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A COMPARATIVE STUDY OF CLASSICAL AND QUANTAL APPROACHES
TO THERMAL AND DIFFUSIVE TRANSPORT IN A DILUTE ATOM-
DIATOM BINARY MIXTURE

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A comparative study of classical and quantal approaches

to thermal and diffusive transport

in a dilute atom-diatom binary mixture

by

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# TABLE OF CONTENTS

# 1. INTRODUCTION

The study of kinetic theory has its roots in the classical physics of the last century. The most significant early pioneers in the field were Maxwell(1) and Boltzmann(2). Their work led to a statistical interpretation of thermodynamics and transport phenomena which ultimately resulted in the ascendency of the kinetic-molecular theory of matter.

The first completely satisfactory attempt at describing transport processes from a kinetic molecular point of view is due to Boltzmann. He proposed an integro-differential equation appropriate to such a description in a paper of 1872(2). This has come to be known as the Boltzmann equation.

However, it was not until the powerful mathematical techniques of functional analysis were developed early in the 20th century that a general method for the solution of Boltzmann's equation became possible. The first attempt at finding such a general solution was made by the mathematician David Hilbert(3). Though his solution failed to produce a satisfactory procedure for the evaluation of transport coefficients, his techniques provided a firm mathematical foundation which paved the way for the simultaneous successes of Chapman(4,5) and Enskog(6). Their contribution was to propose that the time dependence of the singlet distribution

function in a hydrodynamic regime should be a parametric function of the macroscopic thermodynamic state variables and their spatial gradients. The Chapman-Enskog method will be discussed in detail in Chapter 3.

Within the context of this dissertation, it is interesting to note that the Chapman-Enskog approach to the theory of gases in nonequilibrium states predicted the existence of thermal diffusion in dilute gas mixtures before it was observed experimentally[7]. Long known for liquids as the Soret effect, it was first observed in the gas phase by Chapman and Dootson[8].

An interesting development in the kinetic theory as applied to gases with rotational structure came with Senftleben's observation in 1930 of the effect of an applied magnetic field on measurements of the thermal conductivity of oxygen[9]. This effect was also observed for the shear viscosity of oxygen by Engelhardt and Sack[10]. Subsequent experimental work in the 1930s established the "Senftleben effect" as a property characteristic of paramagnetic gases.

An early explanation of the Senftleben effect in terms of a change in the molecular mean free path due to the presence of an applied magnetic field was given by Gorter[11] and later more quantitatively by Zernike and Van Lier[12]. Briefly, the idea is as follows.

The presence of a thermodynamic stress in a dilute molecular fluid results in a preferential alignment of molecular angular momenta. The presence of this polarization in the angular momentum tends to decrease the size of molecular cross sections appropriate to the description of transport processes. The behavior of a rotating molecule in a gas can be illustrated if one imagines the molecule as a spinning disk with axis of rotation parallel to an average magnetic dipole moment and perpendicular to the disk. The application of a field causes the axis to precess about the direction of the field. This precession increases the average molecular cross section by destroying the polarization, hence decreasing the transport coefficient correspondent to the thermodynamic stress. The effect becomes saturated if the applied field is sufficiently strong so that the collisional frequency is much smaller than the precessional frequency.

Apparently, it never occurred to early workers that the Senftleben effect could be generalized to diamagnetic gases. Since there are relatively few examples of paramagnetic gases (NO and $O_2$ being the most notable examples), interest in the study of such a seemingly specialized effect remained limited for many years.

The situation changed drastically in the early 1960s when it was realized that field effects should exist for diamagnetic gases also. Beenakker et al. (13) first observed

a magnetic field effect in the shear viscosity of the diamagnetic gases CO and $N_2$. The corresponding experimental result for the thermal conductivity was subsequently obtained by Gorelik and Sinitsyn(14). This effect in both cases was shown to be similar to the Senftleben effect though it occurred at much higher field strengths because the magnetic moment of a diamagnetic molecule (of the order of a nuclear magneton) is much smaller than that of a paramagnetic molecule (of the order of a Bohr magneton). In addition, it was soon generally realized that the presence of an applied magnetic field acting on a fluid could give rise to transverse components in the transport coefficients due to a lowering of the spatial symmetry of the system. The existence of these components was verified experimentally in 1966 for the shear viscosity by Korving et al.(15) and for the thermal conductivity by Gorelik, Nikolaevskii, and Sinitsyn(16). Finally, it should be mentioned that after some unsuccessful attempts dating back to the 1930s, Senftleben(17) was able to obtain the first successful measurement of the effect of a static electric field on the thermal conductivity of a polar gas. A corresponding measurement of the effect of an electric field on the shear viscosity was obtained by Gallinaro, Meneghetti, and Scoles(18).

The effects of static applied fields (electric or magnetic) on the transport properties of gaseous systems have

come to be known collectively as "Senftleben-Beenakker effects." They are of interest because they provide rather direct information concerning the anisotropy of intermolecular potentials.

The general structure of nonequilibrium thermodynamics as first proposed by Onsager(19,20) and later generalized by Casimir(21) to include the explicit effects of applied fields, provides an interpretive framework appropriate to the understanding of transport in a linear phenomenological regime. Here follows a rudimentary survey of some of the basic ideas.

It is assumed as a postulate of nonequilibrium thermodynamics that fluid systems not too far removed from equilbrium can be represented by a linear phenomenology. This is to say that a flux, $J_i$, of some physical parameter appropriate to a thermodynamic description of the state of the fluid (e.g. thermal energy, mass or fluid velocity) can be linearly related to thermodynamic forces (e.g. temperature gradient, diffusion force, or rate of shear tensor), $X_j$, by the following expression,

$$J_i = -\sum_j L_{ij} X_j \qquad (1-1)$$

where $L_{ij}$ is termed a phenomenological coefficient. The thermodynamic forces are the result of some stress placed on the fluid system such as a temperature, concentration or

velocity gradient.

From the form of Eq. (1-1) it follows that the phenomenological coefficients can be regarded as elements of a matrix. The diagonal coefficients represent direct effects and correspond to the usual transport coefficients such as the thermal conductivity which appears in Fourier's Law of Heat Transport, or the diffusion coefficients which arise in Fick's Laws of Diffusion, etc. These relate the flow of some physical property of the fluid to a stress in that same physical property. For example, the thermal conductivity is the phenomenological coefficient relating a heat flux to a corresponding thermal stress (i.e., a temperature gradient). The off-diagonal elements are phenomenological coefficients which couple the flow of some physical property to a stress in some different physical property. The thermal diffusion coefficient is an example of a phenomenological coefficient for such a coupled effect. It relates a diffusive flux of a molecular species to a thermal stress.

Onsager was able to show that the forces and fluxes could be chosen so that the matrix of phenomenological coefficients would be symmetric. This choice is embodied in the expression,

$$\frac{dS}{dt} = \frac{-1}{T} \sum_i J_i X_i \qquad (1-2)$$

Here, the derivative on the left is the rate of entropy pro-

duction (entropy is maximized at equilibrium) and T is tem-
perature. If Eq. (1-2) is valid for a specific choice of
forces and fluxes, then the corresponding phenomenological
coefficients obey the following symmetry relation,

$$L_{ij} = L_{ji} \tag{1-3}$$

Equation (1-3) is a formal expression of the Onsager
reciprocity relations.

The consideration of an applied field modifies Eq. (1-3)
as follows,

$$L_{ij}(\underline{F}) = L_{ji}(\hat{T}\underline{F}) \tag{1-4}$$

where $\underline{F}$ denotes the field and $\hat{T}\underline{F}$ denotes its time reversed
image. A static electric field, $\underline{E}$, is invariant with respect
to time inversion, thus Eq. (1-4) becomes,

$$L_{ij}(\underline{E}) = L_{ij}(\underline{E}) \tag{1-5}$$

In contrast, since a constant magnetic field, $\underline{H}$, ultimately
arises from the motion of electrical charges, the time
reversed image of $\underline{H}$ is $-\underline{H}$. In light of this fact, Eq. (1-4)
becomes,

$$L_{ij}(\underline{H}) = L_{ij}(-\underline{H}) \tag{1-6}$$

Equation (1-4) embodies the fundamental relations of

nonequilibrium thermodynamics which have come to be known as the Onsager-Casimir reciprocity relations.

The first synthesis of quantum mechanics with the kinetic molecular theory of transport processes is due to Uehling and Uhlenbeck(22,23). In their approach, Boltzmann's equation is modified by replacing the classical expression for the differential scattering cross section appearing within the collision term, with its quantum mechanical analog. This method evades interpretational difficulties encountered when one attempts to define a molecular phase space distribution function in a manner consistent with the Heisenberg uncertainty principle. Green(24) has given a more rigorous statistical mechanical justification of this procedure.

Wang Chang and Uhlenbeck have extended the preceding treatment to the description of dilute polyatomic fluids possessing active internal degrees of freedom(25). The resulting analog of Boltzmann's equation (i.e., the Wang Chang-Uhlenbeck equation) has as its solution a velocity distribution function indexed by an appropriate internal state label. However, the Wang Chang-Uhlenbeck equation is an ad hoc expression which employs, without justification, a quantum mechanical differential cross section in an essentially classical equation.

It is well-known that the expectation value of a mechanical property in quantum mechanics is given as the trace of the matrix product of the density matrix of the system and the appropriate self-adjoint operator. For a dilute gas, bulk mechanical properties can be expressed in terms of operators which consist of a sum of single molecule operators. Thus, the trace formula can be written exclusively in terms of a singlet density matrix. (For mixtures, singlet density matrices appropriate to each species are needed.) In addition, if the bulk state of a dilute gas is sufficiently homogeneous (i.e. its bulk properties vary on a spatial and temporal scale which is much larger than a mean free path or a mean collision time), then it is characterized by a singlet density matrix (or matrices) which can to a good approximation be considered diagonal in total molecular energy. For molecules which have no internal state degeneracy, this amounts to approximate momentum diagonality as well. In the nondegenerate case, one can ignore the contribution of all off-diagonal density matrix elements to the evaluation of expectation values which then can be expressed as averages with the diagonal density matrix elements playing the role of a "quasi-classical" singlet distribution function. It is this "distribution function" which is the solution of the Wang Chang-Uhlenbeck equation. However, the existence of degeneracy in the internal states (e.g. rotational states) of

the gas molecules, implies that some of the off-diagonal density matrix elements cannot be ignored in the evaluation of averages. Thus, description of the relaxation of the gas to equilibrium requires a more fundamental approach. This is discussed in detail in Chapter 2. It suffices here to note that the correct quantum mechanical analog of Boltzmann's equation was obtained first by Waldmann(26) in 1957 and independently later by Snider(27) in 1960. The Waldmann-Snider equation incorporates formal quantum mechanical scattering theory as proposed by Lippman and Schwinger(28) and Gell-Mann and Goldberger(29) into the kinetic molecular theory of transport processes.

The primary objective of this dissertation is to examine various cross sections which arise from the solution of the classical Boltzmann equation and its quantum mechanical analog (Waldmann-Snider equation) for a binary mixture of atoms and diatomic (more generally, linear) molecules close to equilibrium (i.e. within a linear phenomenological regime). This will be done for realistic nonspherical interactions and in the presence of an applied field. (Ar-$CO_2$ He-$CO_2$, and Ar-$N_2$ systems are considered.) A perturbation expansion of the linearized collision operator in the density of the diatomic species will be constructed which will allow an explicit separation of contributions from atom-atom, atom-diatom and diatom-diatom collisions. The discussion will

center on the evaluation of the thermal diffusion coefficient
since this quantity is extremely sensitive to the
nonspherical nature of an interaction. Both classical and
quantal results will be given and compared. Of special
interest in this connection is the application of the
recently developed quantum mechanical sudden approxima-
tions(30,31,32) to the evaluation of transport cross sec-
tions. Also, an analysis of the dynamical approximations in-
herent in the model calculations of the type performed by
Cooper, Dahler, Verlin, Matzen, and Hoffman(33) will be given
in light of results obtained in this work. Finally, wherever
possible, comparison will be made with experimental results
obtained by various workers. In summary, it is the intention
of this investigator to provide results which will afford
valuable insight into the applicability of classical and
quantal approaches to the evaluation of transport coeffi-
cients and also add to the interpretational framework for
assessing the value of model calculations.

## 2. A PARALLEL FORMALISM FOR THE CLASSICAL
## AND QUANTAL KINETIC EQUATIONS FOR DILUTE GASES

### 2.1. A Derivation of the Classical Boltzmann Equation

The original development of Boltzmann's equation was
heuristically derived by considering the randomizing effect
of intermolecular collisions on the temporal evolution of the
velocity distribution in a dilute gas. In order to place the
equation on a firmer theoretical basis, later attempts were
made to derive it directly from Liouville's theorem (i.e. the
conservation of extension in phase space). The first suc-
cessful completion of this task was due to Bogoliubov(34) in
1946 and was followed shortly thereafter by the work of
Kirkwood(35). The method used in the present work is similar
to the approach used by Hoffman and Dahler(36).

The Boltzmann equation is a closed equation for a sin-
glet phase space distribution function. Physically, it pro-
vides a description of relaxation processes occurring in
dilute gas systems. The relaxation of such a system to an
equilibrium state can be understood in terms of processes
occurring on three vastly different time scales. The decay of
nonequilibrium distributions of molecular parameters
which are not conserved in free flight (e.g. rotational phase)
occurs on a short or collisional time scale which is
characterized by the mean duration of a collision $(0(<10^{-12})$

sec.). In contrast, nonequilibrium distributions of free flight invariant parameter (e.g. momentum, kinetic energy) relax on a much longer kinetic time scale characterized by the mean interval between successive collisions ($O(10^{-10}-10^{-9}$ sec. at STP). In a dilute gas, many orders of magnitude separate the collisional and kinetic time scales. A third very long hydrodynamic time scale describes the relaxation of nonequilibrium distributions of summational invariants (e.g. mass, total energy) via macroscopic flows ($O(>10^{-2})$ sec.). In the collisional regime, the time evolution of the system must be described by Liouville's equation incorporating a full set of boundary conditions. In contrast, the kinetic regime can be adequately characterized by a locally uniform singlet distribution function which is a function of free-flight invariant parameters and time ("locally uniform" implies that the function is effectively constant over a distance of the order of a molecular mean free path). The hydrodynamic regime is completely characterized by the macroscopic fluid fields. Boltzmann's equation is appropriate to the description of processes occurring on the kinetic and hydrodynamic time scales but not on the collisional time scale. Unlike Liouville's equation, Boltzmann's equation exhibits temporal irreversibility. This is true because the singlet distribution function which satisfies Boltzmann's equation can be viewed in a crude sense, as a temporal aver-

age over the rigorous distribution function (which satisfies Liouville's equation) on the collisional time scale. Thus, the irreversibility of Boltzmann's equation stems directly from the loss of "fine-grained" dynamical information due to the averaging process (i.e. collisional randomization of nonconserved molecular parameters). Here follows a development of Boltzmann's equation in classical mechanics beginning with the full microscopic description implicit in Liouville's theorem. For simplicity, a single component system is considered. Generalization of the results obtained to multicomponent systems provides no difficulty and will be discussed later.

Fundamental to the statistical mechanical development of gas kinetics is the concept of an N-molecule probability distribution function, $f^{(N)}$. It is parameterized on time and on the coordinates and conjugate momenta of each of the N molecules. The coordinates and momenta can be thought of as comprising the components of a vector in a multidimensional Euclidean space (i.e. N-molecule phase space or $\Gamma$-space.) Thus, $f^{(N)}(\underline{x}^{(N)}, t)$ denotes the probability density of a mechanical state, $\underline{x}^{(N)}$, at time, t, where $\underline{x}^{(N)}$ is a $\Gamma$-space vector and has the form,

$$\underline{x}^{(N)} = (\underline{q}_1, \underline{q}_2, \ldots, \underline{q}_N, \underline{p}_1, \underline{p}_2, \ldots, \underline{p}_N) = (\underline{q}^{(N)}, \underline{p}^{(N)}) \quad (2.1\text{-}1)$$

Here, $\underline{q}_i$ and $\underline{p}_i$ denote generalized coordinates and conjugate

momenta of the $i^{th}$ molecule. For future reference, it should also be noted that $\Gamma$-space can be thought of as the direct sum of N single molecule phase spaces. A point in the single molecule phase space for molecule i ($\mu_i$ space) can be written as,

$$\underline{x}_i = (q_{i1}, q_{i2}, \ldots, q_{i\nu}, p_{i1}, p_{i2}, \ldots, p_{i\nu}) = (\underline{q}_i, \underline{p}_i) \qquad (2.1\text{-}2)$$

where $\underline{q}_{i\beta}$ is the positional coordinate for the $\beta^{th}$ degree of freedom of the $i^{th}$ molecule and $\underline{p}_{i\beta}$ is its conjugate momentum. Here, each molecule has $\nu$ "thermally active" degrees of freedom. Within the context of gas kinetics, these always include translational degrees of freedom. In addition, for diatomic (or linear polyatomic) molecules, two rotational degrees of freedom are active and for a nonlinear polyatom all three rotational degrees of freedom are active. Other molecular degrees of freedom (vibrational, electronic, nuclear) are usually inactive and can be ignored.

The Liouville theorem, which embodies the dynamical information of the classical equations of motion (Hamilton's equations), takes a differential form as a continuity equation for $f^{(N)}$,

$$\frac{\partial f^{(N)}}{\partial t} + \{f^{(N)}, H^{(N)}\} = 0 \qquad (2.1\text{-}3)$$

Here, $H^{(N)}$ is the N-molecule Hamiltonian function and the braces are the Poisson bracket. For general functions of the

phase variables, $\Phi$ and $\Psi$, the Poisson bracket has the explicit form,

$$\{\Phi,\Psi\} = \sum_{i=1}^{N} \sum_{\beta=1}^{\nu} [\frac{\partial\Phi}{\partial q_{i\beta}}\frac{\partial\Psi}{\partial p_{i\beta}} - \frac{\partial\Phi}{\partial p_{i\beta}}\frac{\partial\Psi}{\partial q_{i\beta}}] \qquad (2.1\text{-}4)$$

The motion of a classical N-body system is characterized by nonintersecting trajectories in $\Gamma$-space.

It is possible to describe the probability distribution for a set of s molecules, which is a subset of the N molecules comprising the system, by the definition of a reduced distribution function, $f^{(s)}$. The reduced distribution function is obtained by integrating over the phase variables of the molecules not included in the s-fold cluster. It has the form,

$$f^{(s)}(\underline{x}^{(s)},t) = \frac{1}{(N-s)!} \int d\underline{x}_{s+1} \dots \int d\underline{x}_N f^{(N)}(\underline{x}^{(N)},t) \qquad (2.1\text{-}5)$$

Here, $f^{(N)}$ is taken to be normalized to N!. This normalization is assumed because for an N-fold set of identical molecules there exist N! indistinguishable permutations of molecular labels. Integration of Eq. (2.1-3) over the phase points of the N-s molecules not included in the cluster yields the classical BBGKY hierarchy of coupled equations for which a general member can be written,

$$\frac{\partial f^{(s)}}{\partial t} + \{ ,H^{(s)}\}f^{(s)} = -\sum_{i=1}^{s} \int d\underline{x}_{s+1}\{ ,V_{i,s+1}\}f^{(s+1)} \qquad (2.1\text{-}6)$$

Here, $\{\ ,\Psi\}$, is a linear partial differential operator which when acting on a function, $\Phi$, yields the Poisson bracket, $\{\Phi,\Psi\}$. The derivation of Eq. (2.1-6) depends on the assumption that the potential energy, $V^{(s)}$, of an isolated s-fold molecular cluster can be expressed as a sum of pairwise interactions plus contributions from external fields. Thus, $V^{(s)}$ is assumed to have the form,

$$V^{(s)} = \frac{1}{2}\sum_{i=1}^{s}\sum_{j=i}^{s} V_{ij} + \sum_{i=1}^{s} V_i^{ext} \qquad (2.1-7)$$

where $V_{ij}$ is the interaction potential between the $i^{th}$ and $j^{th}$ molecules and $V_i^{ext}$ is the potential energy of the $i^{th}$ molecule due to external fields. Finally, one notes that the s-molecule Hamiltonian, $H^{(s)}$, is defined by the expression,

$$H^{(s)} = \sum_{i=1}^{s} (\frac{p_i^2}{2M} + K_i^{int}) + V^{(s)} \qquad (2.1-8)$$

where, $K_i^{int}$ is the contribution to the kinetic energy from internal degrees of freedom of the $i^{th}$ molecule and $p_i^2/2M$ is the $i^{th}$ molecule translational kinetic energy. For future reference, the symbol, $K_i^{(1)}$ will be defined here as the total kinetic energy due to molecule i (i.e. $K_i^{(1)} = p_i^2/2M + K_i^{int}$).

The first member of the BBGKY hierarchy gives the total time rate of change of the singlet distribution function, $f^{(1)}$,

as a functional of $f^{(2)}$. It has the form,

$$\frac{\partial f^{(1)}}{\partial t} + \{ ,H_1^{(1)}\}f^{(1)} = -\int d\underline{x}_2\{ ,V_{12}\}f^{(2)} \qquad (2.1\text{-}9)$$

In a similar way, the time rate of change of $f^{(2)}$ is a functional of $f^{(3)}$ and so on up the hierarchy. It is clear that in order to find a closed expression for $f^{(1)}$, the hierarchy must be truncated at the lowest level. This may be accomplished by assuming that any intermolecular potential which is realistically applicable to dilute gas phenomena falls off rapidly as the distance of separation of interacting molecules is increased. This implies that in order to evaluate Eq. (2.1-9) a knowledge of $f^{(2)}$ is needed only in the region where molecule 1 and molecule 2 are close and strongly interacting. Under this condition, many body interactions are negligible and can be ignored in a dilute gas, since having three or more molecules in close proximity is a rare event. This allows the equation of change for $f^{(2)}$ obtained from the hierarchy to be replaced near the interaction region by a continuity equation independent of $f^{(3)}$ (i.e. the two molecule Liouville equation) which is of the form,

$$\frac{\partial f^{(2)}}{\partial t} + \{f^{(2)},H^{(2)}\} = 0 \qquad (2.1\text{-}10)$$

One notes that Eq. (2.10) has the following formal solution,

$$f^{(2)}(\underline{x}^{(2)},t) = e^{-(t-t_o')\{,H^{(2)}\}} f^{(2)}(\underline{x}^{(2)},t_o') \qquad (2.1-11)$$

which immediately yields the result ($\{,H^{(2)}\}$ is a first order differential operator),

$$f^{(2)}(\underline{x}^{(2)},t) = f^{(2)}(\underline{x}^{(2)}(t_o'),t_o') \qquad (2.1-12)$$

where $\underline{x}^{(2)}(t_o')$ is the phase space position of a pair of molecules at a time, $t_o'$, which evolves dynamically to a phase space position, $\underline{x}^{(2)}$, at a later time, t. Equation (2.1-12) is the integrated Liouville equation which describes a system consisting of only two molecules. It implies that the numerical value of the pair distribution function simply translates temporally in phase space as a result of the motion of the system.

At this point, one may introduce the assumption of molecular chaos, which is that for a time, $t_o''$, sufficiently remote in the past one can factorize $f^{(2)}$ in the following way,

$$f^{(2)}(\underline{x}^{(2)}(t_o''),t_o'') =$$

$$f^{(1)}(\underline{x}_1(t_o''),t_o'')f^{(1)}(\underline{x}_2(t_o''),t_o'') \qquad (2.1-13)$$

This is to say that prior to collision, the molecular states are uncorrelated so that the pair distribution can be regarded as a product of singlet distributions. In a dilute gas

regime it is possible to choose a time, $t_o$, which is short enough so that Eq. (2.1-11) is satisfied for $t_o = t_o'$ and long enough so that Eq. (2.1-13) is satisfied for $t_o = t_o''$. Such a $t_o$ cannot be found for a dense fluid since isolated binary encounters are rare events and Eq. (2.1-10) or equivalently, Eq. (2.1-12) becomes inapplicable. This is nothing more than a reaffirmation of the proposition that many body interactions are important in a dense molecular fluid, but not in a dilute one. Returning to the case of a dilute gas, it is clear that Eq. (2.1-11) and (2.1-13) yield the result,

$$f^{(2)}(\underline{x}^{(2)}(t),t) =$$

$$\text{(2.1-14)}$$

$$e^{-(t-t_o)\{\,,H^{(2)}\}} f^{(1)}(\underline{x}_1(t),t_o) f^{(1)}(\underline{x}_2(t),t_o)$$

Here, the pair distribution at a time, t, has been expressed in terms of singlet distributions at a prior time, $t_o$.

It is also possible to write a formal solution for Eq. (2.1-9). If the right hand side is abbreviated by the symbol, J(t), where the argument refers to the explicit time dependence of the collisional term, then $f^{(1)}(\underline{x}_1,t)$ has the form,

$$f^{(1)}(\underline{x}_1,t_0) =$$
$$e^{(t-t_o)\{\,,H_1^{(1)}\}} f^{(1)}(\underline{x}_1,t) + \int_t^{t_o} dt' e^{(t'-t)\{\,,H_1^{(1)}\}} J(t') \quad \text{(2.1-15)}$$

The first term appearing on the right can be interpreted as

arising from collisionless molecular motion and the second term as containing the effect of molecular interactions. It is permissible to neglect the interaction since the time scale involved in this analysis is much less than a mean free time and approaches the time scale characterized by the duration of a collision. On such a short time scale, one can regard the collisional rate of change of $f^{(1)}$ as negligible. This procedure yields the result,

$$f^{(2)}(\underline{x}^{(2)}(t),t) = \underset{\sim}{u}^{(2)}(t_o)f^{(1)}(\underline{x}_1(t),t)f^{(1)}(\underline{x}_2(t),t) \tag{2.1-16}$$

Since the object is to obtain an expression for $f^{(2)}$ in terms of $f^{(1)}$ which is valid in a region of phase space near the collision region, it is appropriate to neglect the effect of external potentials on the time evolution of $f^{(2)}$ and $f^{(1)}$ (i.e. on a collisional time scale external potentials have little effect on molecular trajectories). Thus, $\underset{\sim}{u}^{(2)}(t_o)$ is defined by the expression,

$$\underset{\sim}{u}^{(2)}(t_o) = e^{-(t-t_o)\{\ ,H_o^{(2)}\}}e^{(t-t_o)\{\ ,K_1^{(1)}+K_2^{(1)}\}} \tag{2.1-17}$$

Here, $H_o^{(2)}$ is taken to be $K_1^{(1)} + K_2^{(1)} + V_{12}$, where $K_1^{(1)}$ and $K_2^{(1)}$ are the kinetic energies of molecule 1 and molecule 2,

respectively.

It is clear that the effect of $e^{-(t-t_o)\{\ ,H_o^{(2)}\}}$ is to transform the molecular pair backward dynamically along the two molecule phase trajectory a time interval, $t-t_o$, before any significant interaction occurs. The effect of the operator, $e^{(t-t_o)\{\ ,K_1^{(1)}+K_2^{(1)}\}}$, is to transform the system forward dynamically to the original time, $t$, with the intermolecular potential "turned off". It can be established that the operator, $\underset{\sim}{S}^{(2)}$, defined by

$$\underset{\sim}{S}^{(2)} = \lim_{t_o \to -\infty} \underset{\sim}{U}^{(2)}(t_o) \qquad (2.1\text{-}18)$$

is well-defined if it acts on nonbound regions of the two molecule phase space (In fact, for potentials with a finite cutoff length, $\underset{\sim}{U}^{(2)}(t_o)$ is independent of $t_o$ if the interval $t-t_o$ is sufficiently long so that $t_o$ can be taken as precollisional). Hence, substitution of Eq. (2.1-16) into Eq. (2.1-9) assuming that $t_o$ is in the precollisional past, results in the expression,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H_1^{(1)}\}f^{(1)} = -\int d\underline{x}_2\{\ ,V_{12}\}\underset{\sim}{S}^{(2)}f^{(1)}f_2^{(1)} \qquad (2.1\text{-}19)$$

where $f^{(1)}f_2^{(1)}$ is an abbreviation of $f^{(1)}(\underline{x}_1,t)f^{(1)}(\underline{x}_2,t)$.

If one considers intermolecular potentials which rapidly vanish asymptotically with intermolecular separation, the integral over the spatial position, $\underline{r}_2$, of molecule 2 can be

limited without introducing significant error, to a simply

connected region, $R_{\sigma_{1,2}}$, about molecule 1 which is bounded by

a finite closed surface, $\sigma_{1,2}$. This is to say that the

region, $R_{\sigma_{1,2}}$, is defined such that it contains the spatial

volume within which molecules experience significant

deflection due to intermolecular forces (i.e. the collision

region). Outside of $R_{\sigma_{1,2}}$ there is by definition, negligible

contribution to the integral. The actual shape of $\sigma_{1,2}$ is

immaterial so long as $R_{\sigma_{1,2}}$ contains the collision region.

Thus, a "cutoff" function, $z_{12}$, defined to equal unity inside

$R_{\sigma_{1,2}}$ and zero outside, can be introduced into Eq. (2.1-19)

as follows,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H_1^{(1)}\}f^{(1)} = -\int d\underline{x}_2 z_{12}\{\ ,V_{12}\}\underline{S}^{(2)}f^{(1)}f_2^{(1)} \qquad (2.1-20)$$

Equation (2.1-20) can be further modified as follows,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H_1^{(1)}\}f^{(1)} =$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.1-21)$$

$$\int d\underline{x}_2 z_{12}[\{\ ,K_1^{(1)} + K_2^{(1)}\} - \{\ ,H_o^{(2)}\}]\underline{S}^{(2)}f^{(1)}f_2^{(1)}$$

Here, use has been made of the definition of $H_o^{(2)}$.

In a dilute gas, the distribution function can be taken

to be effectively constant on a spatial scale commensurate

with the effective range of the intermolecular potential

(i.e. within the collision region). This is to say that

collisions can be thought of as occurring at a point. The

application of this assumption means that $f^{(1)}(\underline{x}_1, t) f^{(1)}(\underline{x}_2, t)$ in the right hand side of Eq. (2.1-21) is replaced with $f^{(1)}(\underline{r}_1, \underline{\xi}_1, t) f^{(1)}(\underline{r}_1, \underline{\xi}_2, t)$ where $\underline{r}_1$ is the position of molecule 1, $\underline{\xi}_i$ refers to the phase space variables of molecule i excluding the spatial position vector, and $\underline{\underline{S}}^{(2)}$ (defined by Eq. (2.1-18)) acts only on the $\underline{\xi}_i$ dependence of $f^{(1)}$. An alternate statement of this assumption is that the partial derivative, $\partial f_i^{(1)} / \partial \underline{r}_i$, is negligible in comparison to partial derivatives, $\partial f_i^{(1)} / \partial \underline{\xi}_i$ and $\partial f_i^{(1)} / \partial t$, within the kinetic regime.

The dynamical parameters which comprise $\underline{\xi}_i$ can be divided into two groups. These are the free-flight invariant and noninvariant parameters symbolized by "vectors" $\underline{\chi}_i$ and $\underline{\phi}_i$, respectively. For a dilute gas, the singlet distribution function appropriate to the description of processes occurring on a kinetic time scale (i.e. an $f^{(1)}$ which satisfies Boltzmann's equation) has a weak time dependence which in the following analysis is approximated by zero. Thus, one can write,

$$\dot{\underline{\chi}}_i \cdot \frac{\partial f_i^{(1)}}{\partial \underline{\chi}_i} + \dot{\underline{\phi}}_i \cdot \frac{\partial f_i^{(1)}}{\partial \underline{\phi}_i} = 0 \qquad (2.1\text{-}22)$$

where the "dot above" denotes the total time derivative (e.g. $\dot{\underline{\chi}}_1 = d\underline{\chi}_1 / dt$). Because $\underline{\phi}_i$ varies on the collisional time scale, (i.e. it rapidly changes even while molecules are

widely separated) while $\underline{\chi}_i$ varies on the kinetic time scale,
(i.e. it changes only as a consequence of collisions), it
follows that the components of $\underline{\dot{\phi}}_i$ are large in comparison
with the components of $\underline{\dot{\chi}}_i$. Thus, $\partial f_i^{(1)}/\partial \underline{\dot{\phi}}_i$ is corresponding-
ly small, (i.e. $\underline{\dot{\phi}}_i$ is phase averaged), and hence $f_i^{(1)}$ is ef-
fectively independent of nonfree-flight invariants.
Conversely, $f_i^{(1)}$ exhibits a sensitive dependence on $\underline{\chi}_i$.
Thus, $f_i^{(1)}$ can be regarded as an exclusive function of $\underline{r}_i$,
$\underline{\chi}_i$, and t.

One observes that $\underset{\sim}{S}^{(2)}$ acting on some general dynamical
parameter, $y_{12}$, of the two molecule phase trajectory gives
some well-defined function of $\underline{x}^{(2)}$, $y_{12}^{\star}$. Furthermore, if $y_{12}$
is a function of only single molecule free-flight invariants,
then one obtains,

$$\{ \ , H_o^{(2)} \} y_{12}^{\star} =$$

$$(2.1-23)$$

$$\lim_{t_o \to -\infty} e^{-(t-t_o)\{ \ , H_o^{(2)} \}} \{ \ , H_o^{(2)} \} \ e^{(t-t_o)\{ \ , K_1^{(1)} + K_2^{(1)} \}} y_{12}$$

which yields,

$$\{ \ , H_o^{(2)} \} y_{12}^{\star} = \lim_{t_o \to -\infty} e^{-(t-t_o)\{ \ , H_o^{(2)} \}} \{ y_{12}, V_{12} \} \qquad (2.1-24)$$

Since $V_{12}$ is short range, it follows that the right hand side
of Eq. (2.1-24) vanishes. Within the collision region, $R_{\sigma_{1,2}}$

$R_{\sigma_{1,2}}$, the product, $f_1^{(1)}(\underline{r}_1, \underline{\xi}_1, t) f^{(1)}(\underline{r}_1, \underline{\xi}_2, t)$, is an exclusive function of free-flight invariants and, of course, time. Thus, in Eq. (2.1-21) the term involving $\{\ , H_o^{(2)}\}$ vanishes. This yields the result,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ , H_1^{(1)}\} f^{(1)} =$$

$$\int d\underline{x}_2 z_{12}\{\ , K_1^{(1)} + K_2^{(1)}\} \underline{\underline{S}}^{(2)} f^{(1)} f_2^{(1)}$$

(2.1-25)

where $f^{(1)} f_2^{(1)}$ is now the abbreviation of $f^{(1)}(\underline{r}_1, \underline{\xi}_1, t) \times f^{(1)}(\underline{r}_1, \underline{\xi}_2, t)$. One immediately obtains the result,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ , H_1^{(1)}\} f^{(1)} = \int d\underline{x}_2 [\{\ , K_1^{(1)} + K_2^{(1)}\} z_{12} \underline{\underline{S}}^{(2)} f^{(1)} f_2^{(1)}$$

$$- \{z_{12}, K_1^{(1)} + K_2^{(1)}\} \underline{\underline{S}}^{(2)} f^{(1)} f_2^{(1)}]$$

(2.1-26)

where use has been made of the fact that $\{\ , K_1^{(1)} + K_2^{(1)}\}$ is a linear differential operator.

The differential operator, $\{\ , K_1^{(1)} + K_2^{(1)}\}$, has the explicit form,

$$\{\ , K_1^{(1)} + K_2^{(1)}\} =$$

$$\underline{v}_1 \cdot \frac{\partial}{\partial \underline{r}_1} + \underline{v} \cdot \frac{\partial}{\partial \underline{r}} + \dot{\underline{\phi}}_1 \cdot \frac{\partial}{\partial \underline{\phi}_1} + \dot{\underline{\phi}}_2 \cdot \frac{\partial}{\partial \underline{\phi}_2}$$

(2.1-27)

where the relative position, $\underline{r}$, is defined as $\underline{r}_2 - \underline{r}_1$ and the velocities, $\underline{v}_1$ and $\underline{v}$ are defined as $\dot{\underline{r}}_1$ and $\dot{\underline{r}}$, respectively. (The total time derivative is taken along a free-flight trajectory.) Because $\underline{\chi}_i$ is defined as free-flight invariant,

terms of the form, $\underline{\dot{\chi}}_i \cdot \partial/\partial\underline{\chi}_i$ do not appear in Eq. (2.1-27) since $\underline{\dot{\chi}}_i$ is identically zero. Finally, one should note that since $\{ ,K_1^{(1)}+K_2^{(1)}\}$ is simply the total implicit time differential operator appropriate to free flight motion, Eq. (2.1-27) is valid whether or not the coordinates and momenta appearing on the right are chosen to be canonical conjugate variables.

In classical mechanics, a generalized coordinate which does not appear in the Hamiltonian is termed cyclic or ignorable. It follows directly from Hamilton's equations that the conjugate momentum of a cyclic coordinate is conserved and that the time derivative of a cyclic coordinate is independent of the coordinate itself. Since it is always possible to choose conserved momenta to describe free-flight motion, it follows that $\underline{\phi}_i$ can be chosen to be cyclic, thus allowing $\underline{\phi}_i$ to be interchanged with $\partial/\partial\underline{\phi}_i$ in Eq. (2.1-27). A nontrivial example of this is afforded by consideration of symmetric top molecules. In this case, $\underline{\phi}_i$ is comprised of the Euler angles, $\alpha$ (angle about the space-fixed z-axis) and $\gamma$ (angle about the body-fixed z-axis). The Euler angle, $\beta$, (angle about the line of nodes) is free-flight invariant. Explicit expressions for the rotational Hamiltonian, $\dot{\alpha}$, and $\dot{\gamma}$ are as follows(37),

$$H = \frac{I_1}{2}(\dot{\beta}^2 + \dot{\alpha}^2(\sin\beta)^2) + \frac{I_3}{2}(\dot{\gamma} + \dot{\alpha}\cos\beta)^2 \qquad (2.1-28)$$

$$\dot{\alpha} = \frac{L_\alpha - L_\gamma \cos\beta}{I_1 (\sin\beta)^2} \qquad (2.1-29)$$

$$\dot{\gamma} = \frac{L_\gamma}{I_3} - \cos\beta \left[\frac{L_\alpha - L_\gamma \cos\beta}{I_1 (\sin\beta)^2}\right] \qquad (2.1-30)$$

where $L_\alpha$ and $L_\gamma$ are momenta conjugate to $\alpha$ and $\gamma$, and $I_1$ and $I_3$ are the two principal moments of inertia. One notes immediately that $\dot{\alpha}$ and $\dot{\gamma}$ are independent of $\alpha$ and $\gamma$.

If one substitutes Eq. (2.1-27) into the first term of Eq. (2.1-26), interchanges the time derivatives and partial differential operators and integrates over $\underline{\phi}_1$, one obtains,

$$\frac{\partial f^{(1)}}{\partial t} + \{ ,H_1^{(1)}\}f^{(1)} = \frac{1}{B^2} \int d\underline{\phi}_1 d\underline{\phi}_2 \int d\underline{\chi}_2 \int d\underline{r}_2 \qquad (2.1-31)$$

$$[\frac{\partial}{\partial \underline{r}} \cdot \underline{v}^z{}_{12}\underline{S}^{(2)} f^{(1)} f_2^{(1)} - \{\dot{z}_{12}, K_1^{(1)} + K_2^{(1)}\}\underline{S}^{(2)} f^{(1)} f_2^{(1)}]$$

Here, the singlet distribution function has been renormalized with respect to integration over position and free-flight invariants (i.e. $n = \int d\underline{r} \int d\underline{\chi} f^{(1)} (\underline{r}, \underline{\chi}, t)$ where n is the number density). The constant, B, is defined as $\int d\underline{\phi}$ (e.g. for a symmetric top, $B = \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma = 4\pi^2$). It appears in Eq. (2.1-31) as a consequence of the fact that the orientational parameters, $\underline{\phi}_1$ and $\underline{\phi}_2$, are now not included in the normalization of the distribution function.

Following Curtiss and Dahler(38), one can construct a set of curvilinear coordinates appropriate to the relative position space by means of a family of surfaces which are geometrically similar to $\sigma_{1,2}$ and are scaled by a non-negative dimensionless parameter, $\rho$. By definition, $\sigma_{1,2}$ corresponds to $\rho$ equal to unity. If the scaling parameter is regarded as a function of positional and internal coordinates, $Z_{12}$ can be given the following form as a limit of a continuous function,

$$Z_{12} = \lim_{\nu \to \infty} e^{-\rho^\nu} \qquad (2.1\text{-}32)$$

If one substitutes Eq. (2.1-32) into Eq. (2.1-26), one obtains,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H_1^{(1)}\}f^{(1)} = \lim_{\nu \to \infty} \{\frac{1}{B^2} \int d\underline{\phi}_1 d\underline{\phi}_2 \int d\chi_2 \int d\underline{r}_2$$

$$[\frac{\partial}{\partial \underline{r}} \cdot (\underline{v}\, e^{-\rho^\nu} \underset{\approx}{S}^{(2)} f^{(1)} f_2^{(1)}) + \{e^{-\rho^\nu},K_1^{(1)} + K_2^{(1)}\}\underset{\approx}{S}^{(2)} f^{(1)} f_2^{(1)}] \qquad (2.1\text{-}33)$$

The integral over $\underline{r}_2$ can be restricted to a spherical volume of radius, $a$, about molecule 1, such that the volume encompasses the region $R_{\sigma_{1,2}}$. Since the "cutoff" function has been expressed as the limit of a continuous function, the divergence theorem can be applied to the first term. One obtains the result,

$$0 = \lim_{\nu\to\infty}\{\frac{a^2}{B^2}\int d\underline{\phi}_1 d\underline{\phi}_2 \int d\underline{\chi}_2 \int_{\substack{\text{unit} \\ \text{sphere}}} d\hat{r}\,\underline{v}\cdot\hat{r}e^{-\rho^\nu}\underline{\underline{S}}^{(2)}f^{(1)}f_2^{(1)}\} \quad (2.1\text{-}34)$$

Here, $d\hat{r}$ denotes a differential solid angle taken over the spherical surface.

Recalling the definition of the Poisson bracket and making use of the result just obtained, one can modify Eq. (2.1-33) as follows,

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H_1^{(1)}\}f^{(1)} = \lim_{\nu\to\infty}\{\frac{1}{B^2}\int d\underline{\phi}_1 d\underline{\phi}_2 \int d\underline{\chi}_2$$

$$\int d\underline{r}_2 (\nu\rho^{\nu-1}e^{-\rho^\nu})\dot\rho\underline{\underline{S}}^{(2)}f^{(1)}f_2^{(1)}\} \quad (2.1\text{-}35)$$

As before, the "dot above" denotes a total time derivative taken within the context of free-flight dynamics. The differential volume element $d\underline{r}_2$ takes the following form in terms of the previously introduced curvilinear coordinates,

$$d\underline{r}_2 = \rho^2 d\rho(\underline{\zeta}\cdot\hat{k})dA_{\sigma_{1,2}} \quad (2.1\text{-}36)$$

Here, $\underline{\zeta}$ is defined as a vector from the center of mass of molecule 1 to some point, Q, on the surface, $\sigma_{1,2}$. In the same context, $\hat{k}$ is the outwardly oriented unit vector normal to $\sigma_{1,2}$ at Q, and $dA_{\sigma_{1,2}}$ is a differential area element taken as $\sigma_{1,2}$ about Q. Equation (2.1-36) reduces to the usual

spherical polar form if $\sigma_{1,2}$ is chosen to be a unit sphere. In this case the scaling factor, $\rho$, reduces to the usual radial coordinate. Curtiss and Dahler(38) have given a rigorous justification of Eq. (2.1-36) for all convex choices of $\sigma_{1,2}$.

Substitution of Eq. (2.1-36) into Eq. (2.1-35) followed by integration over $\rho$, yields the result,

$$\frac{\partial f^{(1)}}{\partial t} + \{ ,H^{(1)}\}f^{(1)} =$$

$$\frac{1}{B^2}\int d\underline{\phi}_1 d\underline{\phi}_2 \int d\underline{\chi}_2 \int dA_{\sigma_{1,2}} \dot{\rho}(\underline{\zeta}\cdot\hat{k})\underline{\underline{S}}^{(2)}f^{(1)}f_2^{(1)} \qquad (2.1\text{-}37)$$

where one notes that

$$\lim_{\nu\to\infty}\nu\rho^{\nu-1}e^{-\rho^\nu} = \delta(\rho-1) \qquad (2.1\text{-}38)$$

Equation (2.1-38) is easily established by the argument line,

$$\int_0^\infty d\rho(\lim_{\nu\to\infty}\nu\rho^{\nu-1}e^{-\rho^\nu})F(\rho) = \lim_{\nu\to\infty}\sum_{j=0}^\infty \int_0^\infty d\rho\,\nu\rho^{\nu-1}e^{-\rho^\nu}$$

$$\frac{(\rho-1)^j}{j!}\frac{d^j}{d\rho'^j}F(\rho')\Big|_{\rho'=1} = F(1)\{\lim_{\nu\to\infty}\int_0^\infty d\rho\,\nu\rho^{\nu-1}e^{-\rho^\nu}\} = \qquad (2.1\text{-}39)$$

$$F(1)\lim_{\nu\to\infty}\{-e^{-\rho^\nu}\Big|_0^\infty\} = F(1)$$

Here, it is assumed that the arbitrary function, $F(\rho)$, can be

written as a Taylor series and that the sum, integral, and limit can be arbitrarily permuted.

A relative position, $\underline{r}$, can be expressed in terms of the curvilinear coordinates as follows,

$$\underline{r} = \rho\underline{\zeta} \tag{2.1-40}$$

If one applies the differential operator, $\{\ ,K_1^{(1)} + K_2^{(1)}\}$, to both sides of Eq. (2.1-40), one obtains,

$$\underline{v} = \dot{\rho}\underline{\zeta} + \rho(\dot{\underline{\alpha}}_1 \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}_1} + \dot{\underline{\alpha}}_2 \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}_2}) \tag{2.1-41}$$

Here, $\dot{\alpha}_1$ and $\alpha_2$ denote internal coordinates of molecule 1 and molecule 2. Contraction of both sides of Eq. (2.1-41) with the unit vector, $\hat{k}$, yields the result,

$$\dot{\rho}(\underline{\zeta} \cdot \hat{k}) = (\underline{v} - \rho\dot{\underline{\alpha}}_1 \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}_1} - \rho\dot{\underline{\alpha}}_2 \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}}) \cdot \hat{k} \tag{2.1-42}$$

If one recalls that $\rho$ = unity on $\sigma_{1,2}$, substitution of Eq. (2.1-42) into Eq. (2.1-37) yields the form of Boltzmann's equation obtained by Hoffman and Dahler(36).

$$\frac{\partial f^{(1)}}{\partial t} + \{\ ,H^{(1)}\}f^{(1)} = \frac{1}{B^2}\int d\underline{\phi}_1 d\underline{\phi}_2 \int d\chi_2 \tag{2.1-43}$$

$$\{\int_{\hat{k}\cdot\underline{g}>0} dA_{\sigma_{1,2}} \hat{k}\cdot\underline{g}\underline{\underline{S}}^{(2)} f^{(1)}f_2^{(1)} + \int_{\hat{k}\cdot\underline{g}<0} dA_{\sigma_{1,2}} \hat{k}\cdot\underline{g}f^{(1)}f_2^{(1)}\}$$

where $\underline{g} = \underline{v} - \dot{\underline{\alpha}} \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}_1} - \dot{\underline{\alpha}} \cdot \frac{\partial\underline{\zeta}}{\partial\underline{\alpha}_2}$ and is readily interpreted as

the relative velocity of an incident molecule (i.e. molecule 2) with respect to the surface, $\sigma_{1,2}$. The surface integral has been divided into precollisional ($\hat{k} \cdot g > 0$) and postcollisional ($\hat{k} \cdot g < 0$) contributions and it has been noted that $\underset{\approx}{S}^{(2)}$ is the identity on the precollisional region of $\sigma_{1,2}$. If $\sigma_{1,2}$ is chosen to be a sphere of radius, $b_{max}$ (i.e. maximum impact parameter), and if one allows $b_{max}$ to be indefinitely large, then one obtains the usual form of Boltzmann's equation(2),

$$\frac{\partial f^{(1)}}{\partial t} + \{ \ , H_1^{(1)} \} f^{(1)} =$$

$$\frac{1}{B^2} \int d\underline{\phi}_1 d\underline{\phi}_2 \int d\underline{\chi}_2 \int_0^\infty b\,db \int_0^{2\pi} d\varepsilon \,|\underline{v}|\,(\underset{\approx}{S}^{(2)} - 1) f^{(1)} f_2^{(1)}$$

(2.1-44)

Here, $\underline{v}$ appears because $\underline{\zeta}$ is independent of $\underline{\alpha}_1$ and $\underline{\alpha}_2$ and the definitions of the impact parameter, b, and the angle, $\varepsilon$, are the usual ones given by Chapman and Cowling(39) or Hirschfelder, Curtiss and Bird(40).

It has been tacitly assumed throughout this development that $\sigma_{1,2}$ is differentiable, that is to say that a unique tangent plane can be found for each point on $\sigma_{1,2}$. Hoffman and Dahler(36) have assumed the stronger condition of convexity in their development. For a convex $\sigma_{1,2}$ the surface area element takes the form,

$$dA_{\sigma_{1,2}} = d\hat{k} S_{\sigma_{1,2}}(\hat{k})$$

(2.1-45)

where $d\hat{k}$ denotes a differential change in the unit surface normal (i.e. $d\hat{k}$ is a differential solid angle) and $S_{\sigma_{1,2}}(\hat{k})$ is the Jacobian determinant which describes the topological deformation of the unit sphere into the surface $\sigma_{1,2}$.

In conclusion, the Boltzmann equation can be written in terms of a classical collision kernel, $\Theta$,

$$\frac{\partial f^{(1)}}{\partial t}(\underline{r},\chi_1,t) + \{\ ,H^{(1)}\}f^{(1)}(\underline{r},\chi_1,t) =$$

$$\int d\chi_1' \int d\chi_2 \int d\chi_2' <\chi_1\chi_2|\Theta|\chi_1'\chi_2'>f^{(1)}(\underline{r},\chi_1',t)f^{(1)}(\underline{r},\chi_2',t) \qquad (2.1\text{-}46)$$

where the collision kernel has the form,

$$<\chi_1\chi_2|\underset{\approx}{\Theta}|\chi_1'\chi_2'> = \frac{1}{B^2}\int d\underline{\phi}_1 d\underline{\phi}_2[\underset{\hat{k}\cdot\underline{g}<0}{\int}dA_{\sigma_{1,2}}\hat{k}\cdot\underline{g}\delta(\chi_1-\chi_1')\delta(\chi_2-\chi_2') +$$

$$\qquad (2.1\text{-}47)$$

$$\underset{\hat{k}\cdot\underline{g}>0}{\int}dA_{\sigma_{1,2}}\hat{k}\cdot\underline{g}\int d\chi_1'' \int d\chi_2''\delta(\chi_1-\chi_1'')\delta(\chi_2-\chi_2'')\underset{\approx}{S}^{(2)}\delta(\chi_1'-\chi_1'')\delta(\chi_2'-\chi_2'')]$$

The classical scattering operator, $\underset{\approx}{S}^{(2)}$, is taken to act only on $\chi_1''$ and $\chi_2''$ and not $\chi_1'$ and $\chi_2'$. This expression behaves like a matrix element of a differential operator in a coordinate representation.

Finally, for the sake of completeness, the collision kernel can be related to the specific transition rate defined by Hoffman and Dahler(36),

$$\langle \underline{X}_1 \underline{X}_2 | \Theta | \underline{X}_1' \underline{X}_2' \rangle = \int d\underline{X}_1'' \int d\underline{X}_2'' w(\underline{X}_1 \underline{X}_2 | \underline{X}_1'' \underline{X}_2'')$$

$$[\delta(\underline{X}_1'' - \underline{X}_1') \delta(\underline{X}_2'' - \underline{X}_2') - \delta(\underline{X}_1 - \underline{X}_1') \delta(\underline{X}_2 - \underline{X}_2')]$$

$$(2.1-48)$$

Here, $w(\underline{X}_1 \underline{X}_2 | \underline{X}_1'' \underline{X}_2'')$ denotes the specific transition rate of the collisional process, $\underline{X}_1'', \underline{X}_2'' \rightarrow \underline{X}_1, \underline{X}_2$.

## 2.2. A Derivation of the Waldmann-Snider Equation

As noted in the Introduction, the Waldmann-Snider equation was developed in order to treat dilute gas systems comprised of molecules with degenerate quantum states. Like the Boltzmann equation, it is of an irreversible nature and has a closed form with respect to $f^{(1)}$, which is a singlet Wigner distribution function for the translational degrees of freedom and a singlet density matrix for the internal degrees of freedom.

The Wigner distribution function was proposed in 1932[41] as a real-valued form for a statistical mechanical phase space distribution function compatible with the Heisenberg Uncertainty Principle. It is a function on the classical phase space which gives the correct quantum mechanical ensemble averages, but unlike the classical distribution function, it is not everywhere nonnegative (note that an ensemble average, $\langle \hat{A} \rangle$, is given in quantum mechanics

by a trace of the operator, $\hat{A}$, with the density matrix, $\hat{\rho}$,
$\langle\hat{A}\rangle = Tr(\hat{A}\hat{\rho})$. Thus, one is cautioned that the Wigner dis-
tribution function should not be interpreted in a pointwise
fashion as probability density, but rather in a coarser sense
as probability per minimum uncertainty phase volume. However-
er, one should note that the Wigner distribution function
becomes the phase space distribution function in the corre-
spondence limit. For more information on these interesting
matters, one is directed to the work of Smith(42).

As with classical kinetic theory, one begins the devel-
opment with an equation describing the total temporal evolu-
tion of the state of a gas composed of N-molecules (i.e. the
von Neumann equation). Again, for convenience, consideration
will be limited to a single component. The N-molecule densi-
ty matrix, $\hat{\rho}^{(N)}$, is the quantal analog of the N-molecule
classical distribution function, $f^{(N)}$, and satisfies the
equation,

$$\frac{\partial\hat{\rho}^{(N)}}{\partial t} + (i\hbar)^{-1}[\hat{\rho}^{(N)},\hat{H}^{(N)}] = 0 \qquad (2.2-1)$$

Here, $\hat{H}^{(N)}$ is the N-molecule Hamiltonian operator and square
brackets denote the operator commutator. The expression
given is the quantal analog of the Liouville equation and
follows directly from the quantum mechanical equation of
motion (Schrodinger's equation) in the same way that the
Liouville equation follows from the classical equations of

motion (Hamilton's equations).

The reduced density matrix, $\hat{\rho}^{(s)}$, can be defined in terms of traces over degrees of freedom associated with the molecules labeled by $s+1, s+2, \ldots N$. This is in exact analogy to the integration over the degrees of freedom of molecules labeled by $s+1, s+2, \ldots N$ in the definition of $f^{(s)}$ (cf. Eq. (2.1-5)). Thus, the reduced density matrix is defined by the expression,

$$\hat{\rho}^{(s)} = \frac{1}{(N-s)!} \operatorname*{Tr}_{s+1} \ldots \operatorname*{Tr}_{N} \hat{\rho}^{(N)} \qquad (2.2-2)$$

where $\rho^{(N)}$ is normalized to (i.e. has trace equal to) $N!$ in analogy to the classical case. Taking the trace of Eq. (2.2-1) over the last $N-s$ molecules yields the quantum mechanical BBGKY hierarchy of which a general member has the form,

$$i\hbar \frac{\partial \hat{\rho}^{(s)}}{\partial t} + [\,,\hat{H}^{(s)}]\hat{\rho}^{(s)} = -\sum_{i=1}^{s} \operatorname*{Tr}_{s+1} [\,,\hat{V}_{i,s+1}]\hat{\rho}^{(s+1)} \qquad (2.2-3)$$

Here, the notation, $[\,,\hat{\Psi}]$, defines a linear superoperator (i.e. a tetradic operator) which when acting on an operator, $\hat{\Phi}$, results in the operator commutator, $[\hat{\Phi},\hat{\Psi}]$. Again, as in the classical case, it is assumed that the intermolecular interaction potential is pairwise additive.

$$\hat{V}^{(s)} = \frac{1}{2}\sum_{i=1}^{s}\sum_{j=1}^{s}\hat{V}_{ij} + \sum_{i=1}^{s}\hat{V}_{i}^{ext} \qquad (2.2-4)$$

Thus, the s-molecule Hamiltonian operator is,

$$\hat{H}^{(s)} = \sum_{i=}^{s} (-\frac{\hbar^2}{2M} \nabla^2 + \hat{K}_i^{int}) + \hat{V}^{(s)} \qquad (2.2-5)$$

Here, $\hat{K}_i^{int}$ is the kinetic energy operator appropriate to the internal degrees of freedom of the $i^{th}$ molecule.

In analogy to the classical development, the first member of the BBGKY hierarchy gives the total time rate of change of the singlet density matrix as a functional of the pair density matrix. This is explicit in the expression,

$$i\hbar\frac{\partial \hat{\rho}^{(1)}}{\partial t} + [ ,\hat{H}_1^{(1)}]\hat{\rho}^{(1)} = -\text{Tr}_2[ ,\hat{V}_{12}]\hat{\rho}^{(2)} \qquad (2.2-6)$$

If the gas is dilute, the second member of the quantum mechanical BBGKY hierarchy can be approximated by a two particle von Neumann equation near the interaction region (i.e. quantum mechanical Liouville equation). It has the form,

$$i\hbar\frac{\partial \hat{\rho}^{(2)}}{\partial t} + [ ,\hat{H}^{(2)}]\hat{\rho}^{(2)} = 0 \qquad (2.2-7)$$

As in the classical case, this expression can be formally integrated to obtain the result,

$$\hat{\rho}^{(2)}(t) = e^{(i/\hbar)(t-t_o')}[ ,\hat{H}^{(2)}]\hat{\rho}^{(2)}(t_o') \qquad (2.2-8)$$

In this expression, $\hat{\rho}^{(2)}$ is taken to be a linear operator and $e^{(i/\hbar)(t-t_o')}[\ ,\hat{H}^{(2)}]$ is a linear superoperator which can be written in terms of a direct product of linear operators. To do this, one considers the two particle Schrodinger equation,

$$-i\hbar\frac{\partial}{\partial t}|\Psi> + \hat{H}^{(2)}|\Psi> = 0 \qquad (2.2-9)$$

where $|\Psi>$ is the exact state vector for a two-molecule system. The formal solution of Eq. (2.2-9) is,

$$|\Psi(t)> = e^{-(i/\hbar)(t-t_o')\hat{H}^{(2)}}|\Psi(t_o)> \qquad (2.2-10)$$

Here, $e^{(i/\hbar)(t-t_o')\hat{H}^{(2)}}$ is a linear operator which acts on a state vector. The density matrix can be written in a dyadic form, $\sum_n p_n|\psi_n(t)><\psi_n(t)|$, where $|\psi_n(t)>$ is an eigenket of $\rho^{(2)}$ and is a solution of the pair time dependent Schrodinger equation. The scalar, $p_n$, is the real-valued eigenvalue of $\rho^{(2)}$ and can be given a physical interpretation as the probability of state $|\psi_n(t)>$. One obtains the following result from Eq. (2.2-8),

$$\hat{\rho}^{(2)}(t) = e^{-(i/\hbar)(t-t_o')\hat{H}^{(2)}}\hat{\rho}^{(2)}(t_o')e^{(i/\hbar)(t-t_o')\hat{H}^{(2)}} \qquad (2.2-11)$$

By comparison of Eq. (2.2-11) and Eq. (2.2-8), one is able to make the connection,

$$e^{(i/\hbar)(t-t_0')}[\ ,\hat{H}^{(2)}] =$$

$$e^{-(i/\hbar)(t-t_0')\hat{H}^{(2)}}\otimes e^{-(i/\hbar)(t-t_0')\hat{H}^{(2)}} \tag{2.2-12}$$

here the symbol, $\otimes$, implies a direct product of two linear operators to obtain a superoperator. If $\hat{A}$, $\hat{B}$, and $\hat{C}$ represent arbitrary linear operators, the action of the direct product superoperator, $\hat{A}\otimes\hat{B}$, on $\hat{C}$ is given by $\hat{A}\hat{C}\hat{B}^{\dagger}$.

Assuming Boltzmann statistics, the assumption of molecular chaos in its quantum mechanical form states that for $t_0''$ sufficiently remote in the past, $\bar{\rho}^{(2)}$ can be written in the factorized form,

$$\bar{\rho}^{(2)}(t_0'') = \bar{\rho}^{(1)}(t_0'')\bar{\rho}_2^{(1)}(t_0'') \tag{2.2-13}$$

In Eq. (2.2-13), $\bar{\rho}^{(1)}(t_0'')$ and $\bar{\rho}_2^{(1)}(t_0'')$ are singlet density matrices describing the state of molecule 1 and molecule 2 at a time, $t_0''$, respectively. Again, one notes that in a dilute gas regime $t_0 = t_0' = t_0''$ can be found so that conditions implied by Eqs. (2.2-8) and (2.2-13) are satisfied. One obtains the analog of Eq. (2.1-14) which is,

$$\bar{\rho}^{(2)}(t) =$$

$$e^{-(i/\hbar)(t-t_0)\hat{H}^{(2)}}\bar{\rho}^{(1)}(t_0)\bar{\rho}_2^{(1)}(t_0)e^{(i/\hbar)(t-t_0)\hat{H}^{(2)}} \tag{2.2-14}$$

The formal solution of Eq. (2.2-5), analogous to the classical result is

$$\bar{\rho}^{(1)}(t_o) =$$

$$e^{(i/\hbar)(t-t_o)\hat{H}_1^{(1)}} \bar{\rho}^{(1)}(t_o) e^{-(i/\hbar)(t-t_o)\hat{H}_1^{(1)}} + \qquad (2.2\text{-}15)$$

$$\int_t^{t_o} dt' e^{(i/\hbar)(t'-t)\hat{H}_1^{(1)}} \bar{J}(t') e^{-(i/\hbar)(t'-t)\hat{H}_1^{(1)}}$$

where $J(t')$ is the right hand side of Eq. (2.2-6). As before, the first term on the right arises from collisionless molecular motion and the last term contains the effect of interactions. Here, the superoperators have been written as direct products of operators by using the integral form of the free flight single molecule Schrodinger equation and the definition of $\otimes$. If one ignores the effects of collisions (for exactly the same reasons as in the classical case), it is possible to obtain the analog of Eq. (2.1-16),

$$\bar{\rho}^{(2)}(t) = \bar{u}^{(2)}(t_o)\bar{\rho}^{(1)}(t)\bar{\rho}^{(1)}(t)\bar{u}^{(2)}(t_o)^\dagger \qquad (2.2\text{-}16)$$

Again, one defines $\hat{H}_o^{(2)}$ as $\hat{H}^{(2)} - \hat{V}_1^{ext} - \hat{V}_2^{ext}$, and the operator $\bar{u}^{(2)}(t_o)$ is of the form(43),

$$\bar{u}^{(2)}(t_o) =$$

$$(2.2\text{-}17)$$

$$e^{(i/\hbar)(t_o-t)\tilde{H}_o^{(2)}} \, e^{-(i/\hbar)(t_o-t)(\hat{K}_1^{(1)}+\hat{K}_2^{(1)})}$$

and the superoperator analog of the classical operator defined by Eq. (2.1-17) is $\tilde{U}^{(2)}(t_o) \otimes \tilde{U}^{(2)}(t_o)$.

If $t_o$ is allowed to tend toward the remote past in $\tilde{U}^{(2)}(t_o)$ the Jauch-Moller(44) wave operator, $\hat{\Omega}^{(+)}$, results. In formal quantum mechanical scattering theory, the wave operator, $\hat{\Omega}^{(\pm)}$, is defined by,

$$\hat{\Omega}^{(\pm)} =$$

$$\lim_{t_o \to \mp\infty} e^{(i/\hbar)(t_o-t)\hat{H}_o^{(2)}} \, e^{-(i/\hbar)(t_o-t)(\hat{K}_1^{(1)}+\hat{K}_2^{(1)})} \quad (2.2\text{-}18)$$

If one substitutes Eq. (2.2-16) into Eq. (2.2-5) and takes the limit as $t_o$ tends toward $-\infty$, one obtains the expression,

$$i\hbar\frac{\partial\tilde{\rho}^{(1)}}{\partial t} + [\,,\tilde{H}_1^{(1)}]\tilde{\rho}^{(1)} = -\underset{2}{Tr}[\,,\tilde{V}_{12}]\hat{\Omega}^{(+)}\hat{\rho}^{(1)}\underset{2}{\hat{\rho}^{(1)}}\hat{\Omega}^{(+)\dagger} \quad (2.2\text{-}19)$$

This expression is the exact quantal analog of Eq. (2.1-19). When comparing Eq. (2.1-19) and Eq. (2.2-19) one notes that the action of $\hat{\Omega}^{(+)} \otimes \hat{\Omega}^{(+)}$ on $\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}$ is analogous to the action of $\underset{\approx}{S}^{(2)}$ on $f^{(1)}f_2^{(1)}$. The interpretation is complicated, however, by the fact that classical phase trajectories are nonexistent quantally.

The action of the Jauch-Moller wave operators can be summarized by the expressions,

$$\hat{\Omega}^{(\pm)}\chi = \psi^{(\pm)} \quad , \quad \hat{\Omega}^{(\pm)\dagger}\psi^{(\pm)} = \chi \qquad (2.2\text{-}20)$$

Here, $\chi$ denotes the noninteractive wavefunction and $\psi^{(\pm)}$ denotes a continuum scattering wavefunction. Physically, the wave operator, $\hat{\Omega}^{(+)}$, transforms the wavefunction, $\chi$, describing interactionless molecular motion (e.g. plane wave) to a continuum scattering wavefunction, $\psi^{(+)}$, with identical incoming boundary conditions. Similarly, $\hat{\Omega}^{(-)}$ transforms the interactionless wavefunction, $\chi$, to a continuum wavefunction, $\psi^{(-)}$, with identical outgoing boundary conditions. The adjoint operators reverse the sense of the transformations. (The plus and minus superscripts specify incoming and outgoing plane wave boundary conditions respectively.)

From Eqs. (2.2-20) it might first appear that the Jauch-Moller wave operators are unitary. However, this is not the case if the intermolecular potential admits bound states since,

$$\hat{\Omega}^{(\pm)\dagger}\phi = 0 \qquad (2.2\text{-}21)$$

when $\hat{\Omega}^{(\pm)\dagger}$ operates on a bound state wavefunction, $\phi$ (in the sense of a weak mathematical limit). By expanding any arbitrary function in a complete set of interactionless wavefunctions (i.e. $\{\chi\}$) and also in a complete set of interacting wavefunctions (i.e. $\{\psi\}$ and $\{\phi\}$) and by making use of Eqs.

(2.2-20) and (2.2-21), the wave operators are seen to satisfy the following expressions,

$$\Omega^{(\pm)\dagger}\Omega^{(\pm)} = \hat{1} \qquad (2.2\text{-}22)$$

$$\Omega^{(\pm)}\Omega^{(\pm)\dagger} = \hat{1} - \hat{\Lambda} \qquad (2.2\text{-}23)$$

where the operator, $\hat{\Lambda}$, is a projection operator for the bound states, $\{\phi\}$. The operator, $\hat{\Lambda}$, is known as the unitary defect of the wave operators. If the intermolecular potential is purely repulsive, there are no bound states, and thus $\hat{\Lambda} = 0$.

A complete dynamical description of collision processes is given quantally by matrix elements of the scattering operator (i.e. S-matrix). The S-matrix is defined in terms of the wave operators by the expression,

$$\hat{S} = \Omega^{(-)\dagger}\Omega^{(+)} \qquad (2.2\text{-}24)$$

The scattering operator transforms the incoming (precollisional) asymptotic wavefunction into the outgoing (postcollisional) asymptotic wavefunction. It follows from Eqs. (2.2-22) and (2.2-23) that the relationship,

$$\Omega^{(\pm)\dagger}\hat{\Lambda} = \hat{\Lambda}\Omega^{(\pm)} = 0 \qquad (2.2\text{-}25)$$

is valid. This insures the unitarity of the S-matrix. That is,

$$\hat{S}^{\dagger}\hat{S} = \hat{S}\hat{S}^{\dagger} = \hat{1} \qquad (2.2\text{-}26)$$

An S-matrix element between asymptotic states can be interpreted physically as the probability amplitude of a collisionally induced transition from an incident state written as a ket, to a final state written as a bra. The squared modulus of an S-matrix element is just the probability of such a transition. This interpretation makes it desirable to write the right hand side of Eq. (2.2-19) in terms of the scattering operator rather than the Jauch-Moller wave operators.

In order to carry out this program, it is necessary to use some results from the formal theory of scattering. The continuum wave functions $\psi^{(+)}$ and $\psi^{(-)}$ are exact solutions of the two molecule Schrodinger equation which can be written in the integrated form,

$$\psi_E^{(\pm)} = \chi_E + \hat{G}_E^{(\pm)} \hat{V}_{12} \psi_E^{(\pm)} \qquad (2.2-27)$$

which is known as the Lippman-Schwinger equation (28). Here is an asymptotic state with energy eigenvalue, E. The operator, $\hat{G}_E^{(\pm)}$, is the Green's function for noninteractive scattering and is defined by the expression,

$$\hat{G}_E^{(\pm)} = \lim_{\varepsilon \to 0} [E - \bar{K}_1^{(1)} - \bar{K}_2^{(1)} \pm i\varepsilon]^{-1} \qquad (2.2-28)$$

If one uses contour integration to evaluate a given matrix element of $\hat{G}_E^{(\pm)}$, it is clear that it can be written as a

Cauchy principal value integral plus an explicit essential singularity, in which case $\hat{G}_E^{(\pm)}$ takes the form,

$$\hat{G}_E^{(\pm)} = P([E-\hat{K}_1^{(1)}-\hat{K}_2^{(1)}]^{-1}) \mp \pi i \delta (E-\hat{K}_1^{(1)}-\hat{K}_2^{(1)}) \quad (2.2\text{-}29)$$

Using the definition of the Jauch-Mcller wave operators, and the Lippman-Schwinger equation one obtains an operator expression,

$$\hat{\Omega}^{(\pm)} = \hat{1} + \hat{G}_E^{(\pm)}\hat{V}_{12}\hat{\Omega}^{(\pm)} \quad (2.2\text{-}30)$$

which is appropriate to action on an asymptotic state with energy eigenvalue, E.

The transition operator (i.e. T-matrix) is defined by the operator equation,

$$\hat{T}^{(\pm)} = \hat{V}_{12}\hat{\Omega}^{(\pm)} \quad (2.2\text{-}31)$$

In order to express the quantal collision dynamics in a form which corresponds to the classical collision dynamics, it is necessary to find an explicit relationship between $\hat{T}$ and $\hat{S}$. With this objective in mind, one can easily establish the following identity,

$$e^{\frac{i}{\hbar}\tau\hat{K}^{(2)}} e^{-2\frac{i}{\hbar}\tau\hat{H}_o^{(2)}} e^{\frac{i}{\hbar}\tau\hat{K}^{(2)}} = 1 - \frac{i}{\hbar}\int_0^\tau d\tau' e^{\frac{i}{\hbar}\tau'\hat{K}^{(2)}} \quad (2.2\text{-}32)$$

$$[\tilde{V}_{12} e^{\frac{-2i\tau'}{\hbar} H_o^{(2)}} + e^{\frac{-2i\tau'}{\hbar} \tilde{H}_o^{(2)}} V_{12}] e^{\frac{i}{\hbar}\tau' \tilde{K}^{(2)}}$$

Here, $\tilde{K}^{(2)}$ is defined as $\tilde{K}^{(1)} + \tilde{K}_2^{(1)}$. It follows from Eqs. (2.2-18), (2.2-24), and (2.2-32) that the S-matrix can be written as,

$$\tilde{S} =$$

$$\tilde{1} - \frac{i}{\hbar} \int_0^\infty d\tau e^{\frac{i}{\hbar}\tau K^{(2)}} [V_{12} e^{-2\frac{i}{\hbar}\tau H_o^{(2)}} + e^{-2\frac{i}{\hbar}iH_o^{(2)}} V_{12}] e^{\frac{i}{\hbar}\tau K^{(2)}} \qquad (2.2\text{-}33)$$

An infinite series expression for $\hat{S}$ is obtained by successive substitution of Eq. (2.2-32) into Eq. (2.2-33) followed by evaluation of the integrals. After lengthy manipulation, the following result is obtained,

$$\hat{S} = \hat{1} - 2\pi i \delta(E) \hat{V}_{12} \sum_{j=0}^\infty (\hat{G}_E^{(\pm)} \hat{V}_{12}) \qquad (2.2\text{-}34)$$

The operator series appearing on the right hand side is immediately recognizable as the well-known Born expansion of the T-matrix which is easily obtained from Eqs. (2.2-30) and (2.2-31) by iterative substitution. Thus, the S-matrix is related to the forward scattering T-matrix by the identity,

$$\hat{S} = \hat{1} - 2\pi i \delta(E) \hat{T} \qquad (2.2\text{-}35)$$

Hereafter, $\hat{T}$ will refer to the forward scattering T-matrix,

$\hat{T}^{(+)}$, and the notation $\delta(E)T$ is explicity defined by the expression,

$$\langle m|\delta(E)\hat{T}|n\rangle = \delta(E_n - E_m)\langle m|\hat{T}|n\rangle \qquad (2.2-36)$$

($E_n$ and $E_m$ are total energies of states $|m\rangle$ and $|n\rangle$). The scattering operator has nonzero matrix elements only between states which have the same constants of motion (i.e. $\hat{S}$ is energy diagonal, total angular momentum diagonal, etc.). An expression for the T-matrix in terms of the S-matrix can be obtained by defining operators, $\overline{S}$ and $\overline{T}$, as follows,

$$\overline{S} = \int dE\hat{S} + \hat{T}_{off}, \quad \overline{T} = \int dE\hat{T}. \qquad (2.2-37)$$

Here, $\hat{T}_{off}$ is comprised of off-shell (i.e., nondiagonal in total energy) T-matrix elements, the integral is taken over all possible energy eigenvalues, and the inverse relations for $\hat{S}$ and $\hat{T}$ are,

$$\hat{S} = \delta(E)\overline{S}, \quad \hat{T} = \delta(E)\overline{T}. \qquad (2.2-38)$$

From these definitions one easily obtains,

$$\hat{T} = \frac{i}{2\pi}(\overline{S} - \overline{T}) \qquad (2.2-39)$$

One should note that $\hat{T}$, $\overline{S}$, and $\overline{T}$ have units of energy and that $\hat{S}$ and $\hat{T}$ are dimensionless.

If one combines Eq. (2.2-39) and Eq. (2.2-30), one obtains the result,

$$\hat{\Omega}^{(+)} = \frac{i}{2\pi}\hat{P}([E-\hat{K}_1^{(1)}-\hat{K}_2^{(1)}]^{-1})(\bar{S}-\bar{I}) + \frac{1}{2}(\hat{S}+\hat{I}) \qquad (2.2\text{-}40)$$

Here, E is the energy eigenvalue of the asymptotic state acted on by $\bar{S}-\bar{I}$. Using the identities given in Eqs. (2.2-39) and (2.2-40) allows one to simplify Eq. (2.2-19) in terms of the scattering operator. This yields the following expression,

$$\frac{\partial \hat{\rho}^{(1)}}{\partial t} + (i\hbar)^{-1}[\ ,\hat{H}_1^{(1)}]\hat{\rho}^{(1)} = \frac{1}{\hbar}\text{Tr}_2\{\frac{i}{2\pi}\hat{P}_E(\bar{S}-\bar{I})\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}(\bar{S}^\dagger+\bar{I}) -$$

$$\frac{i}{2\pi}(\bar{S}-\bar{I})\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}(\bar{S}^\dagger-\bar{I})\hat{P}_E^\dagger + \frac{1}{2}(\bar{S}-\bar{I})\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}(\bar{S}^\dagger+\bar{I}) + \qquad (2.2\text{-}41)$$

$$\frac{1}{2}(\hat{S}+\hat{I})\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}(\bar{S}^\dagger-\bar{I})\}$$

where $\hat{P}_E$ is the self-adjoint operator $P([E-K_1^{(1)}-K_2^{(1)}]^{-1})$.

In order to simplify Eq. (2.2-41) further, one notes that the density matrix appropriate to the description of a single dilute gas molecule can be expressed in terms of stationary states as follows,

$$\hat{\rho}^{(1)} = \sum_{nn'} a_{nn'}(t-t_0)|g_n\rangle\langle g_{n'}|e^{-(i/\hbar)(E_n-E_{n'})(t-t_0)} \qquad (2.2\text{-}42)$$

One should note that $\hat{\rho}^{(1)}$ satisfies the lowest order equation of the BBGKY hierarchy and that the state vector, $|g_n\rangle$ is a solution of the single molecule time independent Schrodinger equation. Here $t_0$ is an arbitrary time origin. For a dilute

gas, the assumption of molecular chaos implies that the sin-
glet density matrix is taken as temporally constant on the
collisional time scale. Thus, the quantity, $a_{nn'}(t-t_o)$, can
be replaced in Eq. (2.2-42) by its collisional time scale av-
erage, $\bar{a}_{nn'}$. The resulting expression is averaged over an
interval, $\tau_2 - \tau_1$, which is long compared to the mean duration
of a collision $\tau_{coll}$, but is short compared to the mean in-
terval between collisions, $\tau_\lambda$, that is to say,

$$\bar{\rho}^{(1)} = \frac{1}{\tau_2 - \tau_1} \int_{\tau_1}^{\tau_2} dt \sum_{nn'} \bar{a}_{nn'} |g_n><g_{n'}| e^{-(i/\hbar)(E_n - E_{n'})(t-t_o)}$$

$$\begin{array}{l} \tau_\lambda \gg \\ \tau_{coll} \ll \end{array} \Big\{ \tau_2 - \tau_1 \qquad\qquad (2.2\text{-}43)$$

From this it follows that $\bar{\rho}^{(1)}$ is approximately proportional
to $\delta(E_n - E_{n'})$ (i.e. it is approximately energy diagonal).

Ignoring energy nondiagonalities, one obtains the
result,

$$\frac{\partial\bar{\rho}^{(1)}}{\partial t} + (i\hbar)^{-1}[\ ,\bar{H}_1^{(1)}]\bar{\rho}^{(1)} = \frac{1}{2\hbar}\mathrm{Tr}_2[((\bar{S}-\bar{I})\otimes(\hat{S}+\hat{I}) +$$

$$(\hat{S}+\hat{I})\otimes(\bar{S}-\bar{I}))\bar{\rho}^{(1)}\bar{\rho}_2^{(1)}] \qquad\qquad (2.2\text{-}44)$$

The first two terms cancel each other since application of
approximate energy diagonality gives that $\hat{P}_E(\bar{S}-\bar{I})\bar{\rho}^{(1)}\bar{\rho}_2^{(1)}(S^\dagger-\bar{I})$
is equivalent to $(\bar{S}-\bar{I})\bar{\rho}^{(1)}\bar{\rho}_2^{(1)}(S^\dagger-\bar{I})\hat{P}_E$ in Eq. (2.2-41). This
expression can now be written in terms of a collision

superoperator in analogy to Eq. (2.1-46),

$$\frac{\partial \hat{\rho}^{(1)}}{\partial t} + (i\hbar)^{-1} [\hat{\rho}^{(1)}, \hat{H}_1^{(1)}] = \underset{2}{Tr} \bar{\hat{\Theta}} \hat{\rho}^{(1)} \hat{\rho}_2^{(1)} \qquad (2.2-45)$$

The collision superoperator is of the form,

$$\bar{\hat{\Theta}} = \frac{1}{\hbar}(\bar{S}\otimes\hat{S} - \bar{T}\otimes\hat{T}) \qquad (2.2-46)$$

Due to the energy diagonality of $\hat{\rho}^{(1)}$, the bar and tilde are interchangeable. Thus the simple form of $\bar{\hat{\Theta}}$ follows directly from Eq. (3.2-44). The structure of the quantal collision superoperator bears an obvious similarity to the structure of the classical collision kernel given in Eq. (2.1-47).

Before proceeding to the final stages of the derivation of the Waldmann-Snider equation, it is desirable to introduce a "double bra-ket" notation, $|n[n']^\dagger\rangle\rangle$, which denotes a direct product basis appropriate to a Hilbert space in which the usual linear self-adjoint operators of quantum mechanics appear as vectors. A matrix element in this representation appears as a tetradic form (superoperator) in the usual formulation of quantum mechanics. For example, if superoperator, $\hat{\tilde{A}}$, has a direct product form, $\hat{B}\otimes\hat{C}$, it follows that a superoperator matrix element, $\langle\langle m[m']^\dagger|\hat{\tilde{A}}|n[n']^\dagger\rangle\rangle$, equals a product of ordinary matrix elements, that is $\langle m|\hat{B}|n\rangle\langle n'|\hat{C}^\dagger|m'\rangle$. The lower case letters, m and n, are used here as collective symbols for the appropriate quantum num-

bers.

Continuing with the derivation, one next expresses Eq. (2.2-45) in a momentum representation. If $|p_j^{\sigma_j}\rangle$ is a state appropriate to the $j^{th}$ molecule with definite momentum, $p_j$, and definite internal state given by a set of quantum numbers, $\sigma_j$, Eq. (2.2-45) can be written out explicitly as follows,

$$\frac{\partial}{\partial t}\langle {}^{\sigma_1}_{p_1}|\;\bar{\rho}^{(1)}|\;{}^{\sigma_1'}_{p_1'}\rangle + (i\hbar)^{-1}\langle {}^{\sigma_1}_{p_1}|[\bar{\rho}^{(1)},\bar{K}^{(1)}]|\;{}^{\sigma_1'}_{p_1'}\rangle =$$

$$\sum_{\sigma_2}\int dp_2 \sum_{\substack{\sigma_1'\sigma_2'\\ \sigma_1'\sigma_2'}}\int dp_1'\,dp_2'\,dp_1\,dp_2 \ll {}^{\sigma_1\sigma_2}_{p_1 p_2}\left({}^{\sigma_1'\sigma_2'}_{p_1'p_2'}\right)^{\dagger}\overline{|\bar{\rho}|}\;{}^{\sigma_1\sigma_2}_{p_1 p_2}\left({}^{\sigma_1'\sigma_2'}_{p_1'p_2'}\right)^{\dagger}\gg \quad (2.2-47)$$

$$\langle {}^{\sigma_1}_{p_1}|\;\bar{\rho}^{(1)}|\;{}^{\sigma_1'}_{p_1'}\rangle\langle {}^{\sigma_2}_{p_2}|\;\bar{\rho}^{(1)}|\;{}^{\sigma_2'}_{p_2'}\rangle$$

Now one applies Wigner's Fourier transform(41) which exchanges one of the momentum variables (indices) of a matrix element for a coordinate variable (i.e., transforms to a phase space representation). For a matrix element of an arbitrary operator, $\hat{A}$, in a momentum representation,

$$\langle\sigma|W\{\hat{A}|r,p\}|\sigma'\rangle = 8\int dp'\langle {}^{\sigma}_{p+p'}|\hat{A}|{}^{\sigma'}_{p-p'}\rangle e^{(2i/\hbar)p'\cdot r} \quad (2.2-48)$$

Here, W denotes the Wigner transform, that is, $W\{\hat{A}|r,p\}$ denotes the transformed image of operator, $\hat{A}$. The inverse transform is,

$$\langle{}^{\sigma}_{\underline{p}}|\hat{A}|{}^{\sigma'}_{\underline{p}'}\rangle = \frac{1}{h^3} \int d\underline{r} \langle\sigma|W\{\hat{A}|\underline{r}, \tfrac{1}{2}(\underline{p}+\underline{p}')\}|\sigma'\rangle e^{-(i/h)\underline{r}\cdot(\underline{p}-\underline{p}')} \qquad (2.2\text{-}49)$$

The image, $\hat{W}\{\hat{A}|\cdots\}$, is a function of the classical phase variables, $\underline{r}$ and $\underline{p}$, in the translational degrees of freedom but remains a quantum mechanical operator in the internal degrees of freedom. All quantum mechanical operators can be transformed in this way. For operators that correspond to a simple function of coordinates or momenta, but not both together, the image function-operator, $W\{\hat{A}|\cdots\}$, is identical to the classical form. For operators which are functions of both position and momentum, the image function-operator is a power series in $\hbar$, with the lowest term having the classical form.

If $\hat{A}$ is the singlet density matrix, then $\hat{W}\{\hat{A}|\cdots\}$ is a singlet Wigner phase space distribution function in the translational degrees of freedom, but remains a singlet density matrix in the internal degrees of freedom. The Wigner distribution function is defined as follows,

$$f^{(1)}_{\sigma\sigma'}(\underline{r},\underline{p},t) = \frac{1}{h^3}\langle\sigma|W\{\hat{\rho}^{(1)}|\underline{r},\underline{p},t\}|\sigma'\rangle \qquad (2.2\text{-}50)$$

where the factor, $h^{-3}$, is included to give $f^{(1)}_{\sigma\sigma'}(\underline{r},\underline{p},t)$ units of probability per phase space volume. Using this expression and its inverse in Eq. (2.2-44) yields the result,

$$\frac{\partial f^{(1)}_{\sigma_1 \sigma'_1}}{\partial t}(\underline{r}_1,\underline{p}_1,t) + \sum_{n=0}^{\infty} \frac{(i\hbar)^{2n}}{4^n(2n+1)!}\{f^{(1)}_{\sigma_1\sigma'_1}(\underline{r}_1,\underline{p}_1,t),H^{tr}_1\}^{(2n+1)} +$$

$$(i\hbar)^{-1}\sum_{n_1}[f^{(1)}_{\sigma_1 n_1}(\underline{r}_1,\underline{p}_1,t)H^{int}_{n_1\sigma'_1} - H^{int}_{\sigma_1 n_1}f^{(1)}_{n_1\sigma'_1}(\underline{r}_1,\underline{p}_1,t)] =$$

$$\frac{8}{h^3}\sum_{\sigma_2}\int d\underline{p}_2 \sum_{\substack{\sigma'_1\sigma'_2\\\sigma''_1\sigma''_2}} \int d\underline{p}'_1 d\underline{p}''_2 d\underline{p}''_1 d\underline{p}''_2 \int d\underline{p}'_1 e^{(2i/\hbar)\underline{p}'_1\cdot\underline{r}_1}\int d\underline{r}'_1 e^{-(i/\hbar)\underline{r}'_1\cdot(\underline{p}_1-\underline{p}'_1)}$$

$$\int d\underline{r}'_2 e^{-(i/\hbar)\underline{r}'_2\cdot(\underline{p}_2-\underline{p}'_2)} \ll \begin{matrix}\sigma_1 & \sigma_2\\\underline{p}_1+\underline{p}'_1 & \underline{p}_2\end{matrix}\left(\begin{matrix}\sigma'_1 & \sigma_2\\\underline{p}_1-\underline{p}'_1 & \underline{p}_2\end{matrix}\right)^\dagger\overline{|\Theta|}\begin{matrix}\sigma''_1\sigma''_2\\\underline{p}''_1\underline{p}''_2\end{matrix}\left(\begin{matrix}\sigma''_1\sigma''_2\\\underline{p}''_1\underline{p}''_2\end{matrix}\right)^\dagger \gg$$

$$f^{(1)}_{\sigma''_1\sigma'_1}(\underline{r}'_1,\tfrac{1}{2}(\underline{p}''_1+\underline{p}'_1),t)f^{(1)}_{\sigma''_2\sigma'_2}(\underline{r}'_2,\tfrac{1}{2}(\underline{p}''_2+\underline{p}'_2),t) \qquad (2.2-51)$$

Here $H^{tr}_1$ refers to the classical singlet Hamiltonian function for the translational degrees of freedom and $H^{int}_{\sigma_1 n_1}$ is a matrix element of the quantal singlet Hamiltonian operator for the internal degrees of freedom. The notation defined by the expression,

$$\{A,B\}^{(n)} = \sum_{j=0}^{n}(-1)^j\binom{n}{j}[\frac{\partial^{n-j}}{\partial\underline{p}^{n-j}}(\frac{\partial^j}{\partial\underline{r}^j}B)]\underset{\hbar}{\odot}[\frac{\partial^{n-j}}{\partial\underline{r}^{n-j}}(\frac{\partial^j}{\partial\underline{p}^j}A)] \quad (2.2-52)$$

occurs in the Wigner transform of the commutator bracket, [A,B], and may be thought of as an extension of the definition of the Poisson bracket to order, n.

As in the classical development of Boltzmann's equation, one assumes that there is very little error introduced by re-

placing $f^{(1)}_{\sigma_1\sigma'_1}(\underline{r}'_1,\underline{p}'_1,t)\,f^{(1)}_{\sigma_2\sigma'_2}(\underline{r}'_2,\underline{p}'_2,t)$ with the product,
$f_{\sigma_1\sigma'_1}(\underline{r}_1,\ \underline{p}'_1,t)\,f_{\sigma_2\sigma'_2}(\underline{r}_1,\underline{p}'_2,t)$. One can immediately integrate
over $\underline{r}'_1$, $\underline{r}'_2$, $\underline{p}'_1$, and $\underline{p}'_2$. Making use of the resulting delta
functions, one obtains the following result,

$$\frac{\partial f^{(1)}_{\sigma_1\sigma'_1}}{\partial t}(\underline{r}_1,\underline{p}_1,t) + \{f^{(1)}_{\sigma_1\sigma'_1}(\underline{r}_1,\underline{p}_1,t),H^{tr}_1\} +$$

$$(i\hbar)^{-1}\sum_{\eta_1}[f^{(1)}_{\sigma_1\eta_1}(\underline{r}_1,\underline{p}_1,t)H^{int}_{\eta_1\sigma'_1} - H^{int}_{\sigma_1\eta_1}f^{(1)}_{\eta_1\sigma'_1}(\underline{r}_1,\underline{p}_1,t)] =$$

$$8h^3\sum_{\sigma_2}\int d\underline{p}_2\sum_{\substack{\sigma'_1\sigma'_2\\ \sigma'_1\sigma'_2}}\int\int d\underline{p}'_1 d\underline{p}'_2\int d\underline{p}'_1 e^{(2i/\hbar)(\underline{p}'_1\cdot\underline{r}_1)} \qquad (2.2\text{-}53)$$

$$\ll {}^{\sigma_1}_{\underline{p}_1+\underline{p}'_1}\,{}^{\sigma_2}_{\underline{p}_2}\left({}^{\sigma'_1}_{\underline{p}_1-\underline{p}'_1}\,{}^{\sigma_2}_{\underline{p}_2}\right)^{\dagger}\boxed{\Theta}\,{}^{\sigma'_1\sigma_2}_{\underline{p}'_1\underline{p}'_2}\left({}^{\sigma'_1\sigma'_2}_{\underline{p}'_1\underline{p}'_2}\right)^{\dagger}\gg$$

$$f^{(1)}_{\sigma_1\sigma'_1}(\underline{r}_1,\underline{p}'_1,t)\,f^{(1)}_{\sigma_2\sigma'_2}(\underline{r}_1,\underline{p}'_2,t)$$

Here, terms involving $\{\ ,\ \}^{(n)}$ for $n>1$ have been ignored.
This is rigorous for the kinetic contribution to $H^{tr}_1$ because
the translational kinetic energy has the explicit form, $p^2_1/2M$,
which gives rise only to the usual Poisson bracket. It
is only approximate for the external potential energy contri-
bution to $H^{tr}_1$. However, it should be a very good approxima-
tion because on a molecular scale external potentials can be
expected to have a very slow spatial variation.

Any binary collision process must conserve the overall
momentum, which means that the scattering operator is
rigorously diagonal in this quantity. Applying this

conservation property to the definition of the collision superoperator results in the expression,

$$<<\begin{matrix}\sigma_1\sigma_2\\\underline{p}_1\underline{p}_2\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\\underline{p}_1'\underline{p}_2'\end{pmatrix}^\dagger|\bar{\bar{\Theta}}|\begin{matrix}\sigma_{\bar{1}}\sigma_2\\\underline{p}_{\bar{1}}\underline{p}_2\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\\underline{p}_1'\underline{p}_2'\end{pmatrix}^\dagger>> = \delta(\underline{p}_1+\underline{p}_2-\underline{p}_{\bar{1}}-\underline{p}_{\bar{2}})$$

$$\delta(\underline{p}_1'+\underline{p}_2'-\underline{p}_{\bar{1}}'-\underline{p}_{\bar{2}}')<<\begin{matrix}\sigma_1\sigma_2\\\underline{p}_{12}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\\underline{p}_{12}'\end{pmatrix}^\dagger|\bar{\bar{\Theta}}|\begin{matrix}\sigma_{\bar{1}}\sigma_2\\\underline{p}_{\bar{1}2}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\\underline{p}_{\bar{1}2}'\end{pmatrix}^\dagger>>$$

$$(2.2-54)$$

Here, the notation $\underline{p}_{ij}$ (and $\underline{p}_{ij}'$) denotes the relative momentum between the $i^{th}$ and $j^{th}$ molecules. That is,

$$\underline{p}_{ij} = \frac{\mu_{ij}}{M_j}\underline{p}_j - \frac{\mu_{ij}}{M_j}\underline{p}_i \qquad (2.2-55)$$

where $M_i$ and $M_j$ are the masses of molecule i and molecule j and $\mu_{ij}$ is the reduced mass of the pair, $M_iM_j/(M_i+M_j)$. Substitution of Eq. (2.2-54) into Eq. (2.2-53) and integration over $\underline{p}_1'$ and $\underline{p}_2$ yields the Waldmann-Snider equation[26,27],

$$\frac{\partial f^{(1)}}{\partial t}_{\sigma_1\sigma_1'}(\underline{r},\underline{p}_1,t) + \{f^{(1)}_{\sigma_1\sigma_1'}(\underline{r},\underline{p}_1,t),H_1^{tr}\} +$$

$$(i\hbar)^{-1}\sum_{\eta_1}[f^{(1)}_{\sigma_1\eta_1}(\underline{r},\underline{p}_1,t)H^{int}_{\eta_1\sigma_1'} - H^{int}_{\sigma_1\eta_1}f^{(1)}_{\eta_1\sigma_1'}(\underline{r},\underline{p}_1,t)] =$$

$$h^3\sum_{\substack{\sigma_2'\\\sigma_2}}\int d\underline{p}_2\sum_{\substack{\sigma_{\bar{1}}'\sigma_{\bar{2}}\\\sigma_{\bar{1}}'\sigma_{\bar{2}}'}}\int d\underline{p}_{\bar{1}}\int d\underline{p}_{\bar{2}}\delta_{\sigma_2\sigma_2'}<<\begin{matrix}\sigma_1\sigma_2'\\\underline{p}_{12}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2\\\underline{p}_{12}\end{pmatrix}^\dagger|\bar{\bar{\Theta}}|\begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\\underline{p}_{\bar{1}\bar{2}}\end{matrix}\begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\\underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^\dagger>>$$

$$\delta(\underline{p}_1+\underline{p}_2-\underline{p}_{\bar{1}}-\underline{p}_{\bar{2}})f^{(1)}_{\sigma_{\bar{1}}\sigma_{\bar{1}}'}(\underline{r},\underline{p}_{\bar{1}},t)f^{(1)}_{\sigma_{\bar{2}}\sigma_{\bar{2}}'}(\underline{r},\underline{p}_{\bar{2}},t) \qquad (2.2-56)$$

which is the quantum mechanical analog of the classical
Boltzmann equation.

It is possible to write Eq. (2.2-56) in a form which
very closely resembles the classical expression. To do this,
one first defines the superoperator, $\hat{\bar{\theta}}$,

$$\hat{\bar{\theta}} = \frac{1}{h}(\tilde{S} \otimes \tilde{S}^{\dagger} - \tilde{I} \otimes \tilde{I}) \qquad (2.2\text{-}57)$$

Use of Eq. (2.2-37) allows the tetradic matrix element of $\bar{\bar{\theta}}$
appearing in Eq. (2.2-56) to be written in terms of $\hat{\bar{\theta}}$,

$$<<\begin{matrix}\sigma_1\sigma_2\\ \underline{p}_{12}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\ \underline{p}_{12}\end{pmatrix}^{\dagger}\; |\bar{\bar{\theta}}|\; \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix}\begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^{\dagger}>> =$$

$$\int_0^{\infty}dE<<\begin{matrix}\sigma_1\\ p(E)\hat{\bar{p}}_{12}\end{matrix}\begin{matrix}\sigma_2\\ \underline{p}_{12}\end{matrix}\begin{matrix}\sigma_1'\sigma_2'\end{matrix}^{\dagger}\; |\hat{\bar{\theta}}|\; \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix}\begin{matrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix}^{\dagger}>> \qquad (2.2\text{-}58)$$

where $\hat{\bar{p}}_{12}$ is a unit vector parallel to $\underline{p}_{12}$ and $p(E)$ equals
$[2\mu_{12}(E-E_{\sigma_1\sigma_2}^{(int)})]^{\frac{1}{2}}$. ($E_{\sigma_1\sigma_2}^{(int)}$ denotes the energy of the inter-
nal quantum states, $\sigma_1$ and $\sigma_2$.) The integral over E can be
changed to an integral over p as follows,

$$<<\begin{matrix}\sigma_1\sigma_2\\ \underline{p}_{12}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\ \underline{p}_{12}\end{pmatrix}^{\dagger}\; |\bar{\bar{\theta}}|\; \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix}\begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^{\dagger}>> =$$

$$(2.2\text{-}59)$$

$$\int_0^\infty dp \frac{p}{\mu_{12}} \ll \begin{matrix} \sigma_1 \sigma_2 \\ p\bar{p}_{12} \end{matrix} \begin{pmatrix} \sigma_1' \sigma_2' \\ p_{12} \end{pmatrix}^\dagger |\hat{\theta}| \begin{matrix} \sigma_1' \sigma_2' \\ p_{\hat{1}\hat{2}} \end{matrix} \begin{pmatrix} \sigma_1' \sigma_2' \\ p_{\hat{1}\hat{2}} \end{pmatrix}^\dagger \gg$$

where use has been made of the fact that $dE/dp$ is $p/\mu_{12}$.

It is possible to introduce an integration over definite impact parameter into Eq. (2.2-59) by means of the standard partial wave expansion. ($j_\ell$ denotes a spherical Bessel function and $Y_\ell^m$ a spherical harmonic),

$$e^{\frac{i}{\hbar}\underline{p}\cdot\underline{r}} = 4\pi \sum_{\ell=0}^\infty \sum_{m=-\ell}^\ell i^\ell j_\ell(\frac{pr}{\hbar}) Y_\ell^m(\hat{r}) Y_\ell^{m*}(\hat{p}) \qquad (2.2\text{-}60)$$

which gives,

$$|\underline{p}\rangle = \sum_{\ell=0}^\infty \sum_{m=-\ell}^\ell i^\ell p^{-1} Y_\ell^{m*}(\hat{p}) |p\ell m\rangle \qquad (2.2\text{-}61)$$

If the impact parameter, b, is defined as,

$$b = \frac{\hbar[\ell(\ell+1)]^{\frac{1}{2}}}{p} \qquad (2.2\text{-}62)$$

then $|p\ell m\rangle$ is related to $|b\ell m\rangle$ via the expression (note that $|db/dp| = \hbar[\ell(\ell+1)]^{\frac{1}{2}}/p^2$),

$$|p\ell m\rangle = \frac{[\hbar^2 \ell(\ell+1)]^{\frac{1}{2}}}{p} |b\ell m\rangle \qquad (2.2\text{-}63)$$

This gives the result,

$$|\underline{p}\rangle = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^{\ell} \frac{[\hbar^2 \ell(\ell+1)]^{\frac{1}{2}}}{p^2} Y^{m*} (\hat{p}) |b\ell m\rangle \qquad (2.2\text{-}64)$$

If one substitutes Eq. (2.2-64) into Eq. (2.2-59), regards p as a function of b and $\ell$ (__i.e.__ $p = p_{b\ell} = b^{-1}\hbar[\ell(\ell+1)]^{\frac{1}{2}}$), and changes the integration variable from $p$ to b, one obtains,

$$\langle\langle \begin{matrix}\sigma_1\sigma_2\\ \underline{p}_{12}\end{matrix} \begin{pmatrix}\sigma_1'\sigma_2'\\ \underline{p}_{12}\end{pmatrix}^{\dagger} |\bar{\bar{\theta}}| \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix} \begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^{\dagger}\rangle\rangle = \int_0^{\infty} b db \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell}$$

$$\qquad (2.2\text{-}65)$$

$$(\frac{p_{b\ell}}{\mu_{12}}) \frac{i^{-\ell} p_{b\ell}}{[\hbar^2 \ell(\ell+1)]^{3/4}} Y_{\ell}^{m}(\hat{p}_{12}) \langle\langle \begin{matrix}\sigma_1\sigma_2\\ b\ell m\end{matrix} \begin{pmatrix}\sigma_1'\sigma_2'\\ \underline{p}_{12}\end{pmatrix}^{\dagger} |\hat{\theta}| \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix} \begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^{\dagger}\rangle\rangle$$

An expression for the inner product of a state of definite impact parameter and definite linear momentum is easily obtained from Eq. (2.2-64),

$$\langle b\ell m|\underline{p}'\rangle = \frac{i^{\ell}[\hbar^2 \ell(\ell+1)]^{\frac{1}{2}}}{p'^2} Y_{\ell}^{m*}(\hat{p}') \delta(b - \frac{[\hbar^2 \ell(\ell+1)]^{\frac{1}{2}}}{p'}) \qquad (2.2\text{-}66)$$

Using closure and Eq. (2.2-66), the tetradic matrix element appearing on the right hand side of Eq. (2.2-65) is rewritten entirely in a momentum representation,

$$\langle\langle \begin{matrix}\sigma_1\sigma_2\\ \underline{p}_{12}\end{matrix} \begin{pmatrix}\sigma_1'\sigma_2'\\ \underline{p}_{12}\end{pmatrix}^{\dagger} |\bar{\bar{\theta}}| \begin{matrix}\sigma_{\bar{1}}\sigma_{\bar{2}}\\ \underline{p}_{\bar{1}\bar{2}}\end{matrix} \begin{pmatrix}\sigma_{\bar{1}}'\sigma_{\bar{2}}'\\ \underline{p}_{\bar{1}\bar{2}}\end{pmatrix}^{\dagger}\rangle\rangle = \int_0^{\infty} b db \sum_{\ell=0}^{\infty} (\frac{p_{b\ell}}{\mu_{12}}) \frac{p_{b\ell}^3}{h^2 \ell(\ell+1)}$$

$$\qquad (2.2\text{-}67)$$

$$\frac{(2\ell+1)}{4\pi}\int d\hat{p}_{b\ell}\, P_\ell(\hat{p}_{12}\cdot\hat{p}_{b\ell}) \, \ll \begin{matrix}\sigma_1\sigma_2'\\p_{b\ell}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2\\p_{12}\end{pmatrix}^\dagger |\hat{\theta}| \begin{matrix}\sigma_1'\sigma_2\\p_{\bar{1}\bar{2}}\end{matrix}\begin{pmatrix}\sigma_1'\sigma_2'\\p_{\bar{1}\bar{2}}\end{pmatrix}^\dagger \gg$$

Here, use has been made of the identity,

$$\sum_{m=-\ell}^{\ell} Y_\ell^m(\hat{p}_{12})\, Y_\ell^{m*}(\hat{p}_{b\ell}) = \frac{2\ell+1}{4\pi}\, P_\ell(\hat{p}_{12}\cdot\hat{p}_{b\ell}) \qquad (2.2\text{-}68)$$

where $P_\ell(\cdots)$ is the $\ell$ order Legendre polynomial, and $p_{b\ell}$ is $p_{b\ell}\hat{p}_{b\ell}$.

The tetradic matrix element can be expressed in terms of a phase space representation by means of Eq. (2.2-48).

$$\ll \begin{matrix}\sigma_1\sigma_2\\p_b\end{matrix}\begin{matrix}\sigma_1'\sigma_2'\\p_{12}\end{matrix}^\dagger |\hat{\theta}| \begin{matrix}\sigma_1\sigma_2\\p_{\bar{1}\bar{2}}\end{matrix}\begin{matrix}\sigma_1'\sigma_2'\\p_{\bar{1}\bar{2}}\end{matrix}^\dagger \gg = \frac{1}{h^7}\int d\underline{r}_1'\, d\underline{r}_2'$$

$$\ll \sigma_1\sigma_2(\sigma_1'\sigma_2')^\dagger | W^2\{h\hat{\theta}|\underline{r}_1',\tfrac{1}{2}(p_{b\ell}+p_{\bar{1}\bar{2}})|\underline{r}_2',\tfrac{1}{2}(p_{12}+p_{\bar{1}\bar{2}})\}$$

$$|\sigma_1'\sigma_2(\sigma_1'\sigma_2')^\dagger \gg e^{-\frac{i}{\hbar}\underline{r}_1'\cdot(p_{b\ell}-p_{\bar{1}\bar{2}})} e^{-\frac{i}{\hbar}\underline{r}_2'\cdot(p_{\bar{1}\bar{2}}-p_{12})} \qquad (2.2\text{-}69)$$

Here, $W^2\{\cdots|\cdots|\cdots\}$ is an extension of the earlier notation (cf. Eq. (2.2-48)) and denotes the "squared" Wigner transform which is defined for a general superoperator, $\hat{\hat{G}}$, as follows,

$$W^2\{\hat{\hat{G}}|\underline{r}_1,p_1|\underline{r}_2,p_2\} = 64\int dp_1' \int dp_2' \ll p_1 + p_1'\,(p_2+p_2')^\dagger|\hat{\hat{G}}|$$

$$p_1 - p_1'\,(p_2-p_2')^\dagger \gg e^{(2i/\hbar)(p_1'\cdot\underline{r}_1+p_2'\cdot\underline{r}_2)} \qquad (2.2\text{-}70)$$

It is consistent with the previous localization assumption

(energy diagonality) to replace both $\underline{r}_1'$ and $\underline{r}_2'$ in $W^2\{h\hat{\hat{\Theta}}|\cdots|\cdots\}$ with an asymptotic position, $\underline{r}_b$, which is exclusively a function of the impact parameter. This procedure allows one to evaluate the integrals over $\underline{r}_1'$ and $\underline{r}_2'$,

$$\ll {}_{\underline{p}_{b\ell}}^{\sigma_1\sigma_2} \begin{pmatrix} \sigma_1'\sigma_2' \\ \underline{p}_{12} \end{pmatrix}^{\dagger} |\hat{\Theta}| {}_{\underline{p}_{\bar{1}\bar{2}}}^{\sigma_1\sigma_2} \begin{pmatrix} \sigma_1'\sigma_2' \\ \underline{p}_{\bar{1}\bar{2}} \end{pmatrix}^{\dagger} \gg = \delta(\underline{p}_{b\ell}-\underline{p}_{12})\delta(\underline{p}_{b\ell}-\underline{p}_{\bar{1}\bar{2}})$$

(2.2-71)

$$\frac{1}{h}\ll \sigma_1\sigma_2(\sigma_1'\sigma_2')^{\dagger}|W^2\{h\hat{\Theta}|\underline{r}_b,\underline{p}_{b\ell}|\underline{r}_b,\underline{p}_{b\ell}\}|\sigma_{\bar{1}}\sigma_{\bar{2}}(\sigma_1'\sigma_2')^{\dagger}\gg$$

If one substitutes this result into Eq. (2.2-67) and notes that $P_\ell(1) = 1$, one obtains,

$$\ll {}_{p_{12}}^{\sigma_1\sigma_2} \begin{pmatrix} \sigma_1'\sigma_2' \\ \underline{p}_{12} \end{pmatrix}^{\dagger} |\hat{\Theta}| {}_{\underline{p}_{\bar{1}\bar{2}}}^{\sigma_{\bar{1}}\sigma_{\bar{2}}} \begin{pmatrix} \sigma_1'\sigma_2' \\ \underline{p}_{\bar{1}\bar{2}} \end{pmatrix}^{\dagger} \gg =$$

$$\frac{1}{h^3} \int_0^\infty bdb2\pi|\underline{v}| \sum_{\ell=0}^{\infty} \Delta(p_{b\ell}^2) P_{b\ell} \int d\hat{p}_{b\ell}\delta(\underline{p}_{b\ell}-\underline{p}_{12})$$  (2.2-72)

$$\ll \sigma_1\sigma_2(\sigma_1'\sigma_2')^{\dagger}|W^2\{h\hat{\Theta}|\underline{r}_b,\underline{p}_{b\ell}\}|\sigma_{\bar{1}}\sigma_{\bar{2}}(\sigma_1'\sigma_2')^{\dagger}\gg \delta(p_{b\ell}\hat{p}_{12}-\underline{p}_{\bar{1}\bar{2}})$$

where $\Delta(p_{b\ell}^2)$ equals $\hbar^2(2\ell+1)/b^2$ and $|\underline{v}|$ is the magnitude of the relative velocity (i.e. $\underline{v} = \underline{p}_{12}/\mu_{12}$).

If one compares Eq. (2.2-56) to Eq. (2.1-46), it is evident that the quantal analog of the collision kernel is obtained by combining $h^3\bar{\hat{\Theta}}$ with the center of mass momentum diagonality. Furthermore, from Eqs. (2.2-72), (2.2-57), (2.2-56), and (2.1-47), it follows that the quantal analog of $\underset{\approx}{S}^{(2)}$ is $W^2\{S\otimes S\}\delta_p$ (here $\delta_p$ denotes the center of mass momen-

tum diagonality). Using the form of $\bar{\Theta}$ supplied by Eq. (2.2-72), one finds that the quantal collision kernel is,

$$< {}^{\sigma_1\sigma_1'}_{\underline{p}_1} \; {}^{\sigma_2\sigma_2'}_{\underline{p}_2} |\Theta| \; {}^{\sigma_1^-\sigma_1'}_{\underline{p}_1^-} \; {}^{\sigma_5\sigma_5'}_{\underline{p}_5^-}> = 2\pi \int bdb |\underline{v}| \sum_{\ell=0}^{\infty} \tfrac{1}{2}\Delta(p_{b\ell}^2) p_{b\ell} \int d\tilde{p}_{b\ell}$$

$$\{\delta(\underline{p}_{b\ell}-\underline{p}_{12}) <<\sigma_1\sigma_2(\sigma_1'\sigma_2')^\dagger|w^2\{\tilde{S}\otimes\hat{S}\} - 1|\sigma_1^-\sigma_5(\sigma_1'\sigma_5')^\dagger>>$$

(2.2-73)

$$\delta(\underline{p}_{b\ell} - \underline{p}_{1\bar{5}})\}\delta(\underline{p}_1 + \underline{p}_2 - \underline{p}_1^- - \underline{p}_5^-)$$

In the usual case, translational motion is treated classically, and thus the sum over $\ell$ becomes an integral over $p_{b\ell}^2$ ($p_{b\ell}$ then becomes independent of b).

The Waldmann-Snider equation can be written in a form analogous to Eq. (2.1-44),

$$\frac{\partial\tilde{f}^{(1)}}{\partial t} + \{\tilde{f}^{(1)}, H_1^{tr}\} + \frac{1}{i\hbar} [\tilde{f}^{(1)}, \hat{H}_1^{int}] =$$

(2.2-74)

$$\mathop{Tr}_{\substack{int \\ 2}} \int d\underline{p}_2 \int_0^{\infty} bdb 2\pi |\underline{v}| (w^2\{\tilde{S}\otimes\hat{S}\}\delta p - 1)\tilde{f}^{(1)}\tilde{f}_2^{(1)}$$

Here, the tilde denotes an operator on the internal state domain and $\mathop{Tr}\limits_{\substack{int \\ 2}}$ denotes a trace taken over the internal states of molecule 2. Because of the quantal nature of the internal states, (e.g., rotational angular momentum and orientation cannot be simultaneously specified) the orientational integrals do not appear and the integral over $\varepsilon$ trivially reduces to $2\pi$.

Finally, for the sake of completeness, it should be noted that $\overline{\Theta}$ was originally expressed by Waldmann and Snider in terms of the T-matrix,

$$\overline{\Theta} = \frac{1}{\hbar}(i\hat{1}\otimes\hat{T}^{\dagger} - i\hat{T}\otimes\hat{1} + 2\pi\delta(E)\hat{T}\otimes\hat{T}^{\dagger}) \qquad (2.2\text{-}75)$$

If this form is substituted into Eq. (2.2-56) and only nondegenerate systems are considered, one obtains,

$$\frac{\partial f^{(1)}}{\partial t}\eta_1 (\underline{r}_1,\underline{p}_1,t) + \{f_{\eta_1}^{(1)}(\underline{r}_1,\underline{p}_1,t),H_1^{tr}\} =$$

$$\frac{h^3}{\hbar}\sum_{\eta_2}\int d\underline{p}_2\{-i<\frac{\eta_1\eta_2}{\underline{p}_{12}}|\hat{T}-\hat{T}^{\dagger}|\frac{\eta_1\eta_2}{\underline{p}_{12}}>f_{\eta_1}^{(1)}(\underline{r},\underline{p}_1,t)f_{\eta_2}^{(1)}(\underline{r},\underline{p}_2,t) +$$

$$\sum_{\eta_1',\eta_2'}\int d\underline{p}_1'\int d\underline{p}_2' \, 2\pi|<\frac{\eta_1\eta_2}{\underline{p}_{12}}|\hat{T}|\frac{\eta_1'\eta_2'}{\underline{p}_{12}'}>|^2$$

$$\delta(\underline{p}_1+\underline{p}_2 - \underline{p}_1'-\underline{p}_2')\delta(E-E')f_{\eta_1'}^{(1)}(\underline{r},\underline{p}_1',t)f_{\eta_2'}^{(1)}(\underline{r},\underline{p}_2',t\}. \qquad (2.2\text{-}76)$$

Here, $\eta$ denotes a quantum number appropriate to molecular internal energy states and $E$ denotes total energy (translational + internal).

One easily obtains the following operator identity from Eqs. (2.2-29), (2.2-30), and (2.2-31),

$$\hat{T}^{(\pm)} - \hat{T}^{(\pm)\dagger} = \hat{T}^{(\pm)}(\hat{G}_E^{(\pm)}-\hat{G}_E^{(\pm)\dagger})\hat{T}^{(\pm)\dagger} =$$

$$-2\pi i\hat{T}^{(\pm)}\delta(E-\hat{K}^{(2)})\hat{T}^{(\pm)\dagger} \qquad (2.2\text{-}77)$$

which results in the well-known optical theorem if matrix elements of both sides are taken between energy diagonal

states. Substitution of Eq. (2.2-77) into Eq. (2.2-76) yields the Wang Chang-Uhlenbeck equation(25).

$$\frac{\partial f_{n_1}^{(1)}}{\partial t} (\underline{r},\underline{p}_1,t) + \{f_{n_1}^{(1)}(\underline{r},\underline{p}_1,t),H_1^{tr}\} =$$

$$\int d\underline{p}_2 \sum_{n_2} \int d\underline{p}_1' \sum_{n_1'} \int d\underline{p}_2' \sum_{n_2'} \left[\frac{4\pi^2}{h}\middle| < \begin{array}{c} n_1 n_2 \\ \underline{p}_{12} \end{array} |\hat{T}| \begin{array}{c} n_1' n_2' \\ \underline{p}_{12}' \end{array} >\middle|^2 \delta(\underline{p}_1+\underline{p}_2-\underline{p}_1'-\underline{p}_2')\right.$$

$$\delta(E-E')] \, h^3 \{f_{n_1'}^{(1)}(\underline{r},\underline{p}_1',t) f_{n_2'}^{(1)}(\underline{r},\underline{p}_2',t) -$$

$$f_{n_1}^{(1)}(\underline{r},p_1,t) f_{n_2}^{(1)}(\underline{r},\underline{p}_2,t) \quad\quad\quad (2.2-78)$$

The quantity in the square brackets is a quantal expression for the specific transition rate, $w(\cdots|\cdots)$, (cf. Eq. (2.1-48)) which is appropriate to the collisional process,

$$\underline{p}_1',\underline{p}_2',n_1',n_2' \rightarrow \underline{p}_1,\underline{p}_2,n_1,n_2.$$

## 2.3. Formal Correspondences and Symmetry Properties of the Generalized Collision Kernel

In the preceding two sections of this chapter, the classical Boltzmann equation, Eq.(2.1-44) and the Waldmann-Snider equation, Eq. (2.2-74), and its singlet density matrix counterpart, Eq. (2.2-45), which describe the temporal behavior of dilute gas under appropriate conditions have been developed. In the light of demonstrated structural analogies between them, it comes as no surprise that one formal expression can be written which embodies all. The purpose of this kind of approach is to reveal the underlying similarity of

the classical and quantal kinetic equations without the cumbersome mathematical machinery associated with the detailed dynamics. With this in mind, one can represent these three equations by a single expression as follows,

$$\frac{\partial}{\partial t}<1|f> + <1|\{\{f,H^{(1)}\}\}> =$$

<div align="right">(2.3-1)</div>

$$\int d1'\int d2\int d2'<I|2><12|\underset{\approx}{\varphi}|1'2'><1'|f><2'|f>$$

Here, $|f>$ stands for the singlet distribution function-density matrix and can be thought of as a vector in a function-operator space, $H_j$ (j refers to molecular labels 1 or 2). This is analogous to the usual construction of state vectors found in quantum mechanics. Basis vectors (function-operators) appropriate to $H_j$ are denoted in Eq. (2.3-1) by the symbols $|j>$ and $|j'>$. This basis is assumed to be complete. The symbol, $\int dj$, denotes integration-summation over a continuous-discrete set of indices which label the basis vectors and the symbol, I, is the multiplicative identity-operator. Finally, $\{\{f,H^{(1)}\}\}$ gives the implicit time derivative of the singlet distribution function-density matrix. It is identified quantally as an operator commutator, $(i\hbar)^{-1}[\rho^{(1)},H^{(1)}]$ and classically as a Poisson bracket, $\{f^{(1)},H^{(1)}\}$.

The collision operator-superoperator, $\underset{\approx}{\varphi}$, can be regarded as an operator on a direct product function-operator space, $H_{12} = H_1 \otimes H_2$. It follows that a complete basis appropriate

to $H_{12}$ is given by the direct products of bases for $H_{12}$ and $H_2$. Thus, in Eq. (2.3-1), basis functions of $H_{12}$ are denoted by $|12\rangle = |1\rangle|2\rangle$.

The function operator space, $H_j$ (or $H_{12}$), is defined to have an $L^2$ norm with regard to functions and a Hilbert-Schmidt norm with regard to operators. This space is larger than necessary since any admissable distribution "state vector" must, in fact, converge under the $L^1$ norm and/or belong to the trace class of operators (i.e. any physically realistic distribution has a finite normalization). In the present notation one obtains:

$$N_f = \int d1 \langle 1|f\rangle \qquad (2.3-2)$$

where $N_f$ is a scalar constant (conventionally $N_f$ is the local molecular number density of the gas, n, however other normalizations are possible). The advantage of using the larger $L^2$/Hilbert-Schmidt norm instead of the $L^1$/trace class norm lies in the fact that the former admits a well-defined inner product. Finally, for future reference, one should note that the function-operator space appropriate to the usual Chapman-Enskog kinetic theory differs from $H_j$ as the result of the inclusion of a weight in the norm.

It is well-known that physically realistic Hamiltonian function-operators are invariant with respect to any rotation of the external reference frame. Thus, the classical scat-

tering operator, $\underset{\approx}{S}^{(2)}$, and the quantal scattering

superoperator, $S \otimes S^\dagger$, are also rotationally invariant. As a

consequence, $\underset{\approx}{\Theta}$, exhibits rotational invariance which can be

formalized in the following expression.

$$\underset{\approx}{\Theta} = \underset{\approx}{R} \; \Theta \; \underset{\approx}{R}^\dagger \qquad\qquad (2.3\text{-}3)$$

Here, $\underset{\approx}{R}$ is the unitary rotation operator defined on $H_{12}$.

Similarly, if an isolated molecular system is composed

of nonchiral molecules, it is mechanically invariant with re-

spect to inversion through an arbitrary symmetry center or

reflection through an arbitrary plane. Again, $\underset{\approx}{S}^{(2)}$ and $\tilde{S} \otimes \tilde{S}^\dagger$

exhibit this invariance and $\underset{\approx}{\Theta}$ obeys the expression,

$$\underset{\approx}{\Theta} = \underset{\approx}{P} \; \Theta \; \underset{\approx}{P}^\dagger \qquad\qquad (2.3\text{-}4)$$

In this case, $\underset{\approx}{P}$ is the unitary parity operator defined on

It can further be noted that $P$ (unlike $R$) is a self-inverse

operator (<u>i.e.</u> $\underset{\approx}{P} = \underset{\approx}{P}^\dagger$).

The last symmetry principle to be considered in this

discussion is that of time reversal invariance (microscopic

reversibility). It is particularly important since it pro-

vides the proof of the Onsager-Casimir reciprocity relations.

The effect of time reversal is to replace $\underset{\approx}{S}^{(2)}$ or $\tilde{S} \otimes \tilde{S}^\dagger$

with its adjoint, that is $\underset{\approx}{S}^{(2)\dagger}$ or $S^\dagger \otimes S$. This is easily seen

if one reverses the sense of time in the defining equations,

Eq. (2.1-18) and Eq. (2.2-24). This yields the result,

$$\Theta^{\dagger} = \underset{\sim}{T} \underset{\sim}{\Theta} \underset{\sim}{T}^{\dagger} \qquad (2.3\text{-}5)$$

where $\underset{\sim}{T}$ is the unitary time reversal operator defined on $H_{12}$. As with parity, time reversal is also self-inverse (i.e., $\underset{\sim}{T} = \underset{\sim}{T}^{\dagger}$). Thus, one can write,

$$\underset{\sim}{T} \underset{\sim}{\Theta} = \underset{\sim}{\Theta}^{\dagger} \underset{\sim}{T} \qquad (2.3\text{-}6)$$

which implies that the product operators, $\underset{\sim}{T}\underset{\sim}{\Theta}$ and $\underset{\sim}{\Theta}\underset{\sim}{T}$, are self-adjoint under the $L^2$/Hilbert-Schmidt norm.

## 2.4. The Macroscopic Conservation Equations and the H-theorem

The average value of single molecule physical parameters can be computed via the expression,

$$\langle A \rangle = \langle A | f \rangle = \int d1 \langle A | 1 \rangle \langle 1 | f \rangle \qquad (2.4\text{-}1)$$

Here, A is a time independent function-operator corresponding to an arbitrary physical observable and $\langle A \rangle$ is its average value in an ensemble described by f. From the explicit form of $\langle A | 1 \rangle$ and $\langle f | 1 \rangle$. it follows that $\langle A \rangle$ is an average over a function, A, and a probability distribution function and/or a trace of an operator product of $\hat{A}$ with a density matrix. An equation of change for $\langle A \rangle$ is obtained by contracting A into both sides of Eq. (2.3-1) and symmetrizing with respect to molecular labeling. It has the form,

$$\langle A | \frac{df}{dt} \rangle = \frac{1}{2} \langle A_1^{(2)} + A_2^{(2)} | \underset{\sim}{\theta} | ff \rangle \qquad (2.4\text{-}2)$$

where the total time derivative is defined by,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \{\{ \, , H^{(1)} \}\} \qquad (2.4\text{-}3)$$

The definition of quantities appearing on the right hand side of Eq. (2.4-2) are,

$$\langle 12 | A_1^{(2)} + A_2^{(2)} \rangle = \langle 1 | A \rangle \langle 2 | I \rangle + \langle 1 | I \rangle \langle 2 | A \rangle \qquad (2.4\text{-}4)$$

and

$$\langle 12 | ff \rangle = \langle 1 | f \rangle \langle 2 | f \rangle \qquad (2.4\text{-}5)$$

Since A is not an explicit function of time, one obtains the result,

$$\frac{\partial}{\partial t} \langle A \rangle + \langle A | \{\{f, H^{(1)}\}\} \rangle = \frac{1}{2} \langle A_1^{(2)} + A_2^{(2)} | \underset{\sim}{\theta} | ff \rangle \qquad (2.4\text{-}6)$$

In the case that A represents a summationally invariant physical parameter, then $A_1^{(2)} + A_2^{(2)}$ can be regarded as an eigenvector of $\underset{\sim}{\theta}$ with a zero eigenvalue. This results directly from the conservation properties implicit in $\underset{\sim}{S}^{(2)}$ or $\hat{S} \otimes \hat{S}^\dagger$. Thus, one obtains a macroscopic conservation equation for $\langle A \rangle$,

$$\frac{\partial}{\partial t} \langle A \rangle + \langle A | \{\{f, H^{(1)}\}\} \rangle = 0 \qquad (2.4\text{-}7)$$

Specific examples of Eq. (2.4-7) occur if A is mass, linear momentum or kinetic energy in which case one obtains the hydrodynamic equations of continuity, motion and energy balance.

The H-theorem gives a quantitative statement of the irreversible behavior of the kinetic equation applicable to the temporal description of a dilute gas. In particular, the H-function is defined by the expression ($\ell$n is the natural logarithm),

$$H = \langle \ell nf | f \rangle = \int d1 \langle \ell nf | 1 \rangle \langle 1 | f \rangle \qquad (2.4-8)$$

Here, H is a real-valued function of time. The total time derivative of H is written as follows,

$$\frac{dH}{dt} = \int d1 \langle \ell nf + I | 1 \rangle \frac{d}{dt} \langle 1 | f \rangle \qquad (2.4-9)$$

Using Eq. (2.3-1) one can express the time derivative of H in terms of the collision kernel,

$$\frac{dH}{dt} = \frac{1}{2} \langle \ell nff | \underline{\varrho} | ff \rangle + \langle I | \underline{\varrho} | ff \rangle \qquad (2.4-10)$$

Here, the right hand side has been symmetrized with respect to molecular labeling by making use of the identity,

$$\langle 12 | \ell nff \rangle = \langle 1 | \ell nf \rangle \langle 2 | I \rangle + \langle 1 | I \rangle \langle 2 | \ell nf \rangle \qquad (2.4-11)$$

It should be noted that a function of an operator (e.g. $\ell$nf

where f is the density matrix) can be defined by transforming
the operator to a diagonal representation via unitary
conjugation, applying the function to the diagonal elements
(i.e. eigenvalues), and then transforming back to the origi-
nal representation. With this in mind, it is clear that Eq.
(2.4-11) follows for a product of singlet distribution
function-density matrices from the elementary definition of
the logarithm of a product. Finally, one obtains the follow-
ing expression from Eq. (2.4-10),

$$\frac{dH}{dt} = \frac{1}{2} \langle \ell n ff | \underset{\approx}{\Theta} | ff \rangle \qquad (2.4-12)$$

since I is a zero eigenvector of $\underset{\ast}{\Theta}$ (and $\underset{\approx}{\Theta}^{\dagger}$).

In the classical case, it is easily shown (using inte-
gration by parts) that $\underset{\approx}{S}^{(2)}$ can be regarded as a unitary op-
erator. Quantally, an analogous property can be established
for $\hat{S} \otimes \hat{S}^{\dagger}$ directly from the unitarity of the usual S-matrix.
If the symbol, $\underset{\approx}{S}$, is a generalized notation for $\underset{\approx}{S}^{(2)}$ and/or
$\hat{S} \otimes \hat{S}^{\dagger}$ (i.e. $\underset{\approx}{S}$ is unitary on $H_{12}$) and if $A^{(2)}$ and $B^{(2)}$ repre-
sent arbitrary $H_{12}$ vectors (i.e. classical functions and/or
quantum mechanical operators), then one can write,

$$\langle A^{(2)} | \underset{\approx}{\Theta} | B^{(2)} \rangle = \int d\tau \langle A^{(2)} | \underset{\approx}{S} - \underset{\approx}{I} | B^{(2)} \rangle \qquad (2.4-13)$$

Here, the symbol, $\underset{\approx}{I}$, denotes the $H_{12}$ identity operator and
the symbol, $\int d\tau$, denotes the appropriate integrations over
impact parameter or relative translational energy

and orientational parameters (if appropriate). If one arbitrarily adds zero (i.e. $\frac{1}{2}\langle ff|\underset{\sim}{\theta}|I\rangle$) to the right hand side of Eq. (2.4-12) and substitutes Eq. (2.4-13), one obtains,

$$\frac{dH}{dt} =$$

$$\frac{1}{2}\int d\tau\,[\langle \ell n\underset{\sim}{s}(ff)|ff\rangle - \langle \ell ff|ff\rangle - \langle \underset{\sim}{s}(ff)|I\rangle + \langle ff|I\rangle] \quad (2.4-14)$$

The operator-superoperator, $\underset{\sim}{S}$, can be brought into the argument of the natural logarithm due to the fact that it can be written as the limit of a product of exponential forms.

If ff is a positive real and/or positive definite self-adjoint function-operator, it follows that $\underset{\sim}{S}(ff)$ is also positive real and/or positive definite self-adjoint. Thus, one can write,

$$\frac{dH}{dt} = -\frac{1}{2}\int d\tau\, \sum_{ij} B_{ij}\,[\ell n(\frac{\lambda_i}{\lambda_j^\star}) - 1 + \frac{\lambda_j^\star}{\lambda_i}]\lambda_i \quad (2.4-15)$$

where $\lambda_i$ and $\lambda_j^\star$ are components of ff and S(ff), respectively. Classically, $\lambda_i$ and $\lambda_j^\star$ are functional values (i.e. nonnegative real numbers) of $f^{(1)}f_2^{(1)}$ and $\underset{\sim}{S}^{(2)}f^{(1)}f^{(1)}$ and quantally, they are eigenvalues (i.e. again nonnegative real numbers) of $\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}$ and $\hat{S}\hat{\rho}^{(1)}\hat{\rho}_2^{(1)}\hat{S}^\dagger$. The quantity, $B_{ij}$, can be identified classically as a delta function, $\delta_{ij}$, and quantally as a transition probability, $|S_{ij}|^2$. As an immediate consequence of Eq. (2.4-15) and the fact that

$\ell nx - 1 + \frac{1}{x}$ is nonnegative for all real positive values of x,

it follows that,

$$\frac{dH}{dt} \leqslant 0 \qquad\qquad (2.4-16)$$

Thus, H is shown to be a nonincreasing real function of time.

It can be shown that for any dilute gas system which has a finite average energy, the H-function must be bounded in time from below. This means that as such a system evolves temporally, it relaxes to a steady state. The time derivative of the H-function vanishes. Thus, in equilibrium, $\ell$nf must be a linear combination of summationally invariant physical observables. These are mass, linear momentum and total energy. The hydrodynamic parameters, mass density, $\rho$, (this should not be confused with density matrix) streaming velocity, $\underline{u}$, and thermodynamic temperature are given by the ensemble averages,

$$\rho = \langle \underline{I} \rangle M \qquad\qquad (2.4-17)$$

$$\underline{u} = \rho^{-1} \langle \underline{p} \rangle \qquad\qquad (2.4-18)$$

$$T = (M/\rho C_v) \langle p^2/2M + K^{int} \rangle \qquad\qquad (2.4-19)$$

Here, M is molecular mass, $\underline{p}$ is the linear momentum function operator, $K^{int}$ is the internal kinetic energy function operator, and $C_v$ is the constant volume heat capacity per molecule. These ensemble averages can be used to fix the coefficients of the linear combination of summational invariants

appropriate to $\ell nf^{(eq)}$. This yields the usual Maxwellian form,

$$\underline{f}^{(eq)} = \frac{n}{Z} e^{-(1/2MkT)(\underline{p}-M\underline{u})^2} e^{-K^{int}/kT} \qquad (2.4-20)$$

Here, Z is the molecular canonical ensemble partition function, k is Boltzmann's constant, and n is the number density which is $\rho/M$. From the above definition of the macroscopic parameters, it is clear that the singlet distribution function-operator can be regarded as being normalized to the number density. This will be assumed hereafter in this work.

The definition of entropy in equilibrium statistical mechanics is,

$$s = -k<\ell nf^{(eq)} | \underline{f}^{(eq)}> \qquad (2.4-21)$$

This definition is readily extended for the dilute gas case under consideration to,

$$s = -kH = -k<\ell nf | f> \qquad (2.4-22)$$

where f is now not necessarily the equilibrium distribution function-operator. Thus, the H-theorem can be interpreted as a generalization of the Second Law of Thermodynamics (i.e. entropy can never decrease) in that the irreversible relaxation of a molecular fluid to equilibrium is characterized by entropy production.

## 3. THE KINETIC THEORY

### 3.1. Linearization of the Kinetic Equation

In the preceding chapter, it was shown that the Waldmann-Snider equation and the Boltzmann equation both could be formally expressed by Eq. (2.3-1). Furthermore, this formulation is easily generalized to mixtures by assigning a species index (hereafter denoted by a Greek letter) to the basis vectors of $H_j$ ($j$ = 1 or 2). Thus, one can generalize Eq. (2.3-1) as follows,

$$\frac{\partial}{\partial t}<1\alpha|f> + <1\alpha|\{\{f,H^{(1)}\}\}> =$$
$$\sum_\beta \int d1' \int d2 \int d2' <I|2\beta><1\alpha2\beta|\underset{\sim}{\Theta}|1'\alpha2'\beta><1'\alpha|f><2'\beta|f> \quad (3.1-1)$$

where explicit use has been made of the fact that molecules do not react during collisions (i.e. $<1\alpha2\beta|\underset{\sim}{\Theta}|1'\alpha'2'\beta'>$ = $<1\alpha2\beta|\underset{\sim}{\Theta}|1'\alpha2'\beta>\delta_{\alpha\alpha'}\delta_{\beta\beta'}$). The distribution function-operator, f (hereafter referred to simply as the "distribution") can be thought of as a vector in a "composition space" which has components of the form,

$$f_\alpha = \int d1 <1\alpha|f> \quad (3.1-2)$$

It is clear from Eq. (3.1-2) that f can be thought of as a vector in a subspace, $H_j^\alpha$ (of the full space, $H_j$), which is appropriate to species, $\alpha$.

As stated in the Introduction, within the scope of this work, transport processes are described by a linear phenomenology. Accordingly, a suitable linearized form of Eq. (3.1-1) can be obtained via application of the standard Chapman-Enskog method. The method is based on the postulate that the spatial and temporal dependence of the distribution applicable to a dilute gas near equilibrium is implicitly contained in the hydrodynamic fields (i.e. density, streaming velocity, and temperature).

Heuristically, one can gain insight into the approach of a dilute gas system to equilibrium by imagining that a volume of gas is divided up into cells, each of which has a volume that is negligible macroscopically but is of sufficient size microscopically so as to contain a large number of molecules. The cells can be imagined to have cyclic boundary conditions so that the system satisfies the usual mechanical conservation relations. Clearly, the only time dependence of the distribution in this hypothetical situation is due solely to molecular collisions. These have the effect of bringing the distribtuion rapidly (i.e. within just a few collision times) to a Maxwellian form (cf. Eq. (2.4-21)).

The idealized situation just described is approximated by a real system for which the hydrodynamic field gradients are small (i.e. the system is near equilibrium). In such a system, any given molecule suffers a large number of

collisions during a time interval sufficiently long so as to allow it to drift an appreciable distance due to random motion of the molecules. Thus, the time dependence of the distribution is dominated by the gradient independent contribution due to collisions. Accordingly, the time dependence of the distribution due to the existence of a hydrodynamic field gradient (i.e. a macroscopic flux) can be viewed as a small perturbation on the collisional time dependence.

One carries through with the Chapman-Enskog method by defining a dimensionless perturbation parameter, $\varepsilon$, which "marks" any time dependence that is due to a gradient of a hydrodynamic field. Thus, one can write Eq. (3.1-3) as follows,

$$\varepsilon\langle 1\alpha|\frac{\partial}{\partial t} + \underline{v}\cdot\frac{\partial}{\partial \underline{r}} + \underline{X}^{ext}\cdot\frac{\partial}{\partial \underline{p}}|f\rangle = -\langle 1\alpha|\{\{f,H^{int}\}\}\rangle +$$

$$\sum_{\beta}\int d1'\int d2\int d2'\langle I|2\beta\rangle\langle 1\alpha 2\beta|\underline{\theta}|1'\alpha 2'\beta\rangle\langle 1'\alpha|f\rangle\langle 2'\beta|f\rangle \qquad (3.1-3)$$

Here, the streaming term (i.e. the translational part of $\langle 1\alpha|\{\{f,H^{(1)}\}\}\rangle$) is marked by $\varepsilon$ since it describes the time rate of change of the distribution due to macroscopic forces. One should also note that $\underline{X}^{ext}$ is defined as a weak external force (e.g. gravitational) which has an appreciable effect only on the hydrodynamic motion of the system (i.e. molecular trajectories between collisions are not appreciably affected by $\underline{X}^{ext}$). The term $\langle 1\alpha|\{\{f,H^{int}\}\}\rangle$ contains the effect of externally applied fields on internal molecular motion (in

the present work, rotational). In contrast to the effect of $\underline{x}^{ext}$ on translational motion, an applied field can significantly alter internal motion during an intercollisional interval. (This is the source of the Senftleben-Beenakker effects.) Thus, $\{\{f,H^{int}\}\}$ is conveniently grouped with the collisional term (i.e. not "marked" by $\epsilon$) since its size depends only on the strength of the applied field and can become of the same order as the collisional term.

To apply the Chapman-Enskog method, the following series expansions of f and $\partial/\partial t$ are proposed,

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \ldots \qquad (3.1-4)$$

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \epsilon \frac{\partial_1}{\partial t} + \epsilon^2 \frac{\partial_2}{\partial t} + \ldots \qquad (3.1-5)$$

where, $f^{(k)}$ and $\partial_k/\partial t$ denote contributions to f and $\partial/\partial t$ which are of total power k in the macroscopic gradient operator (i.e. $k^{th}$ order in the hydrodynamic field gradients). If one substitutes Eqs. (3.1-4) and (3.1-5) into Eq. (3.1-3) and equates terms of like power in $\epsilon$, one obtains a hierarchy of equations of the form,

$$D^{(k)} = -\{\{f^{(k)},H^{int}\}\} + \sum_{k'=0}^{k} J(f^{(k-k')},f^{(k')}) \qquad (3.1-6)$$

where,

$$D^{(k)} = \begin{cases} (0 \text{ for } k = 0) \\ \sum_{k'=0}^{k=0} \frac{\partial k'}{\partial t} f^{(k-k'-1)} + \end{cases}$$

(3.1-7)

$$\underline{v} \cdot \frac{\partial}{\partial \underline{r}} f^{(k)} + \underline{X}^{ext} \cdot \frac{\partial}{\partial \underline{p}} f^{(k)} \qquad (\text{for } k \neq 0)$$

and,

$$J(f^{(k')}, f^{(k)}) = \sum_{\alpha\beta} \int d1' \int d2 \int d2' \langle I | 2\beta \rangle$$

$$\langle 2\beta | \underline{\varrho} | 1'\alpha 2'\beta \rangle \langle 1'\alpha | f^{(k')} \rangle \langle 2'\beta | f^{(k)} \rangle$$

(3.1-8)

Equations (3.1-6), (3.1-7) and (3.1-8) are expressions of the standard Enskog expansion applicable to quantum mechanical as well as classical kinetic theory.

For the sake of completeness, it can be noted here that the Chapman-Enskog method fails in the case of a highly rarified gas (i.e., the Knudsen regime) in which molecules travel a large distance between collisions.

For dilute gas systems in a linear phenomenological regime, the perturbation in ε needs only to be carried to first order. With this in mind, one can define a distortion function-operator, ϕ, (hereafter termed simply as the "distortion") as follows,

$$f^{(1)} = \tfrac{1}{2}(f^{(0)}\phi + \phi f^{(0)})$$

(3.1-9)

This general symmetrized form is due to Snider(43). However,

in the present work the simpler definition,

$$f^{(1)} = f^{(0)}\phi = \phi f^{(0)} \tag{3.1-10}$$

is adopted. To justify this in anticipation of later developments, it is sufficient to state here that for a dilute gas, $\phi$ is a function of space-fixed components of the translational and angular momenta. In contrast, $f^{(0)}$ is a function of the total energy and thus commutes with $\phi$. (Classically, of course, commutation is not an issue.)

From Eqs. (3.1-6) and (3.1-10) one obtains the following zeroth and first order expressions,

$$0 = -\{\{f^{(0)}, H^{int}\}\} + J(f^{(0)}, f^{(0)}) \tag{3.1-11}$$

$$\mathcal{D} =$$
$$-\{\{f^{(0)}\phi, H^{int}\}\} + J(f^{(0)}\phi, f^{(0)}) + J(f^{(0)}, f^{(0)}\phi) \tag{3.1-12}$$

where for notational economy the superscript has been dropped from $\mathcal{D}$. Equation (3.1-12) can be written in a explicitly linear form by means of the linear operators, $\underset{\approx}{F}$ and $\underset{\approx}{\Gamma}$, which are defined by,

$$\underset{\approx}{F}|\phi> = |\{\{f^{(0)}\phi, H^{int}\}\}> \tag{3.1-13}$$

$$\underset{\approx}{\Gamma}|\phi> = -|J(f^{(0)}\phi, f^{(0)})> - |J(f^{(0)}, f^{(0)}\phi)> \tag{3.1-14}$$

Thus, one obtains the expression,

$$|\mathcal{D}> = -\underset{\approx}{F}|\phi> - \underset{\approx}{\Gamma}|\phi> \tag{3.1-15}$$

where $\underset{\approx}{F}$ describes the effect of an applied external field and $\underset{\approx}{\Gamma}$ describes the effect of collisions. These two operators can be combined to form a generalized linear collision operator, $\underset{\approx}{\Lambda} = -\underset{\approx}{F}-\underset{\approx}{\Gamma}$, such that,

$$|\mathcal{D}> = \underset{\approx}{\Lambda}|\phi> \qquad (3.1-16)$$

The solution of Eq. (3.1-16) provides theoretical expressions appropriate to linear transport coefficients.

## 3.2. The Zeroth Order Approximation to the Distribution and the General Force-Flux Relations

In order to solve Eq. (3.1-16), a solution to Eq. (3.1-11) must be found. To do this, one first notes that Eq. (3.1-11) can be considered as an approximation of the more rigorous expression,

$$0 = -\{\{f^{(0)}, H^{int}\}\} + J_F(f^{(0)}, f^{(0)}) \qquad (3.2-1)$$

where $J_F$ is defined in terms of a collision kernel, $\underset{\approx F}{\Theta}$, which rigorously includes the effect of an applied field on the collision dynamics ($J_F$ and $\underset{\approx F}{\Theta}$ replace $J$ and $\underset{\approx}{\Theta}$ in Eq. (3.1-18)). One can establish an H-theorem for $\underset{\approx F}{\Theta}$ using the same line of argument as in Section 2.4. It follows that,

$$0 = J_F(f^{(0)}, f^{(0)}) \qquad (3.2-2)$$

where the $\alpha$-species component of $f^{(0)}$ (cf. Eq. (3.1-2) is,

$$f_\alpha^{(0)} = n_\alpha \frac{e^{-(\underline{p}-M_\alpha\underline{u})^2/2M_\alpha kT}}{[2\pi M_\alpha kT]^{-3/2}} \times \frac{e^{-H_\alpha^{int}/kT}}{z_\alpha^{int}} \qquad (3.2-3)$$

Here, $z_\alpha^{int}$ is the contribution to the partition function for species $\alpha$ due to internal degrees of freedom. It is clear that $f^{(0)}$ satisfies the equation,

$$0 = \{\{f^{(0)}, H^{int}\}\} \qquad (3.2-4)$$

since it is an analytic function of internal degrees of freedom exclusively through $H^{int}$. Hence, $f^{(0)}$ satisfies Eq. (3.2-1).

It is clear that in the absence of an applied field,

$$f_\alpha^{(0)} = f_{0\alpha}^{(0)} = n_\alpha \frac{e^{-(\underline{p}-M_\alpha\underline{u})^2/2M_\alpha kT}}{[2\pi M_\alpha kT]^{-3/2}} \times \frac{e^{-K_\alpha^{int}/kT}}{z_{0\alpha}^{int}} \qquad (3.2-5)$$

where,

$$0 = J(f_0^{(0)}, f_0^{(0)}) \qquad (3.2-6)$$

Here, $f_0^{(0)}$ and $z_{0\alpha}^{int}$ denote the field free limits of $f^{(0)}$ and $z_\alpha^{int}$, respectively. If it is valid to neglect the effect of applied fields on the collision dynamics, then it follows that $f_0^{(0)}$ can be replaced by $f^{(0)}$ in Eq. (3.2-6). Thus, $f^{(0)}$

is the general solution of Eq. (3.1-11).

It will be shown explicitly in the subsequent development that the particular choice of $H^{int}$ appropriate to this work has the property that $\{\{K^{int}, H^{int}\}\}$ vanishes. Under this condition, $f_0^{(0)}$ is also a solution of Eq. (3.1-11). Noting this, $f^{(0)}$ and $f_0^{(0)}$ will be treated hereafter in this work as interchangeable and the five quantities, $n$, $u_x$, $u_y$, $u_z$, and $T$ ($u_x$, $u_y$, and $u_z$ are cartesian components of $\underline{u}$) will be taken as adjustable parameters depending on position and time.

The local equilibrium approximation to the distribution is obtained if the following auxiliary conditions are imposed,

$$n_\alpha = \langle I | f_\alpha \rangle = \langle I | f_\alpha^{(0)} \rangle \qquad (3.2-7)$$

$$\underline{u} = \sum_\alpha (n_\alpha M_\alpha)^{-1} \langle \underline{p} | f_\alpha \rangle = \sum_\alpha (n_\alpha M_\alpha)^{-1} \langle \underline{p} | f_\alpha^{(0)} \rangle \qquad (3.2-8)$$

$$T = \sum_\alpha (n_\alpha C_v^{(\alpha)})^{-1} \langle p^2/2M_\alpha + K_\alpha^{int} | f_\alpha \rangle = \qquad (3.2-9)$$
$$\sum_\alpha (n_\alpha C_v^{(\alpha)})^{-1} \langle p^2/2M_\alpha + K_\alpha^{int} | f_\alpha^{(0)} \rangle$$

where the right hand sides of these expressions by definition correspond to local values of the number density for species $\alpha$, the streaming velocity and the thermodynamic temperature, respectively. Here, $C_v^{(\alpha)}$ is the molecular constant volume heat capacity for species $\alpha$. The auxiliary conditions imply that the local values of the hydrodynamic fields are com-

pletely determined by the zeroth order approximation to the distribution and hence contain no contributions from the distortion.

Due to the collisional conservation of summational invariants, the operator, $\underset{\sim}{\Lambda}$, which appears in Eq. (3.1-16) is singular. This has been previously noted for the full collision kernel (i.e. $\underset{\sim}{\Theta}$ has zero eigenvectors corresponding to the summational invariants). It is well-known that a singular matrix equation can be termed as "consistent" or "inconsistent" which means, respectively, that solutions either do or do not exist. For a linear inhomogeneous matrix equation, consistency is guaranteed if all solutions of the corresponding homogeneous adjoint equation are orthogonal to the inhomogeneity. Thus, if one considers the expression,

$$0 = \underset{\sim}{\Lambda}^{\dagger} |\psi\rangle \qquad (3.2-10)$$

it follows that Eq. (3.1-16) is consistent if and only if,

$$\langle \mathcal{D} |\psi\rangle = 0 \qquad (3.2-11)$$

where $|\psi\rangle$ represents an arbitrary solution vector of the homogeneous adjoint equation. Equation (3.2-10) is satisfied if $\psi$ is identified as molecular mass, linear momentum, or kinetic energy (or any linear combination of these quantities). If one evaluates Eq. (3.2-11) explicitly for each of the summational invariants, one obtains the expressions,

$$\frac{d_0 \rho_\alpha}{dt} = -\rho_\alpha \nabla \cdot \underline{u} \qquad (3.2-12)$$

$$\frac{d_0 \underline{u}}{dt} = -\frac{1}{\rho} \nabla nkT + \sum_\beta \frac{n_\beta}{\rho} \underline{X}_\beta^{(ext)} \qquad (3.2-13)$$

$$\frac{d_0 T}{dt} = -\frac{nkT}{C_v} \nabla \cdot \underline{u} \qquad (3.2-14)$$

Here, $\rho_\alpha$ is the mass density ($\rho_\alpha = n_\alpha M_\alpha$) for species $\alpha$, $n$ and $\rho$ are total number and mass densities for the mixture ($n = \sum_\beta n_\beta$, $\rho = \sum_\beta \rho_\beta$), and $C_v$ is defined as the molecular heat capacity for the mixture ($C_v = \sum_\beta \frac{n}{n_\beta} c_v^{(\beta)}$). The differential operator, $\frac{d_0}{dt}$, is the zeroth order substantial derivative,

$$\frac{d_0}{dt} = \frac{\partial_0}{\partial t} + \underline{u} \cdot \nabla \qquad (3.2-15)$$

These orthogonality conditions are immediately recognizable as the Euler or ideal hydrodynamic equations which means that $n_\alpha$, $\underline{u}$, and $T$ must evolve temporally according to nondissipative hydrodynamics. This is, of course, consistent with their identification as macroscopic fields.

The peculiar velocity of a molecule of component $\alpha$ is defined by the expression,

$$\underline{C}_\alpha = \underline{p}/M_\alpha - \underline{u} \qquad (3.2-16)$$

This expression can be substituted directly into Eq. (3.1-7) to obtain,

$$\mathcal{D}_\alpha = \frac{\partial_0}{\partial t} f_\alpha^{(0)} + (\underline{u} + \underline{C}_\alpha) \cdot (\frac{\partial}{\partial \underline{r}}\Big|_{\underline{C}_\alpha} - \underline{\nabla}\underline{u} \cdot \frac{\partial}{\partial \underline{C}_\alpha}\Big|_{\underline{r}}) f_\alpha^{(0)}$$

$$+ \frac{\underline{X}_\alpha^{(ext)}}{M_\alpha} \cdot \frac{\partial}{\partial \underline{C}_\alpha}\Big|_{\underline{r}} f_\alpha^{(0)} \qquad (3.2\text{-}17)$$

By using the identities $1 = f^{(0)}(f^{(0)})^{-1}$ and $d\ell n f^{(0)} = (f^{(0)})^{-1} df^{(0)}$, Eq. (3.2-17) can be rewritten as follows,

$$\mathcal{D}_\alpha = f_\alpha^{(0)} \{\frac{\partial_0}{\partial t} + (\underline{u} + \underline{C}_\alpha) \cdot (\frac{\partial}{\partial \underline{r}}\Big|_{\underline{C}_\alpha} - \underline{\nabla}\underline{u} \cdot \frac{\partial}{\partial \underline{C}_\alpha}\Big|_{\underline{r}})$$

$$\qquad\qquad (3.2\text{-}18)$$

$$+ \frac{\underline{X}_\alpha^{(ext)}}{M_\alpha} \cdot \frac{\partial}{\partial \underline{C}_\alpha}\Big|_{\underline{r}} \} \ell n f_\alpha^{(0)}$$

where, from Eq. (3.2-5), $\ell n f_\alpha^{(0)}$ equals,

$$\ell n f_\alpha^{(0)} = \ell n n_\alpha - \frac{3}{2}\ell n T - \ell n z_{\theta\alpha}^{int} - M_\alpha C_\alpha^2/2kT$$

$$\qquad\qquad (3.2\text{-}19)$$

$$- K_\alpha^{int}/kT + \text{constants}$$

Upon application of the differential operators, $\frac{\partial_0}{\partial t}$, $\frac{\partial}{\partial \underline{r}}\Big|_{\underline{C}_\alpha}$ and $\frac{\partial}{\partial \underline{C}_\alpha}\Big|_{\underline{r}}$, to Eq. (3.2-19), one obtains the following results,

$$\frac{\partial_0}{\partial t}\ell n f_\alpha^{(0)} = \frac{\partial_0}{\partial t}\ell n n_\alpha - \frac{\partial_0}{\partial t}\ell n z_{0\alpha}^{int} + \frac{M_\alpha \underline{C}_\alpha}{kT} \cdot \frac{\partial_0 \underline{u}}{\partial t} +$$

$$\qquad\qquad (3.2\text{-}20)$$

$$- (\frac{M_\alpha C_\alpha^2}{2kT} + \frac{K_\alpha^{int}}{kT} - \frac{3}{2})\frac{\partial_0}{\partial t}\ell n T$$

$$\frac{\partial}{\partial \underline{r}} \ell n f_\alpha^{(0)} =$$

$$\frac{\partial}{\partial \underline{r}} \ell n n_\alpha - \frac{\partial}{\partial \underline{r}} \ell n z_{0\alpha}^{int} + (\frac{M_\alpha C_\alpha^2}{2kT} + \frac{K_\alpha^{int}}{kT} - \frac{3}{2}) \frac{\partial}{\partial \underline{r}} \ell n T \qquad (3.2\text{-}21)$$

$$\frac{\partial}{\partial \underline{C}_\alpha} \ell n f_\alpha^{(0)} = - \frac{M_\alpha}{kT} \underline{C}_\alpha \qquad (3.2\text{-}22)$$

Now, one notes that the molecular partition function for internal degrees of freedom is an explicit function of the temperature. Thus, use of the chain rule allows the gradient of $\ell n z_{0\alpha}^{int}$ to be written in terms of the temperature gradient,

$$\frac{\partial}{\partial \underline{r}} \ell n z_{0\alpha}^{int} = \frac{\partial T}{\partial \underline{r}} \frac{\partial}{\partial T} \ell n z_{0\alpha}^{int} \qquad (3.2\text{-}23)$$

and the quantity, $\partial \ell n z_{0\alpha}^{int} / \partial T$ can be evaluated by the standard formula of equilibrium statistical mechanics,

$$\bar{E}_\alpha^{int} = kT^2 \frac{\partial}{\partial T} \ell n z_{0\alpha}^{int} \qquad (3.2\text{-}24)$$

Here, $\bar{E}_\alpha^{int}$ is the canonical ensemble average of the energy per molecule of $\alpha$, which is due to internal degrees of freedom.

One can substitute Eqs. (3.2-20), (3.2-21), (3.2-22), and (3.2-24) into Eq. (3.2-18) and use the Euler hydrodynamic

equations to eliminate the zeroth order time derivatives, thus obtaining,

$$
\underline{\mathcal{D}}_\alpha = f_\alpha^{(0)} \{ (-1 - \frac{n E_\alpha k}{C_v}) \underline{\nabla} \cdot \underline{u} + \frac{M_\alpha}{kT} \underline{C}_\alpha \underline{C}_\alpha : \underline{\nabla u} + (E_\alpha - 1) \underline{C}_\alpha \cdot \underline{\nabla} \ell n T +
$$

$$
\frac{n}{n_\alpha} \underline{C}_\alpha \cdot \underline{d}_\alpha \}
$$

(3.2-25)

where $E_\alpha$ is defined as,

$$
E_\alpha = \frac{M_\alpha C_\alpha^2}{2kT} + \frac{K_\alpha^{int}}{kT} - \frac{3}{2} - \frac{E_\alpha^{int}}{kT}
$$

(3.2-26)

The vector, $\underline{d}_\alpha$, is defined as the diffusion driving force for component $\alpha$. It has the explicit form,

$$
\underline{d}_\alpha = \underline{\nabla}(\frac{n_\alpha}{n}) + (\frac{n_\alpha}{n} - \frac{\rho_\alpha}{\rho}) \frac{1}{nkT} \underline{\nabla}(nkT)
$$

$$
+ \frac{\rho}{nkT} (\sum_\beta \frac{n_\beta}{\rho} \underline{X}_\beta^{(ext)} - \frac{\underline{X}_\alpha^{(ext)}}{M_\alpha})
$$

(3.2-27)

The three terms which comprise $\underline{d}_\alpha$ can be given the following physical interpretations. The first term is the gradient of the mole fraction and corresponds to the driving force of ordinary diffusion as defined by Fick's First Law. The second term describes a situation in which the hydrostatic pressure is not uniform. In such a case, lighter molecules tend to migrate preferentially toward regions of low pressure. The third term describes a situation in which external forces acting on molecules of different species are unequal. This

implies that if the external forces are constant, the components tend to become stratified.

The inhomogenity defined by Eq. (3.1-7) has been expressed explicity by Eq. (3.2-25) in terms of the thermodynamic forces, $\underline{v} \cdot \underline{u}$, $\underline{v}\underline{u}$, $\underline{v}\ell nT$ and $\underline{d}_\alpha$. The components of $\underline{v}\underline{u}$ and $\underline{v}\ell nT$ are linearly independent; however, the diffusion forces form a linearly dependent set of vectors since,

$$\sum_\alpha \underline{d}_\alpha = 0 \qquad (3.2-28)$$

This expression follows directly from the definitions of total number and mass densities as sums of number and mass densities of each component.

It is desirable to remove the linear dependence inherent in Eq. (3.2-25) due to the diffusion forces. This is accomplished by using Eq. (3.2-28) to formally add zero to $\underline{d}_\alpha$,

$$\underline{d}_\alpha = \sum_\beta (\delta_{\alpha\beta} - \frac{\rho_\alpha}{\rho})\underline{d}_\beta \qquad (3.2-29)$$

Here, the factor $\rho_\alpha/\rho$ has been included explicitly, because it combines with factors appearing in Eq. (3.2-25) in a particularly desirable way upon substitution of Eq. (3.2-29) into Eq. (3.2-25). This will be discussed in more detail later. If one carries out this substitution, one obtains,

$$\mathcal{D}_\alpha = f_\alpha^{(0)} \{ (\tfrac{2}{3}W_\alpha^2 - \frac{nE_\alpha k}{C_v} - 1)\underline{\nabla}\cdot\underline{u} + 2(\underline{W}_\alpha\underline{W}_\alpha - \frac{W_\alpha^2}{3}\underline{U}):\overset{\circ}{\underline{\nabla u}} +$$

$$(E_\alpha - 1)[2kT/M_\alpha]^{\frac{1}{2}}\underline{W}_\alpha\cdot\underline{\nabla}\ell nT + nM_\alpha[2kT/M_\alpha]^{\frac{1}{2}}\underline{W}_\alpha\cdot\underset{\beta}{\sum}(\delta_{\alpha\beta} - \frac{\rho_\beta}{\rho})\frac{\underline{d}_\beta}{\rho_\beta}\} \qquad (3.2\text{-}30)$$

where the dimensionless peculiar velocity is defined by the expression,

$$\underline{W}_\alpha = [M_\alpha/2kT]^{\frac{1}{2}}\underline{C}_\alpha \qquad (3.2\text{-}31)$$

and $\underline{U}$ denotes the identity tensor. The velocity gradient, $\underline{\nabla}\underline{u}$, has been written explicitly in terms of its irreducible components. (The symbol, $\overset{\circ}{\underline{G}}$, is adopted here as a uniform notation for the symmetric traceless component of a general second rank tensor, $\underline{G}$.)

It should be noted before proceeding that the method in which the linear dependence of the diffusion forces was eliminated will lead naturally to linear force-flux relations which explicitly exhibit the Onsager-Casimir reciprocity relations. Physically, this is a particularly satisfying result. However, this method of removing the linear dependence is not unique, but is rather, one of an infinite number of methods. In particular, another useful way of removing the linear dependence is embodied in the expression,

$$\underline{d}_\alpha = \underset{\beta}{\sum}(\delta_{\alpha\beta} - 1)\underline{d}_\beta \qquad (3.2\text{-}32)$$

If Eq. (3.2-32) is substituted into Eq. (3.2-25) (instead of Eq. (3.2-29)), one obtains the force-flux relations which correspond to the usual formulation of Fick's First Law (but do not explicitly exhibit the Onsager-Casimir relations).

If one substitutes Eq. (3.2-30) into Eq. (3.1-16) and takes note that the thermodynamic forces are linearly independent and that $\underset{\approx}{\Lambda}$ is a linear operator, it follows that the distortion can be cast into the form,

$$\phi = D\underline{\nabla}\cdot\underline{u} + \overset{\circ}{\underline{\underline{B}}} : \underline{\nabla}\underline{u} + [2kT]^{\frac{1}{2}}\underline{A}\cdot\underline{\nabla}\ell nT - n\sum_{\beta}\underline{\zeta}^{(\beta)}\cdot\frac{\underline{d}_\beta}{\rho_\beta} \qquad (3.2-33)$$

Here, the symbols $\underline{A}$, $\overset{\circ}{\underline{\underline{B}}}$, $D$, and $\underline{\zeta}^{(\beta)}$ specify contributions to the distortion due to the presence of specific thermodynamic forces. If one substitutes Eq. (3.2-33) into Eq. (3.1-16), one obtains,

$$|\mathcal{D}^D\rangle = \underset{\approx}{\Lambda}|D\rangle \qquad (3.2-34)$$

$$|\overset{\circ}{\underline{\mathcal{D}}}{}^{B}\rangle = \underset{\approx}{\Lambda}|\overset{\circ}{\underline{B}}\rangle \qquad (3.2-35)$$

$$|\underline{\mathcal{D}}^A\rangle = \underset{\approx}{\Lambda}|\underline{A}\rangle \qquad (3.2-36)$$

$$|\underline{\mathcal{D}}^{\zeta^{(\beta)}}\rangle = \underset{\approx}{\Lambda}|\underline{\zeta}^{(\beta)}\rangle \qquad (3.2-37)$$

where the inhomogeneities are defined,

$$\mathcal{D}^D_\alpha = f_\alpha^{(0)}\left(\frac{2}{3}w_\alpha^2 - \frac{nE_\alpha k}{C_v} - 1\right) \qquad (3.2-38)$$

$$\mathcal{D}_{-\alpha}^{B} = 2f_\alpha^{(0)} \, (\underline{W}_\alpha \underline{W}_\alpha - \tfrac{1}{3}W_\alpha^2 \underline{U}) \qquad (3.2\text{-}39)$$

$$\mathcal{D}_{-\alpha}^{A} = f_\alpha^{(0)} \, (E_\alpha - 1) M_\alpha^{-\frac{1}{2}} \underline{W}_\alpha \qquad (3.2\text{-}40)$$

$$\mathcal{D}_{-\alpha}^{\zeta(\beta)} = f_\alpha^{(0)} \, [2M_\alpha kT]^{\frac{1}{2}} \underline{W}_\alpha \, (\frac{\rho_\beta}{\rho} - \delta_{\alpha\beta}) \qquad (3.2\text{-}41)$$

Thus, the evaluation of the distortion and hence the transport coefficients, is a well-posed problem which can be carried out by the construction of $\underset{\approx}{\Lambda}$ in an appropriate basis followed by the solution of the resulting matrix equation (i.e. Eqs. (3.2-34) through (3.2-37)). The mechanics of this procedure are discussed in detail in Sections 3.4 and 3.5.

In a dilute gas, the flux vector of some physical quantity, $x_\alpha$, for species $\alpha$, is given by the ensemble average, $\langle x_\alpha \underline{C}_\alpha \rangle$, which is to say,

$$\langle x_\alpha \underline{C}_\alpha \rangle = \langle f | x_\alpha \underline{C}_\alpha \rangle \qquad (3.2\text{-}42)$$

If the distribution is expanded via the Chapman-Enskog method, then any flux vector can be also written in terms of the expansion for which a general term of order k has the form,

$$\langle x_\alpha \underline{C}_\alpha \rangle^{(k)} = \langle f^{(k)} | x_\alpha \underline{C}_\alpha \rangle \qquad (3.2\text{-}43)$$

The description of a linear phenomenology requires a knowl-

edge of $\langle x_\alpha \underline{C}_\alpha \rangle$ only through first order. Thus,
nondissipative (k = 0) and dissipative (k = 1) contributions
can be written as follows,

$$\langle x_\alpha \underline{C}_\alpha \rangle^{(0)} = \langle I | f^{(0)} x_\alpha \underline{C}_\alpha \rangle \qquad (3.2\text{-}44)$$

$$\langle x_\alpha \underline{C}_\alpha \rangle^{(1)} = \langle \phi | f^{(0)} x_\alpha \underline{C}_\alpha \rangle \qquad (3.2\text{-}45)$$

where I and $\phi$ represent the identity and the distortion, re-
spectively. Since $f^{(0)}$ is of a Maxwellian form (cf. Eq.
(3.2-51)), any nondissipative flux vector, $\langle x_\alpha C_\alpha \rangle^{(0)}$,
vanishes unless $x_\alpha$ is an odd function of $\underline{C}_\alpha$ (e.g. the
nondissipative partial pressure tensor, $\langle M_\alpha \underline{C}_\alpha \underline{C}_\alpha \rangle^{(0)} = n_\alpha kTU$;
nondissipative mass and heat flux vectors vanish).

Linear force-flux relations can be established by sub-
stitution of $\underline{x}_\alpha$ equal to $M_\alpha \underline{C}_\alpha$, $M_\alpha$ and $\frac{1}{2} M_\alpha C_\alpha^2 + K_\alpha^{int}$ (i.e. the
summational invariants) into Eq. (3.2-45) to obtain expres-
sions for the dissipative pressure tensor, $\underline{\pi}$, component
mass flux vector, $\underline{J}_\alpha$, and heat flux vector, $\underline{q}$. One obtains,

$$\underline{\pi} = \sum_\alpha \langle M_\alpha \underline{C}_\alpha \underline{C}_\alpha \rangle^{(1)} = kT \langle \phi | \underline{\underline{D}}^\beta + \frac{1}{3} \underline{D}^D \underline{U} \rangle \qquad (3.2\text{-}46)$$

$$\underline{J}_\alpha = \langle M_\alpha | \underline{C}_\alpha \rangle = -\langle \phi | \underline{D}^{\zeta(\alpha)} \rangle \qquad (3.2\text{-}47)$$

$$\underline{q} = \sum_\alpha \langle (\frac{1}{2} M_\alpha C_\alpha^2 + K_\alpha^{int}) \underline{C}_\alpha \rangle = [2k^3 T^3]^\frac{1}{2} \langle \phi | \underline{D}^A \rangle \qquad (3.2\text{-}48)$$

where use has been made of the explicit form of the
inhomogeneities (i.e., Eq. (3.2-38) through (3.2-41)) and the

auxiliary conditions (i.e., Eq. (3.2-7), (3.2-8), and (3.2-9)). One should note that there is the same number of force-flux pairs and hydrodynamic fields. Derivation of the force-flux relations is completed by substitution of Eqs. (3.2-33) through (3.2-37) into the preceding expressions(45).

$$\overset{o}{\underline{\pi}} = -[2k^3T^3]^{\frac{1}{2}}\underline{\nabla}\ell nT\cdot\langle\underline{A}|\underline{\Lambda}|\overset{o}{\underline{B}}\rangle - kT\underline{\nabla}^o\underline{u}:\langle\overset{o}{\underline{B}}|\underline{\Lambda}|\overset{o}{\underline{B}}\rangle -$$

$$kT\underline{\nabla}\cdot\underline{u}\langle D|\underline{\Lambda}|\overset{o}{\underline{B}}\rangle + nkT\sum_\alpha\frac{d_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\alpha)}|\underline{\Lambda}|\overset{o}{\underline{B}}\rangle \qquad (3.2-49)$$

$$\pi = -[2k^3T^3]^{\frac{1}{2}}\underline{\nabla}\ell nT\cdot\langle\underline{A}|\underline{\Lambda}|D\rangle - kT\underline{\nabla}^o\underline{u}:\langle\overset{o}{\underline{B}}|\underline{\Lambda}|D\rangle -$$

$$kT\underline{\nabla}\cdot\underline{u}\langle D|\underline{\Lambda}|D\rangle + nkT\sum_\alpha\frac{d_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\alpha)}|\underline{\Lambda}|D\rangle \qquad (3.2-50)$$

$$\underline{J}_\beta = [2kT]^{\frac{1}{2}}\underline{\nabla}\ell nT\cdot\langle\underline{A}|\underline{\Lambda}|\underline{\zeta}^{(\beta)}\rangle + \underline{\nabla}^o\underline{u}:\langle\overset{o}{\underline{B}}|\underline{\Lambda}|\underline{\zeta}^{(\beta)}\rangle +$$

$$\underline{\nabla}\cdot\underline{u}\langle D|\underline{\Lambda}|\underline{\zeta}^{(\beta)}\rangle - n\sum_\alpha\frac{d_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\alpha)}|\underline{\Lambda}|\underline{\zeta}^{(\beta)}\rangle \qquad (3.2-51)$$

$$\underline{q} = -2k^2T^2\underline{\nabla}\ell nT\cdot\langle\underline{A}|\underline{\Lambda}|\underline{A}\rangle - [2k^3T^3]^{\frac{1}{2}}\underline{\nabla}^o\underline{u}:\langle\overset{o}{\underline{B}}|\underline{\Lambda}|\underline{A}\rangle$$

$$-[2k^3T^3]^{\frac{1}{2}}\underline{\nabla}\cdot\underline{u}\langle D|\underline{\Lambda}|\underline{A}\rangle + [2k^3T^3]^{\frac{1}{2}}n\sum_\alpha\frac{d_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\alpha)}|\underline{\Lambda}|\underline{A}\rangle \qquad (3.2-52)$$

Here, the tensor, $\underline{\pi}$, has been decomposed into a symmetric traceless component, $\overset{o}{\underline{\pi}}$, and a trace, $\pi$, where $\underline{\pi} = \overset{o}{\underline{\pi}} + \frac{1}{3}\pi\underline{U}$ (for dilute gases $\underline{\pi}$ has no antisymmetric component).

Equations (3.2-49) through (3.2-52) are the linear phenomenological relationships, as given generally in Eq.

(1-1), which are appropriate for dilute gases. If the matrix elements of are transposed so that the Eqs. (3.2-49) through (3.2-52) are written as conventional matrix equations, one can identify the phenomenological coefficients explicitly as matrix elements of $\underset{\sim}{\Lambda}^{\dagger}$,

$$L_{ij} = \langle \phi_i | \underset{\sim}{\Lambda}^{\dagger} | \phi_j \rangle \qquad (3.2-53)$$

where $\phi_i$ is the part of the distortion characteristic of the force-flux pair $X_i - J_i$.

## 3.3. Diffusion, Thermal Conduction, Soret and Dufour Effects in a Binary Mixture of Atoms and Diatoms

The formalism developed in Chapter 2 and the first two sections of this chapter is completely general to mixtures of any number of components with arbitrary internal degrees of freedom and in the presence of an applied field. Here, and for the remainder of this work, consideration is limited to a binary mixture of a monatomic species, $\alpha$, and a diatomic species (more generally, linear), $\beta$, in the presence of a magnetic field. The diatom will be treated kinematically as a rigid rotor.

A monatom-diatom-magnetic field system exhibits invariance with respect to coordinate inversion. Thus, the collision operator, $\underset{\sim}{\Lambda}$, commutes with parity, $\underset{\sim}{P}$, implying that

$\underset{\sim}{\Lambda}$ cannot couple distortions which have different parity ei-genvalues. Immediately, from Eqs. (3.2-51) and (3.2-52) one obtains,

$$\underline{J}_\gamma = [2kT]^{\frac{1}{2}}\underline{\nabla}\ell nT \cdot \langle \underline{A}|\underset{\sim}{\Lambda}|\underline{\zeta}^{(\gamma)}\rangle - n\frac{\underline{d}_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\gamma)}|\underset{\sim}{\Lambda}|\underline{\zeta}^{(\gamma)}\rangle -$$

$$n\frac{\underline{d}_\beta}{\rho_\beta}\cdot\langle\underline{\zeta}^{(\beta)}|\underset{\sim}{\Lambda}|\underline{\zeta}^{(\gamma)}\rangle \qquad (3.3\text{-}1)$$

$$\underline{q} = -2k^2T^2\underline{\nabla}\ell nT\cdot\langle\underline{A}|\underset{\sim}{\Lambda}|\underline{A}\rangle + [2k^3T^3]^{\frac{1}{2}}n\frac{\underline{d}_\alpha}{\rho_\alpha}\cdot\langle\underline{\zeta}^{(\alpha)}|\underset{\sim}{\Lambda}|\underline{A}\rangle +$$

$$[2k^3T^3]^{\frac{1}{2}}n\frac{\underline{d}_\beta}{\rho_\beta}\cdot\langle\underline{\zeta}^{(\beta)}|\underset{\sim}{\Lambda}|\underline{A}\rangle \qquad (3.3\text{-}2)$$

The phenomenological coefficients appear here as second rank tensors. One can write Eqs. (3.3-1) and (3.3-2) conventionally in terms of the thermal conductivity, $\underset{=}{\lambda}$, thermal diffusion (Soret) coefficient, $\underset{=}{D}_\gamma^T$, diffusive thermal (Dufour) coefficient, $\underset{=}{K}_\gamma^T$, and diffusion coefficient, $\underset{=}{\Omega}_{\gamma\gamma'}$, as follows,

$$\underline{J}_\gamma = -\frac{1}{T}\underset{=}{D}_\gamma^T\cdot\underline{\nabla}T - \frac{nkT}{\rho_\alpha}\underset{=}{\Omega}_{\gamma\alpha}\cdot\underline{d}_\alpha - \frac{nkT}{\rho_\beta}\underset{=}{\Omega}_{\gamma\beta}\cdot\underline{d}_\beta \qquad (3.3\text{-}3)$$

$$\underline{q} = -\frac{1}{T}\underset{=}{\lambda}\cdot\underline{\nabla}T - \frac{nkT}{\rho_\alpha}\underset{=}{K}_\alpha^T\cdot\underline{d}_\alpha - \frac{nkT}{\rho_\beta}\underset{=}{K}_\beta^T\cdot\underline{d}_\beta \qquad (3.3\text{-}4)$$

where $\underset{=}{\lambda}$, $\underset{=}{D}_\gamma^T$, $\underset{=}{K}_\gamma^T$, and $\underset{=}{\Omega}_{\gamma\gamma'}$ have the explicit definition,

$$\underset{=}{\lambda} = 2(kT)^2\langle\underline{A}|\underset{\sim}{\Lambda}^\dagger|\underline{A}\rangle \qquad (3.3\text{-}5)$$

$$\underset{=}{D}_\gamma^T = -[2kT]^{\frac{1}{2}}\langle\underline{\zeta}^{(\gamma)}|\underset{\sim}{\Lambda}^\dagger|\underline{A}\rangle \qquad (3.3\text{-}6)$$

$$\underline{K}_\gamma^T = -[2kT]^{\frac{1}{2}} \langle \underline{A} | \underline{\underline{\Lambda}}^\dagger | \underline{\varsigma}^{(\gamma)} \rangle \qquad (3.3\text{-}7)$$

$$\underline{\Omega}_{\gamma\gamma'} = \frac{1}{kT} \langle \underline{\varsigma}^{(\gamma)} | \underline{\underline{\Lambda}}^\dagger | \underline{\varsigma}^{(\gamma')} \rangle \qquad (3.3\text{-}8)$$

Digressing momentarily, it is interesting to note that the usual binary diffusion coefficient, $\underline{\underline{D}}_{\gamma\gamma'}$, is related to $\underline{\underline{\Omega}}_{\gamma\gamma'}$ as follows,

$$\underline{\underline{D}}_{\gamma\gamma'} = -nkT\left(\frac{1}{\rho_{\gamma'}} \underline{\underline{\Omega}}_{\gamma\gamma'} - \frac{1}{\rho_\gamma} \underline{\underline{\Omega}}_{\gamma\gamma}\right) \qquad (3.3\text{-}9)$$

Matzen has given a detailed discussion of the general relationship between $\underline{\underline{D}}_{\gamma\gamma'}$ and $\underline{\underline{\Omega}}_{\gamma\gamma'}$ in a multicomponent mixture in his dissertation[45].

Explicit relationships (_i.e._ the Onsager-Casimir relations[19,20,21]) can be found between some of the previously mentioned phenomenclogical coefficients as a consequence of microscopic reversibility. If one notes first that $\underline{\underline{F}} = -\underline{\underline{F}}^\dagger$ due to its definition as a Poisson bracket or an operator commutator, and if $H^{int}$ is taken as proportional to the field, then the identity,

$$\underline{\underline{T}} \, \underline{\underline{\Lambda}} \, (\underline{F}) = \underline{\underline{\Lambda}}^\dagger (\tau\underline{F}) \, \underline{\underline{T}} \qquad (3.3\text{-}10)$$

is easily established via Eqs. (2.3-5), (3.1-8), and (3.1-16). Here, $\underline{\underline{T}}$ is the time reversal operator, $\underline{F}$ is the applied field, and $\tau$ is the time reversal eigenvalue of $\underline{F}$. If one notes that the thermal and diffusive distortions have

the same time reversal eigenvalue, Eq. (3.3-10) immediately yields,

$$\underline{D}_\gamma^T = \underline{K}_\gamma^T \qquad (3.3-11)$$

$$\underline{\Omega}_{\gamma\gamma'} = \underline{\Omega}_{\gamma'\gamma} \qquad (3.3-12)$$

where $\underline{H}$ denotes an applied magnetic field.

In addition to the Onsager-Casimir relations, further relationships between the diffusion and thermal diffusion coefficients can be found as a consequence of the linear dependence of the diffusion forces. One finds from Eqs. (3.2-37) and (3.2-41) that $\sum_\gamma \underline{\zeta}^{(\gamma)}$ vanishes in general (i.e. $\underline{\zeta}^{(\alpha)} = -\underline{\zeta}^{(\beta)}$ in the present case). Thus, it follows that,

$$\underline{D}_\alpha^T = -\underline{D}_\beta^T \qquad (3.3-13)$$

and,

$$\underline{\Omega}_{\alpha\alpha} = -\underline{\Omega}_{\alpha\beta} = \underline{\Omega}_{\beta\beta} = -\underline{\Omega}_{\beta\alpha} \qquad (3.3-14)$$

Again digressing, it is interesting to note that Eqs. (3.3-13) and (3.3-9) yield the result,

$$\underline{D}_{\alpha\beta} = -nkT\left(\frac{\rho}{\rho_\alpha\rho_\beta}\right)\underline{\Omega}_{\alpha\beta} \qquad (3.3-15)$$

where $\underline{D}_{\alpha\beta} = \underline{D}_{\beta\alpha}$ and $\underline{D}_{\alpha\alpha}$ and $\underline{D}_{\beta\beta}$ vanish.

In conclusion, it is clear from the preceding development that the phenomenological coefficients describing ordi-

nary diffusion, the Soret effect, the Dufour effect and heat conduction are all embodied in the three second rank tensor quantities, $\underline{\underline{\lambda}}$, $\underline{\underline{D}}_\beta$, and $\underline{\underline{\Omega}}_{\alpha\beta}$. In the absence of an applied field, the isotropy of space requires that $\underline{\underline{\lambda}}$, $\underline{\underline{D}}_\beta^T$, and $\underline{\underline{\Omega}}_{\alpha\beta}$ are all proportional to the isotropic second rank tensor, $\underline{\underline{U}}$. However, the application of a field destroys three dimensional spatial isotropy although one still observes two dimensional isotropy in a plane perpendicular to the direction of the field, $\hat{K}$ ($\hat{K} = \underline{H}/|\underline{H}|$). If $\underline{\underline{T}}$ is adopted as a general notation for $\underline{\underline{\lambda}}$, $\underline{\underline{D}}_\beta^T$, or $\underline{\underline{\Omega}}_{\alpha\beta}$, in the presence of a field it takes the form,

$$\underline{\underline{T}} = T_\perp(\underline{\underline{U}}-\hat{k}\hat{k}) + T_\parallel\hat{k}\hat{k} + T_{tr}(\hat{k}\times\underline{\underline{U}}) \qquad (3.3\text{-}16)$$

where $T_\perp$, $T_\parallel$, and $T_{tr}$ are scalars. Specifically, $T_\perp$ and $T_\parallel$ describe transport which is, respectively, perpendicular and parallel to the field direction. The "transverse" phenomenological coefficient, $T_{tr}$, describes transport which is both perpendicular to the field direction and to the thermodynamic stress (field gradient) giving rise to the flux.

## 3.4. Formal Inversion of the Generalized Linear Collision Operator

It follows from Eqs. (3.3-5) through (3.3-8) that the phenomenological coefficient, $\underline{\underline{T}}$ (i.e. $\underline{\lambda}$, $\underline{\underline{D}}_\beta^T$, or $\underline{\underline{\Omega}}_{\alpha\beta}$) can be written formally as,

$$\underline{\underline{T}} = C_T \langle \underline{\underline{F}} | \underline{\underline{\Lambda}}^\dagger | \underline{\underline{G}} \rangle \qquad (3.4-1)$$

where $C_T$ is a numerical coefficient and $\underline{F}$ and $\underline{G}$ are distortions (i.e. in the present case, $\underline{A}$, $\underline{\zeta}^{(\alpha)}$, or $\underline{\zeta}^{(\beta)}$). If use is made of Eqs. (3.2-34) through (3.2-37) one obtains,

$$\underline{\underline{T}} = C_T \langle \underline{D}^F | \underline{\underline{G}} \rangle \qquad (3.4-2)$$

where $\underline{D}^F$ is the inhomogeneity conjugate to the distortion, $\underline{F}$ (i.e., $\underline{D}^F$ is $\underline{D}^A$, $\underline{D}^{\zeta\,(\alpha)}$, or $\underline{D}^{\zeta\,(\beta)}$). As stated in Section 3.2, the phenomenological coefficient (i.e., $\underline{\underline{T}}$) can be evaluated explicitly by construction of the appropriate distortion (i.e., $\underline{G}$). However, because $\underline{\underline{\Lambda}}$ is a singular operator the expression (i.e. Eq. (3.1-16)),

$$| \underline{D}^G \rangle = \underline{\underline{\Lambda}} | \underline{\underline{G}} \rangle \qquad (3.4-3)$$

cannot be inverted directly. As stated previously, this singularity arises from mechanical conservation principles and is manifested in the fact that the summational invariants are zero eigenvectors of $\underline{\underline{\Lambda}}$. To remedy this, one can define the nonsingular operator, $\underline{\underline{L}}$, as the sum, $\underline{\underline{\Lambda}} + \underline{\underline{\Lambda}}$, where,

$$\underset{\approx}{A} = \sum_{\nu} a_1^{(\nu)} |f_\nu^{(0)}\rangle\langle f_\nu^{(0)}| \delta_{\nu\mu} + \sum_{\nu} \underline{a}_2^{(\nu)} : \sum_{\nu} |\underline{p}_\nu f_\nu^{(0)}\rangle\langle\underline{p}_\mu f_\mu^{(0)}|$$

$$+ \sum_{\nu} a_3^{(\nu)} \sum_{\mu} |h_\nu f_\nu^{(0)}\rangle\langle h_\mu f_\mu^{(0)}| \qquad (3.4-4)$$

Here, $h_\beta = p_\beta^2/2M_\beta + K_\beta^{int} - 3kT/2 - \overline{E}_\beta^{int}$ and $h_\alpha = p_\alpha^2/2M_\alpha - 3kT/2$, and $a_1^{(\nu)}$, $\underline{a}_2^{(\nu)}$, and $a_2^{(\nu)}$ are arbitrary scalar and tensor constants which will be specified later, and the sums are taken over $\alpha$ and $\beta$. Thus, the nonsingularity of $\underset{\approx}{L}$ is guaranteed by the auxiliary conditions (i.e., Eqs. (3.2-7), (3.2-8), and (3.2-9)) which require that the only nonzero eigenvalues of $\underset{\approx}{A}$ must be linearly independent combinations of the summational invariants. Thus, an appropriate number of additional linearly independent conditions (one for each summational invariant) are provided by the auxiliary conditions and are combined with the singular operator, $\underset{\approx}{\Lambda}$, to construct the nonsingular operator, $\underset{\approx}{L}$. It follows explicitly from the auxiliary conditions (i.e., $f^{(1)}$ gives no contribution to hydrodynamic fields) and Eq. (3.1-16) that

$$|\mathcal{D}\rangle = \underset{\approx}{L} |\phi\rangle \qquad (3.4-5)$$

or in particular,

$$|\underline{\mathcal{D}}^G\rangle = \underset{\approx}{L} |\underline{G}\rangle \qquad (3.4-6)$$

Thus, $\underset{\sim}{T}$ can be written,

$$\underset{\sim}{T} = c_T \langle \underline{D}^F | \underset{\approx}{L}^{-1} | \underline{D}^G \rangle \tag{3.4-7}$$

where $\underset{\approx}{L}^{-1}$ is well-defined as the inverse of $\underset{\approx}{L}$.

A formal expression for $\underset{\approx}{L}^{-1}$ can be obtained if $\underset{\approx}{L}$ is written as an operator sum(46),

$$\underset{\approx}{L} = \underset{\approx 0}{L} + \underset{\approx}{W} \tag{3.4-8}$$

where $\underset{\approx 0}{L}$ is defined as the "spherical" contribution to $\underset{\approx}{L}$ and the remainder, $\underset{\approx}{W}$, is defined as the "nonspherical" contribution. (The motivation behind these designations will become clear in later development.) It is assumed that $\underset{\approx 0}{L}$ is nonsingular and thus one obtains,

$$\underset{\approx}{1} = \underset{\approx 0}{L}^{-1} \underset{\approx 0}{L} = \underset{\approx 0}{L}^{-1} \underset{\approx}{L} - \underset{\approx 0}{L}^{-1} \underset{\approx}{W} \underset{\approx}{1} \tag{3.4-9}$$

Repetitive substitution of Eq. (3.4-9) into itself yields,

$$\underset{\approx}{L}^{-1} = \underset{\approx 0}{L}^{-1} \sum_{j=0}^{\infty} (\underset{\approx}{W} \underset{\approx 0}{L}^{-1})^j \tag{3.4-10}$$

Equation (3.4-10) is useful only if $\underset{\approx 0}{L}^{-1}$ is easily constructed and if $\underset{\approx}{W}$ can be considered as a small perturbation (in the "nonsphericity") on $\underset{\approx 0}{L}$ (i.e. the series converges rapidly). It will become evident in later development that both of these criteria are met for cases of interest in this work.

If one defines a dimensionless ordering parameter, $\eta$, (ultimately to be set equal to unity) which marks the diatom

density, $n_\beta$, then $\underset{\approx}{L}$ can be cleanly separated into a sum of operators, $\underset{\approx}{L}^{(0)}$, $\underset{\approx}{L}^{(1)}$, and $\underset{\approx}{L}^{(2)}$, which involve, respectively, only atom-atom, atom-diatom, and diatom-diatom collisions,

$$\underset{\approx}{L} = \underset{\approx}{L}^{(0)} + \eta \underset{\approx}{L}^{(1)} + \dot{\eta}^2 \underset{\approx}{L}^{(2)} \qquad (3.4\text{-}11)$$

Likewise, the inhomogeneity, $\underline{D}^G$, and the distortion, $\underline{G}$, can be written as power series in $\eta$ (or equivalently in the diatom density),

$$\underline{D}^G = \underline{D}^{G(0)} + \eta \underline{D}^{G(1)} + \eta^2 \underline{D}^{G(2)} + \dots \qquad (3.4\text{-}12)$$

$$\underline{G} = \underline{G}^{(0)} + \eta \underline{G}^{(1)} + \eta^2 \underline{G}^{(2)} + \dots \qquad (3.4\text{-}13)$$

If one substitutes Eqs. (3.4-12) and (3.4-13) into Eq. (3.4-11) and equates coefficients of like power in $\eta$, one obtains a hierarchy of equations,

$$\left| \begin{matrix} \underline{D}_\alpha^{G(j)} \\ \underline{D}_\beta^{G(j)} \end{matrix} \right\rangle = \left[ \begin{matrix} \underset{\approx}{L}_{\alpha\alpha}^{(0)} & 0 \\ \hline 0 & 0 \end{matrix} \right] \left| \begin{matrix} \underline{G}_\alpha^{(j)} \\ \underline{G}_\beta^{(j)} \end{matrix} \right\rangle + \left[ \begin{matrix} \underset{\approx}{L}_{\alpha\alpha}^{(1)} & \underset{\approx}{L}_{\alpha\beta}^{(1)} \\ \hline \underset{\approx}{L}_{\beta\alpha}^{(1)} & \underset{\approx}{L}_{\beta\beta}^{(1)} \end{matrix} \right] \left| \begin{matrix} \underline{G}_\alpha^{(j-1)} \\ \underline{G}_\beta^{(j-1)} \end{matrix} \right\rangle$$

$$+ \left[ \begin{matrix} 0 & 0 \\ \hline 0 & \underset{\approx}{L}_{\beta\beta}^{(2)} \end{matrix} \right] \left| \begin{matrix} \underline{G}_\alpha^{(j-2)} \\ \underline{G}_\beta^{(j-2)} \end{matrix} \right\rangle \qquad (3.4\text{-}14)$$

where Eq. (3.4-14) has been written explicitly in terms of "composition space" components. This expression can be rearranged to yield,

$$\left| \begin{matrix} \underline{G}_\alpha^{(j)} \\ \frac{1}{\eta}\underline{G}_\beta^{(j-1)} \end{matrix} \right\rangle = \left[ \begin{array}{c|c} (\underset{\approx}{L}_{\alpha\alpha}^{(0)})^{-1} & 0 \\ \hline 0 & \frac{1}{\eta}(\underset{\approx}{L}_{\beta\beta}^{(1)})^{-1} \end{array} \right] \left\{ \left| \begin{matrix} \underline{D}_\alpha^{G(j)} \\ \underline{D}_\beta^{G(j)} \end{matrix} \right\rangle - \left[ \begin{array}{c|c} \underset{\approx}{L}_{\alpha\alpha}^{(1)} & \underset{\approx}{L}_{\alpha\beta}^{(1)} \\ \hline \underset{\approx}{L}_{\beta\alpha}^{(1)} & 0 \end{array} \right] \right.$$

$$\left. \left| \begin{matrix} \underline{G}_\alpha^{(j-1)} \\ \underline{G}_\beta^{(j-1)} \end{matrix} \right\rangle - \left[ \begin{array}{c|c} 0 & 0 \\ \hline 0 & \underset{\approx}{L}_{\beta\beta}^{(2)} \end{array} \right] \left| \begin{matrix} \underline{G}_\alpha^{(j-2)} \\ \underline{G}_\beta^{(j-2)} \end{matrix} \right\rangle \right\} \qquad (3.4\text{-}15)$$

where one notes that $\underline{G}^{(k)}$, $\underline{D}_\alpha^{G(k)}$, and $\underline{D}_\beta^{G(k+1)}$ all vanish if $k$ is less than zero. Thus, $\underline{G}$ has been constructed as a series of successive approximations of increasing power in the diatom density. Before proceeding, one should note that the operator, $\underset{\approx}{L}$, defined as

$$\underset{\approx}{L} = \left[ \begin{array}{c|c} \underset{\approx}{L}_{\alpha\alpha}^{(0)} & 0 \\ \hline 0 & \eta\underset{\approx}{L}_{\beta\beta}^{(1)} \end{array} \right] \qquad (3.4\text{-}16)$$

can be inverted formally to obtain the inverse operator, $\underset{\approx}{L}^{-1}$,

$$\underset{\approx}{L}^{-1} = \left[ \begin{array}{c|c} (\underset{\approx}{L}_{\alpha\alpha}^{(0)})^{-1} & 0 \\ \hline 0 & \frac{1}{\eta}(\underset{\approx}{L}_{\beta\beta}^{(1)})^{-1} \end{array} \right] \qquad (3.4\text{-}17)$$

by means of the same "nonsphericity" perturbation technique (cf. Eqs. (3.4-8) through (3.4-10)) outlined previously

(where $\underset{\approx}{T}_0$ and $\underset{\approx}{W}_0$ are defined in complete analogy to $\underset{\approx}{T}$ and $\underset{\approx}{W}$).

One can write $\underset{=}{T}$ as a series in $\eta$ by substitution of Eqs. (3.4-12) and (3.4-13) into Eq. (3.4-2),

$$\underset{=}{T} = \sum_{j=0}^{\infty} \eta^j \underset{=}{T}^{(j)} = C_T \sum_{j=0}^{\infty} \sum_{k=0}^{j} \eta^j \langle \underset{=}{D}^{F(k)} | \underset{=}{G}^{(j-k)} \rangle \qquad (3.4-18)$$

The utility of this kind of expansion can be appreciated in the analysis of the effect of interactions between unlike molecules (i.e., atoms and diatoms). Specifically, $\underset{=}{T}^{(1)}$ involves the effect of atom-diatom interactions but does not involve diatom-diatom interactions and can be written in terms of a limiting slope,

$$\underset{=}{T}^{(1)} = \lim_{n_\beta \to 0} \left( n_\beta \frac{\partial}{\partial n_\beta} \underset{=}{T} \right)_{n_\alpha} = \lim_{x_\beta \to 0} \left( x_\beta \frac{d}{dx_\beta} \underset{=}{T} \right) \qquad (3.4-19)$$

Here, $X_\beta$ is the diatom mole fraction, $n_\beta / n$.

To conclude this section, Eq. (3.4-18) will be applied specifically to the thermal conductivity, $\underset{=}{\lambda}$, to illustrate its utility. Thus, one obtains,

$$\underset{=}{\lambda} = \sum_{j=0}^{\infty} \eta^j \underset{=}{\lambda}^{(j)} \qquad (3.4-20)$$

Now, using simple collision number arguments, it is possibile to write an empirical expression for the thermal conductivity of an atom-diatom mixture as follows,

$$\underline{\lambda} = X_\alpha^2 \underline{\lambda}_{\alpha\alpha} + 4X_\alpha X_\beta \underline{\lambda}_{\alpha\beta} + X_\beta^2 \underline{\lambda}_{\beta\beta} \qquad (3.4\text{-}21)$$

where $X_\alpha$ is the atom mole fraction. The tensor quantities, $\underline{\lambda}_{\alpha\alpha}$ and $\underline{\lambda}_{\beta\beta}$, are pure component thermal conductivities for the $\alpha$ and $\beta$ species, respectively, and thus involve only interactions between like molecules. In contrast, $\underline{\lambda}_{\alpha\beta}$ involves only interactions between unlike molecules and can be viewed physically as the thermal conductivity of an equimolar mixture of $\alpha$ and $\beta$ species for which the $\alpha$-$\alpha$ and $\beta$-$\beta$ interactions have been hypothetically "turned off" (i.e., only $\alpha$-$\beta$ collisions occur). If one notes the definition of the mole fractions, $X_\alpha$ and $X_\beta$, in terms of the densities, $n_\alpha$ and $n_\beta$, and assumes that the atomic species is the major component, then one can use the geometric series to write Eq. (3.4-21) in the form,

$$\underline{\lambda} = \underline{\lambda}_{\alpha\alpha} + \eta(2\underline{\lambda}_{\alpha\beta} - \underline{\lambda}_{\alpha\alpha})\frac{2n_\beta}{n_\alpha} + \ldots \qquad (3.4\text{-}22)$$

Here, the marking parameter is inserted explicitly. Comparison of this expression to Eq. (3.4-20) allows the identifications,

$$\underline{\lambda}_{\alpha\alpha} = \underline{\lambda}^{(0)} \qquad (3.4\text{-}23)$$

$$\underline{\lambda}_{\alpha\beta} = \frac{n_\alpha}{4n_\beta}\underline{\lambda}^{(1)} + \frac{1}{2}\underline{\lambda}^{(0)} \qquad (3.4\text{-}24)$$

Thus, the effect of unlike collisions can be directly investigated by means of the diatom density expansion.

## 3.5. Expansion of the Thermal and Diffusive Distortions Using Irreducible Tensors, Sonine and Wang Chang-Uhlenbeck Polynomials

One begins this discussion by investigating the concrete form for the $L^2$/Hilbert-Schmidt inner product appropriate to an atom-diatom mixture. If X and Y denote arbitrary composition vectors, the components of which are real functions of the free-flight invariants exclusively, then classically $\langle X|Y \rangle$ can be defined(36),

$$\langle X|Y \rangle = \frac{1}{4\pi}\int d\hat{e}\int dW_\beta \int_0^\infty d\Omega_1 \int_0^\infty d\Omega_2 X_\beta Y_\beta + \int dW_\alpha X_\alpha Y_\alpha \qquad (3.5-1)$$

where $\underline{W}_\alpha$ and $\underline{W}_\beta$ are dimensionless peculiar velocities as defined by Eq. (3.2-31) and $\hat{e}$ is the unit vector parallel to the diatomic internuclear axis. The variables, $\Omega_1$ and $\Omega_2$ are defined as,

$$\Omega_1 = \ell_1/[2I_\beta kT]^{\frac{1}{2}} \qquad (3.5-2)$$

$$\Omega_2 = \ell_2/[2I_\beta kT]^{\frac{1}{2}} \qquad (3.5-3)$$

where $\ell_1$ and $\ell_2$ are components of the diatomic rotational

angular momentum appropriate to the two thermally active rotational degrees of freedom and $I_\beta$ is the diatomic moment of inertia. Because $X_\beta + Y_\beta$ are independent of $\hat{e}$, one can make a change of integration variable to obtain,

$$\langle X | Y \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int d\underline{W}_\beta \int \frac{d\underline{\Omega}_\beta}{|\underline{\Omega}_\beta|} X_\beta Y_\beta + \int d\underline{W}_\alpha X_\alpha Y_\alpha \qquad (3.5\text{-}4)$$

where $\phi$ is a phase angle describing the position of the diatom internuclear axis relative to a space-fixed coordinate system. The reduced rotational angular momentum, $\underline{\Omega}_\beta$, is defined in analogy to $\Omega_1$ and $\Omega_2$.

$$\underline{\Omega}_\beta = \underline{\ell}_\beta / [2I_\beta kT]^{\frac{1}{2}} \qquad (3.5\text{-}5)$$

where $\underline{\ell}_\beta$ is the space-fixed diatom rotational angular momentum. Since $\phi$ is not a free-flight invariant, Eq. (3.5-4) gives,

$$\langle X | Y \rangle = \frac{1}{2} \int d\underline{W}_\beta \int \frac{d\underline{\Omega}_\beta}{|\underline{\Omega}_\beta|} X_\beta Y_\beta + \int d\underline{W}_\alpha X_\alpha Y_\alpha \qquad (3.5\text{-}6)$$

Quantally, $\langle X | Y \rangle$ is defined ($\hat{X}_\beta$ and $\hat{Y}_\beta$ commute),

$$\langle X | Y \rangle = \frac{\pi \theta_r}{T} \int d\underline{W}_\beta \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \langle jm | \hat{X}_\beta \hat{Y}_\beta | jm \rangle + \int d\underline{W}_\alpha X_\alpha Y_\alpha \qquad (3.5\text{-}7)$$

where $\theta_r$ equals $\hbar^2 / 2I_\beta kT$ and $|jm\rangle$ is an eigenfunction of the reduced rotational angular momentum magnitude and z component operators $\hat{\Omega}_\beta$ and $\hat{\Omega}_{z\beta}$.

Digressing briefly one notes that an analytic function, F, of a three dimensional vector, $\underline{x}$, can be written as the following series,

$$F(\underline{x}) = \sum_{n=0}^{\infty} F^{(n)}(x) \underset{n}{\odot} [\underline{x}]^{(n)} \qquad (3.5\text{-}8)$$

Here, $F^{(n)}(x)$ is an n-rank tensor function of the magnitude of $\underline{x}$ and $[\underline{x}]^{(n)}$ is by definition, the n-rank irreducible component of the n-ad, $(\underline{x})^n$. The symbol, $\underset{n}{\odot}$, denotes n successive scalar contractions taken between pairs of indices starting with the last index (i.e. on the right) of $F^{(n)}(x)$ and the first index (i.e. on the left) of $[\underline{x}]^{(n)}$ and proceeding in order to the first index of $F^{(n)}(x)$ and the last index of $[\underline{x}]^{(n)}$. This is the so-called "adjacent" tensor contraction convention and will be uniformly adopted throughout this work unless otherwise stated.

The irreducible tensor, $[\underline{x}]^{(n)}$, is symmetric and traceless on all pairs of indices. It is easily shown that the $[\underline{x}]^{(n)}$ are mutually orthogonal under integration over the angles of $\underline{x}$. Also, the expansion given in Eq. (3.5-8) remains valid in the case that $\underline{x}$ is a vector operator. In this case, the resulting irreducible tensor operators now form a mutually orthogonal set under the trace operation. A brief discussion of the properties and form of the irreducible tensors appears in Appendix A.

The normalized Sonine polynomials, $S_a^b(x)$, satisfy the following orthogonality condition,

$$\int_0^\infty dx \; x^a S_a^{(b)}(x) S_a^{(b')}(x) e^{-x} = \delta_{bb'} \qquad (3.5-9)$$

and have the explicit form,

$$S_a^{(b)}(x) = [b! \Gamma(a+b+1)]^{\frac{1}{2}} \sum_{j=0}^{b} \frac{(-x)^j}{(b-j)! j! \Gamma(a+j+1)} \qquad (3.5-10)$$

Similarly, the normalized Wang Chang-Uhlenbeck polynomials, $S_a^{(b)}(\hat{\Omega}_\beta^2)$, satisfy a corresponding orthogonality condition,

$$\frac{\theta_r}{T} \sum_{j=0}^{\infty} \sum_{m=-j}^{j} <jm| \hat{\Omega}_\beta^{2a} e^{-\hat{\Omega}_\beta^2} S_a^{(b)}(\hat{\Omega}_\beta^2) S_a^{(b')}(\hat{\Omega}_\beta^2) |jm> = \delta_{bb'} \qquad (3.5-11)$$

The coefficients of the Wang Chang-Uhlenbeck polynomials are easily determined using an appropriate orthogonalization scheme (e.g. Schmidt orthogonalization). The zeroth and first order polynomials are,

$$S_a^{(0)}(\hat{\Omega}_\beta^2) = [\frac{1}{\varepsilon(a)}]^{\frac{1}{2}} \qquad (3.5-12)$$

$$S_a^{(1)}(\hat{\Omega}_\beta^2) = \left[ \frac{\varepsilon(a)}{\varepsilon(a+2)\varepsilon(a)-(\varepsilon(a+1))^2} \right] \left( \frac{\varepsilon(a+1)}{\varepsilon(a)} - \hat{\Omega}_\beta^2 \right) \qquad (3.5-13)$$

where,

$$\epsilon(a) = \frac{\theta_r}{T} \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \langle jm | \hat{\Omega}_\beta^{2a} e^{-\hat{\Omega}_\beta^2} | jm \rangle \quad (3.5\text{-}14)$$

It is easily shown that the correspondence limit of $\epsilon(a)$ is $\Gamma(a+1)$ from which it follows that the Sonine polynomials are the correspondence limit of the Wang Chang-Uhlenbeck polynomials.

The Sonine and/or Wang Chang-Uhlenbeck polynomials can be combined with irreducible tensors to construct a general set of basis function-operators which are given by the following expressions,

$$\psi_\alpha^{(ps)} = [2^p \Gamma(p+3/2)]^{\frac{1}{2}} S_{p+\frac{1}{2}}^{(s)}(W_\alpha^2) [\underline{W}_\alpha]^{(p)} \quad (3.5\text{-}15)$$

$$\psi_\beta^{(pqst)} = [2^{p+q+1} \pi^{\frac{1}{2}} \Gamma(p+3/2)\Gamma(q+3/2)]^{\frac{1}{2}} S_{p+\frac{1}{2}}^{(s)} \quad (3.5\text{-}16)$$
$$(W^2) S_q^{(+)} (\hat{\Omega}^2) [\underline{W}_\beta]^{(p)}[\underline{\Omega}_\beta]^{(q)}$$

Here the classical form of $\psi_\beta^{(pqst)}$ has been given. For comparison, the quantal form can be written,

$$\psi_\beta^{(pqst)} = [2^{p+q+1} \pi^{\frac{1}{2}} \Gamma(p+3/2)\Gamma(q+3/2) N_{qt}]^{\frac{1}{2}} S_{p+\frac{1}{2}}^{(s)} \quad (3.5\text{-}17)$$
$$(W_\beta^2) S_q^{(t)} (\hat{\Omega}_\beta^2) [\underline{W}_\beta]^{(p)} [\underline{\Omega}_\beta]^{(q)}$$

where the constant $N_{qt}$ is a quantal correction for the normalization constant (e.g. $N_{00} = 1/\epsilon(0)$). Clearly, Eq.

(3.5-16) is the correspondence limit of Eq. (3.5-17).

The preceding basis function-operators by definition, satisfy the following orthogonality relations,

$$\int d\underline{W}_\alpha \psi_\alpha^{(ps)} \psi_\alpha^{(PS)} \frac{e^{-W_\alpha^2}}{\pi^{3/2}} = \Delta^{(p)} \delta_{pP} \delta_{sS} \tag{3.5-18}$$

and

$$\frac{1}{2} \int d\underline{W}_\beta \int \frac{d\underline{\Omega}_\beta}{\Omega_\beta} \psi_\beta^{(pqst)} \psi_\beta^{(PQST)} \frac{e^{-W_\beta^2 - \Omega_\beta^2}}{\pi^{5/2}}$$

$$= \Delta^{(p,q)} \delta_{pP} \delta_{qQ} \delta_{sS} \delta_{tT} \tag{3.5-19}$$

or

$$\frac{\theta_r}{T} \int d\underline{W}_\beta \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \langle jm| \psi_\beta^{(pqst)} \psi_\beta^{(PQST)} e^{-\Omega_\beta^2} |jm\rangle \frac{e^{-W_\beta^2}}{\pi^{3/2}} =$$

$$\Delta^{(p,q)} \delta_{pP} \delta_{qQ} \delta_{sS} \delta_{tT} \tag{3.5-20}$$

Here, $\Delta^{(p)}$ is defined as a three-dimensional isotropic tensor of rank 2p which has the tensor symmetry of $[\underline{x}]^{(p)}$ on its first and last p indices. If one notes that the tensor, $[\underline{x}]^{(p)}$ forms a basis for an irreducible representation of the three-dimensional rotation group, $C^+(3)$, it follows that the tensor, $\Delta^{(p)}$, is the identity element in this representation (i.e. $\Delta^{(p)} \underset{p}{\otimes} [\underline{x}]^{(p)} = [\underline{x}]^{(p)}$). Using this definition of $\Delta^{(p)}$, the tensor, $\Delta^{(p,q)}$, is defined as an isotropic tensor of rank 2(p+q) which has the tensor symmetry of the direct product

tensor, $[\underline{x}]^{(q)}[\underline{y}]^{(p)}$, on its first $p+q$ indices and of $[\underline{y}]^{(p)}[\underline{x}]^{(q)}$ on its last $p+q$ indices. It can be constructed from $\Delta^{(p)}$ and $\Delta^{(q)}$ by "sandwiching" $\Delta^{(p)}$ between the first and last sets of $q$ indices of $\Delta^{(q)}$. Accordingly, $\Delta^{(p,q)}$ is the identity element of this direct product representation, (i.e. $\Delta^{(p,q)}\underset{p+q}{\odot}[\underline{x}]^{(q)}[\underline{y}]^{(p)} = [\underline{x}]^{(q)}[\underline{y}]^{(p)}$). The properties and form of these isotropic tensors are discussed in Appendix B.

A distortion, $\underline{G}$, can be written in terms of the basis function-operators as follows(47,48),

$$\underline{G}_\alpha = \sum_{p=0}^{\infty} \sum_{s=0}^{p} \Psi_\alpha^{(ps)} \underset{p}{\odot} \langle \Psi_\alpha^{(ps)} | \delta_\alpha \underline{G} \rangle \qquad (3.5\text{-}21)$$

$$\underline{G}_\beta = \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{s=0}^{p} \sum_{t=0}^{q} \Psi_\beta^{(pqst)} \underset{p+q}{\odot} \langle \Psi_\beta^{(pqst)} | \delta_\beta \underline{G} \rangle \qquad (3.5\text{-}22)$$

where $\delta_\gamma$ is defined as $f_\gamma^{(0)}/n_\gamma$. By convention, when a basis function-operator, $\Psi_\beta^{(pqst)}$, appears to the right of a contraction or within a bra it will undergo a bulk transposition of tensor indices (i.e. $[\underline{W}_\beta]^{(p)}[\underline{\Omega}_\beta]^{(q)} \rightarrow [\underline{\Omega}_\beta]^{(q)}[\underline{W}_\beta]^{(p)}$). Equations (3.5-21) and (3.5-22) lead immediately to the matrix equation,

$$\langle \Psi_\nu^{(pqst)} | \underline{D}^G \rangle =$$

$$(3.5\text{-}23)$$

$$\sum_{\substack{PQST \\ \mu}} \langle \Psi_\nu^{(pqst)} | \underset{\approx}{L} | \Psi_\mu^{(PQST)} \rangle_{P \ne Q} \langle \Psi_\mu^{(PQST)} | \delta_\mu \underline{G} \rangle$$

By convention, the angular momentum indices q,t or Q,T are ignored if $\nu$ or $\mu$, respectively, is $\alpha$. Clearly, Eq. (3.5-23) is a concrete representation of the abstract expression Eq. (3.4-6). Thus, the solution of the linearized Boltzmann/Waldmann-Snider equation is now embodied in the evaluation of the matrix elements of the operator, $\underset{\approx}{L}$, and construction of its inverse in an irreducible tensor Sonine or Wang Chang-Uhlenbeck polynomial representation.

The thermal and diffusive inhomogeneities given in Eqs. (3.2-40) and (3.2-41) can be written explicitly in terms of the basis function-operators as follows,

$$\underline{D}_\alpha^A = [\frac{5}{4M_\alpha}]^{\frac{1}{2}} f_\alpha^{(0)} \psi_\alpha^{(11)} \qquad (3.5-24)$$

$$\underline{D}_\beta^A = f_\beta^{(0)} ( [\frac{5}{4M_\beta}]^{\frac{1}{2}} \psi_\beta^{(1010)} + [\frac{\epsilon^*}{2M_\beta}]^{\frac{1}{2}} \psi_\beta^{(1001)} ) \qquad (3.5-25)$$

$$\underline{D}_\alpha^{\zeta(\gamma)} = f_\alpha^{(0)} [M_\alpha kT]^{\frac{1}{2}} (\frac{\rho_\gamma}{\rho} - \delta_{\alpha\gamma}) \psi_\alpha^{(10)} \qquad (3.5-26)$$

$$\underline{D}_\beta^{\zeta(\gamma)} = f_\beta^{(0)} [M_\beta kT]^{\frac{1}{2}} (\frac{\rho_\gamma}{\rho} - \delta_{\beta\gamma}) \psi_\beta^{(1000)} \qquad (3.5-27)$$

where $\epsilon^* = (\epsilon(2) - (\epsilon(1))^2/\epsilon(0))$. It follows from these expressions, Eqs. (3.3-5) through (3.3-8) and Eq. (3.1-16) that the phenomenological coefficients can be written explicitly in terms of the coefficients of the expansion of the distor-

tion (*i.e.* Eqs. (3.5-22) and (3.5-23)). One obtains,

$$\underline{\lambda} = 2(kT)^2 \{ n_\alpha [\frac{5}{4M_\alpha}]^{\frac{1}{2}} \underline{A}_\alpha^{(11)} + n_\beta [\frac{5}{4M_\beta}]^{\frac{1}{2}} \underline{A}_\beta^{(1010)} + \\ n_\beta [\frac{\epsilon^*}{2M_\beta}]^{\frac{1}{2}} \underline{A}_\beta^{(1001)} \}$$

(3.5-28)

$$\underline{D}_\beta^T = [2M_\beta]^{\frac{1}{2}} n_\beta kT \underline{A}_\beta^{(1000)}$$

(3.5-29)

$$\underline{\Omega}_{\alpha\beta} = -[\frac{M_\beta}{kT}]^{\frac{1}{2}} n_\beta \; \underline{\zeta}_\beta^{(\alpha)(1000)}$$

(3.5-30)

where, $\underline{A}_\alpha^{(ps)}$ is $\langle \Psi_\alpha^{(ps)} | \delta_\alpha \underline{A} \rangle$, $\underline{A}_\beta^{pqst}$ is $\langle \Psi_\beta^{(pqst)} | \delta_\beta \underline{A} \rangle$, and $\underline{\zeta}_\beta^{(\alpha)(pqst)}$ is $\langle \Psi_\beta^{(pqst)} | \delta_\beta \underline{\zeta}^{(\alpha)} \rangle$. Also, use has been made of the auxiliary condition,

$$0 = n_\alpha M_\alpha^{\frac{1}{2}} \langle \Psi_\alpha^{(10)} | \delta_\alpha \phi \rangle + n_\beta M_\beta^{\frac{1}{2}} \langle \Psi_\beta^{(1000)} | \delta_\beta \phi \rangle$$

(3.5-31)

One can conclude from Eqs. (3.5-28), (3.5-29) and (3.5-30) that the complete construction of the distortion is not necessary since the phencmenological coefficients have been written explicitly in terms of just a few of its components. Thus, the full basis can be truncated to a manageable finite size with little error. To be specific, in this work the truncated basis consists of the seven function-operators, $\Psi_\alpha^{(10)}$, $\Psi_\alpha^{(11)}$, $\Psi_\beta^{(1000)}$, $\Psi_\beta^{(1010)}$, $\Psi_\beta^{(1001)}$, $\Psi_\beta^{(1100)}$, and $\Psi_\beta^{(1200)}$. The first five explicitly appear in the thermal and diffusive inhomogeneities and are of obvious importance. The remaining two are anisotropic in the rotational angular momentum and are included in order for the Senftleben-Beenakker

effects to be treated.

The task of constructing matrix elements of $\underset{\approx}{L}^{-1}$ now remains. To do this, first an explicit form appropriate to $H^{int}$ must be given. It obviously vanishes for the atomic species. For the diatomic species in an applied magnetic field, $\underline{H}$, one can write,

$$H_{\beta}^{int} = \gamma_{\beta} [2I_{\beta}kT]^{\frac{1}{2}} \underline{\Omega}_{\beta} \cdot \underline{H} \qquad (3.5-32)$$

where $\gamma_{\beta}$ is the gyromagnetic ratio of a $\beta$ molecule. This form is applicable in both quantum and classical mechanics with $H_{\beta}^{int}$ and $\underline{\Omega}_{\beta}$ being linear operators or dynamical variables as is appropriate. Considering the quantal case, from Eq. (3.1-13) it is clear that a matrix element of $\underset{\approx}{F}$ takes the form,

$$\langle \Psi_{\nu}^{(pqst)} | \underset{\approx}{F} | \Psi_{\mu}^{(PQST)} \rangle =$$

$$\frac{\gamma_{\beta}}{i\hbar} \langle \Psi_{\beta}^{(pqst)} | f_{\beta}^{(0)} [\Psi_{\beta}^{(PQST)}, \underline{\ell}_{\beta} \cdot \underline{H}] \rangle \delta_{\nu\beta} \delta_{\mu\beta} \qquad (3.5-33)$$

Here, $\underline{\ell}_{\beta}$ is the space-fixed rotational angular momentum operator. Clearly, $f_{\beta}^{(0)}$ commutes with $\underline{\ell}_{\beta} \cdot \underline{H}$ and the basis function-operators and thus can be taken outside of the commutator. Angular momentum operators obey the well-known commutation relation,

$$[\underline{\ell}_{\beta}, \underline{\ell}_{\beta} \cdot \underline{H}] = -i\hbar \underline{\ell}_{\beta} \times \underline{H} \qquad (3.5-34)$$

If one combines this expression with the following commutator

identity,

$$[\hat{A}\hat{B},\hat{C}] = \hat{A}[\hat{B},\hat{C}] + [\hat{A},\hat{C}]\hat{B} \qquad (3.5\text{-}35)$$

where $\hat{A}$, $\hat{B}$, and $\hat{C}$ are general quantum mechanical operators, one obtains the result,

$$[(\underline{\ell}_\beta)^n, \underline{\ell}_\beta \cdot \underline{H}] = -i\hbar \sum_{j=0}^{n} (\underline{\ell}_\beta)^j \times \underline{H}(\underline{\ell}_\beta)^{n-j} = -i\hbar(\underline{\ell}_\beta)^n \times_n \underline{H} \quad (3.5\text{-}36)$$

The symbol $\times_n$ is defined in relation to the sum as by Cooper(46). That is to say that $\times_n$ denotes a sum of n terms obtained by crossing a vector (in this case $\underline{H}$) into each of the n right hand indices of a tensor (in this case $(\underline{\ell}_\beta)^n$). From the above result and its definition as the symmetric traceless part of the polyad, $(\underline{\ell}_\beta)^n$, one can easily establish that $[\underline{\ell}_\beta]^{(n)}$ obeys a similar expression,

$$[[\underline{\ell}_\beta]^{(n)}, \underline{\ell}_\beta \cdot \underline{H}] = -i\hbar[\underline{\ell}_\beta]^{(n)} \times_n \underline{H} \qquad (3.5\text{-}37)$$

Thus, a matrix element of has the explicit form,

$$\langle \Psi_\nu^{(pqst)} | \underline{F} | \Psi_\mu^{(PQST)} \rangle = -\gamma_\beta \langle \Psi_\nu^{(pqst)} | f_\beta^{(0)} \Psi_\mu^{(PQST)} \rangle \times_Q \underline{H} \delta_{\nu\beta} \delta_{\mu\beta}$$

$$= -n_\beta \gamma_\beta \Delta^{(p,q)} \times_q \underline{H} \delta_{pP} \delta_{qQ} \delta_{sS} \delta_{tT} \delta_{\nu\beta} \delta_{\mu\beta} \qquad (3.5\text{-}38)$$

In the correspondence limit, Eq. (3.5-37) becomes,

$$\{[\underline{\ell}_\beta]^{(n)}, \underline{\ell}_\beta \cdot \underline{H}\} = -[\underline{\ell}_\beta]^{(n)} \times_n \underline{H} \qquad (3.5\text{-}39)$$

where the braces denote the Poisson bracket. This is identi-

cal to the result obtained by Cooper(46). In conclusion, one should note that for $H^{int}$, as defined by Eq. (3.5-32), the quantity $\{\{K^{int}, H^{int}\}\}$ vanishes as was stated at the beginning of the chapter.

Next, one should note that the operator, $\underset{\sim}{A}$, (defined in Eq. (3.4-4)) can be written exclusively in terms of direct products of the basis function-operators, $\psi_\alpha^{(00)}$, $\psi_\alpha^{(\ 0)}$, $\psi_\alpha^{(10)}$, $\psi_\beta^{(0000)}$, $\psi_\beta^{(1000)}$, $\psi_\beta^{(0010)}$, and $\psi_\beta^{(0001)}$, where

$$\underset{\sim}{p}_\nu = [M_\nu kT]^{\frac{1}{2}}\psi_\nu^{(1000)} + M_\nu\psi_\nu^{(0000)}\underline{u} \qquad (3.5\text{-}40)$$

$$h_\nu = -\frac{2kT}{\sqrt{7}}\psi_\nu^{(0010)} - [\varepsilon^*]^{\frac{1}{2}}kT\psi_\nu^{(0001)} + [\frac{M_\nu}{kT}]^{\frac{1}{2}}\psi_\nu^{(1000)}\cdot\underline{u}$$

$$+ \frac{M_\nu u^2}{2kT}\psi_\nu^{(0000)} \qquad (3.5\text{-}41)$$

Thus, $\underset{\sim}{A}$ has nonzero matrix elements only in the subspace spanned by the above seven basis functions of which only two, $\psi_\alpha^{(10)}$ and $\psi_\beta^{(1000)}$, are in common with the truncated basis used in the present work. In principle, the arbitrary scalar and tensor constants, $a_1^{(\nu)}$, $\underset{=}{a}_2^{(\nu)}$, and $a_3^{(\nu)}$ must be nonvanishing if the nonsingularity of $\underset{\sim}{L}$ is to be guaranteed. However, in practice, one needs $\underset{\sim}{L}$ to be nonsingular only in the subspace spanned by the truncated basis. Thus, under this less stringent condition, it is convenient to set all of the constants equal to zero except for $\underset{=}{a}_2^{(\alpha)}$. Now, so that $\underset{\sim}{A}$ will have the same dimension as $\underset{\sim}{\Gamma}$ (i.e. $cm^{-3}$ $sec^{-1}$) $\underset{=}{a}_2^{(\alpha)}$ is explicitly defined as

$$a_2^{(\alpha)} = \frac{|\underline{u}|}{n_\alpha M_\alpha kT\, V^{1/3}} \qquad (3.5\text{-}42)$$

where $V$ is the macroscopic volume of the system. Thus, in the truncated basis, $\underset{\approx}{A}$ has the explicit form,

$$\underset{\approx}{A} = \frac{|\underline{u}|}{n_\alpha V^{1/3}}\{\,|f_\alpha^{(0)}\psi_\alpha^{(10)}\rangle\langle f_\alpha^{(0)}\psi_\alpha^{(10)}|\; + $$

$$[\frac{M_\beta}{M_\alpha}]^{\frac{1}{2}}|f_\alpha^{(0)}\psi_\alpha^{(10)}\rangle\langle f_\beta^{(0)}\psi_\beta^{(1000)}|\}:\underline{\underline{U}} \qquad (3.5\text{-}43)$$

This expression is obtained by substitution of Eq. (3.5-4) into Eq. (3.4-4) and retention of the appropriate terms.

As a consequence of the three dimensional rotational invariance of the full collision kernel, it is easily demonstrated that $\underset{\approx}{\Gamma}$ is also rotationally invariant. This implies that any matrix element of $\underset{\approx}{\Gamma}$ forms a basis for the totally symmetric representation of the three dimensional rotation group, $O^+(3)$. Thus, all matrix elements of $\underset{\approx}{\Gamma}$ are three dimensional isotropic tensors. Furthermore, since the domain and range of $\underset{\bullet}{\Gamma}$ are the scalar field, its action preserves tensor symmetry. This is to say that the tensor symmetry of $\langle\psi_\nu^{(pqst)}|\underset{\approx}{\Gamma}|\psi_\mu^{(PQST)}\rangle$ is identical to that of the direct product, $[\underline{\Omega}_\nu]^{(q)}[\underline{W}_\nu]^{(p)}[\underline{W}_\mu]^{(P)}[\underline{\Omega}_\mu]^{(Q)}$.

If a molecular system interacts through a spherically symmetric intermolecular potential, it follows that rotational angular momentum is collisionally conserved.

Thus, in this case, the matrix elements of $\underset{\approx}{\Gamma}$ are nonvanishing if and only if the direct products, $[\underline{W}_\nu]^{(p)}[\underline{W}_\mu]^{(P)}$ and $[\underline{\Omega}_\nu]^{(q)}[\underline{\Omega}_\mu]^{(Q)}$ independently form bases for a representation of $O^+(3)$ which contains the totally symmetric irreducible representation. In this case, the matrix elements are of the following form,

$$\langle \Psi_\nu^{(pqst)} | \underset{\approx}{\Gamma} | \Psi_\mu^{(PQST)} \rangle = -g_{\nu\mu}^{(p,q)} \binom{st}{ST} \delta_{pP} \delta_{qQ} \Delta^{(p,q)} \quad (3.5\text{-}44)$$

where $g_{\nu\mu}^{(pq)}\binom{st}{ST}$ is a scalar coefficient.

Now one observes that in general matrix elements of $\underset{\approx}{F}$ and $\underset{\approx}{A}$ vanish unless $[\underline{W}_\nu]^{(p)}[\underline{W}_\mu]^{(P)}$ and $[\underline{\Omega}_\nu]^{(q)}[\underline{\Omega}_\mu]^{(Q)}$ form bases which contain the totally symmetric representation, which suggests that matrix elements of $\underset{\approx}{L}_0$ (cf. Eq. (3.4-8)) should be defined by the expression,

$$\langle \Psi_\nu^{(pqst)} | \underset{\approx}{L}_0 | \Psi_\mu^{(PQST)} \rangle = -\Delta^{(p,q)}_{\substack{p\neq q}} \langle \Psi_\nu^{(pqst)} | \underset{\approx}{\Gamma} | \Psi_\mu^{(PQST)} \rangle$$

$$_{P\neq Q}\Delta^{(P,Q)} \delta_{pP} \delta_{qQ} - \langle \Psi_\nu^{(pqst)} | \underset{\approx}{F}' | \Psi_\mu^{(PQST)} \rangle +$$

$$\langle \Psi^{(pqst)} | \underset{\approx}{A} | \Psi_\mu^{(PQST)} \rangle \quad (3.5\text{-}45)$$

From this it follows that matrix elements of $\underset{\approx}{W}$ are,

$$\langle \Psi_\nu^{(pqst)} | \underset{\approx}{W} | \Psi_\mu^{(PQST)} \rangle =$$
$$\langle \Psi_\nu^{(pqst)} | \underset{\approx}{L} | \Psi_\mu^{(PQST)} \rangle - \langle \Psi_\nu^{(pqst)} | \underset{\approx}{L}_0 | \Psi_\mu^{(PQST)} \rangle \quad (3.5\text{-}46)$$

Here, the isotropic tensors, $\Delta^{(p,q)}$, act as projection operators for the direct product representation. The above defi-

nition explains the motivation for the designation of $\underset{\approx}{L}_0$ as the "spherical" part of $\underset{\approx}{L}$ since it rigorously contains all contributions to $\underset{\approx}{L}$ which do not vanish for a spherical inter-action potential. In contrast, $\underset{\approx}{W}$, is the remaining "nonspherical" contribution and rigorously vanishes for spherical potentials.

Now if one notes that,

$$-\Delta^{(p,q)}{}_{p\mp q}\underset{p\mp q}{\odot}\langle\psi_\nu^{(pqst)}|\underset{\approx}{\Gamma}-\underset{\approx}{A}|\psi_\mu^{pqST)}\rangle\underset{p\mp q}{\odot}\Delta^{(p,q)} =$$
$$\ell_{\nu\mu}^{(p,q)}\binom{st}{ST}\Delta^{(p,q)} \tag{3.5-47}$$

It follows that a matrix element of $\underset{\approx}{L}^{-1}$ must satisfy the ex-pression,

$$\sum_{\eta=\alpha}^{\beta}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\langle\psi_\nu^{(pqst)}|\underset{\approx}{L}_0^{-1}|\psi_\eta^{(pnqm)}\rangle\underset{p\mp q}{\odot}(\Delta^{(p,q)}\ell_{\eta\mu}^{(p,q)}\binom{nm}{ST}+$$
$$\Delta^{(p,q)}\underset{q\mp}{\times}\underset{}{H}\ b_{\eta\mu}^{(p,q)}\binom{nm}{ST}) = \Delta^{(p,q)} \tag{3.5-48}$$

where $b_{\eta\mu}^{(p,q)}\binom{nm}{ST}$ is defined as $n_\beta\gamma_\beta\delta_{ns}\delta_{mT}\delta_{\eta\beta}\delta_{\mu\beta}$. (This follows directly from Eq. (3.5-38).

Equation (3.5-48) can be formally inverted if one defines a new set of orthonormal basis function-operators which explicitly diagonalize, $\underset{\approx}{L}_0+\underset{\approx}{F}$ (i.e. the eigenvectors of $\underset{\approx}{L}_0+\underset{\approx}{F}$). If these function-operators are denoted by the symbol, $\Phi_i^{(p,q)}$, where i is an appropriately chosen label, one obtains the following expression due to Cooper(46),

$$\langle \phi_i^{(p,q)} | \underset{\approx}{L}_0^{-1} | \phi_i^{(p,q)} \rangle_{p\mp q} (\Delta^{(p,q)} \ell_i^{(p,q)} + \Delta^{(p,q)} \times_{\underline{q}} \underline{H} \ b_i^{(p,q)}) = $$
$$\Delta^{(p,q)} \qquad\qquad\qquad (3.5\text{-}49)$$

Here, $\ell_i^{(p,q)}$ is the eigenvalue of $\underset{\sim}{L}_0 + \underset{\sim}{F}$ appropriate to the eigenvector, $\phi_i^{(p,q)}$.

In order to construct $\langle \phi_i^{(p,q)} | \underset{\approx}{L}_0^{-1} | \phi_i^{(p,q)} \rangle$, it is necessary to introduce a linearly independent set of tensors of rank 2q which have the tensor symmetry of $[\underline{\Omega}_\beta]^{(q)}$ on the first and last sets of q indices and which are isotropic with respect to two dimensional rotations about the field direction. These tensors are denoted by $\gamma_m^{(q)}$ where m ranges from -q to q. A brief discussion of their form and properties is given in Appendix B. It suffices to say here that the $\gamma_m^{(q)}$ are isomorphic with the usual three dimensional spherical harmonics and satisfy the following relations,

$$\gamma_m^{(q)} \underset{q}{\otimes} \gamma_{m'}^{(q)} = \gamma_m^{(q)} \delta_{mm'} \qquad (3.5\text{-}50)$$

$$\Delta^{(q)} = \sum_{m=-q}^{q} \gamma_m^{(q)} \qquad (3.5\text{-}51)$$

$$\Delta^{(q)} \times_{\underline{q}} \underline{H} = -|\underline{H}| \sum_{m=-q}^{q} im\gamma_m^{(q)} \qquad (3.5\text{-}52)$$

where i in Eq. (3.5-52) is $\sqrt{-1}$ (45).

Thus, the matrix element of $\underset{\approx}{L_0^{-1}}$ appearing in Eq. (3.5-49) can be written as follows,

$$\langle \phi_i^{(p,q)} | \underset{\approx}{L_0^{-1}} | \phi_i^{(p,q)} \rangle = \sum_{m=-q}^{q} \lambda_m^{pqi} y_m^{(p,q)} \qquad (3.5-53)$$

where $y_m^{(p,q)}$ is of rank $2(p+q)$ and is defined by "sandwiching" $\Delta^{(p)}$ between the first and last q indices at $y_m^{(q)}$. If one combines Eqs. (3.5-53) and (3.5-49) and makes use of Eqs. (3.5-50), (3.5-51), and (3.5-52), one obtains,

$$\lambda_m^{pqi} = \frac{\ell_i^{(p,q)} + im|\underline{H}|b_i^{(p,q)}}{(\ell_i^{(p,q)})^2 + m^2(|\underline{H}|b_i^{(p,q)})^2} \qquad (3.5-54)$$

which can be substituted into Eq. (3.5-53) to obtain an explicit expression for the inverse collision operator.

It is often the case that the off-diagonalities of $\underset{\approx}{L_0}$ can be ignored in Eq. (3.5-48) and thus, that the basis function-operators, $\psi_\nu^{(pqst)}$, can themselves be considered to be eigenfuctions of $\underset{\approx}{L_0}$. In this case Eq. (3.5-53) becomes,

$$\langle \psi_\nu^{(pqst)} | \underset{\approx}{L_0^{-1}} | \psi_\nu^{(pqst)} \rangle =$$

$$\sum_{m=-q}^{q} \frac{1}{\ell_{\nu\nu}^{(p,q)}\binom{st}{st}} \left\{ \frac{1 + im\, d_\nu^{(pqst)}}{1 + m^2(d_\nu^{(pqst)})^2} \right\} y_m^{(p,q)} \qquad (3.5-55)$$

where $d_\nu^{(pqst)} = n_\beta \gamma_\beta |\underline{H}| \delta_{\nu\beta} / \ell_{\nu\nu}^{(p,q)}\binom{st}{ST}$. This result will be used to obtain explicit expressions for the transport coefficients.

## 3.6. The Effective Cross Sections and Some Specific Results

At the end of the last section, a general method applicable to the approximate inversion of $\underset{\sim}{L}$ was developed. The same method can be applied to the inversion of the operator, $\underset{\sim}{T}$, defined in Eq. (3.4-16). In either case, the inverse operator, hence, the transport coefficient, are ultimately evaluated in terms of effective collision cross sections. The effective collision cross sections can be defined in terms of the operators, $\underset{\sim}{\Gamma}^{(2)}$ and $\underset{\sim}{\Gamma}^{(1,\eta)}$, which in the atom-diatom case are related to $\underset{\approx}{\Gamma}$ as follows,

$$\underset{\ast}{\Gamma} = \underset{\ast}{\Gamma}^{(2)} + \underset{\ast}{\Gamma}^{(1,\alpha)} + \underset{\ast}{\Gamma}^{(1,\beta)} \qquad (3.6\text{-}1)$$

The matrix elements of $\underset{\approx}{\Gamma}^{(2)}$ and $\underset{\approx}{\Gamma}^{(1,\eta)}$ have the explicit definitions,

$$\langle \psi_\nu^{(pqst)} | \underset{\approx}{\Gamma}^{(2)} | \psi_\mu^{(PQST)} \rangle =$$
$$-\langle \psi_\nu^{(pqst)} | J(f_\nu^{(0)}, f_\mu^{(0)} \psi_\mu^{(PQST)}) \rangle \qquad (3.6\text{-}2)$$

and

$$\langle \psi_\nu^{(pqst)} | \underset{\approx}{\Gamma}^{(1,\eta)} | \psi_\mu^{(PQST)} \rangle =$$
$$-\langle \psi_\nu^{(pqst)} | J(f_\mu^{(0)} \psi_\mu^{(PQST)}, f_\eta^{(0)}) \rangle \delta_{\nu\mu} \qquad (3.6\text{-}3)$$

where one notes that they are equivalent to the standard tensor collision integrals or bracket integrals,

$$\{ \psi_\nu^{(pqst)}, \psi_\mu^{(PQST)} \}_{\nu,\eta}^{(1,r)} =$$
$$\qquad (3.6\text{-}4)$$

$$[n_\nu n_\mu]^{-1} <\Psi_\nu^{(pqst)} |\underset{\approx}{\Gamma}^{(r,\eta)} | \Psi_\mu^{(PQST)}>$$

Here, r is 1 or 2 and $\underset{\sim}{\Gamma}^{(2,\eta)}$ is just $\underset{\approx}{\Gamma}^{(2)}$. The effective cross section, $G\binom{pqst}{PQST}|_\eta^\nu)_{\nu\eta}$, is a scalar, and is defined as follows(49),

$$G\binom{pqst}{PQST}|_\mu^\nu)_{\nu\eta} \quad \Delta^{(p,q|P,Q)} =$$

$$\frac{1}{v_{\nu\eta} n_\nu n_\eta} (\delta_{\nu\mu}\delta_{1r} + \delta_{\eta\mu}\delta_{2r}) \qquad (3.6-5)$$

$$\Delta^{(p,q)}_{p\overset{\circ}{q}} <\Psi_\nu^{(pqst)} |\underset{\approx}{\Gamma}^{(r,\eta)} | \Psi_\mu^{(PQST)}>_{P\overset{\circ}{Q}} \Delta^{(P+Q)}$$

where $\Delta^{(p,q|P,Q)}$ is an isotropic tensor of rank p+q+P+Q with the tensor symmetry of the tetradic direct product,

$[\underline{\Omega}_\nu]^{(q)} [\underline{W}_\nu]^{(p)} [\underline{W}_\mu]^{(P)} [\underline{\Omega}_\mu]^{(Q)}$, and $v_{\mu\eta}$ is the relative thermal velocity,

$$v_{\nu\eta} = [\frac{8kT}{\pi} \frac{(M_\nu + M_\eta)}{M_\nu M_\eta}]^{\frac{1}{2}} \qquad (3.6-6)$$

which is appropriate to collisions between $\nu$ and $\eta$ species.

A field free transport coefficient, $\underset{\approx}{T}$, is isotropic and can be written as a scalar (i.e. $\underset{\approx}{T} = T\underline{U}$). In terms of effective collision cross sections, one obtains from Eq. (3.5-54)

$$\lambda = \frac{5(nkT)^2}{2|\ell|^2} \left\{ \frac{n_\alpha^2}{M_\alpha} v_{\beta\beta} X_\beta^2 G\binom{1010}{1010}|_\beta^\beta)_{\beta\beta} + \frac{n_\beta^2}{M_\beta} v_{\alpha\alpha} X_\alpha^2 G\binom{1010}{1010}|_\alpha^\alpha)_{\alpha\alpha} \right.$$

$$+ \left(\frac{n_\alpha}{M_\alpha^{\frac{1}{2}}} - \frac{n_\beta}{M_\beta^{\frac{1}{2}}}\right)^2 v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\alpha}_{1010|\beta}\right)_{\alpha\beta} + \Bigg\}$$

$$\cdot \frac{\varepsilon^*}{M_\beta}(kT)^2 n_\beta^2 [v_{\beta\beta}X_\beta^2 G\left(^{1001|\beta}_{1001|\beta}\right)_{\beta\beta} + v_{\alpha\beta}X_\alpha X_\beta G\left(^{1001|\alpha}_{1001|\beta}\right)_{\alpha\beta}]^{-1}$$

$$\tag{3.6-7}$$

where,

$$|\ell| = n^2[(v_{\alpha\alpha}X_\alpha^2 G\left(^{1010|\alpha}_{1010|\alpha}\right)_{\alpha\alpha} + v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\alpha}_{1010|\beta}\right)_{\alpha\beta}) \times$$

$$(v_{\beta\beta}X_\beta^2 G\left(^{1010|\beta}_{1010|\beta}\right)_{\beta\beta} + v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\alpha}_{1010|\beta}\right)_{\alpha\beta}) -$$

$$(v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\alpha}_{1010|\beta}\right)_{\alpha\beta})^2]^{\frac{1}{2}}$$

$$\tag{3.6-8}$$

and,

$$D_\beta^T = -\sqrt{\frac{5}{2}} \frac{n^2 n_\beta^2 kT}{G\left(^{1000|\beta}_{1000|\beta}\right)_{\alpha\beta}|\ell|^2}\left(G\left(^{1000|\beta}_{1010|\beta}\right)_{\alpha\beta}(v_{\alpha\alpha}X_\alpha^2 G\left(^{1010|\alpha}_{1010|\alpha}\right)_{\alpha\alpha}\right.$$

$$+ v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\alpha}_{1010|\beta}\right)_{\alpha\beta}) + \frac{X_\alpha}{X_\beta}\left[\frac{M_\beta}{M_\alpha}\right]^{\frac{1}{2}} G\left(^{1000|\beta}_{1010|\beta}\right)_{\alpha\beta}(v_{\beta\beta}X_\beta^2 G\left(^{1010|\alpha}_{1010|\alpha}\right)_{\alpha\alpha}$$

$$\left. + v_{\alpha\beta}X_\alpha X_\beta G\left(^{1010|\beta}_{1010|\beta}\right)_{\alpha\beta}\right)$$

$$\tag{3.6-9}$$

and finally,

$$D_{\alpha\beta} = \frac{kT}{X_\alpha}[v_{\alpha\beta}G\left(^{1000|\beta}_{1000|\beta}\right)_{\alpha\beta}]^{-1}$$

$$\tag{3.6-10}$$

One notes that $D_{\alpha\beta}$ is related to $\Omega_{\alpha\beta}$ by Eq. (3.3-15).

Expressions appropriate to the description of the Senftleben-Beenakker effects are obtained via Eq. (3.5-54). Retaining terms of no greater than second order in $\underset{\approx}{W}$ yields,

$$\frac{T_{tr}}{D_{\alpha\beta}} = \psi_{11}^T \frac{\xi_{11}}{1+\xi_{11}^2} - \psi_{12}^T \left( \frac{\xi_{12}}{1+\xi_{12}^2} + \frac{4\xi_{12}}{1+4\xi_{12}} \right) \qquad (3.6-11)$$

$$\frac{T_\perp - T}{D_{\alpha\beta}} = \psi_{11}^T \frac{\xi_{11}^2}{1+\xi_{11}^2} - \psi_{12}^T \left( \frac{\xi_{12}^2}{1+\xi_{12}^2} + \frac{8\xi_{12}^2}{1+4\xi_{12}^2} \right) \qquad (3.6-12)$$

$$\frac{T_\parallel - T}{D_{\alpha\beta}} = 2\psi_{11}^T \frac{\xi_{11}^2}{1+\xi_{11}^2} - 2\psi_{12}^T \frac{\xi_{12}^2}{1+4\xi_{12}^2} \qquad (3.6-13)$$

where the field parameter, $\xi_{pq}$, is,

$$\xi_{pq} =$$

$$\frac{g_\beta \mu_N kT}{\hbar} \left[ X_\beta v_{\beta\beta} G \left( \begin{matrix} pq00 \\ pq00 \end{matrix} \Big| \begin{matrix} \beta \\ \beta \end{matrix} \right)_{\beta\beta} + X_\alpha v_{\alpha\beta} G \left( \begin{matrix} pq00 \\ pq00 \end{matrix} \Big| \begin{matrix} \beta \\ \beta \end{matrix} \right)_{\alpha\beta} \right]^{-1} \frac{H}{P} \qquad (3.6-14)$$

Here, P is the hydrostatic pressure, nkT, $g_\beta$ is the diatom rotational g-factor, and $\mu_N$ is the nuclear magneton. The polarizations, $\psi^T$, can be written in terms of the field parameter and other effective cross sections,

$$\psi_{pq}^\lambda = \qquad (3.6-15)$$

$$(1 - \tfrac{1}{2}\delta_{p1}\delta_{q2}) \frac{\hbar\xi_{pq}}{M_\beta g_\beta \mu_N} \left(\frac{P}{H}\right) X_\alpha X_\beta v_{\alpha\beta} G \left( \begin{matrix} 1000 \\ 1000 \end{matrix} \Big| \begin{matrix} \beta \\ \beta \end{matrix} \right)_{\alpha\beta} P^2$$

$$\psi \, {}^{D^T_\beta}_{pq} =$$

$$(1 - \tfrac{1}{2}\delta_{p1}\delta_{q2}) \, \frac{\hbar \xi_{pq}}{g_\beta \mu_N kT} \, (\frac{P}{H}) \, x_\alpha x_\beta v_{\alpha\beta} \, G\left({}^{1000}_{pq00}\Big|{}^\beta_\beta\right)_{\alpha\beta} P \qquad (3.6\text{-}16)$$

$$\psi \, {}^{D_{\alpha\beta}}_{pq} = (1 - \tfrac{1}{2}\delta_{p1}\delta_{q2}) \, \frac{\hbar\xi_{pq}}{g_\beta\mu_N kT}(\frac{P}{H}) \, \frac{x_\alpha^2 v_{\alpha\beta}\,[G\left({}^{1000}_{pq00}\Big|{}^\beta_\beta\right)_{\alpha\beta}]^2}{G\left({}^{1000}_{1000}\Big|{}^\beta_\beta\right)_{\alpha\beta}} \qquad (3.6\text{-}17)$$

where,

$$P = \left[\frac{\bar{E}^{int}_\beta}{kT}\right]^{\frac{1}{2}} \left\{ x_\beta v_{\beta\beta} G\left({}^{1001}_{pq00}\Big|{}^\beta_\beta\right)_{\beta\beta} + x_\alpha v_{\alpha\beta} G\left({}^{1001}_{pq00}\Big|{}^\beta_\beta\right)_{\alpha\beta} \right\} \times$$

$$\left[ x_\beta v_{\beta\beta} G\left({}^{1001}_{1001}\Big|{}^\beta_\beta\right)_{\beta\beta} + x_\alpha v_{\alpha\beta} G\left({}^{1001}_{1001}\Big|{}^\beta_\beta\right)_{\alpha\beta} \right]^{-1} -$$

$$\left[\frac{5}{2}\right]^{\frac{1}{2}} \left\{ \left[ x_\beta v_{\beta\beta} G\left({}^{1010}_{pq00}\Big|{}^\beta_\beta\right)_{\beta\beta} + x_\alpha v_{\alpha\beta} G\left({}^{1010}_{pq00}\Big|{}^\beta_\beta\right)_{\alpha\beta} \right] \times \right.$$

$$\left[ x_\alpha v_{\alpha\alpha} G\left({}^{1010}_{1010}\Big|{}^\alpha_\alpha\right)_{\alpha\alpha} + x_\beta v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\alpha_\alpha\right)_{\alpha\beta} - x_\alpha \sqrt{\frac{M_\beta}{M_\alpha}}\, v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\alpha_\beta\right)_{\alpha\beta} \right]$$

$$- x_\alpha v_{\alpha\beta} G\left({}^{1010}_{pq00}\Big|{}^\alpha_\beta\right)_{\alpha\beta} \left[ x_\beta v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\alpha_\beta\right)_{\alpha\beta} - x_\beta \sqrt{\frac{M_\beta}{M_\alpha}}\, v_{\beta\beta} G\left({}^{1010}_{1010}\Big|{}^\beta_\beta\right)_{\beta\beta} \right.$$

$$\left. \left. - x_\alpha \sqrt{\frac{M_\beta}{M_\alpha}}\, v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\beta_\beta\right)_{\alpha\beta} \right] \right\} \left[ \left[ x_\beta v_{\beta\beta} G\left({}^{1010}_{1010}\Big|{}^\beta_\beta\right)_{\beta\beta} \right. \right.$$

$$\left. + x_\alpha v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\beta_\beta\right)_{\alpha\beta} \right] \left[ x_\alpha v_{\alpha\alpha} G\left({}^{1010}_{1010}\Big|{}^\alpha_\alpha\right)_{\alpha\alpha} + x_\beta v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\alpha_\alpha\right)_{\alpha\beta} \right]$$

$$\left. - x_\alpha x_\beta (v_{\alpha\beta} G\left({}^{1010}_{1010}\Big|{}^\alpha_\beta\right)_{\alpha\beta})^2 \right] \qquad (3.6\text{-}18)$$

Comparison of Eqs. (3.6-15), (3.6-16), and (3.6-17) yields
the result,

$$|\psi^{D^{T}}{}_{\beta}| = \left[\frac{X_{\beta}M_{\beta}}{X_{\alpha}kT} \ \psi^{\lambda} \ \psi^{D}{}_{\alpha\beta}\right]^{\frac{1}{2}} \qquad (3.6-19)$$

Thus, the cross polarization is seen to be proportional to the geometric average of the direct polarizations. Similar expressions have been given by t'Hooft et al. (50,51).

To zeroth order (i.e. infinite dilution) in the diatomic species, Eq. (3.4-15) gives,

$$\underline{A}_{\alpha}^{(0)} = (\underline{L}_{\alpha\alpha}^{(0)})^{-1} \ \underline{D}_{\alpha}^{A(0)} \qquad (3.6-20)$$

and,

$$\underline{A}_{\beta}^{(0)} = (\underline{L}_{\beta\beta}^{(1)})^{-1} (\underline{D}_{\beta}^{A(1)} - \underline{L}_{\beta\alpha}^{(1)} (\underline{L}_{\alpha\alpha}^{(0)})^{-1} \ \underline{D}_{\alpha}^{A(0)}) \qquad (3.6-21)$$

As stated previously, $\underline{T}$ (defined in Eq. (3.4-16)) can be inverted by the same method (i.e. expansion in the nonsphericity) as used to invert $\underline{L}$. In fact, the inversion of $\underline{T}$ is less complicated than the inversion of $\underline{L}$ since $\underline{T}$ is already block diagonal in the components. However, construction of $\underline{A}^{(0)}$ is complicated by the complex form of the inhomogeneity vector acted on by $(\underline{L}_{\beta}^{(1)})^{-1}$ in Eq. (3.6-21). From these expressions, one obtains the result,

$$\lambda^{(0)} = \frac{5(kT)^{2}}{2M_{\alpha}} \ [v_{\alpha\alpha}G(\begin{smallmatrix}1010\\1010\end{smallmatrix}|{\alpha\atop\alpha})_{\alpha\alpha}]^{-1} \qquad (3.6-22)$$

where $\lambda^{(0)}$ is the pure component thermal conductivity, $\lambda_{\alpha\alpha}$

$(D_\beta^{T(0)}$ and $\Omega_{\alpha\beta}^{(0)}$ vanish). Since the thermal diffusion coefficient is of special interest due to its sensitivity to the anisotropy of the molecular interaction, an explicit expression for $D_\beta^{T(1)}$ is given,

$$D_\beta^{T(1)} = n_\beta^2 kT \langle \Psi_\beta^{(1000)} | (L_{\beta\beta}^{(1)})^{-1} | \Phi_\beta^A \rangle \qquad (3.6\text{-}23)$$

where,

$$\Phi_\beta^A = \sqrt{\varepsilon^*} \, \Psi_\beta^{(1001)} + \Psi_\beta^{(1010)} \left\{ \sqrt{\frac{5}{2}} - \langle \Psi_\beta^{(1010)} | L_{\beta\alpha}^{(1)} | \Psi_\alpha^{(10)} \rangle \right.$$
$$\left. \frac{[M_\alpha M_\beta]^{\frac{1}{2}}}{n_\alpha n_\beta} \frac{\sqrt{2}\lambda^{(0)}}{5(kT)^2} \right\} \qquad (3.6\text{-}24)$$

The matrix elements which appear can be written in terms of effective cross sections appropriate to the $\alpha$-$\beta$ interaction. Thus the limiting form of $D_\beta^T$ is directly determined by the thermal conductivity of the pure monatomic gas and the scattering dynamics of $\alpha$-$\beta$ collisions. The field dependence is wholly contained in the matrix element of $(L_{\beta\beta}^{(1)})^{-1}$.

Since the matrix elements of $\Gamma^{(r,\eta)}$ which appear in the definition of the bracket integrals and effective cross sections (i.e. Eqs. (3.6-4) and (3.6-5)) are isotropic tensors, they are completely determined by their scalar contractions. Each of these, in turn, can be written as a linear combination of the scalar contractions of their irreducible parts which have the form,

$$C_{p\ q\ s\ t;\sigma}^{p'q's't';\nu}(J;r,\eta) =$$

$$\hspace{6cm} (3.6\text{-}25)$$

$$\sum_{\mu} < [\psi_{\nu}^{(p'q's't')}]_{\mu}^{J} | \underset{\approx}{\Gamma}^{(r,\eta)} | [\psi_{\sigma}^{(pqst)}]_{\mu}^{J} >$$

where $[\psi_{\nu}^{(pqst)}]_{\mu}^{J}$ is the $\mu^{th}$ component of the irreducible con-
tribution of rank J in $\psi_{\nu}^{(pqst)}$. The coefficients of the
linear combination depend upon the specific contraction of
$<\psi_{\nu}^{(pqst)} | \underset{\approx}{\Gamma}^{(r,\ )} | \psi_{\sigma}^{(PQST)}>$ under consideration. Since the
basis function-operators are direct products of irreducible
tensors of rank p and q, it follows that J can only assume
values $|p-q| \leqslant J \leqslant p+q$. Likewise, $\psi_{\sigma}^{(PQST)}$ constrains J by
$|P-Q| \leqslant J \leqslant P+Q$, and a nonzero scalar contraction exists
only if both relations are satisfied simultaneously.

The scalar contraction of Eq. (3.6-25) can be partially
evaluated by performing the center of mass integration. To
do this, it is necessary to express the basis explicitly in
terms of center of mass and reduced relative momenta. One
can proceed by first considering the Sonine polynomials.
From Eq. (3.5-10), one can write,

$$S_{p+\frac{1}{2}}^{(s)}(W_{\eta}^{2}) = \sum_{u=0}^{s} a^{ups}(W_{\eta}^{2})^{u} \hspace{2cm} (3.6\text{-}26)$$

where,

$$a^{ups} = (-1)^u \frac{\{s!\Gamma(p+s+3/2)\}^{\frac{1}{2}}}{(s-u)!u!\Gamma(p+u+3/2)} \qquad (3.6-27)$$

The reduced momentum, $\underline{W}_\eta$, is related to the reduced center of mass momentum, $\underline{\Gamma}$, and reduced relative momentum, $\underline{\gamma}$, as follows,

$$\underline{W}_\eta = \chi_\eta \underline{\Gamma} - (-1)^r (1-\chi_\eta^2)^{\frac{1}{2}} \underline{\gamma} \qquad (3.6-28)$$

where $\chi_\eta = M_\eta/(M_\alpha + M_\beta)$ and r is the molecular label of species $\eta$. It follows from this that $W_\eta^2$ depends on the angles of $\underline{\gamma}$ and $\underline{\Gamma}$ only through the dot product $x = \hat{\gamma} \cdot \hat{\Gamma}$ and hence, the Sonine polynomials can be written as an expansion in the Legendre polynomials,

$$S_{p+\frac{1}{2}}^{(s)}(W_\eta^2) = \sum_\ell [S_{p+\frac{1}{2}}^{(s)}(W_\eta^2)]_\ell \, P_\ell(x)$$

$$= \sum_{\ell,m} (-1)^m \frac{(2\ell-1)!!}{\ell!} \left(\frac{1}{\Gamma\gamma}\right)^\ell [S_{p+\frac{1}{2}}^{(s)}(W_\eta^2)]_\ell [\underline{\Gamma}]_m^\ell [\underline{\gamma}]_m^\ell \quad (3.6-29)$$

The last equality is established by making use of the addition theorem for spherical harmonics and the relationship between spherical harmonics and irreducible natural tensors. Using Eqs. (3.6-27) and (3.6-28), the expansion coefficient, $[S_{p+\frac{1}{2}}^{(s)}(W_\eta^2)$ can be evaluated as follows,

$$[S_{p+\frac{1}{2}}^{(s)}(W_\eta^2)]_\ell = \frac{2\ell+1}{2} \int_{-1}^{1} dx \, P_\ell(x) \, S_{p+\frac{1}{2}}^{(s)}(W_\eta^2) \qquad (3.6-30)$$

$$= \left(\frac{2\ell+1}{2}\right) \sum_{u=0}^{s} \sum_{v,w} A_{psuvw}^{\eta;r} \Gamma^{2(u-w)-v} \gamma^{2w+v} \int_{-1}^{1} dx \, x^{v} P_{\ell}(x)$$

where the coefficient,

$$A_{psuvw}^{\eta;r} = \qquad (3.6-31)$$

$$a^{ups} \frac{u!}{v!w!(u-v-w)!} \chi_{\eta}^{2(u-w)-v} [1-\chi_{\eta}^{2}]^{\frac{2w+v}{2}} [2(-1)^{r-1}]^{v}$$

results from a trinomial expansion of $W_{\eta}^{2}$. Substitution of Eq. (3.6-30) into Eq. (3.6-29) yields,

$$S_{p+\frac{1}{2}}^{(s)}(W_{\eta}^{2}) = \sum_{\substack{u=0 \\ v+w \leq u}}^{s} \sum_{v,w} \sum_{\ell=0}^{v} \sum_{m} (-1)^{m} a_{\ell}^{v} A_{psuvw}^{\eta;r}$$

$$\times \Gamma^{2(u-w)-v-\ell} \gamma^{2w+v-\ell} [\underline{\Gamma}]_{m}^{\ell} [\underline{\gamma}]_{-m}^{\ell} \qquad (3.6-32)$$

where,

$$a_{\ell}^{v} = \frac{(2\ell+1)!!}{(2\ell)!} \int_{-1}^{1} dx \, x^{v} P_{\ell}(x)$$

$$= \frac{1}{2}[1+(-1)^{\ell+v}] \frac{(2\ell+1)! v! \left(\frac{v+\ell}{2}\right)!}{(\ell!)^{2} \left(\frac{v-\ell}{2}\right)! (v+\ell+1)!} \qquad (3.6-33)$$

The standard formula for the irreducible tensor components of the direct product of two (commuting) irreducible tensor operators, $[\underline{A}]^{(p)}$ and $[\underline{B}]^{(q)}$ is,

$$[\,[\underline{A}]^{(\ell)}\,[\underline{B}]^{(\ell')}\,]_\mu^J \;=$$

$$\sum_{m\,m'}\;(-1)^{\ell'-\ell+\mu}(2J+1)^{\frac12}\begin{pmatrix}\ell & \ell' & J\\ m & m' & -\mu\end{pmatrix}\cdot[\underline{A}]_m^\ell\;[\underline{B}]_{m'}^{\ell'}\quad (3.6\text{-}34)$$

and the inverse relation,

$$[\underline{A}]_m^\ell\;[\underline{B}]_{m'}^{\ell'}\;=\qquad\qquad\qquad\qquad (3.6\text{-}35)$$

$$\sum_{J,\mu}\;(-1)^{\ell'-\ell+\mu}(2J+1)^{\frac12}\begin{pmatrix}\ell & \ell' & J\\ m & m' & -\mu\end{pmatrix}[\,[\underline{A}]^{(\ell)}\,[\underline{B}]^{(\ell')}\,]_\mu^J\;.$$

For the special case of $\underline{A} = \underline{B}$, the latter reduces to,

$$[\underline{A}]_m^\ell\;[\underline{A}]_{m'}^{\ell'}\;=$$

$$\sum_{J,\mu}\;(-1)^\mu\begin{pmatrix}\ell & \ell' & J\\ m & m' & -\mu\end{pmatrix}c(\ell,\ell',J)A^{\ell+\ell'-J}[\underline{A}]_\mu^J\quad (3.6\text{-}36)$$

where,

$$c(\ell,\ell',J)\;=$$

$$2^{\frac12(\ell+\ell'-J)}(2J+1)\frac{\ell!\,\ell'!}{J!}\left(\frac{(2J)!}{(2\ell)!\,(2\ell')!}\right)^{\frac12}\begin{pmatrix}\ell & \ell' & J\\ 0 & 0 & 0\end{pmatrix}_{(3.6\text{-}37)}$$

if the vector operator, $\underline{A}$, commutes with itself. Equation (3.6-36) can be easily established by relating $[\underline{A}]_m^\ell$ to $Y_m^\ell$ and using the standard expression for the expansion of the product of two spherical harmonics in terms of spherical harmon-

ics.

One now proceeds by using Eq. (3.6-34) to express the irreducible tensors $[[\underline{W}_\eta]^{(p)}[\underline{\Omega}_\eta]^{(q)}]^J$ in terms of $[\underline{W}_\eta]^{(p)}$ and $[\underline{\Omega}_\eta]^{(q)}$. Making use of Eq. (3.6-28), one can write $[\underline{W}_\eta]^{(p)}$ in the binomial expansion,

$$[W_\eta]^p_{m_p} = \sum_k^p B_\eta^{pk} \; [[\underline{\Gamma}]^k[\underline{\chi}]^{(p-k)}]^p_{m_p} \qquad (3.6\text{-}38)$$

where,

$$B_\eta^{pk} = \binom{p}{k} (\chi_\eta)^k \{(-1)^{r+1}(1-\chi_\eta^2)^{\frac{1}{2}}\}^{p-k} . \qquad (3.6\text{-}39)$$

One then carries out the sequence of steps:

a) One first couples the $\underline{\Gamma}$ dependence of Eqs. (3.6-32) and (3.6-38) using Eq. (3.6-36).

b) Next one couples the $\underline{\chi}$ dependence of Eqs. (3.6-32) and (3.6-38) using Eq. (3.6-36).

c) Finally one couples the $\underline{\chi}$ dependence of b) to the decoupled $\underline{\Omega}$ dependence of $[[W_\eta]^{(p)}[\underline{\Omega}_\eta]^{(q)}]$.
Having carried out these three steps together with standard recombinations of 3-j symbols, one obtains the following expression,

$$[\Psi_\eta^{(pqst)}]^J_\mu = (-1)^m \sum_{\substack{G \; K \\ M_G \; Q}} (2K+1)^{\frac{1}{2}} \begin{pmatrix} G & J & K \\ M_G & -\mu & Q \end{pmatrix}$$

$$(3.6\text{-}40)$$

$$\times \sum_{\substack{u,v,w \\ g,k,\ell}} A_{\underline{M}}^{\eta}(J,G,K) \ \Gamma^{2u-G-2w+k-v}[\underline{\Gamma}]_{M_G}^{G} \ [\phi^{(M)}]_{Q}^{K'}$$

where the coefficient $A_{\underline{M}}^{\eta}(J,G,K)$ is defined by,

$$A_{\underline{M}}^{\eta}(J,G,K) = (-1)^{g+q+p+k}[(2J+1)(2p+1)]^{\frac{1}{2}}$$

$$\times A_{psuvw}^{\eta} \ a_{\ell}^{v} c(\ell,k,G) c(\ell,p-k,g) \ B_{pk}^{\eta} \times \qquad (3.6-41)$$

$$[2^{p+q+1}-\pi^{\frac{1}{2}}\Gamma(p+3/2)\Gamma(q+3/2)N_{qt}]^{\frac{1}{2}} \begin{pmatrix} g & p & G \\ k & \ell & p-k \end{pmatrix} \begin{pmatrix} G & J & K \\ q \cdot g & p \end{pmatrix}$$

and the basis function-operator, $[\phi^{(M)}]_{Q}^{K}$, is defined,

$$[\phi^{(M)}]_{Q}^{K} = S_{q}^{(t)}(\Omega_{\eta}^{2})\gamma^{p-g+2w-k+v}[[\underline{Y}]^{(g)} [\underline{\Omega}_{\eta}]^{(q)}]_{Q}^{K} \quad (3.6-42)$$

Here, $\overline{M}$ is a collective notation for the set of variables, $\{p,q,s,t,u,v,w,g,k,\ell\}$ which are the original basis function-operator indices (i.e. pqst) plus the indices introduced in the reduction of $\psi_{\eta}^{(pqst)}$ that are not final tensor indices (i.e. $\{u,v,w,g,k,\ell\}$), and M represent the subset of these indices, g, j = p-g+2w-k+v, q and t which are indices of $\phi^{(M)}$ analogous to the indices pqst in the definition of $\psi_{\eta}^{(pqst)}$.

Making use of the fact that

$$\int d\underline{\Gamma} \ e^{-\Gamma^2} [\underline{\Gamma}]_{M_G}^{G} [\underline{\Gamma}]_{-M_G'}^{G'}(-1)^{M_G'} \ \Gamma^{2N}$$

$$= \pi^{\frac{3}{2}} \frac{2^{G}(G!)^2}{(2G)!} \frac{[2(G+N)+1]!}{4^{G+N}(G+N)!} \ \delta_{GG'} \ \delta_{M_G M_G'} \qquad (3.6-43)$$

results in the expression,

$$C^{p'q's't';\nu}_{p\ q\ s\ t\ ;\sigma}(J;r,\eta) = \sum_{\substack{[M] \\ [M']}} \sum_{KQ} C^{\overline{M}';\nu}_{\overline{M};\sigma}(J,K) \qquad (3.6\text{-}44)$$

$$\langle [\Phi^{(M')}]^K_Q | \Gamma^{(r,\eta)}_{\underline{\ }} | [\Phi^{(M)}]^K_Q \rangle$$

where,

$$C^{\overline{M}';\nu}_{\overline{M};\sigma}(J,K) =$$

$$\frac{[2L(M,M')+1]!}{4^{L(M,M')}(L(M,M'))!} \sum_G \frac{(G!)^2 2^G}{(2G)!} A^{\sigma}_{M}(J,G,K) A^{\nu}_{M'}(J,G,K) \qquad (3.6\text{-}45)$$

where,

$$\sum_{[M]} \cdots = \sum_{uvwgk\ell} \cdots \qquad (3.6\text{-}46)$$

That is, a sum over all dummy indices of M, and L(M,M') is
u+u--w-w'+ (k+k'-v-v') which is always an integer for nonzero

values of $G^{\overline{M}';}_{\overline{M};}(J,K)$.

In conclusion, the resulting form of Eq. (3.6-44)

prompts the introduction of the notation, $\{\overline{\Psi}'_\nu \odot \overline{\Psi}_\mu\}^{(1,r)}_{\nu\ \eta}$, to

denote a general scalar contraction or scalar collision inte-

gral. Here, $\overline{\Psi}'_\nu$ and $\overline{\Psi}_\mu$ are tensor functions of dynamical var-

iables and are of the same rank. Thus,

$$\{\overline{\Psi}'_\nu \odot \overline{\Psi}_\mu\}^{(1,r)}_{\nu,\eta} = \frac{1}{n_\nu n_\eta} \langle \overline{\Psi}'_\nu | \Gamma^{(r,\eta)}_{\underline{\ }} | \overline{\Psi}_\mu \rangle \odot U \qquad (3.6\text{-}47)$$

where U is an isotropic tensor defined such that $\overline{\Psi}'_\nu \overline{\Psi}_\mu \odot U =$

$\overline{\Psi}'_\nu \odot \overline{\Psi}_\mu$. (The symbol $\odot$ means that all possible contractions

are taken.)

The effective collision cross section appropriate to the above scalar collision integral is defined,

$$G(\overline{\Psi}'_\nu \circledcirc \overline{\Psi}_\mu)^{(1,r)}_{\nu,\eta} = \frac{1}{v_{\nu\eta}}\{\overline{\Psi}_\nu \circledcirc \overline{\Psi}_\mu\}^{(1,r)}_{\nu,\eta} \qquad (3.6-48)$$

Finally, the reader should note that if $\overline{\Psi}'_\nu$ and $\overline{\Psi}_\mu$ are functions of translational momenta only through $\underline{\gamma}$, then the $(1,r)$ superscripts become superfluous and can be ignored.

# 4. EVALUATION OF SCALAR COLLISION INTEGRALS AND PHENOMENOLOGICAL CROSS SECTIONS

## 4.1. General Considerations

In order to obtain numerical values for the previously developed expressions appropriate to the phenomenological coefficients, one must evaluate appropriate effective cross sections (i.e. scalar collision integrals). This is accomplished by the explicit construction of the collision kernel, followed by the application of analytic or numerical methods.

In this chapter, effective cross sections applicable to the description of atom-diatom systems will be evaluated by application of a number of different dynamical approaches.

The scalar collision integrals, hence, the effective collision cross sections, can be viewed as thermal averages of energy-dependent cross sections under a Maxwellian distribution. Explicit evaluation of the energy-dependent (or phenomenological) cross sections is of interest since these quantities provide detailed information concerning the role of rotational degrees of freedom in collisional processes. The preceding statement is especially true of cross sections which are appropriate to the description of Senftleben-Beenakker effects.

## 4.2. Central Potentials in Classical Mechanics

Evaluation of scalar collision integrals and phenomenological cross sections assuming a spherically symmetric interaction potential from a classical mechanical point of view has already been extensively studied(52). If one approximates an atom-diatom interaction with a central potential, there is no possibility for the description of inelastic interactions. This feature, of course, makes such a potential inappropriate to the description of Senftleben-Beenakker effects. However, a brief discussion of central potential dynamics is included here as a reference for later development (also central potentials are completely adequate to the description of atom-atom collisions).

For molecular systems which are adequately described by classical mechanics, the collision kernel can be written using Eq. (2.1-46). In this case, only the linear momenta are meaningful dynamical parameters so that $X_1$, $X_2$, $X_1'$, and $X_2'$ can be identified as individual molecular momenta, $\underline{p}_1$, $\underline{p}_2$, $\underline{p}_1'$, and $\underline{p}_2'$. If one assumes that the convex surface, $\sigma_{1,2}$, is spherical with a radius of $b_{max}$, (i.e. maximum impact parameter), the collision kernel takes the explicit form,

$$\langle \underline{p}_1 \underline{p}_2 | \Theta | \underline{p}' \underline{p}_2' \rangle =$$

$$b_{max}^2 \int_{\hat{k}\cdot\underline{p}>0} d\hat{k}\, \hat{k}\cdot\underline{p}/\mu\{\delta(\underline{p}'-\underline{p}^*) - \delta(\underline{p}'-\underline{p})\}\delta(\underline{P}-\underline{P}') \quad (4.2-1)$$

Here, $\underline{p}$ and $\underline{P}$ are defined as relative and center of mass momenta derived from $\underline{p}_1$ and $\underline{p}_2$ (i.e. $\underline{p} = (M_1 \underline{p}_2 - M_2 \underline{p}_1) \times 1/(M_1 + M_2)$ and $\underline{P} = \underline{p}_2 + \underline{p}_1$) and $\mu$ is the reduced mass. The momenta $\underline{p}'$ and $\underline{P}'$ are related to $\underline{p}_1'$ and $\underline{p}_2'$ in exactly the same way. The vector quantity, $\underline{p}^{\star}$ is defined as the precollisional relative momentum which is dynamically related to the postcollisional momentum, $\underline{p}$.

Equation (4.2-1) is substituted into Eq. (3.6-4) and then integrals over total momenta, $\underline{P}$ and $\underline{P}'$, are performed. One obtains the following expression,

$$\{\overline{\Psi}_{\nu}'\!\odot\overline{\Psi}_{\tau}\}_{\nu,\omega} = b_{max}\pi^{-3/2}[\frac{2kT}{\mu_{\eta\omega}}]^{\frac{1}{2}}\int d\underline{\gamma}\int d\hat{k}\hat{k}\cdot\underline{\gamma}e^{-\gamma^2}\overline{\Psi}_{\nu}'(\overline{\Psi}_{\tau}-\overline{\Psi}_{\omega}^{\star}) \quad (4.2-2)$$

where $\overline{\Psi}_{\nu}'$ and $\overline{\Psi}_{\tau}$ are tensor functions of the dimensionless relative momentum, $\underline{\gamma}$.

The scalar collision integral, $\{\overline{\Psi}_{\nu}'\!\odot\overline{\Psi}_{\tau}\}_{\nu\omega}$, can be written in terms of Chapman-Cowling omega integrals which are defined as follows (39,40),

$$\Omega^{(\ell,s)}(T) = [\frac{kT}{2\pi\mu}]^{\frac{1}{2}}\int_0^{\infty} d\gamma e^{-\gamma^2}\gamma^{2s+3}Q^{(\ell)}(E) \quad (4.2-3)$$

The quantity $Q^{(\ell)}(E)$ has units of area and can be identified as a phenomenological cross section (referred to hereafter as the "Q-cross section"). It is a function of the relative

kinetic energy, $E = kT\gamma^2$, and has the form,

$$Q^{(\ell)}(E) = 2\pi b_{max}^2 \int_0^1 (1-(\cos\chi)^\ell)\cos\theta \, d(\cos\theta) \qquad (4.2-4)$$

Here, $\theta$ is the angle between the surface normal, $\hat{k}$, and the relative momentum (i.e. $\cos\theta = \hat{k} \, \gamma/|\gamma|$). The scattering angle, $\chi$, is defined by the expression,

$$\chi(E,\cos\theta) =$$

$$\pi - 2b_{max}\cos\theta \int_{r_m}^{\infty} \frac{dr}{r^2[1-(\frac{b_{max}\cos\theta}{r})^2 - \frac{V(r)}{E}]^{\frac{1}{2}}} \qquad (4.2-5)$$

In this expression, $V(r)$ is the intermolecular potential and $r_m$ is the distance of closest approach. ($r_m$ is a function of $E$ and $\cos\theta$.)

These expressions can be evaluated analytically for a few simple types of intermolecular potentials (e.g. a "hard" potential) but in general they must be calculated by a suitable numerical technique. An efficient algorithm using a Curtiss-Clenshaw quadrature technique has been developed by O'Hara and Smith(53).

## 4.3. Hard Convex Ovaloid Potentials in Classical Mechanics

In the last section, it was noted that scalar collision integrals can be evaluated analytically for hard sphere potentials. This is because of the inherent simplicity of impulsive collision dynamics. Making use of this simplicity, Hoffman(54) was able to greatly reduce the complexity of the scalar collision integrals for any hard convex interaction under the assumption that contributions from collisions with multiple impulses (chattering collisions) can be neglected. This assumption is valid for interactions which have a predominantly spherical component, but breaks down for significantly nonspherical interactions. A quantitative discussion of this point appears in Section 4.5.

An explicit expression for the collision kernel, using this approach can be obtained from Eq. (2.1-46) by constructing the convex surface, $\sigma_{1,2}$, so as to enclose an appropriate "excluded volume". The surface, $\sigma_{1,2}$, is defined as the locus of points occupied by the center of mass of an incident molecule (molecule 2) if the point of contact between interacting molecules is allowed to range over the whole surface of the target (molecule 1) with both molecules having a fixed orientation and the center of mass of the target being fixed. It can be shown geometrically that the convexity of molecules 1 and 2 guarantee that $\sigma_{1,2}$ is also convex.

Any convex surface is conveniently described in terms of a supporting function, h, which is defined as follows,

$$h = \underline{\zeta} \cdot \hat{k} \qquad (4.3-1)$$

Here, $\underline{\zeta}$ is a vector from a fixed origin (in this case, the center of mass of the target molecule) to a point on the surface, and $\hat{k}$ is a unit vector perpendicular to the surface at the point. Equation (4.3-1) can be inverted to yield the explicit expression for the radius vector,

$$\underline{\zeta} = h\hat{k} + \frac{\partial h}{\partial \hat{k}} \qquad (4.3-2)$$

Here, the differential operator $\frac{\partial}{\partial \hat{k}}$ is explicitly defined as $r\frac{\partial}{\partial \underline{r}} - \underline{r}\frac{\partial}{\partial \underline{r}}$ where $\underline{r} = r\hat{k}$.

Since $\sigma_{1,2}$ is convex, it follows that a differential element of surface area on $\sigma_{1,2}$, $dA_{\sigma_{1,2}}$, is related to a differential solid angle, $d\hat{k}$, by the expression,

$$dA_{\sigma_{1,2}} = S_{\sigma_{1,2}} d\hat{k} \qquad (4.3-3)$$

where $S_{\sigma_{1,2}}$ is defined in Eq. (2.1-45). The tensor, $\partial \underline{\zeta}/\partial \hat{k}$, has nonzero components only in the two dimensional subspace perpendicular to $\hat{k}$. From the definition of the determinant in terms of the Levi-Civita density, it follows that can be written in the form,

$$S_{\sigma_{1,2}} = -\frac{1}{2}(\frac{\partial \underline{\zeta}}{\partial \hat{k}} \times \hat{k}) : (\frac{\partial \underline{\zeta}}{\partial \hat{k}} \times \hat{k}) \qquad (4.3-4)$$

When the molecules are in contact, it follows that the radius vector of $\sigma_{1,2}$ can be defined as follows,

$$\underline{\zeta} = \underline{\zeta}_1 - \underline{\zeta}_2 = h_1 \hat{k}_1 + \frac{\partial h_1}{\partial \hat{k}_1} - h_2 \hat{k}_2 - \frac{\partial h_2}{\partial \hat{k}_2} \qquad (4.3-5)$$

Here, $h_1$ and $h_2$ denote supporting functions for molecule 1 and molecule 2, respectively, and $\hat{k}_1$ and $\hat{k}_2$ are corresponding unit surface normals taken at the point of contact. At this point, the convex bodies representing the interacting molecules share a common tangent plane. Since $\hat{k}_1$ and $\hat{k}_2$ must both be normal to this plane, it is clear that $\hat{k}_1 = -\hat{k}_2$. Thus the unit vector, $\hat{k} = \hat{k}_1$, is perpendicular to $\sigma_{1,2}$ at the endpoint of $\underline{\zeta}$ and the supporting function, $h$, appropriate to $\sigma_{1,2}$ can be regarded as a sum of the molecular supporting function (i.e. $h = h_1 + h_2$).

For an atom-diatom system, the atomic species will be modeled by a hard sphere and the molecular species by an ellipsoid of revolution. The spherical and axial symmetries implied by these models require the supporting functions to have the forms,

$$h_\alpha = r_0 \; ; \; h_\beta = h_\beta(\hat{k} \cdot \hat{e}) \qquad (4.3-6)$$

where $r_0$ is the radius of the sphere and $\hat{e}$ is the unit vector parallel to the molecular symmetry axis. The collision

kernel appropriate to atom-atom interactions retains the same form as given in Eq. (4.2-1). The atom-diatom collision kernel then is,

$$\langle \underline{p}_1 \underline{\ell}_1 \underline{p}_2 | \Theta | \underline{p}_1' \underline{\ell}_1' \underline{p}_2' \rangle = \frac{\ell_1'}{\pi} \int_0^{2\pi} d\eta \{ \int_{\substack{\hat{k} \cdot \underline{g} \leqslant 0 \\ \text{unit} \\ \text{hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) \hat{k} \cdot \underline{g} \delta(\underline{p}'-\underline{p}) \delta(\underline{\ell}_1'-\underline{\ell}_1)$$

$$+ \int_{\substack{\hat{k} \cdot \underline{g} > 0 \\ \text{unit} \\ \text{hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) \hat{k} \cdot \underline{g} \delta(\underline{p}'-\underline{p}^{\star}) \delta(\underline{\ell}_1'-\underline{\ell}_1^{\star}) \} \delta(\underline{p}-\underline{p}')$$

(4.3-7)

Here, $\underline{p}$, $\underline{p}'$, $\underline{p}^{\star}$, $\underline{p}$, and $\underline{p}'$ are defined as in Eq. (4.2-1) and $\ell_1^{\star}$ is defined as the precollisional rotational angular momentum (i.e. $\underline{\ell}_1^{\star}$ is related to $\underline{\ell}_1$ in the same way that $\underline{p}^{\star}$ is related to $\underline{p}$). The Jacobian of the surface transformation, $S_{\sigma_{1,2}}(\hat{k})$, is given by, ,

$$S_{\sigma_{1,2}}(\hat{k}) = S_{h_\beta} + 2r_0 h_\beta + r_0^2 \qquad (4.3-8)$$

which results from substitution of Eq. (4.3-5) into Eq. (4.3-4). Here, $S_{n\beta}$ is defined such that a unit surface area on the diatom ovaloid, $dA_{n\beta}$, is related to a unit solid angle, $d\hat{k}$, by $S_{n\beta}$ (i.e., $dA_{n\beta} = S_{n\beta} d\hat{k}$).

The velocity relative to the surface, $\underline{g}$, is defined in Eq. (2.1-41) as $\underline{v}-\dot{\underline{\alpha}}_1 \cdot \partial \underline{\zeta}_1/\partial \underline{\alpha}_1 - \dot{\underline{\alpha}}_2 \cdot \partial \underline{\zeta}_2/\partial \underline{\alpha}_2$. In Eq. (4.3-7) the diatomic molecule is arbitrarily labeled by 1 and the atom is

labeled by 2 which implies that $\underline{\alpha}_1$ can be identified as $\hat{e}$ and $\underline{\alpha}_2$ can be ignored (i.e. there are no orientation angles for the atom). Furthermore, $\underline{\zeta}_2$ is not a function of $\hat{e}$. The only internal degree of freedom of the system consists of the rotation of the diatom with angular velocity, $\underline{\ell}_1/I_\beta$. It is well-known that the time derivative of any body-fixed vector due to the rotation of the body can be obtained by the cross product of the angular velocity with this body-fixed vector. Thus, $\underline{g}$ has the form,

$$\underline{g} = \frac{\underline{p}}{\mu_{\alpha\beta}} - \frac{\underline{\ell}_1 \times \underline{\zeta}_1}{I_\beta} \qquad (4.3\text{-}9)$$

where $\mu_{\alpha\beta}$ is the reduced mass of the atom-molecule pair. If one substitutes Eq. (4.3-2) into Eq. (4.3-9) and evaluates $\hat{k} \cdot \underline{g}$, one obtains the following expression,

$$\hat{k} \cdot \underline{g} = \frac{\hat{k} \cdot \underline{p}}{\mu_{\alpha\beta}} - \frac{1}{I_\beta} \hat{k} \cdot \underline{\ell} \times \frac{\partial h_\beta}{\partial \hat{k}} \qquad (4.3\text{-}10)$$

This expression and Eq. (4.3-8), when substituted into Eq. (4.3-7), yield a Boltzman collision kernel from which the following form of the scalar collision integral

$$\{\Psi_\nu' , \varphi \Psi_\tau\}_{\nu\omega} = -\frac{1}{4}\pi^{-7/2}[\frac{2kT}{\mu_{\nu\omega}}]^{\frac{1}{2}} \int \Omega^{-1} d\underline{\Omega} \int d\underline{\gamma} e^{-\gamma^2-\Omega^2} \int_0^{2\pi} d\eta$$

$$\int_{\substack{\hat{k}\cdot\underline{g}\leq 0 \\ \text{unit hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) (\hat{k}\cdot\underline{\gamma} - \underline{a}\cdot\underline{\Omega}) \Psi_\nu' \varphi \Psi_\tau + \int_{\substack{\hat{k}\cdot\underline{g}\geq 0 \\ \text{unit hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) \qquad (4.3\text{-}11)$$

$$(\hat{k} \cdot \underline{\gamma} - \underline{a} \cdot \underline{\Omega}) \Psi_\nu' \odot \Psi_\tau^{\star}$$

is obtained. The vector quantity, $\underline{a}$, is defined by the expression,

$$\underline{a} = -[\frac{\mu_{\alpha\beta}}{I_\beta}]^{\frac{1}{2}} \hat{k} \times \hat{e} \frac{dh_\beta}{dz}(z) \qquad (4.3-12)$$

where z is defined as $\hat{k} \cdot \hat{e}$.

Following Hoffman(54), it is possible to define a vector, $\underline{\varepsilon}$, in a five dimensional Euclidean space, $E^5$, in which $\underline{\varepsilon}$ is comprised of the three body-fixed components of and the two active body-fixed components of $\underline{\Omega}$. (The body-fixed z-axis is assumed to parallel to $\hat{e}$.) In addition, a unit vector, $\hat{\kappa}$, can be defined in $F^5$ by the expression,

$$\hat{\kappa} = (\hat{k}, -\underline{a})/D \qquad (4.3-13)$$

where D is defined as $[1 + a^2]^{\frac{1}{2}}$. This is consistent since $\underline{a}$ has only two nonzero body-fixed components, both of which are in the same plane as $\underline{\Omega}$.

One can define two 3x5 rectangualr "projection" operators, $^3P_\gamma^5$ and $^3P_\Omega^5$ which are functions of the components of $\hat{e}$ and act between the abstract 5-space, $F^5$, and the usual physical 3-space, $E^3$, as follows(55):

$$^3P^5_\gamma \cdot \underline{\varepsilon} = \underline{\gamma}; \quad ^3P^5_\Omega \cdot \underline{\varepsilon} = \underline{\Omega} \qquad (4.3\text{-}14)$$

where $\varepsilon = (\underline{\gamma}, \underline{\Omega})$. Since the tensor quantities, $\overline{\Psi}'_\nu$ and $\overline{\Psi}_\tau$ are exclusive functions of $\underline{\gamma}$ and $\underline{\Omega}$, it follows that $^3P^5_\gamma$ and $^3P^5_\Omega$ can be used to construct composite operators which act between $E^5$ and $E^3$ as follows,

$$^3P^5_{\overline{\Psi}'_\nu} \underset{u}{\odot} (\underline{\varepsilon})^u = \overline{\Psi}'_\nu \; ; \; ^3P^5_{\overline{\Psi}_\tau} \underset{v}{\odot} (\underline{\varepsilon})^v = \overline{\Psi}_\tau \qquad (4.3\text{-}15)$$

Here, u and v are the total powers of $\overline{\Psi}'_\nu$ and $\overline{\Psi}_\tau$ in the dynamical variables. If one contracts $^3P^5_{\overline{\Psi}'_\nu}$ with $^3P^5_{\overline{\Psi}_\eta}$ in the three dimensional manifold, one obtains an operator, $^3P^5_{\overline{\Psi}'_\nu \odot \Psi_\eta}$ such that,

$$^3P^5_{\overline{\Psi}'_\nu \odot \overline{\Psi}_\tau} \underset{u+v}{\odot} (\underline{\varepsilon})^{u+v} = \overline{\Psi}'_\nu \odot \overline{\Psi}_\tau \qquad (4.3\text{-}16)$$

Thus, Eq. (4.3-11) takes the form,

$$\{\overline{\Psi}'_\nu \odot \overline{\Psi}_\tau\}_{\nu,\omega} = -\frac{1}{4} \pi^{-7/2} [\frac{2kT}{\mu_{\nu\omega}}]^{1/2} \int d\underline{\varepsilon} e^{-\varepsilon^2} \int_{\substack{\text{unit} \\ \text{hemisphere}}} d\hat{e} \; ^3P^5_{\overline{\Psi}'_\nu \odot \Psi_\tau} \underset{u+v}{\odot}$$

$$(4.3\text{-}17)$$

$$\int_{\substack{\underline{k}\cdot\underline{g}\leqslant 0 \\ \text{unit} \\ \text{hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) D(\underline{\varepsilon})^u (\underline{\varepsilon})^v \underline{\varepsilon}\cdot\hat{k} + \int_{\substack{\hat{k}\cdot\underline{g}>0 \\ \text{unit} \\ \text{hemisphere}}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) D(\underline{\varepsilon})^u (\underline{\varepsilon}^\star)^v \underline{\varepsilon}\cdot\hat{k}$$

The operator $^3P^5_{\overline{\Psi}'_\nu \odot \Psi_\tau}$ will be abbreviated as P in subsequent expressions.

In the case of a hard anisotropic potential, the unit vector, $\hat{\kappa}$, can be interpreted as a generalization of the apse vector one encounters in the dynamics of elastic interactions. For an elastic interaction, all components of the relative momentum are conserved in collision except for the component of the relative momentum parallel to the apse vector which reverses sign. Correspondingly, for hard anisotropic molecules, the collision dynamics are quantitatively described by a reversal of the sign of $\varepsilon_\kappa = \hat{\kappa} \cdot \hat{\varepsilon}$ while the other components remain unchanged. Thus, if $\underline{c}$ is defined as $\varepsilon - \varepsilon_\kappa \hat{\kappa}$ (<u>i.e.</u> $\underline{\varepsilon} = \underline{c} + \varepsilon_\kappa \hat{\kappa}$), then $\varepsilon^* = \underline{c} - \varepsilon_\kappa \hat{\kappa}$. This allows the expression for the scalar collision integrals to be written as follows,

$$\{\overline{\Psi}'_\nu, \overline{\Psi}_\tau\}_{\nu,\omega} =$$

$$-\frac{1}{4} \pi^{-7/2} [\frac{2kT}{\mu}]^{\frac{1}{2}}_{\nu\omega} \int_{\substack{unit \\ sphere}} d\hat{e} \int_{\substack{unit \\ sphere}} d\hat{k} S_{\sigma_{1,2}} (\hat{k}) D\underline{P}_{\underline{u+v}}^{\Theta} (u,v)_5 \qquad (4.3\text{-}18)$$

Here, $(u,v)$ is a tensor quantity of rank $u+v$ defined by the expression,

$$(u,v)_n =$$

$$\int_{E^{n-1}} d\underline{c} e^{-c^2} \int_0^\infty d\varepsilon_\kappa e^{-\varepsilon_\kappa^2} [(\underline{c}-\varepsilon_\kappa \hat{k})^u - (\underline{c}+\varepsilon_\kappa \hat{k})^u] (\underline{c}-\varepsilon_\kappa \hat{k})^v \varepsilon_\kappa \qquad (4.3\text{-}19)$$

In the expression for $(u,v)_n$, $\underline{c}$ is treated as a vector in an $E^{n-1}$ space orthogonal to $\hat{k}$ where $\hat{k}$ is a basis vector of $E^n$. (For the case in point, n equals 5.) Equations (4.3-18) and (4.3-19) are obtained from Eq. (4.3-17) by noting that the conditions previously placed on the integration over $\hat{k}$ can be replaced by equivalent conditions on the integration over $\varepsilon_K$. Following this, the integration variable, $\varepsilon_K$, in the precollisional term is exchanged for $-\varepsilon_K$ so that all integrations over $\varepsilon_K$ are between limits of 0 to $\infty$.

Equation (4.3-19) can be simplified by noting

$$(c\hat{c} \pm \varepsilon_K \hat{k})^n = \sum_{j=0}^{n} (\pm 1)^j c^{n-j} \varepsilon_K^j \{(\hat{c})^{n-j}(\hat{k})^j\} \qquad (4.3-20)$$

where c is the magnitude of $\underline{c}$, $\hat{c}$ is $\underline{c}/c$ and $\{(\hat{c})^{n-j}(\hat{k})^j\}$ is defined as the sum of all distinguishable permutations of the tensor indices of the direct product $(\hat{c})^{n-j}(\hat{k})^j$. If one substitutes Eq. (4.3-20) into Eq. (4.3-19) and makes use of the following identity for arbitrary integers n and s,

$$\int_{\substack{unit \\ n-1 \text{ sphere}}} d\hat{c}\,(\hat{c})^s \int_0^{\infty} dc\, c^{n+s-1} e^{-c^2} = [\frac{\pi^n}{2^s}]^{\frac{1}{2}} \{(\underline{\underline{I}}_{n-1})^{s/2}\} \quad s \text{ even}$$
$$= 0 \qquad s \text{ odd} \qquad (4.3-21)$$

(Here, $\underline{\underline{I}}_{n-1}$ is the identity tensor on $E^{n-1}$), one obtains the

result,

$$(u,v)_n = [-\frac{1}{2^{\frac{1}{2}}}]^{u+v} \frac{\pi}{2} \sum_{\substack{j=1 \\ j \cdot odd}}^{\frac{n-1}{2}} \sum_{\substack{k=j \\ k \text{ even if } u+v \text{ even} \\ k \text{ odd if } u+v \text{ odd}}}^{n \quad v+j}$$

$$2^{k/2} k\Gamma(\frac{k}{2}) P_{u,v}[(\hat{k})^j \{(\underline{\underline{I}}_n - \hat{k}\hat{k})^{\frac{1}{2}(u+v-k)}\} (R)^{k-j}]$$

(4.3-22)

Here, $P_{u,v}[\cdots]$ means "the sum of all distinct permutations of the first u and last v tensor indices of the tensor appearing in the brackets."

Equation (4.3-18) can be reduced to a single quadrature if one notes that the $S_{\sigma_{1,2}}(\hat{k})$, D, and $P_{\underline{u+v}}^{\odot}(u,v)_5$ are functions of $\hat{k}$ and $\hat{e}$ only through the dot product, $\hat{k} \cdot \hat{e}$. One obtains the result,

$$\{\underline{\Psi}_\nu'; \underline{\Psi}_\tau\}_{\nu,\omega} = -2\pi^{-3/2}[\frac{2kT}{\mu_{\nu\omega}}]^{\frac{1}{2}} \int_{-1}^{1} dz S_{\sigma_{1,2}}(z) D \underline{P}_{\underline{u+v}}^{\odot}(u,v)_5 \quad (4.3-23)$$

One can evaluate $P_{\underline{u+v}}^{\odot}(u,v)_5$ using Eq. (4.3-14) and the following identities,

$$^3P_\gamma^5 \cdot \underline{\underline{I}}_5 = \underline{\underline{U}} \; ; \; ^3P_\gamma^5 \cdot \hat{k} = \hat{k}/D \qquad (4.3-24)$$

$$^3P_\Omega^5 \cdot \underline{\underline{I}}_5 = \underline{\underline{U}} - \hat{e}\hat{e} \; ; \; ^3P_\Omega^5 \cdot \hat{k} = -\underline{a}/D \qquad (4.3-25)$$

where, $\underline{\underline{U}}$ is the usual $E^3$ identity operator. Proceeding in

this way and noting that $\underline{a} \cdot \hat{k}$ vanishes, one finds that the scalar collision integrals for an atom-diatom interaction can be written as linear combinations of the following basic integrals,

$$\chi^{(n)} = \int_{-1}^{1} dz S_{\sigma_{1,2}}(z) D^{-n} \qquad (4.3\text{-}26)$$

$$T^{(n,m)} = \int_{-1}^{1} dz S_{\sigma_{1,2}}(z) z^m D^{-n} \qquad (4.3\text{-}27)$$

$$G = \left[\frac{\mu_{\alpha\beta}}{I_\beta}\right]^{\frac{1}{2}} (b^2 - a^2) \int_{-1}^{1} dz S_{r_0}^{a,b}(z) \frac{z^2(1-z^2)}{h_\beta D^2} \qquad (4.3\text{-}28)$$

These integrals can be evaluated numerically by use of Gaussian quadrature techniques.

## 4.4. Realistic Anisotropic Potentials in Classical Mechanics

In the two sections immediately preceding this one, discussion is given which concerns the evaluation of the scalar collision integrals (and hence the effective cross sections) using very restricted classes of molecular interactions (i.e., central and/or "hard" convex intermolecular potentials). These limitations were imposed because the simplicity of the dynamics implied by these potentials allow partial analytical evaluation of the scalar collision integrals. In

order to evaluate the scalar collision integrals for realistic anisotropic potentials, cne must resort to numerical techniques such as Monte Carlo or Diophantine integration.

Before discussing the numerical techniques, appropriate expressions for the atom-diatom collision kernel and atom-diatom scalar collision integrals must be given. The evaluation of realistic atom-diatom scalar collision integrals is complicated by the infinite interaction range of a realistic interaction potential which means that $\sigma_{1,2}$ cannot be chosen in such a way as to represent a physically meaningful "excluded volume" as was the case in the discussion of hard ovaloids. Thus, $\sigma_{1,2}$ is conveniently chosen to be spherical since there is no advantage to be gained in exchange fcr a preferential nonspherical choice. This results in the following form for the atcm-diatom collision kernel,

$$\langle \underline{p}_1 \underline{\ell}_1 \underline{p}_2 | \Theta | \underline{p}_1' \underline{\ell}_1' \underline{p}_2' \rangle = \frac{\ell_1' b_{max}^2}{4\pi} \int_0^{2\pi} d\eta \int_{\hat{k}\cdot\underline{p}>0} d\hat{k} \ \hat{k}\cdot\underline{p}/\mu_{\alpha\beta} \{\delta(\underline{p}'-\underline{p}^\star)\delta(\underline{\ell}_1'-\underline{\ell}_1^\star)$$

$$- \delta(\underline{p}'-\underline{p})\delta(\underline{\ell}_1'-\underline{\ell}_1)\}\delta(\underline{p}-\underline{p}') \qquad (4.4-1)$$

Here, $b_{max}$ denotes the radius of $\sigma_{1,2}$ (i.e. maximum impact parameter.) An expression for an arbitrary atom-diatom scalar collision integral has the form,

$$\{\Psi_\nu \cdot \Phi \Psi_\tau\}_{\nu,\omega} = \tfrac{1}{4} b_{max}^2 \pi^{-7/2} [\frac{2kT}{\mu_{\nu\omega}}]^{\frac{1}{2}} \int \frac{d\Omega}{\Omega} \int d\underline{\gamma} e^{-\Omega^2 - \gamma^2}$$

$$\int_0^{2\pi} d\eta \int_{\hat{k} \cdot \underline{\gamma} > 0} d\hat{k} \; \hat{k} \cdot \underline{\gamma} \Psi_\nu^i (\Psi_\tau - \Psi_\tau^{\star}) \qquad (4.4\text{-}2)$$

This expression is analogous to Eq. (4.3-11).

The expression given in Eq. (4.4-2) is formulated in terms of integrals over postcollisional parameters. It can be equivalently formulated in terms of integrals over precollisional parameters. In fact, such a formulation is perhaps more appealing since it involves scattering out of rather than into a dynamically prepared state. The transformation from a postcollisional to a precollisional expression proceeds as follows.

A dynamical trajectory through the region contained within $\sigma_{1,2}$ can be symbolized as follows,

$$z^{\star} \rightarrow z \qquad (4.4\text{-}3)$$

Here, $z^{\star}$ and $z$ denote the sets of dynamical parameters, $\{\underline{\gamma}^{\star}, \Omega^{\star}, \eta^{\star}, \hat{k}^{\star}\}$ and $\{\underline{\gamma}, \underline{\Omega}, \eta, \hat{k}\}$. In order for this trajectory to exist, $\hat{k}^{\star} \cdot \underline{\gamma}^{\star}$ must be negative and $\hat{k} \cdot \underline{\gamma}$ must be positive (i.e. $z^{\star}$ must be precollisional and $z$ must be postcollisional). The time reversal symmetry of classical mechanics implies that the time reversed image of any given trajectory is mechanically allowed. Thus, one can write the

following expression,

$$\overline{Z} \rightarrow \overline{Z}^{\star} \qquad (4.4-4)$$

where $\overline{Z}$ and $\overline{Z}^{\star}$ denote the time reversed sets, $\{-\gamma,-\underline{\Omega},\eta,\hat{k}\}$ and $\{-\gamma^{\star},-\underline{\Omega}^{\star},\eta^{\star},\hat{k}^{\star}\}$, respectively. It should be noted that $\eta^{\star}$, $\eta$, $\hat{k}^{\star}$, and $\hat{k}$ are evaluated at the point where the trajectory pierces $\sigma_{1,2}$.

One can define the following functional relations,

$$Z_i(Z) = Z^{\star} \qquad (4.4-5)$$

$$Z_f(Z^{\star}) = Z \qquad (4.4-6)$$

In a similar way, one obtains the expressions,

$$Z_i(\overline{Z}^{\star}) = \overline{Z}, \quad Z_f(\overline{Z}) = \overline{Z}^{\star} \qquad (4.4-7)$$

from which it follows that,

$$Z_i(Z) = \overline{Z}_f(\overline{Z}) \qquad (4.4-8)$$

The quantity $\Psi_{\tau}^{\star}$ appearing in Eq. (4.4-2) can be thought of as a function of $z^{\star}$. Hence, $\overline{Z}_f(\overline{Z})$ can be substituted for $z^{\star}$. If one exchanges the integration variables $\underline{\gamma},\underline{\Omega}$ for $-\underline{\gamma},-\underline{\Omega}$ one obtains the result,

$$\{\Psi_{\nu}' \circ \Psi_{\tau}\}_{\nu,\omega} = -\frac{1}{4}b_{max}^2 \pi^{-7/2} \left[\frac{2kT}{\mu}\right]^{\frac{1}{2}} \int \frac{d\underline{\Omega}}{\underline{\Omega}} \int d\underline{\gamma} e^{-\Omega^2-\gamma^2}_{\nu\omega} \qquad (4.4-9)$$

$$\int_0^{2\pi} d\eta \int_{\hat{k}\cdot\underline{\gamma}\leqslant 0} d\hat{k}\ \hat{k}\cdot\underline{\gamma}\Psi_\nu'\odot(\Psi_\tau-\Psi_\tau^\star)\,(-1)^n$$

Here, n equals 1 if $\Psi_\nu'\odot\Psi_\tau$ changes sign under time reversal and it equals 0 if $\Psi_\nu'\odot\Psi_\tau$ does not change sign. The solid star denotes a postcollisional quantity, $\Psi_\tau^\star$, which is dynamically related to a precollisional quantity, $\Psi_\tau$.

The impact parameter, b, can be defined as $b_{max}\hat{k}\cdot\underline{\gamma}/\gamma$. From this definition, it follows that the double integral over the angles of $\hat{k}$ appearing in Eq. (4.4-9) can be replaced by integrals over the impact parameter, b, and an angle, $\varepsilon$. One obtains the result,

$$\{\Psi_\nu'\odot\Psi_\tau\}_{\nu\omega} = [\frac{2kT}{\mu_{\nu\omega}}]^{\frac{1}{2}}\ \frac{1}{4}\ \pi^{-7/2}\int_0^\infty\Omega d\Omega e^{-\Omega^2}\int_0^\infty\gamma^3 d\gamma e^{-\gamma^2}\int_{\substack{unit\\sphere}}d\hat{\Omega}$$

$$\int_{\substack{unit\\sphere}}d\hat{\gamma}\int_0^{2\pi}d\eta\int_0^{b_{max}}bdb\int_0^{2\pi}d\varepsilon\Psi_\nu'(\Psi_\tau-\Psi_\tau^\star)\,(-1)^n \qquad (4.4\text{-}10)$$

The angle, $\varepsilon$, is taken about an axis defined by the direction of the precollisional linear momentum, $\underline{\gamma}$.

The Q-cross section, $Q(\Psi_\nu'\odot\Psi_\tau)$ can be defined in a manner analogous to that given in Eq. (4.2-4) by

$$Q(\Psi_\nu'\odot\Psi_\tau) =$$

$$\frac{\gamma^{-s-s'}}{32\,\pi^3}\int_{\substack{unit\\sphere}}d\hat{\gamma}\int_{\substack{unit\\sphere}}d\hat{\Omega}\int_0^{2\pi}d\eta\int_0^{b_{max}}bdb\int_0^{2\pi}d\varepsilon\Psi_\nu'\odot(\Psi_\tau-\Psi_\tau^\star)\,(-1)^n \qquad (4.4\text{-}11)$$

where s and s' are taken respectively as the order of $\Psi_\nu'$ and

$\overline{\Psi}_\tau$ in $|\underline{Y}|$. Thus, in analogy to Eq. (4.2-3),

$$\{\overline{\Psi}'_\nu \underset{\circ}{\overset{\circ}{\circ}} \overline{\Psi}_\tau\}_{\nu\omega} =$$

$$[\frac{kT}{2\pi\mu_{\nu\omega}}]^{\frac{1}{2}} \int_0^\infty d\gamma e^{-\gamma^2} \gamma^{s+s'+3} \int_0^\infty \Omega d\Omega e^{-\Omega^2} [16Q(\overline{\Psi}'_\nu \underset{\circ}{\overset{\circ}{\circ}} \overline{\Psi}_\tau)] \qquad (4.4-12)$$

It is clear that $Q(\overline{\Psi}'_\nu \underset{\circ}{\overset{\circ}{\circ}} \overline{\Psi}_\tau)$ can be regarded as a function of two independent variables, namely the reduced translational and rotational kinetic energies.

Evaluation of scalar collision integrals and/or Q-cross sections for a realistic anisotropic interaction requires evaluation of nontrivial nine-fold or seven-fold quadratures respectively. The standard numerical techniques which are well-suited for the efficient evaluation of a single quadrature are impractical in these cases due to the sheer number of times a particular integrand must be evaluated in order to attain a reasonably accurate result. In particular, the number of points, $\Delta$, at which an arbitrary integrand is sampled in order to obtain a given accuracy rises roughly as $\Delta^N$ where N is the multiplicity of the quadrature. Additionally, this problem is exacerbated by the fact that realistic collision dynamics in general are very complicated and can be evaluated only with much effort. These difficulties can be partially overcome by the use of Monte Carlo techniques.

An integral of an arbitrary function, G, of a vector, $\xi$, in an n dimensional Euclidean space, $E^n$, over limits defined by an n-cube of unit volume, obeys the following inequality,

$$\frac{1}{N}\sum_{j=1}^{N}G(\underline{\xi}_j^{max}) \geqslant \int_0^1 - \int_0^1 d\underline{\xi}G(\underline{\xi}) \geqslant \frac{1}{N}\sum_{j=1}^{N}G(\underline{\xi}_j^{min}) \qquad (4.4-13)$$
$$\text{n-cube}$$

Here, the n-cube is taken to be divided into N partitions of equal volume. The vectors, $\underline{\xi}_j^{max}$ and $\underline{\xi}_j^{min}$, define particular points (not necessarily unique) in the $j^{th}$ partition for which the value of $G(\underline{\xi})$ is maximum and minimum respectively. From the mean value theorem, it follows that a vector, $\overline{\underline{\xi}}_j$, can be found within each partition such that the following equality is valid,

$$\frac{1}{N}\sum_{j=1}^{N}G(\overline{\underline{\xi}}_j) = \int_0^1 - \int_0^1 d\underline{\xi}G(\underline{\xi}) \qquad (4.4-14)$$
$$\text{n-cube}$$

The Monte Carlo estimate, $S_G^N$, of the above quantity can be defined by evaluating $G(\underline{\xi})$ at N points randomly chosen within the unit n-cube followed by a summation over the selected points. It has the form(56),

$$S_G^N = \frac{1}{N}\sum_{j=1}^{N}G(\underline{\xi}_j) \qquad (4.4-15)$$

If each term appearing in the sum on the right hand side of Eq. (4.4-15) is written as a Taylor series expanded about one of the corresponding values, $\underline{\xi}_j$, (where the index, j, is assigned so that $N^{-1}\sum_j |\underline{\xi}_j - \overline{\underline{\xi}}_j|$ is minimized) one obtains the result,

$$S_G^N - I_G = \frac{1}{N}\sum_{j=1}^{N} \sum_{k=1}^{\infty} \frac{(\underline{\xi}_j - \overline{\underline{\xi}}_j)^k}{k!} \circledcirc_k (\frac{d}{d\overline{\underline{\xi}}_j})^k G(\overline{\underline{\xi}}_j) \qquad (4.4\text{-}16)$$

Clearly, one notes that the first term of the Taylor series is just $I_G$ where $I_G$ symbolizes the integral appearing on the right hand side of Eq. (4.4-14).

If the number of partitions, N, (i.e. the number of randomly chosen points, $\underline{\xi}_j$) is allowed to increase without limit, it follows that the quantity, $|\underline{\xi}_j - \overline{\underline{\xi}}_j|$ tends to zero. This is to say that as N tends toward infinity that the distance between an exact integrating point, $\overline{\underline{\xi}}_j$, and a randomly chosen point, $\underline{\xi}_j$, becomes indefinitely small.

An important adjunct to the direct Monte Carlo estimate, $S_G^N$, is a reliable estimate of the random error inherent in $S_G^N$. It follows from the central limit theorem of statistics that the probability distribution followed by any observable quantity which is derived from measurements which are subject only to random fluctuations is a normal Gaussian. The Monte

Carlo estimate, $S_G^N$, can be regarded as just such an observation (i.e. subject to random fluctuations). Thus, the square root of the variance of this quantity as it is normally defined by statisticians is a suitable measure of the expected error in $S_G^N$. The variance, $\sigma^2$, is defined as follows,

$$\sigma^2 = \int d\underline{\xi}_1 - \int d\underline{\xi}_N (S_G^N - I_G)^2 \qquad (4.4\text{-}17)$$

Here, each of the integrals are taken over the usual unit n-cube.

If one substitutes the explicit form of $S_G^N$ from Eq. (4.4-15) and performs the integrations, one obtains the result,

$$N\sigma^2 = \sigma_G^2 = \int_0^1 - \int_0^1 d\underline{\xi} (G(\underline{\xi}) - I_G)^2 \qquad (4.4\text{-}18)$$
$$\text{n-cube}$$

Thus, the expected error in the Monte Carlo estimate is proportional to $N^{-\frac{1}{2}}$. A suitable estimator for the expected error is $\delta_G^N$ where $\delta_G^N$ is defined by the expression, (i.e., $\delta_G^N$ is the Monte Carlo estimate of $\sigma_G$),

$$\delta_G^N = [\frac{1}{N} \sum_{j=1}^N (G(\underline{\xi}_j) - S_G^N)^2]^{\frac{1}{2}} \qquad (4.4\text{-}19)$$

In practice, $S_G^N$ and $\delta_G^N$ can be evaluated simultaneously for some set of N randomly chosen points.

Both the scalar collision integrals and the phenomenological cross sections for a realistic potential can be evaluated as Monte Carlo estimates. Explicit forms for the estimators are obtained if one defines the following set of variables,

$$\xi_1 = \frac{\eta}{2\pi} \ , \ \xi_2 = \frac{\varepsilon}{2\pi} \qquad (4.4\text{-}20)$$

$$\xi_3 = \frac{1-\cos\theta_\Omega}{2} \ , \ \xi_4 = \frac{\phi_\Omega}{2\pi} \qquad (4.4\text{-}21)$$

$$\xi_5 = \frac{1-\cos\theta_\gamma}{2} \ , \ \xi_6 = \frac{\phi_\gamma}{2\pi} \qquad (4.4\text{-}22)$$

$$\xi_7 = \frac{b}{b_{max}} \qquad (4.4\text{-}23)$$

$$\xi_8 = 1 - e^{-\Omega^2} \qquad (4.4\text{-}24)$$

$$\xi_9 = 1 - (1+\gamma^2)e^{-\gamma^2} \qquad (4.4\text{-}25)$$

Here, $\theta_\Omega$, $\phi_\Omega$, $\theta_\gamma$, and $\phi_\gamma$ denote the angles of $\hat{\Omega}$ and $\hat{\gamma}$. If one defines a seven dimensional vector, $\underline{\xi}^{(7)}$, and a nine dimensional vector, $\underline{\xi}^{(9)}$, as being comprised of components given by $\xi_1$ through $\xi_7$ and $\xi_1$ through $\xi_9$, respectively, Eqs. (4.4-10) and (4.4-11) take the following forms,

$$\{\overline{\Psi}_\nu' \wp \overline{\Psi}_\tau\}_{\nu,\omega} = $$
$$[\frac{2kT}{\mu_{\nu\omega}}]^{\frac{1}{2}} \ 4\pi^{\frac{1}{2}} b_{max} \int_0^1 - \int_0^1 d\underline{\xi}^{(9)} \ b\overline{\Psi}_\wp'(\overline{\Psi}_\tau - \overline{\Psi}_\tau^\star) \ (-1)^n \qquad (4.4\text{-}26)$$
$$9\text{-cube}$$

$$Q(\overline{\Psi}_{\nu}'\varphi\overline{\Psi}_{\tau}) = \frac{2\pi b_{max}}{\gamma^{s+s'}} \int_0^1 -\int_0^1 d\underline{\xi}^{(7)} b\overline{\Psi}_{\nu}^{\flat}\phi(\Psi_\tau - \Psi_\tau^{\star})(-1)^n \qquad (4.4-27)$$
$$\text{7-cube}$$

Algorithms designed to evaluate Eqs. (4.4-26) and (4.4-27) as Monte Carlo estimates consist of three stages. First, a randomly chosen set of integration points (i.e. $\underline{\xi}^{(7)}$, $\underline{\xi}^{(9)}$) is generated by an appropriate pseudo-random number generator. Second, these are converted to dynamical parameters by inversion of Eqs. (4.4-20) through (4.4-25) and $\overline{\Psi}_\tau^{\star}$ is evaluated by numerical integration of Hamilton's equations within the collision region. Third, the resulting set of collision trajectories is used to compute Monte Carlo estimates via Eq. (4.4-15).

It should be noted here that $\xi_7$ is defined as $b/b_{max}$ rather than $b^2/b^2_{min}$ which causes the integrands appearing in Eqs. (4.4-26) and (4.4-27) to contain the impact parameter, b, as a weighting factor. The result of this procedure is that the evaluation of these integrands is biased toward regions on the precollisional hemisphere characterized by low values of the impact parameter. This bias is desirable because the strongest and hence most significant interactions occur precisely for this case. This is an example of a general technique known as importance sampling which can be used

to improve simple Monte Carlo estimates by biasing the random sampling of a particular estimand toward regions which contain the most significant contributions to the overall estimate (56).

## 4.5. The Method of Control Variates and a Quantitative Discussion of the Effect of Chattering Collisions

In the last section the Monte Carlo estimate of a multi-dimensional definite integral was given. It was found that such an estimate converges at a rate which is inversely proportional to the square root of the number of random points at which the integrand is evaluated. While this convergence rate represents a vast improvement over alternative quadrature methods, in practice, an integrand characterized by a moderate variation must still be evaluated at a large number of points (usually several thousand) in order to obtain a reasonably accurate result.

It seems likely that if a significant correlation exists between a "difficult" problem which requires the application of a Monte Carlo technique and a "simpler" problem which can be solved either analytically or with some efficient numerical technique, that this correlation can be exploited to improve the convergence of the simple Monte Carlo estimate. This idea can be quantitatively applied to the evaluation of

definite integrals by modification of Eq. (4.4-15) as
follows,

$$S_G^N(G') = \frac{1}{N}\sum_{j=1}^{N}(G(\underline{\xi}_j) - G'(\underline{\xi}_j)) + I_{G'} \qquad (4.5-1)$$

Here, $G'(\underline{\xi})$ is termed a "control variate" of $G(\underline{\xi})$ and is a
function of $\underline{\xi}$ which exhibits a positive correlation with the
functional behavior of $G(\underline{\xi})$ (56). It should be emphasized
that G and G' are evaluated over the same set of randomly
chosen points. The quantity, $I_{G'}$, is defined by the expres-
sion,

$$I_{G'} = \int_0^1 - \int_0^1 d\underline{\xi} G'(\underline{\xi}) \qquad (4.5-2)$$
$$\text{n-cube}$$

and must be able to be evaluated to an arbitrary accuracy via
an appropriate analytic or numerical method.

It is found in the cases considered in this work, that
the method of control variates improves typical Monte Carlo
estimates of scalar collision integrals or energy-dependent
cross sections by reducing expected error estimates,
typically, by a factor of two to four for a given set of N
randomly chosen integration points. The degree of improve-
ment is a measure of how closely the primary and control in-
tegrands are correlated. It is useful to give as an example
of the control variate method a calculation of the Chapman-

Cowling omega integral, $\Omega^{(1,1)\star}$, for a Lennard-Jones 6-12 potential as a Monte Carlo estimate for a reduced temperature of 1.824 and using the value of $\Omega^{(1,1)\star}$ appropriate to hard sphere models of varying radius, R, as a control variate. The expected error estimates are plotted in Fig. 4.1 versus the reduced hard sphere radius, R/σ. (σ is the usual Lennard-Jones force constant.) The actual deviations of the control variate Monte Carlo estimates appear as isolated points. Both quantities are evaluated for two sets of 10,000 randomly chosen integration points. The obvious minimization of the expected error at R/σ equal to 0.95 illustrates the applicability of the control variate technique. The expected error estimate is reduced for the optimum hard sphere radius by a factor of three over the corresponding uncorrected value. Since the expected error converges as $N^{-\frac{1}{2}}$, this three-fold improvement of precision corresponds to a primary uncorrected Monte Carlo estimate obtainable by a nine-fold increase in the number of integration points evaluated (i.e., 90,000 versus 10,000).

One possible choice for a control variate which is applicable to the evaluation of scalar collision integrals or phenomenological cross sections of a realistic anisotropic potential is the corresponding integral evaluated for a spherically symmetric potential. A shortcoming of this choice is that no significant improvement can be expected in
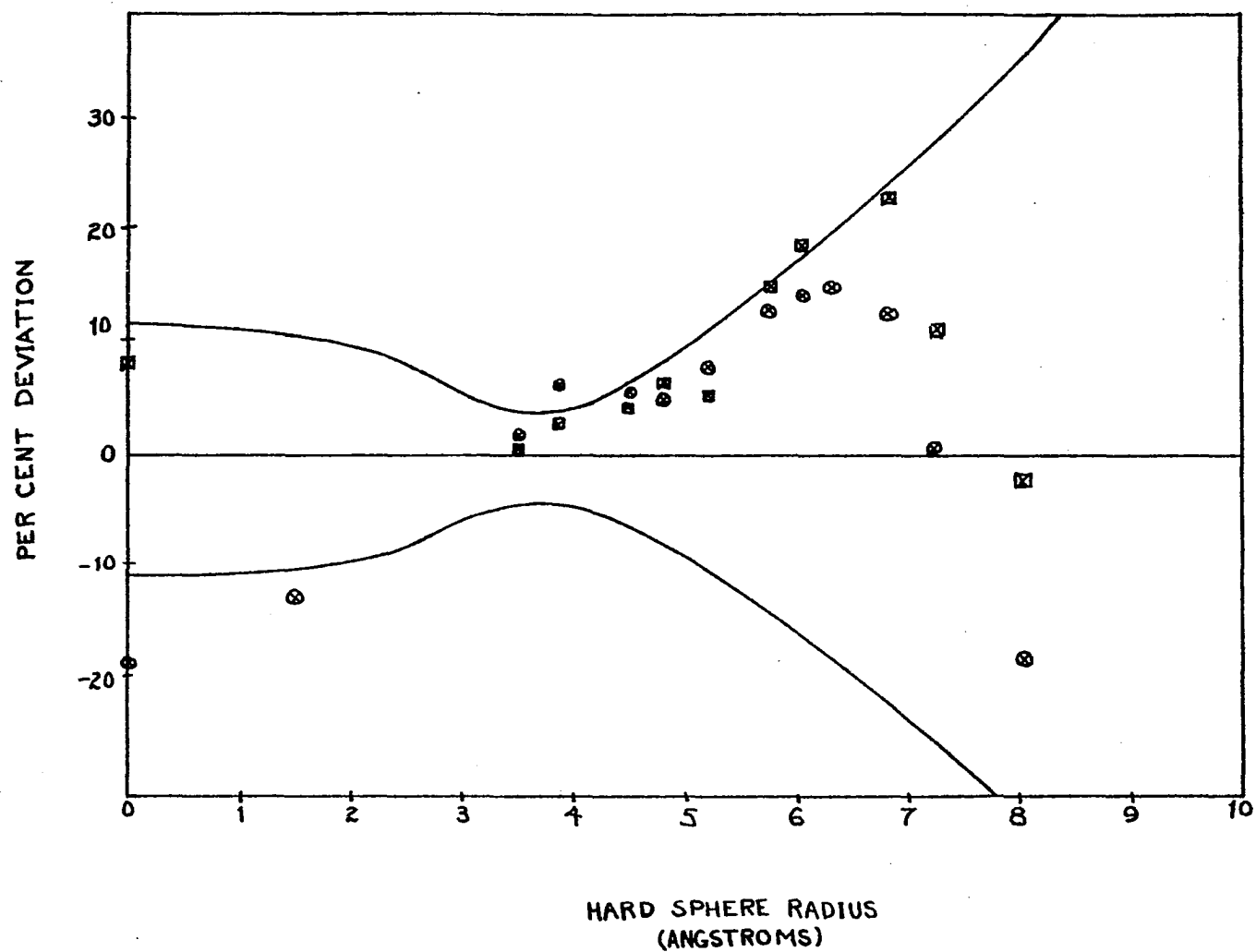
Fig. 4.1. Expected and Actual Monte Carlo-Control Variate Error estimates of $\Omega^{(1,1)}\star$

estimates of quantities which involve only the anisotropy of the interaction. Accurate values of the control variate can be easily obtained by suitable analytic or numerical techniques.

Another possible choice for a control variate applicable to the above situation is the corresponding quantity evaluated for a hard ovaloid interaction. One should be able to obtain improvement of all estimates since anisotropic contributions to the interaction potential are explicitly taken into account. However, as was noted previously, the "projection" operator techniques developed to evaluate the scalar collision integrals for hard ovaloid interactions in Section 4.3 possess a systematic error due to the neglect of "chattering" collisions. In principle, it is undesirable to ever introduce systematic error deliberately into a Monte Carlo calculation. In practice, systematic errors which are negligible compared to the probable random error inherent in the calculation will not affect the numerical result. The utility of hard ovaloid control variates can be judged on this criterion.

For hard intermolecular potentials, chattering interactions are unambiguously defined as binary collision events which involve more than a single impulse. Chattering cannot occur for hard sphere interactions. The frequency of chattering is, as expected, directly related to the degree of

anisotropy inherent in the intermolecular potential.

The chattering frequency can be approximated by a suitable Monte Carlo estimate which consists of the ratio of the number of chattering collisions to the total number of collisions for some set of randomly chosen classical trajectories. A description of the algorithm used to construct hard sphere-hard ellipsoid trajectories is given in Appendix C. Results obtained by this method for hard sphere-hard ellipsoid interactions are summarized in Fig. 4.2. Here, the kinematic parameters are appropriate to an Ar-$CO_2$ system. Of the potential parameters, the sphere radius, $r_0$, and ellipsoid semimajor axis, b, are held fixed with values of 1.91 Å (3.6 bohrs) and 4.23 Å (8.0 bohrs), respectively, and the semiminor axis, a, is allowed to vary from 1.59 Å (3.0 bohrs) up to b. The collision frequency is evaluated as a function of impact parameter and ellipsoid eccentricity, e,

$$ e = \sqrt{\frac{b^2-a^2}{b^2}} \qquad (4.5-3) $$

It is evident from the results appearing in Fig. 4.2 that the chattering frequency can become significant for moderately eccentric ellipsoids. Figure 4.3 illustrates the definition of the hard sphere-hard ellipsoid potential parameters.

To assess the systematic error inherent in the "projection" operator technique applicable to the evaluation
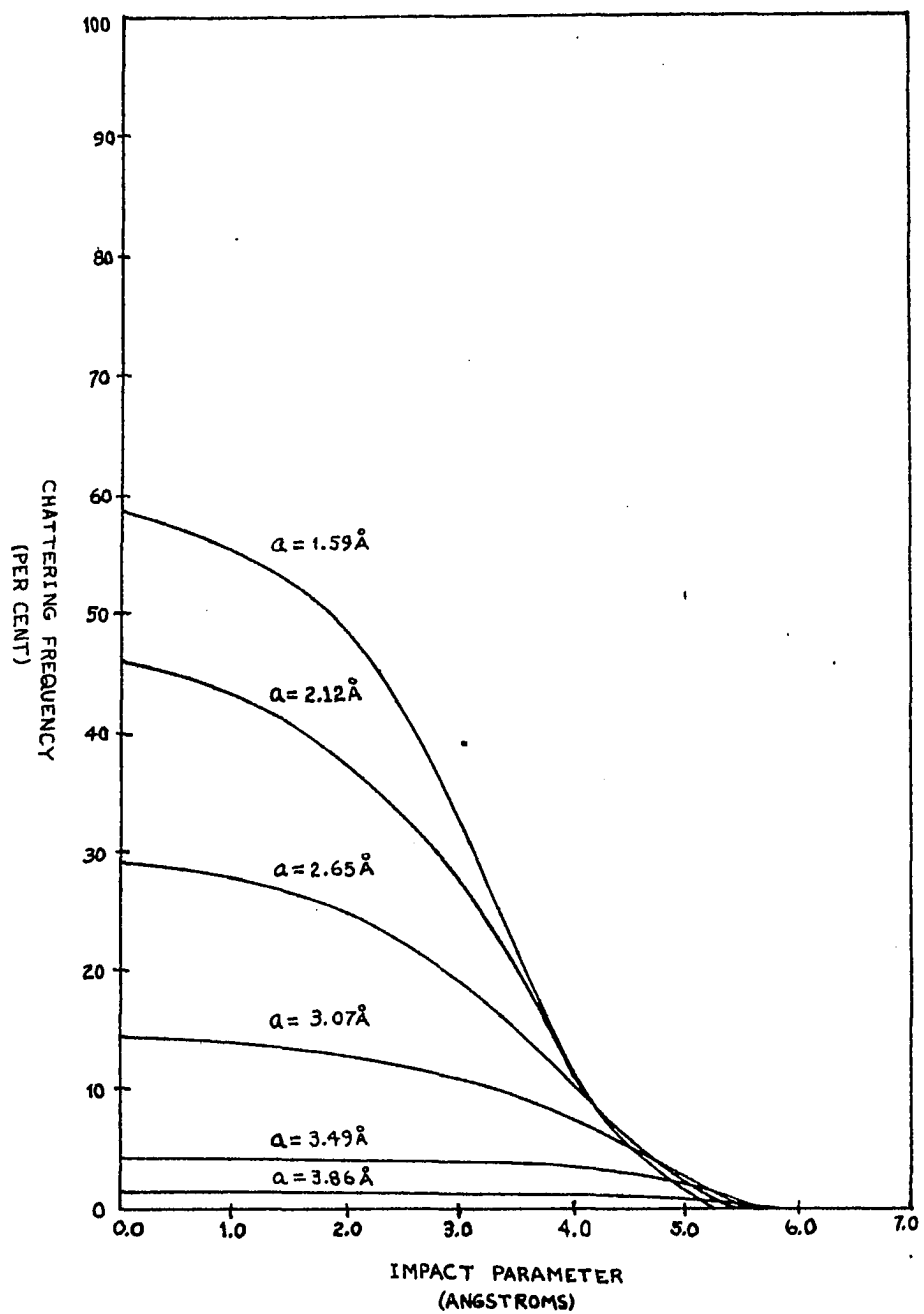
Fig. 4.2. Chattering Frequency for a Hard Sphere-Hard-Ellipsoid Interaction
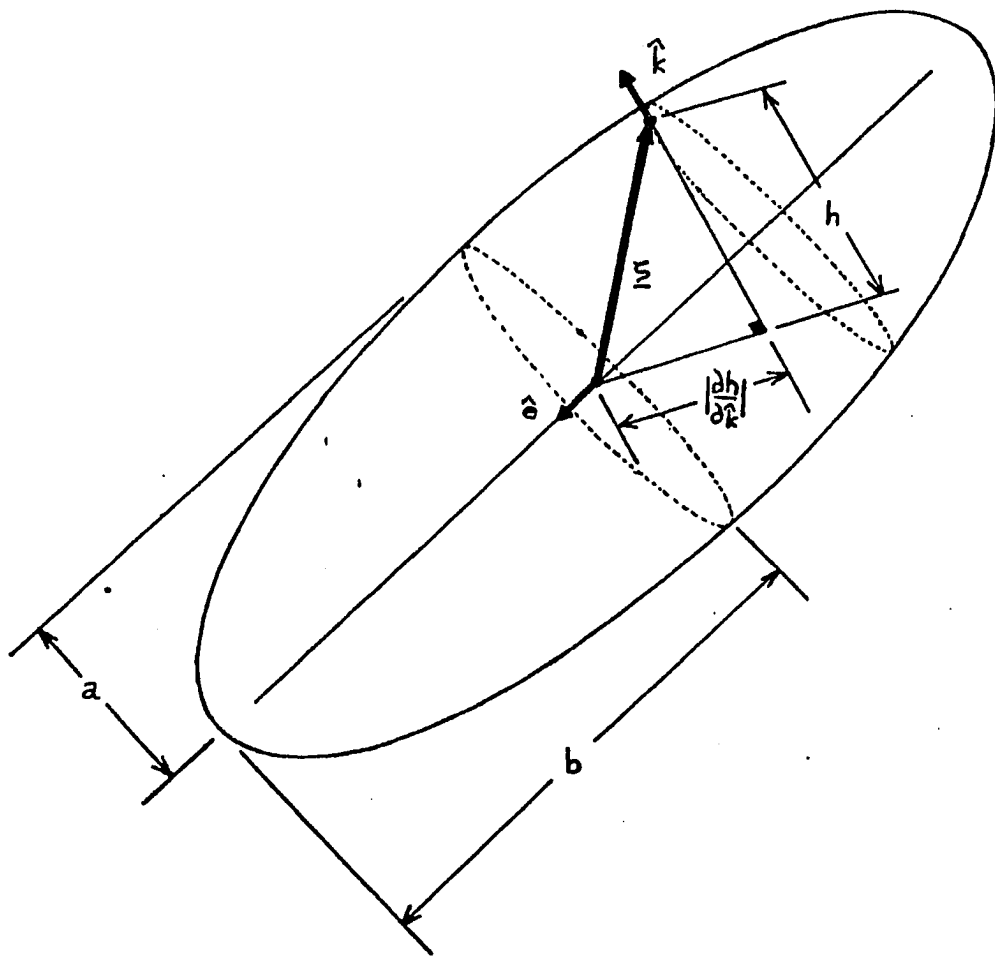
Fig. 4.3. Geometry of an Ellipsoid of Revolution

of hard ellipsoid-hard sphere effective collision cross sec-
tions, Monte Carlo estimates of a selected few of these cross
sections have been obtained. Again, $Ar-CO_2$ kinematics is
assumed and $r_0$ and b are held constant at 1.91 Å and 4.23 Å,
respectively. A summary of results based on 10,000
trajectories is given in Tables 4.1, 4.2, and 4.3, and Figs.
4.4, 4.5, 4.6, and 4.7. In each case Monte Carlo estimates
are compared with values obtained via Eqs. (4.3-26),
(4.3-27), and (4.3-28). In the plots, Monte Carlo estimates
(isolated points with appropriate error bars) and
"projection" operator results (solid curves) are given versus
eccentricity. Deviates which are significantly greater than
the expected random error become apparent at an approximate
value of e = 0.55. If one defines R = b/a, this value of e
corresponds to an R of about 1.2. Finally, as expected,
chattering has a greater effect on cross sections which have
no spherical contribution.

It has been found by Cooper, Hoffman, Matzen and
Verlin(33) that typical values of R appropriate to the calcu-
lation of transport coefficients for hard ellipsoidal models
of first row diatomics range from approximately 1.1 to 1.3.
Thus, the use of the effective collision cross sections for
hard ellipsoid-hard sphere potentials as a control variate is
marginal at best when applied to the estimation of realistic
$Ar-N_2$ cross sections and is unwarranted when applied to the

Table 4.1. Hard Sphere-Hard Ellipsoid[a] Effective Cross Sections: Comparison of Monte Carlo Estimates and Projection Operator Results

| Cross Section[b] | Monte Carlo Estimate[c] | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G\left(\begin{smallmatrix}1000\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 36.5 (1.8) | 32.9 | -9.6 |
| $G\left(\begin{smallmatrix}1100\\1100\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 31.9 (3.2) | 36.1 | 13.2 |
| $G\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 149.5 (5.1) | 229.6 | 53.6 |
| $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 71.8 (3.7) | 111.6 | 55.4 |
| $G\left(\begin{smallmatrix}1000\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 1.32 (14.3) | 0.318 | -75.9 |
| $G\left(\begin{smallmatrix}1010\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1010\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -2.79 (7.9) | -8.49 | 204.3 |
| $G\left(\begin{smallmatrix}1001\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1001\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -1.99 (5.6) | -1.68 | -15.6 |

[a] Sphere radius = 1.91 Å; ellipsoid semimajor axis = 4.23 Å; ellipsoid semiminor axis = 2.12 Å.

[b] All cross sections given in angstroms squared.

[c] Values in parentheses are percent relative standard deviation.

Table 4.1.   (continued)

| Cross Section | Monte Carlo Estimate | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 262.8 (3.2) | 261.2 | -0.61 |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | -29.3 (4.5) | -80.5 | 174.7 |
| $G(\underline{\gamma}\underline{\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma}\underline{\Omega})_{\alpha\beta}$ | 16.8 (11.3) | 16.0 | -4.8 |

Table 4.2.   Hard Sphere-Hard Ellipsoid[a] Effective Cross Sections:   Comparison of Monte Carlo Estimates and Projection Operator Results

| Cross Section[b] | Monte Carlo Estimate[c] | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G(^{1000}_{1000}|^{\beta}_{\beta})_{\alpha\beta}$ | 52.3 (1.6) | 50.2 | -1.0 |
| $G(^{1100}_{1100}|^{\beta}_{\beta})_{\alpha\beta}$ | 41.5 (3.5) | 41.5 | 0.01 |

a   Sphere radius = 1.91 Å; ellipsoid semimajor axis = 4.23 Å; ellipsoid semiminor axis = 3.06 Å.

b   All cross sections given in angstroms squared.

c   Values in parentheses are percent relative standard deviation.

Table 4.2. (continued)

| Cross Section | Monte Carlo Estimate | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 145.8(4.7) | 170.4 | 16.9 |
| $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 61.1(2.6) | 71.3 | 16.7 |
| $G\left(\begin{smallmatrix}1000\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ <br> $G\left(\begin{smallmatrix}1200\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 0.743(30.2) | 0.204 | -72.5 |
| $G\left(\begin{smallmatrix}1010\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ <br> $G\left(\begin{smallmatrix}1200\\1010\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -3.59(7.2) | -5.32 | 48.5 |
| $G\left(\begin{smallmatrix}1001\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ <br> $G\left(\begin{smallmatrix}1200\\1001\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -7.73(2.5) | -7.20 | -6.86 |
| $G\left([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)}\right)_{\alpha\beta}$ | 357.7(2.7) | 361.9 | 1.2 |
| $G\left(\gamma^2,\Omega^2\right)_{\alpha\beta}$ <br> $G\left(\Omega^2,\gamma^2\right)_{\alpha\beta}$ | -50.3(3.7) | -68.5 | 36.2 |
| $G\left(\underline{\gamma}\underline{\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)}\right)_{\alpha\beta}$ <br> $G\left(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma}\underline{\Omega}\right)_{\alpha\beta}$ | 23.2(16.4) | 21.6 | -6.9 |

Table 4.3.  Hard Sphere-Hard Ellipsoid[a] Effective Cross
            Sections:  Comparison of Monte Carlo Estimates
            and Projection Operator Results

| Cross Section[b] | Monte Carlo Estimate[c] | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G\left(\begin{matrix}1000\\1000\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | 69.4 (1.5) | 71.3 | 2.7 |
| $G\left(\begin{matrix}1100\\1100\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | 67.9 (3.2) | 70.0 | 3.1 |
| $G\left(\begin{matrix}1200\\1200\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | 109.2 (4.7) | 115.9 | 6.1 |
| $G\left(\begin{matrix}0200\\0200\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | 4.34 (3.4) | 4.47 | 3.0 |
| $G\left(\begin{matrix}1000\\1200\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ $G\left(\begin{matrix}1200\\1000\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | 0.586 (32.8) | 0.259 | -55.8 |
| $G\left(\begin{matrix}1010\\1200\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ $G\left(\begin{matrix}1200\\1010\end{matrix}\middle\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | -0.379 (29.7) | -0.271 | -28.5 |

[a]  Sphere radius = 1.91 Å; ellipsoid semimajor axis = 4.23 Å; ellipsoid semiminor axis = 4.02 Å.

[b]  All cross sections given in angstroms squared.

[c]  Values in parentheses are percent relative standard deviation.

Table 4.3.   (continued)

| Cross Section | Monte Carlo Estimate | Projection Operator Result | Percent Deviation |
|---|---|---|---|
| $G\begin{pmatrix} 1001 & \beta \\ 1200 & \beta \end{pmatrix}_{\alpha\beta}$ $G\begin{pmatrix} 1200 & \beta \\ 1001 & \beta \end{pmatrix}_{\alpha\beta}$ | $-1.69(21.6)$ | $-1.18$ | $-30.2$ |
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | $436.9(3.0)$ | $452.7$ | $3.6$ |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | $-4.96(4.0)$ | $-5.08$ | $2.4$ |
| $G(\underline{\gamma\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma\Omega})_{\alpha\beta}$ | $7.25(6.4)$ | $7.66$ | $5.7$ |

Fig. 4.4. Monte Carlo and Projection Operator Values of $|G(\underline{\gamma}\gamma^2;\underline{\Omega}\underline{\gamma}\cdot\underline{\Omega})$

Fig. 4.5. Monte Carlo and Projection Operator Values of $G(\Omega^2,\Omega^2)$
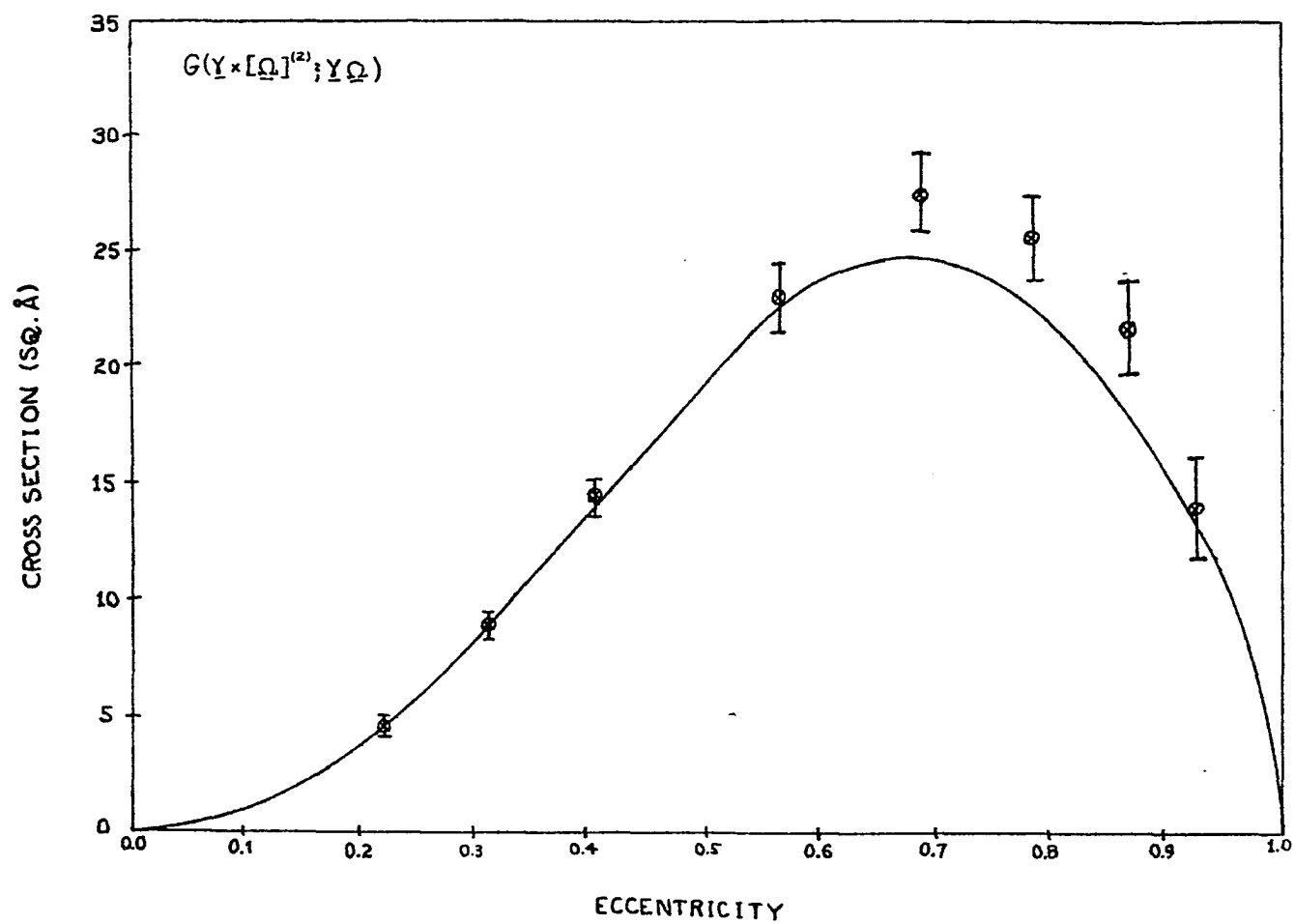
Fig. 4.6. Monte Carlo and Projection Operator Values of $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma}\underline{\Omega})$
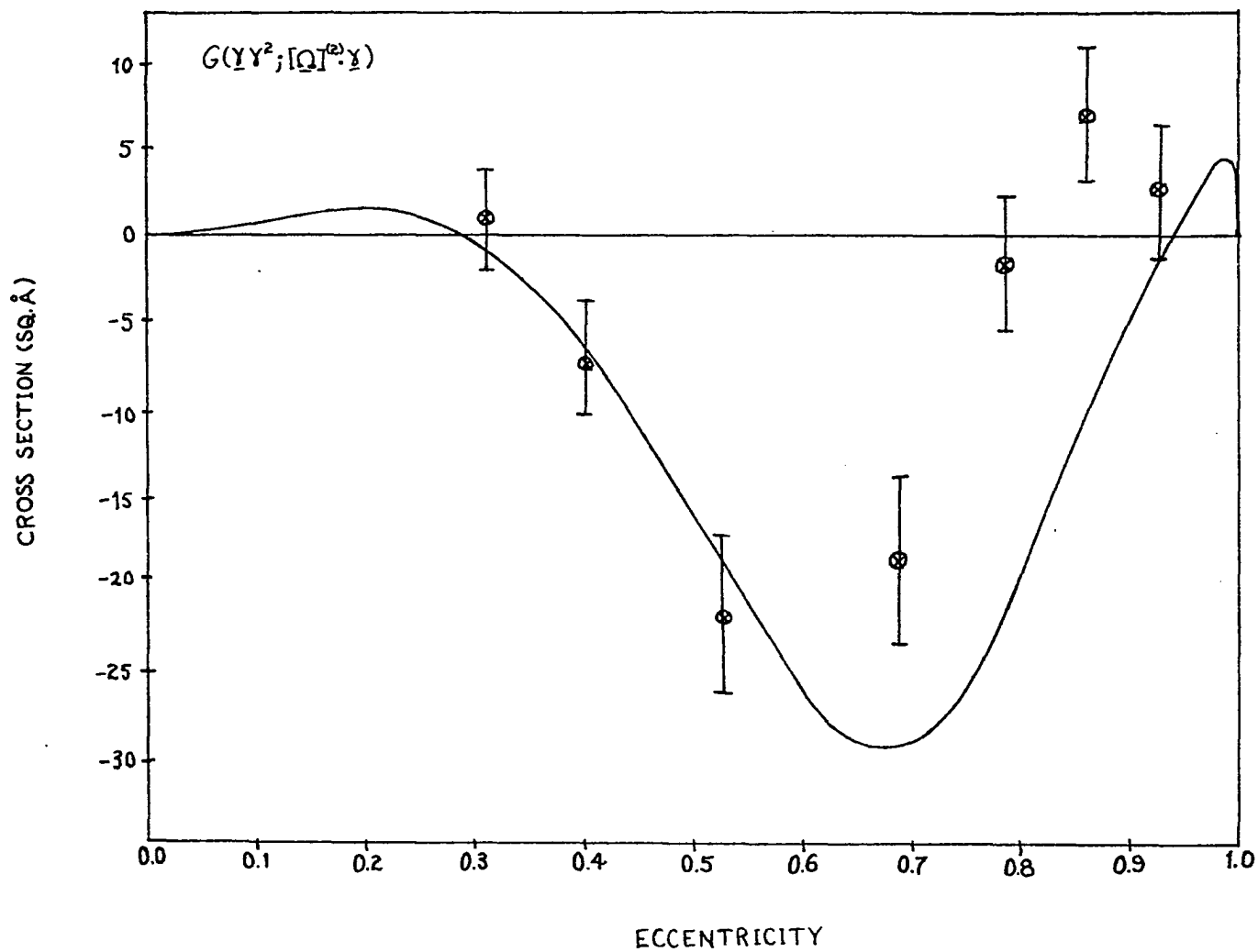
Fig. 4.7. Monte Carlo and Projection Operator Values of $G(\underline{\gamma}\gamma^2;[\underline{\Omega}]^{(2)}\cdot\underline{\gamma})$

estimation of realistic $Ar-CO_2$ and $He-CO_2$ cross sections since such a procedure would likely introduce systematic errors which are larger than the random errors inherent in Monte Carlo integration.

In contrast, the effective cross sections obtained from a Lennard-Jones 6-12 potential can be used as control variates since the Curtis-Clenshaw quadrature techniques of O'Hara and Smith(53) can be used to evaluate them accurately. Optimum values of the two Lennard-Jones force constants, $\epsilon$ and $\sigma$, appropriate to the control variate can be found by treating the expected error estimate as a function of the force constants. The optimum values occur when the expected error estimate is simulaneously minimized in both $\epsilon$ and $\sigma$. This procedure is illustrated by Fig. 4.8. It is generally found that the optimal values of the force constants are obtained when the difference between the primary Monte Carlo estimate and the control variate is at (or very near) a minimum. This does not come as a great surprise since Eq. (4.5-1) shows that $S_G^N(G')$ is comprised primarily of an exact result, $I_{G'}$, plus a small Monte Carlo correction.
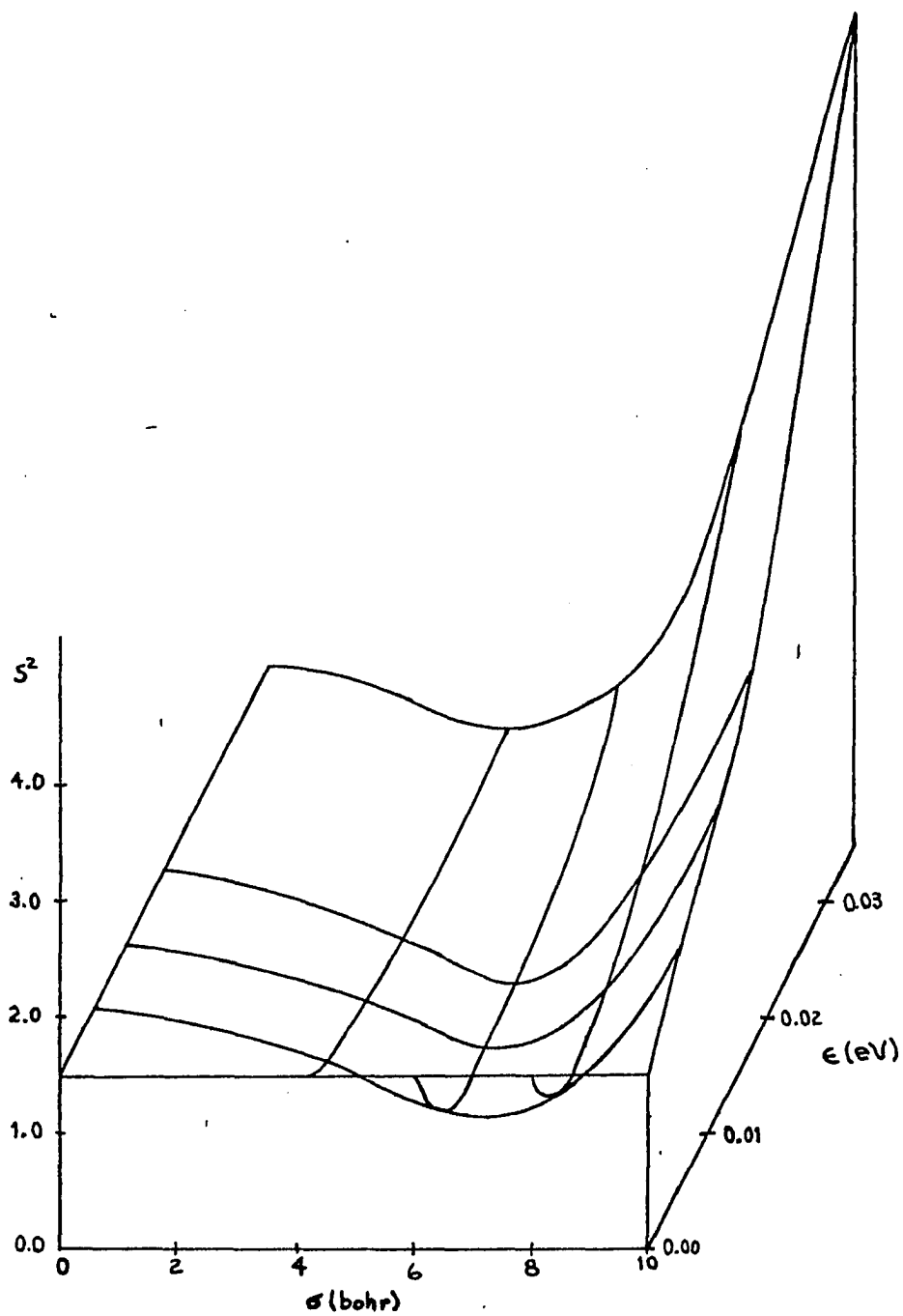
Fig. 4.8. Variance of the Monte Carlo-Control Variate Estimates of $\{\underline{\gamma};\underline{\gamma}\}$ as a Function of Lennard-Jones Force Constants

## 4.6. Realistic Anisotropic Potentials in Quantum Mechanics

The quantum mechanical expressions for the scalar collision integrals and phenomenological cross sections can be obtained using the expression for the Waldmann-Snider collision kernel which appears in Eq. (2.2-48). In this expression, the internal state quantum numbers are denoted collectively as $\sigma_1$ and $\sigma_2$. Within the Born-Oppenheimer and rigid rotor approximations, the only internal state quantum numbers for an atom-diatom system are $j$ and $m$ where $\sqrt{\hbar\, j(j+1)}$ is the rotational angular momentum and $\hbar m$ is the component of rotational angular momentum along a space-fixed quantization axis. Thus, the collision kernel can be written as follows,

$$\left\langle \begin{matrix} j_f m_f j_i m_i \\ p_1, p_2 \end{matrix} \middle| \Theta \middle| \begin{matrix} j'_f m'_f j'_i m'_i \\ p'_1, p'_2 \end{matrix} \right\rangle =$$

$$g h^2 \int_0^\infty dp_{12} \left\langle\!\left\langle \begin{matrix} j_f m_f \\ p_{12} \end{matrix}\!\left(\begin{matrix} j_i m_i \\ p_{12}\hat{p}_{12} \end{matrix}\right)^\dagger \middle| S\otimes S^\dagger - \hat{1}\otimes\hat{1} \middle| \begin{matrix} j'_f m'_f \\ p'_{12} \end{matrix}\!\left(\begin{matrix} j'_i m'_i \\ p'_{12} \end{matrix}\right)^\dagger \right\rangle\!\right\rangle \qquad (4.6-1)$$

$$\delta(p_1 + p_2 - p'_1 - p'_2)$$

Here, the "prime" denotes precollisional quantities and "unprime" denotes postcollisional quantities. The subscripts

"i" and "f" are conventionally defined as by Ben-Reuven and other workers(57,58) and denote initial and final states of spectroscopic transitions which occur during a collision. (Obviously, if $j_i m_i = j_f m_f$ and $j_i' m_i' = j_f' m_f'$ no transition takes place.) Such notation is appropriate to the description of dilute gas interacting with a radiation field (e.g. pressure broadening of spectral lines). Although radiation fields are not considered in the usual description of gas transport phenomena, the "i" and "f" provide a convenient means of keeping track of indices.

The scalar collision integrals are defined as follows,

$$\{\overline{\Psi}_\nu'\overset{\odot}{\Theta}\overline{\Psi}_\eta\}_{\nu,\omega} = \hbar^2 [2\pi\mu_{\nu\omega}kT]^{-3/2} \left(\frac{\theta_r}{T}\right)^2 \sum_{j_i m_i} \sum_{j_f m_f} \int d\underline{\gamma} \int d\underline{\gamma}'$$

$$e^{-\gamma'^2} \exp(-\frac{\theta_r}{T} j_i'(j_i'+1)) < j_i m_i |\overline{\Psi}_\nu^+| j_f m_f > \tag{4.6-2}$$

$$<< \begin{matrix} j_f m_f \\ \gamma \end{matrix} \begin{pmatrix} j_i m_i \\ \gamma \end{pmatrix}^\dagger | \overline{1}\otimes\overline{1}-\overline{S}\otimes\overline{S}^\dagger | \begin{matrix} j_f' m_f' \\ \gamma' \end{matrix} \begin{pmatrix} j_i' m_i' \\ \gamma' \end{pmatrix}^\dagger >> < j_f' m_f' |\overline{\Psi}_\eta'| j_i' m_i' >$$

Here, $\overline{\Psi}_\nu'$ and $\overline{\Psi}_\eta'$ are tensor functions of $\underline{\gamma}$ and $\underline{\hat{\Omega}}$.

It follows from Eq. (3.6-44) that $\{\overline{\Psi}_\nu'\overset{\odot}{\Theta}\overline{\Psi}_\eta\}_{\nu,\omega}$ can be written as follows,

$$\{\overline{\Psi}_\nu'\overset{\odot}{\Theta}\overline{\Psi}_\eta\}_{\nu,\omega} = \sum_{\substack{[M] \\ [M']}} \sum_{K} \sum_{\substack{K_\ell, K_j \\ K_\ell', K_j'}} \sum_{Q=-K}^{K} C^K[\begin{matrix} K_\ell K_j M \\ K_\ell' K_j' M' \end{matrix}]$$

$$\{ [\Phi_M^{K_\ell, K_j K}]_Q, [\Phi_{M'}^{K_\ell', K_j' K}]_Q\}_{\nu,\omega} \tag{4.6-3}$$

Here, $C^K[{}^{K_\ell K_j M}_{K'_\ell K'_j M'}]$ is a scalar coefficient of the type defined in Eq. (3.6-45) and $[\Phi_M^{K_\ell,K_j}]_Q^K$ is equivalent to $[\Phi^{(M)}]_Q^K$ defined by Eq. (3.6-42) for which $g \equiv K_\ell$, $q \equiv K_j$, and $M \equiv \{j,t\}$. The sum over $[M]$ is defined,

$$\sum_{[M]} \cdots = \sum_{uvwk\ell} \cdots \qquad (4.6-4)$$

which is equivalent to Eq. (3.6-46) with the sum over g (i.e. $K_\ell$) left out. Thus, in order to construct the effective collision cross sections appropriate to the evaluation of the transport coefficients, one must evaluate scalar collision integrals of the form,

$$\{[\Phi_M^{K_\ell,K_j}]_Q^K, [\Phi_{M'}^{K'_\ell,K'_j}]_Q^K\}_{v\omega} = h^2[2\pi\mu_{v\omega}kT]^{-3/2}\left(\frac{\theta_r}{T}\right)^2$$

$$\sum_{\substack{j_i m_i \\ j'_i m'_i}} \sum_{\substack{j_f m_f \\ j'_f m'_f}} \int d\underline{\gamma}_i \int d\underline{\gamma}_f \int d\underline{\gamma}'_i \int d\underline{\gamma}'_f \, e^{-\gamma_i'^2} \exp\left(-\frac{\theta_r}{T}j'_i(j'_i+1)\right)$$

$$<{}^{j_i m_i}_{\underline{\gamma}_i}\Big|[\Phi_M^{K_\ell,K_j}]_Q^{K\dagger}\Big|{}^{j_f m_f}_{\underline{\gamma}_f}><<{}^{j_f m_f}_{\underline{\gamma}_f}\left({}^{j_i m_i}_{\underline{\gamma}_i}\right)^\dagger\Big|\overline{\overline{1\otimes\hat{1}-\overline{S}\otimes\hat{S}}}^\dagger\Big|{}^{j'_f m'_f}_{\underline{\gamma}'_f}\left({}^{j'_i m'_i}_{\underline{\gamma}'_i}\right)^\dagger>>$$

$$<{}^{j'_f m'_f}_{\underline{\gamma}'_f}\Big|[\Phi_{M'}^{K'_\ell,K'_j}]_Q^K\Big|{}^{j'_i m'_i}_{\underline{\gamma}'_i}> \qquad (4.6-5)$$

Here, the matrix elements are given in terms of a dimensionless plane wave representation.

It is advantageous to convert the expression in terms of plane wave states appearing as Eq. (4.6-5) to one in terms of spherical waves. This can be accomplished by using the standard plane wave expansion,

$$e^{i\underline{k}\cdot\underline{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} i^{\ell} j_{\ell}(kr) Y_{\ell}^{\mu}(\hat{r}) Y_{\ell}^{\mu^{*}}(\hat{k}) \qquad (4.6-6)$$

Here, $j_{\ell}(x)$ is a spherical Bessel function of order, $\ell$. If one assumes a Dirac delta function normalization for continuously indexed state vectors, Eq. (4.6-6) can be written without as follows,

$$|\underline{k}\rangle = \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} i^{\ell} k^{-1} Y_{\ell}^{\mu^{*}}(\hat{k}) |k\ell\mu\rangle \qquad (4.6-7)$$

Here, a phase convention for spherical wave states which gives rise to symmetric S-matrix elements as defined by Arthurs and Dalgarno(59) has been adopted. For the sake of completeness, one notes that Eqs. (4.6-6) and (4.6-7) are related by the identities,

$$\langle \underline{r}|\underline{k}\rangle = 2\pi^{-3/2} e^{i\underline{k}\cdot\underline{r}} \qquad (4.6-8)$$

$$\langle \underline{r}|k\ell\mu\rangle = [\tfrac{2}{\pi}]^{\frac{1}{2}} k j_{\ell}(kr) Y_{\ell}^{\mu}(\hat{r}) \qquad (4.6-9)$$

Equation (4.6-7) yields the expression,

$$\left|\frac{jm}{\underline{\gamma}}\right\rangle = [\tfrac{2kT}{\gamma}]^{\frac{1}{2}} \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} i^{\ell} Y_{\ell}^{m^{*}}(\hat{\gamma}) \left|\frac{jm}{E\ell\mu}\right\rangle \qquad (4.6-10)$$

where one notes that the dimensionless relative linear momen-
tum, $\underline{\gamma}$ equals $\hbar k/[2\mu_{\alpha\beta}kT]^{\frac{1}{2}}$ and the relative translational
kinetic energy, E equals $kT\gamma^2$. If one substitutes Eq.
(4.6-10) into Eq. (4.6-5), one obtains an expression in terms
of an uncoupled translational energy-spherical wave represen-
tation as follows,

$$\{[\Phi_M^{K_\ell,K_j}\,K]_Q\,,\,[\Phi_M^{K'_\ell,K'_j}\,K]_Q\}_{\nu,\omega} =$$

$$h^2[2\pi\mu_{\nu\omega}kT]^{-\frac{1}{2}}\left(\frac{\theta_r}{T}\right)^2\sum_{\substack{j_i m_i\\j'_i m'_i}}\sum_{\substack{j_f m_f\\j'_f m'_f}}\sum_{\substack{\ell_i\mu_i\\\ell'_i\mu'_i}}\sum_{\substack{\ell_f\mu_f\\\ell'_f\mu'_f}}\int_0^\infty dE_i\int_0^\infty dE'_i\int_0^\infty dE_f\int_0^\infty dE'_f$$

$$\exp(-E'_i/kT)\exp\left(-\frac{\theta_r}{T}j'_i(j'+1)\right)\left<{}^{j_i m_i}_{E_i\ell_i\mu_i}\right|[\Phi_M^{K_\ell,K_j}\,K\dagger]_Q\left|{}^{j_f m_f}_{E_f\ell_f\mu_f}\right>$$

$$<<{}^{j_f m_f}_{E_f\ell_f\mu_f}\left({}^{j_i m_i}_{E_i\ell_i\mu_i}\right)^\dagger\left|\bar{1}\otimes\bar{1}-\bar{S}\otimes\bar{S}^\dagger\right|{}^{j'_f m'_f}_{E'_f\ell'_f\mu'_f}\left({}^{j'_i m'_i}_{E'_i\ell'_i\mu'_i}\right)^\dagger>>$$

$$\left<{}^{j'_f m'_f}_{E'_f\ell'_f\mu'_f}\right|[\Phi_{M'}^{K'_\ell,K'_j}\,K]_Q\left|{}^{j'_i m'_i}_{E'_i\ell'_i\mu'_i}\right> \qquad (4.6-11)$$

The irreducible tensor operators are explicitly diagonal in
the relative translational kinetic energy.

The matrix elements of the irreducible tensor operators
can be written in terms of standard spherical components
using Eq. (4.6-4). One obtains an expression in which con-

tributions from rotational and translational motion are neatly separated. Thus, the irreducible tensor matrix elements have the explicit form,

$$\left\langle {}_{E_f \ell_f \mu_f}^{j_f m_f} \Big| [\Phi_M^{K_\ell,K_j}]_Q^K \Big| {}_{E_i \ell_i \mu_i}^{j_i m_i} \right\rangle = \sum_{Q_\ell Q_j} (-1)^{K_\ell - K_j + Q} (2K+1)^{\frac{1}{2}}$$

$$(4.6-12)$$

$$\begin{pmatrix} K_\ell & K_j & K \\ Q_\ell & Q_j & -Q \end{pmatrix} \langle E_f \ell_f \mu_f | \gamma^j [\underline{Y}]_{Q_\ell}^{K_\ell} | E_i \ell_i \mu_i \rangle \langle j_f m_f | S_q^{(t)} (\hat{\Omega}^2) [\underline{\Omega}]_{Q_j}^{K_j} | j_i m_i \rangle$$

As a consequence of the Wigner-Eckart theorem(60), the tensor operator matrix elements appearing on the right hand side of Eq. (4.6-12) have a simple geometrical dependence on magnetic quantum numbers, $m_i$, $m_f$, $\mu_i$ and $\mu_f$. If the matrix element of $\gamma^j [\underline{Y}]_{Q_\ell}^{K_\ell}$ is expressed in a relative momentum representation, it can be evaluated directly. One obtains the result,

$$\langle E_f \ell_f \mu_f | \gamma^j [\underline{Y}]_{Q_\ell}^{K_\ell} | E_i \ell_i \mu_i \rangle = (E_f/kT)^{\frac{1}{2}K_\ell + \frac{1}{2}j}$$

$$N(K_\ell) i^{\ell_f - \ell_i} (-1)^{\mu_f} \begin{pmatrix} \ell_i & \ell_f & K_\ell \\ \mu_i & -\mu_f & Q_\ell \end{pmatrix} \begin{pmatrix} \ell_i & \ell_f & K_\ell \\ 0 & 0 & 0 \end{pmatrix}$$

$$(4.6-13)$$

$$\frac{1}{2}\pi^{-\frac{1}{2}} [(2\ell_i+1)(2\ell_f+1)(2K_\ell+1)]^{\frac{1}{2}} \delta(E_i - E_f)$$

The scalar quantity, $N(K_\ell)$, comes from the definition of standard spherical tensor components in terms of spherical harmonics. (This definition appears explicitly as Eq. (8-9) in Appendix A.) It has the form,

$$N(K_\ell) = 2^{3/2} \left[ \frac{\pi K_\ell! (K_\ell+1)! 2^{K_\ell}}{(2K_\ell+2)!} \right]^{\frac{1}{2}} \qquad (4.6-14)$$

It follows directly from the Wigner-Eckart theorem that a matrix element of $S_q^{(t)} (\bar{\Omega}^2) [\hat{\Omega}]_{Q_j}^{K_j}$ can be written in terms of a standard reduced matrix element which is independent of magnetic quantum numbers. If "reduced" or "double-bar" matrix elements are defined as by Edmonds(60), one obtains the expression,

$$\langle j_f m_f | S_q^{(t)} (\bar{\Omega}^2) [\underline{\hat{\Omega}}]_{Q_j}^{K_j} | j_i m_i \rangle = \langle j_f || S_q^{(t)} (\bar{\Omega}^2) [\hat{\Omega}]^{(K_j)} || j_i \rangle$$

$$(-1)^{j_f - m_f} \begin{pmatrix} j_i & j_f & K_j \\ m_i & -m_f & Q_j \end{pmatrix} \qquad (4.6-15)$$

The reduced tensor operator matrix elements, $\langle \cdots || S_q^{(t)} (\bar{\Omega}^2) [\underline{\hat{\Omega}}]^{(K_j)} || \cdots \rangle$ are scalar quantities.

The scalar collision integrals can be formulated in terms of the rotationally invariant Arthurs and Dalgarmo S-matrix elements if the tetradic matrix element of $\hat{I} \otimes \hat{I} - \hat{S} \otimes \hat{S}^\dagger$ is written in an appropriate totally coupled basis. If one uses the coupling scheme given by Ben-Reuven(57), one obtains expressions for the following rotational and translational basis vectors,

$$|j_f j_i^\dagger ; K_j Q_j \rangle\!\rangle = \sum_{m_i m_f} (-1)^{j_i + K_j - m_f} (2K_j+1)^{\frac{1}{2}} \begin{pmatrix} j_i & j_f & K_j \\ -m_i & m_f & -Q_j \end{pmatrix}$$

$$|j_f m_f\rangle\langle j_i m_i| \qquad\qquad (4.6\text{-}16)$$

$$|E_f \ell_f (E_i \ell_i)^\dagger ; K_\ell Q_\ell \rangle\!\rangle = \sum_{\mu_i \mu_f} (-1)^{\ell_i + K_\ell - \mu_f} (2K_i+1)^{\frac{1}{2}} \qquad (4.6\text{-}17)$$

$$\begin{pmatrix} \ell_i & \ell_f & K_\ell \\ -\mu_i & \mu_f & -Q_\ell \end{pmatrix} |E_f \ell_f \mu_f\rangle\langle E_i \ell_i \mu_i|$$

One notes here that these couplings can be summarized vectorially as $\underline{j}_f - \underline{j}_i = \underline{K}_\ell$ and $\underline{\ell}_f - \underline{\ell}_i = \underline{K}_\ell$. The basis vectors defined by Eqs. (4.6-16) and (4.6-17) can be further combined in order to form a totally coupled basis as follows,

$$|E_f E_i^\dagger , (j_f j_i^\dagger) K_j , (\ell_f \ell_i^\dagger) K_\ell ; KQ \rangle\!\rangle = \sum_{Q_j Q_\ell} (-1)^{K_j - K_\ell + Q} \qquad (4.6\text{-}18)$$

$$(2K+1)^{\frac{1}{2}} \begin{pmatrix} K_j & K_\ell & K \\ Q_j & Q_\ell & -Q \end{pmatrix} |j_f j_i^\dagger ; K_j Q_j \rangle\!\rangle |E_f \ell_f (E_i \ell_i)^\dagger ; K_\ell Q_\ell \rangle\!\rangle$$

The coupling can be summarized vectorially as $\underline{K}_\ell + \underline{K}_j = \underline{K}$.

This "K-K" basis set defined by Eq. (4.6-18), does not provide a convenient basis in which to construct rotationally invariant quantities. It is, however, related by a unitary transformation to a totally coupled basis set which does provide a suitable basis. This "J-J" basis set can be con-

structed according to the following vector coupling scheme,

$\underline{j}_f + \underline{\ell}_f = \underline{J}_f$, $\underline{j}_i + \underline{\ell}_i = \underline{J}_i$, $\underline{J}_f - \underline{J}_i = \underline{K}$. The unitary trans-

formation relating the K-K basis set to the J-J basis set can

be written in terms of the Wigner 9-j symbols as follows,

$$|E_f E_i^\dagger, (j_f \ell_f) J_f, [(j_i \ell_i) J_i J^\dagger]; KQ\rangle\rangle = \sum_{K_j K_\ell} [(2J_f+1)(2J_i+1)$$

$$(4.6\text{-}19)$$

$$(2K_j+1)(2K_\ell+1)]^{\frac{1}{2}} \begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix} (E_f E_i^\dagger, (j_f j_i^\dagger) K_j, (\ell_f \ell_i^\dagger) K_\ell; KQ\rangle\rangle$$

In terms of the J-J basis, the tetradic matrix element of $\hat{1}\otimes\overline{1}-\overline{S}\otimes\hat{S}^\dagger$ has the particularly simple form,

$$\langle\langle E_f E_i^\dagger, (j_f \ell_f) J_f, [(j_i \ell_i) J_i]^\dagger; KQ | \overline{1}\otimes\hat{1}$$

$$- \overline{S}\otimes\hat{S}^\dagger | E_f' E_i', (j_f' \ell_f') J_f', [(j_i' \ell_i') J_i']^\dagger, K'Q'\rangle\rangle =$$

$$(4.6\text{-}20)$$

$$\delta_{KK'}\delta_{QQ'}\delta_{J_i' J_i}\delta_{J_f' J_f}[\delta_{j_i' j_i}\delta_{j_f' j_f}\delta_{\ell_i' \ell_i}\delta_{\ell_f' \ell_f} -$$

$$S_{j_f \ell_f; j_f' \ell_f'}^{J_f} S_{j_i \ell_i; j_i' \ell_i'}^{J_i *}]\delta(E_i - E_i')$$

Here, $E_i$ and $E_i'$ represent the total energies (translational

plus rotational) of the system in states "i" and "i'", and

$S_{j_f \ell_f; j_f' \ell_f'}^{J_f}$ and $S_{j_i \ell_i; j_i' \ell_i'}^{J_i}$ are S-matrix elements as defined by

Arthurs and Dalgarno. The superoperator, $\hat{1}\otimes\overline{1}-\overline{S}\otimes\hat{S}^\dagger$ is diago-

nal in K, Q, $J_i$, and $J_f$ due to the overall rotational

invariance of physical systems. The energy diagonality comes

from the "hatted" operators and has been thoroughly discussed previously.

Equation (4.6-11) can be written in terms of a generalized phenomenological cross section by using Eqs. (4.6-12), (4.6-13), (4.6-14), and (4.6-15) to simplify the trial tensor function-operators in terms of scalar reduced tensor operator matrix elements and Wigner 3-j symbols. This is followed by use of Eqs. (4.6-16), (4.6-17), (4.6-18) and (4.6-19) in order to transform the uncoupled basis appearing in Eq. (4.6-11) to a totally coupled one. Use of Eq. (4.6-20) allows the evaluation of the tetradic matrix element as discussed in the last paragraph and results in the final expression,

$$
\{[\Phi_M^{K_\ell, K_j} \, ]_Q^K, [\Phi_{M'}^{K'_\ell, K'_j} \, ]_Q^K\}_{\nu,\omega} = [\frac{8kT}{\pi\mu_{n\omega}}]^{\frac{1}{2}} K_\ell! K'_\ell! \, [\frac{2^{K_\ell + K'_\ell + 2}}{(2K_\ell)!(2K'_\ell)!}]^{\frac{1}{2}}
$$

$$
\sum_{j_i j'_i} \sum_{j_f j'_f} \exp(-\frac{\theta_r}{T} j'_i(j'_i+1)) \langle j_i || S_q^{(t)} (\tilde{\Omega}^2) [\underline{\tilde{\Omega}}]^{(K_j)} || j_f \rangle \qquad (4.6-21)
$$

$$
\langle j'_f || S_{q'}^{(t')} (\tilde{\Omega}^2) || j'_i \rangle \int_0^\infty d\gamma' e^{-\gamma'^2} \gamma'^{s'+3} \gamma^s \, \sigma_{j_i j_f; j'_i j'_f}^{K_\ell K_j; K'_\ell K'_j} (K, E'_i E_i)
$$

Here, $\gamma'$ is defined as $\frac{E'_i}{kT}$, and thus $\gamma = \frac{E'_i}{kT} - \frac{\theta_r}{T} j_i(j_i+1)$ where $E'$ is defined as $E'_i + \frac{\theta_r}{T} j'_i(j'_i+1)$. The integers s and s' are defined as $j+K_\ell$ and $j'+K'_\ell$ respectively. (j and j' are indices appropriate to the basis and should not be confused with angular momentum quantum numbers.) The generalized

phenomenological cross section which is independent of Q, is defined as follows,

$$\sigma_{J_i J_f; J_i' J_f'}^{K_\ell K_j; K_\ell' K_j'}(K, E_f', E_i') = \frac{\pi}{\kappa_i'^2} \sum_{\substack{\ell_i \ell_f \ell_i' \ell_f' \\ J_i J_f}} (-1)^{\ell_f + \ell_f' \; \ell_f' - \ell_i' - \ell_f + \ell_i}$$

$$(2J_i + 1)(2J_f + 1)[(2\ell_i + 1)(2\ell_f + 1)(2\ell_i' + 1)(2\ell_f' + 1)]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell_i & \ell_f & K_\ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_i' & \ell_f' & K_\ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_f' & \ell_f' & J_f' \\ j_i' & \ell_i' & J_i' \\ K_j' & K_\ell' & K \end{Bmatrix} \begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix} \qquad (4.6\text{-}22)$$

$$[\delta_{j_i' j_f} \delta_{j_i' j_i} \delta_{\ell_f' \ell_f} \delta_{\ell_i' \ell_i} - S_{j_f \ell_f; j_f' \ell_f'}^{J_f}(E_f') S_{j_i \ell_i; j_i' \ell_i'}^{J_i *}(E_i')]$$

The partial wavenumber, $\kappa_i'$ is defined as $[2\mu_{\alpha\beta}E_i'/\hbar]^{\frac{1}{2}}$. The Arthurs and Dalgarno S-matrix elements are evaluated at total energies of $E_f'$ and $E_f'$.

For the sake of completeness, it should be noted that the generalized phenomenological cross section as defined by Eq. (4.6-22) has a wider application than the evaluation of transport coefficients as is proposed in this work, in particular, to the description of collisionally induced radiative processes. (Pressure broadening of spectroscopic line shapes is a good example(57).) As mentioned previously, the effects of a radiation field are not considered in the usual description of gas transport phenomena. In this case the "i" and "f" subscripts are ignored.

The generalized phenomenological cross section exhibits the following symmetry relations,

$$\sigma_{j_i'j_f'j_ij_f}^{K_\ell'K_j';K_\ell K_j}(K,E_f,\bar{E}_i) =$$

$$\frac{K_i'}{K_i}^2 (-1)^{K_\ell+K_\ell'} \sigma_{j_ij_f;j_i'j_f'}^{K_\ell K_j;K_\ell'K_j'}(K,E_f',E_i') \qquad (4.6-23)$$

$$\sigma_{j_ij_f;j_i'j_f'}^{K_\ell K_j;K_\ell'K_j'}(K,E_f',E_i') =$$

$$\frac{K_i'}{K_f'}^2 (-1)^{K_j+K_\ell+K_j'+K_\ell'} \sigma_{j_ij_f;j_i'j_f'}^{K_\ell K_j;K_\ell'K_j'*}(K,E_f',E_i') \qquad (4.6-24)$$

These relations are obtained by using parity, the symmetric nature of the Arthurs and Dalgarno S-matrix, and certain properties of the Wigner 3-j symbols. Further inspection shows that if $j_i = j_f$ and $j_i' = j_f'$ as for the construction of transport coefficients, then $K_\ell+K_\ell'$ must be even or the cross section vanishes. Furthermore, for this case, if $K_j+K_j'$ is odd, the cross section is imaginary and if $K_j+K_j'$ is even, it is real. If $j_i \neq j_f$ and $j_i' \neq j_f'$, then the cross section can be complex.

The scalar collision integral defined by Eq. (4.6-21) can be written in terms of a "Q" cross section which is analogous to the classical expression given by Eq. (4.4-11). One obtains the result,

$$\{[\Phi_M^{K_\ell,K_j}]_{Q'}^K, \ [\Phi_{M'}^{K'_\ell,K'_j}]_Q^K\}_{\nu,\omega} = [\frac{kT}{2\pi\mu_{\nu\omega}}]^{\frac{1}{2}} \int_0^\infty d\gamma' e^{-\gamma'^2} \gamma'^{s'+s+3}$$

$$\frac{2}{T} \frac{\theta_r}{} \sum_{\substack{j_i j_i' \\ j_f j_f'}} exp(-\frac{\theta_r}{T} j_i'(j_i'+1)) \frac{(2j_i'+1)}{2K+1} Q^{(K)} \begin{array}{c} K_\ell \ K_j; \ M \\ K_\ell' \ K_j'; \ M' \end{array} \quad (4.6\text{-}25)$$

If one compares this expression to Eq. (4.6-21) one can define the Q cross section in terms of the generalized phenomenological cross section as follows,

$$Q^{(K)} \begin{pmatrix} K_\ell K_j; M \\ K_\ell' K_j'; M' \end{pmatrix} = 16K_\ell! K_\ell'! [\frac{2^{K_\ell+K_\ell'}}{(2K_\ell)!(2K_\ell')!}]^{\frac{1}{2}} \frac{(2K+1)}{(2j_i+1)}$$

$$<j_i||S_q^{(t)}(\hat{\Omega}^2)[\underline{\hat{\Omega}}]^{(K_j)}||j_f><j_f'||S_{q'}^{(t')}(\hat{\Omega}^2)[\underline{\hat{\Omega}}]^{(K_j')}||j_i'> \quad (4.6\text{-}26)$$

$$(\frac{\gamma}{\gamma'})^s \sigma_{j_i j_f; j_i' j_f'}^{K_\ell K_j; K_\ell' K_j'}(K, E_i, E_i)$$

This expression is a direct generalization of the cross section, $Q^{(\ell)}$.

It is possible to obtain the spherical limit of the generalized phenomenological cross section if one notes that the S-matrix elements can be written in terms of a phase shift as follows,

$$S_{j_f\ell_f; j_f'\ell_f'}^{J_f}(E_f) = \delta_{j_f'j_f}\delta_{\ell_f'\ell_f} exp[-2i\eta_{\ell_f}] \quad (4.6\text{-}27)$$

Substitution of this expression into Eq. (4.6-22) yields the

result,

$$\sigma_{j_i j_f; j_i' j_f'}^{K_\ell K_j; K_\ell' K_j'}(K, E_f', E_i') = \delta_{j_i' j_i} \delta_{j_f' j_f} \delta_{K_j' K_j} \delta_{K_\ell' K_\ell} \frac{\pi}{\kappa_i^2}$$

$$\sum_{\ell_i \ell_f} \frac{(2\ell_i + 1)(2\ell_f + 1)}{(2K_j + 1)(2K_\ell + 1)} \begin{pmatrix} \ell_i & \ell_f & K_\ell \\ 0 & 0 & 0 \end{pmatrix}^2 [1 - \exp[2i(\eta_{\ell_i} - \eta_{\ell_f})]]$$

(4.6-28)

For the cross sections appropriate to transport phenomena, the "i" and "f" subscripts can be ignored which results in the expression,

$$\sigma_{j'j';jj}^{K_\ell K_j; K_\ell' K_j'}(K, E_f', E_i') = \delta_{j'j} \delta_{K_j' K_j} \delta_{K_\ell' K_\ell} \frac{\pi}{\kappa_i^2}$$

$$\sum_{\ell_i} \sum_{\ell_f > \ell_i} \frac{(2\ell_i + 1)(2\ell_f + 1)}{(2K_j + 1)(2K_\ell + 1)} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix}^2 [\sin(\eta_{\ell_i} - \eta_{\ell_f})]^2$$

(4.6-29)

Clearly, the cross section is exclusively real valued in this case.

## 4.7. Approximate Quantum Mechanical Generalized Phenomenological Cross Sections

Recent work has resulted in some very useful quantal approximations for use in treating rotational excitation in atom-molecule collisions(31,32). Of these, the coupled states (CS) and infinite order sudden (IOS) seem to hold the

most promise for application to transport phenomena. This is because IOS and CS cross sections can be computed reasonably fast (as compared to close coupling (CC) cross sections) but yet compare well with accurate CC or classical trajectory (CT) cross sections.

Briefly, all sudden approximations arise by the application of a suitable angular momentum decoupling assumption to the set of coupled, exact quantum dynamical equations describing atom-molecule collision dynamics. Such decoupling represents a great simplification because it reduces the large number of coupled equations which arise for even modestly energetic collisions.

One obtains the CS approximation by replacing the orbital angular momentum operator appearing in the centrifugal potential of the atom-molecule Schrodinger equation by an average orbital angular momentum eigenvalue. The validity of this approximation is related to the rate of change of the classical turning point with respect to orbital angular momentum. This can be seen if one recalls that the underlying assumption of the CS approximation is that the relative kinetic energy is sufficiently large so that the precise value of the centrifugal potential is unimportant. (i.e., just the case for which the rate of change of the classical turning point with respect to angular momentum tends to become small.) Indeed, it is found that the CS approximation

is quite good for steep, repulsive single turning point regions of an interaction potential, but should be considered suspect in the three turning point region for potentials with wells.

The IOS approximation is a further approximation of the CS approximation. It is valid in tne case that both the centrifugal potential and the rotational kinetic energy are unimportant when compared to the relative kinetic energy. Further discussion of the sudden approximations and other approximation techniques is beyond the scope of this work. For a more complete discussion of approximate quantum mechanical scattering techniques the reader is referred to the work of Kouri(61). The results of this work will be used to simplify the generalized phenomenological cross section appearing in the last section.

The generalized phenomenological cross section given in Eq. (4.6-22) can be readily converted to its CS form by standard techniques. The first step in this conversion requires substituting the CS expression for the Arthurs-Dalgarno S-matrix into Eq. (4.7-1),

$$S^{J_f}_{j_f \ell_f; j_f' \ell_f'} = i^{2\bar{\ell}_f - \ell_f - \ell_f'} \sum_{\lambda_f} [(2\ell_f+1)(2\ell_f'+1)]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell_f' & j_f' & J_f \\ 0 & \lambda_f & -\lambda_f \end{pmatrix} \begin{pmatrix} \ell_f & j_f & J_f \\ 0 & \lambda_f & -\lambda_f \end{pmatrix} S_{\bar{\ell}_f \lambda_f}(j_f | j_f') \qquad (4.7-1)$$

Here, $\mathcal{L}_f$ can be chosen to be any function of $\ell_f$ and $\ell'_f$. (However, to preserve time reversal symmetry $\mathcal{L}_f$ should be symmetric in $\ell_f$ and $\ell'_f$.) The phase convention used here has been shown to be correct by Khare(62). This convention gives the proper behavior for degeneracy-averaged differential cross sections. If one expresses the Wigner 9-j symbols in Eq. (4.6-22) in terms of Wigner 6-j symbols using the following relation,

$$
\begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix} =
$$

$$
\sum_S (-1)^{2S}(2S+1) \begin{Bmatrix} j_f & j_i & K_j \\ K_\ell & K & S \end{Bmatrix} \begin{Bmatrix} \ell_f & \ell_i & K_j \\ j_i & S & J_i \end{Bmatrix} \begin{Bmatrix} J_f & J_i & K \\ S & j_f & \ell_f \end{Bmatrix}
$$

(4.7-2)

and recombines appropriate pairs of 3-j and 6-j symbols according to the relation,

$$
\begin{pmatrix} \ell_f & j_f & J_f \\ 0 & \lambda_f & -\lambda_f \end{pmatrix} \begin{Bmatrix} J_f & J_i & K \\ S & j_f & \ell_f \end{Bmatrix} = \sum_{\mu_i \mu} (-1)^{K+J_i+S+\mu} \begin{pmatrix} \ell_f & J_i & S \\ 0 & \mu_i & -\mu_i \end{pmatrix}
$$

$$
\begin{pmatrix} K & J_f & S \\ -\mu & \lambda_f & \mu_i \end{pmatrix} \begin{pmatrix} K & J_i & J_f \\ \mu & -\mu_i & -\lambda_f \end{pmatrix}
$$

(4.7-3)

one is able to sum over $J_f$. The Secrest labeling scheme, (i.e., the so-called "L-average" labeling $\mathcal{L} = \frac{1}{2}(\ell_i+\ell'_i) = \ell_{av}$)

results in the following expression for the generalized
phenomenological cross section evaluated within the CS ap-
proximation.

$$\sigma^{K_\ell K_j ; K_\ell' K_j'}_{j_i j_f ; j_i' j_f'} (K, E_f', E_i') = \frac{\pi}{\kappa_i'^2} \sum_{SS'} (-1)^{K_\ell' + S + S'} (2S+1)(2S'+1)$$

$$\begin{Bmatrix} j_f & j_i & K_j \\ K_\ell & K & S \end{Bmatrix} \begin{Bmatrix} j_f' & j_i' & K_j' \\ K_\ell' & K & S' \end{Bmatrix} \sum_{\substack{\ell_i \ell_i' \ell_f \ell_f' \\ J_i}} (-1)^{\ell_f' + \ell_i + \overline{\ell}_i - \overline{\ell}_f}$$

$$(2J_i+1)(2\ell_i+1)(2\ell_f+1)(2\ell_i'+1)(2\ell_f'+1)$$

$$\begin{pmatrix} \ell_f & \ell_i & K_\ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f' & \ell_i' & K_\ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_f & \ell_i & K_\ell \\ j_i & S & J_i \end{Bmatrix} \begin{Bmatrix} \ell_f' & \ell_i' & K_\ell' \\ j_i' & S' & J_i \end{Bmatrix}$$

$$\sum_{\lambda_i \lambda_f \mu_i \mu_f} \begin{pmatrix} \ell_i' & j_i' & J_i \\ 0 & \lambda_i & -\lambda_i \end{pmatrix} \begin{pmatrix} \ell_i & j_i & J_i \\ 0 & \lambda_i & -\lambda_i \end{pmatrix} \begin{pmatrix} \ell_f & J_i & S' \\ 0 & \mu_i & -\mu_i \end{pmatrix}$$

$$\begin{pmatrix} \ell_f' & J_i & S' \\ 0 & \mu_i & -\mu_i \end{pmatrix} \begin{pmatrix} K & j_f & S \\ -\mu_i -\lambda_f & \lambda_f & \mu_i \end{pmatrix} \begin{pmatrix} K & j_f' & S' \\ -\mu_i -\lambda_f & \lambda_f & \mu_i \end{pmatrix}$$

$$[\delta_{j_f' j_f} \delta_{j_i' j_i} - S_{\overline{\ell}_f \lambda_f}(j_f | j_f') S^*_{\overline{\ell}_i \lambda_i}(j_i | j_i')] \qquad (4.7-4)$$

From a computational viewpoint, this expression does not
appear to hold any great advantage over calculation of S-
matrix elements using Eq. (4.7-1) followed by direct substi-
tution into Eq. (4.6-22).

If instead of choosing L-average labeling, one chooses $\mathcal{L}_f = \ell_i$ and $\mathcal{L}'_f = \ell'_i$ (this is termed the "L-initial" labeling scheme), considerable simplification results. By appropriately applying expression similar to Eq. (4.7-3) and (4.7-4), the summations over $\ell_i$, $\ell_f$, $J_i$, S and S' can be performed and the much simpler form of the generalized phenomenological cross section,

$$\sigma_{j_i j_f; j'_i j'_f}^{K_\ell K_j; K'_\ell K'_j}(K, E'_f, E'_i) = \frac{\pi}{\kappa_i'^2} \sum_{\substack{\ell'_i \ell'_f \\ \lambda_i \lambda_f}} (-1)^{j_i + j'_i + K_j + K'_j + K_\ell}$$

$$(2\ell'_i + 1)(2\ell'_f + 1) \begin{pmatrix} \ell'_f & \ell'_f & K'_\ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} j'_i & j'_f & K' \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix}$$

$$\begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K'_\ell & K'_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix}$$

$$[\delta_{j'_i j_i} \delta_{j'_f j_f} - S_{\ell'_f \lambda_f}(j_f | j'_f) S^*_{\ell'_i \lambda_i}(j_i | j'_i)]$$

(4.7-5)

is obtained. It should be noted that had $\mathcal{L}_i = \ell_i$ and $\mathcal{L}_f = \ell_f$ (i.e., the "L-final" labeling scheme) been chosen, an expression analogous to Eq. (4.7-5) with $\ell'_i$ and $\ell'_f$ replaced by $\ell_i$ and $\ell_f$ would result. These two expressions are the same only if $K_\ell$ and $K'_\ell$ are equal.

The CS expression given in Eq. (4.7-4) for "L-average" labeling can be reduced easily to the corresponding IOS expression by noting that the IOS approximation to $S_{\ell_f \lambda_f}(j_f | j'_f)$

is given by the following expression,

$$S_{\bar{\ell}_f \lambda_f}(j_f | j_f') = \sum_{L_f} (-1)^{\lambda_f} [(2_{j_f}+1)(2_{j_f}'+1)]^{\frac{1}{2}} \begin{pmatrix} j_f & j_f' & L_f \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} j_f & j_f' & L_f \\ \lambda_f & -\lambda_f & 0 \end{pmatrix} S_{L_f}^{\bar{\ell}_f}$$

(4.7-6)

Here, $S_{L_f}^{\bar{\ell}_f}$ is the $L_f$th Legendre polynomial expansion coefficient of the S-matix for the fixed-angle uncoupled radial equation having orbital parameter, $\bar{\ell}_f$. If one substitutes Eq. (4.7-6) and its equivalent form for $S_{\ell_i \lambda_i}^*(j_i | j_i')$ followed by appropriate recombinations of 3-j and 6-j symbols using expressions similar to Eq. (4.7-3), one is able to perform the summations over $J_i$, S, and S' which appear in Eq. (4.7-4). The resulting IOS form of the generalized phenomenological cross section is,

$$\sigma_{j_i j_f; j_i' j_f'}^{K_\ell K_j; K_\ell' K_j'}(K, E_f', E_i') = \frac{\pi}{\kappa_i'^2} \sum_{\mu\mu'\lambda\lambda'} (-1)^{\mu'+\lambda+\lambda'+K_j+K_j'}$$

$$[(2j_i+1)(2j_f+1)(2j_i'+1)(2j_f'+1)]^{\frac{1}{2}} \begin{pmatrix} j_f & K_j & j_i \\ -\mu & \lambda+\mu' & \mu-\mu'-\lambda \end{pmatrix}$$

(4.7-7)

$$\begin{pmatrix} j_f' & K_j' & j_i' \\ -\mu & \lambda'+\mu' & \mu-\mu'-\lambda' \end{pmatrix} \begin{pmatrix} K_\ell & K_j & K \\ \lambda & -\lambda-\mu' & \mu' \end{pmatrix} \begin{pmatrix} K_\ell' & K_j' & K \\ \lambda' & -\lambda'-\mu' & \mu' \end{pmatrix}$$

$$\sum_{L_i L_f} \begin{pmatrix} j_f' & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ \mu & -\mu & 0 \end{pmatrix}$$

$$
\begin{pmatrix} j_i' & j_i & L_i \\ \lambda & -\mu+\mu & \mu-\mu'-\lambda' & \lambda'-\lambda \end{pmatrix} (-1)^{L_i+L_f} \sum_{\substack{\ell_i \ell_f \\ \ell_i' \ell_f'}} (-1)^{\ell_i - \ell_i' + \mathcal{L}_i - \mathcal{L}_f}
$$

$$
[(2\ell_i+1)(2\ell_f+1)(2\ell_i'+1)(2\ell_f'+1)]^{\frac{1}{2}} \begin{pmatrix} \ell_i' & K_\ell' & \ell_f' \\ 0 & 0 & 0 \end{pmatrix}
$$

$$
\begin{pmatrix} \ell_i & K_\ell & \ell_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_i & \ell_i' & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_i & \ell_i' & L_i \\ \lambda & -\lambda' & \lambda'-\lambda \end{pmatrix} \begin{pmatrix} \ell_i & K_\ell & \ell_f \\ \lambda & -\lambda & 0 \end{pmatrix}
$$

$$
\begin{pmatrix} \ell_i' & K_\ell' & \ell_f' \\ \lambda' & -\lambda' & 0 \end{pmatrix} [\delta_{L_i 0} \delta_{L_f 0} - S_{L_f}^{\mathcal{L}_f} S_{L_i}^{\mathcal{L}_i^*}]
$$

This expression simplifies further only for special choices of $K_j$, $K_j'$, $K_\ell$, and $K_\ell'$. As with the "L-average" CS expression, it would appear that this expression affords little if any improvement over numerical evaluation of the generalized phenomenological cross section via calculation of the S-matrix elements using Eqs. (4.7-6) and (4.7-1) followed by direct substitution into Eq. (4.6-22). In fact, it was found by this worker that in practice, the indirect method is actually more efficient from a computational viewpoint than a direct numerical evaluation of Eq. (4.7-7).

Considerable simplification of Eq. (4.7-7) results if instead of an "L-average" labeling, one chooses and "L-initial" labeling (i.e., $\mathcal{L}_i = \ell_i'$ and $\mathcal{L}_f = \ell_f'$). The summations over $\ell_i$ and $\ell_f$ can be performed which results in the following IOS expression for the generalized phenomenological

cross section,

$$\sigma^{K_\ell K_j ; K'_\ell K'_j}_{j_i j_f ; j'_i j'_f}(K, E'_f, E'_i) = \frac{\pi}{\kappa_i'^2} \sum_{\lambda_i \lambda_f} (-1)^{\lambda_i + \lambda_f + K_\ell + j_i + j'_i}$$

$$[(2j_f+1)(2j_i+1)(2j'_f+1)(2j'_i+1)]^{\frac{1}{2}} \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix}$$

$$\begin{pmatrix} j'_i & j'_f & K'_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix}$$

$$\begin{pmatrix} K & K'_\ell & K'_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \sum_{L_i L_f} \begin{pmatrix} j'_i & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'_f & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \qquad (4.7\text{-}8)$$

$$\begin{pmatrix} j'_f & j_f & L_f \\ -\lambda_f & \lambda_f & 0 \end{pmatrix} \begin{pmatrix} j'_i & j_i & L_i \\ -\lambda_i & \lambda_i & 0 \end{pmatrix} \sum_{\ell'_i \ell'_f} (-1)^{\ell'_f + \ell'_i} (2\ell'_i+1)(2\ell'_f+1)$$

$$\begin{pmatrix} \ell'_i & K'_\ell & \ell'_f \\ 0 & 0 & 0 \end{pmatrix}^2 [\delta_{L_i 0} \delta_{L_f 0} - S^{\ell'_f}_{L_f} S^{\ell'_i *}_{L_i}]$$

As was the case with the CS "L-initial" expression, an analogous expression for "L-final" labeling can be derived which has the same form as the expression given above except that $\ell'_i$ and $\ell'_f$ are replaced by $\ell_i$ and $\ell_f$ respectively and $K'_\ell$ in the last 3-j symbol is replaced by $K_\ell$. It should be noted that the IOS "L-initial" and "L-final" expressions are equal only if $K_\ell$ is equal to $K'_\ell$. The transport coefficient cross sections for which $j_i = j_f$ and $j'_i = j'_f$ also do not simplify further(63).

# 5. NUMERICAL RESULTS

## 5.1. Introduction

As an introduction to the numerical results obtained by use of the preceding theory, a short, qualitative discussion of the Senftleben-Beenakker effects is given. This is followed by a discussion of the convergence of the perturbation expansion in the nonsphericity parameter and finally a summary of the numerical results is to be presented.

The Senftleben-Beenakker effects on the thermal conductivity, Soret, Dufour, and diffusion coefficients are quantitatively characterized by parallel, perpendicular, and transverse components as shown in Eq. (3.3-16). In the low field limit, the parallel and perpendicular components are equal. Conversely, in the high field limit, saturation occurs with the parallel and perpendicular components approaching different limiting values. The transverse component vanishes in both high and low field limits. It reaches a maximum value at an intermediate field strength for which molecular precession and collision frequencies are of the same order of magnitude. If one allows $\underline{T}$ to represent any one of the above-mentioned transport coefficients, one can define the following dimensionless parameters,

$$\nu_{\perp}^{T} = \frac{T_{\perp} - T_{0}}{T_{\perp}^{(s)} - T_{0}} \qquad (5.1-1)$$

$$\nu_\parallel^T = \frac{T_\parallel - T_0}{T_\perp^{(s)} - T_0} \qquad (5.1\text{-}2)$$

$$\nu_{tr}^T = \frac{T_{tr}}{T_\perp^{(s)} - T_0} \qquad (5.1\text{-}3)$$

Here, the scalar coefficients, $T_\perp$, $T_\parallel$, and $T_{tr}$, are defined as in Eq. (3.3-16). The quantity, $T_\perp^{(s)}$, is the saturation limit of $T_\perp$, and $T_0$ is given by,

$$T_0 = \lim_{H \to 0} T_\perp = \lim_{H \to 0} T_\parallel \qquad (5.1\text{-}4)$$

where H is the magnetic field strength. The quantities $\nu_\perp^T$, $\nu_\parallel^T$, and $\nu_{tr}^T$ are universal functions of H/P (P is the hydrostatic pressure) and can be plotted versus this quantity as is shown in Fig 5.1. This plot is representative of the Senftleben-Beenakker effects observable in a dilute atom-diatom mixture.

If one includes only the dominant $\underline{W}[\underline{\Omega}]^{(2)}$ polarization in the expansion set used to construct the collision operator, then one finds that the saturation limit of $\nu_\parallel^T$ is 2/3. ($\nu_\perp^T$ has been defined such that it has a saturation limit of unity.) Under the same conditions, one finds that $\nu_{tr}^T$ reaches a maximum of 0.475059 at a critical value of the magnetic field strength, $H_{crit}$. The value of $H_{crit}/P$ in an atom-
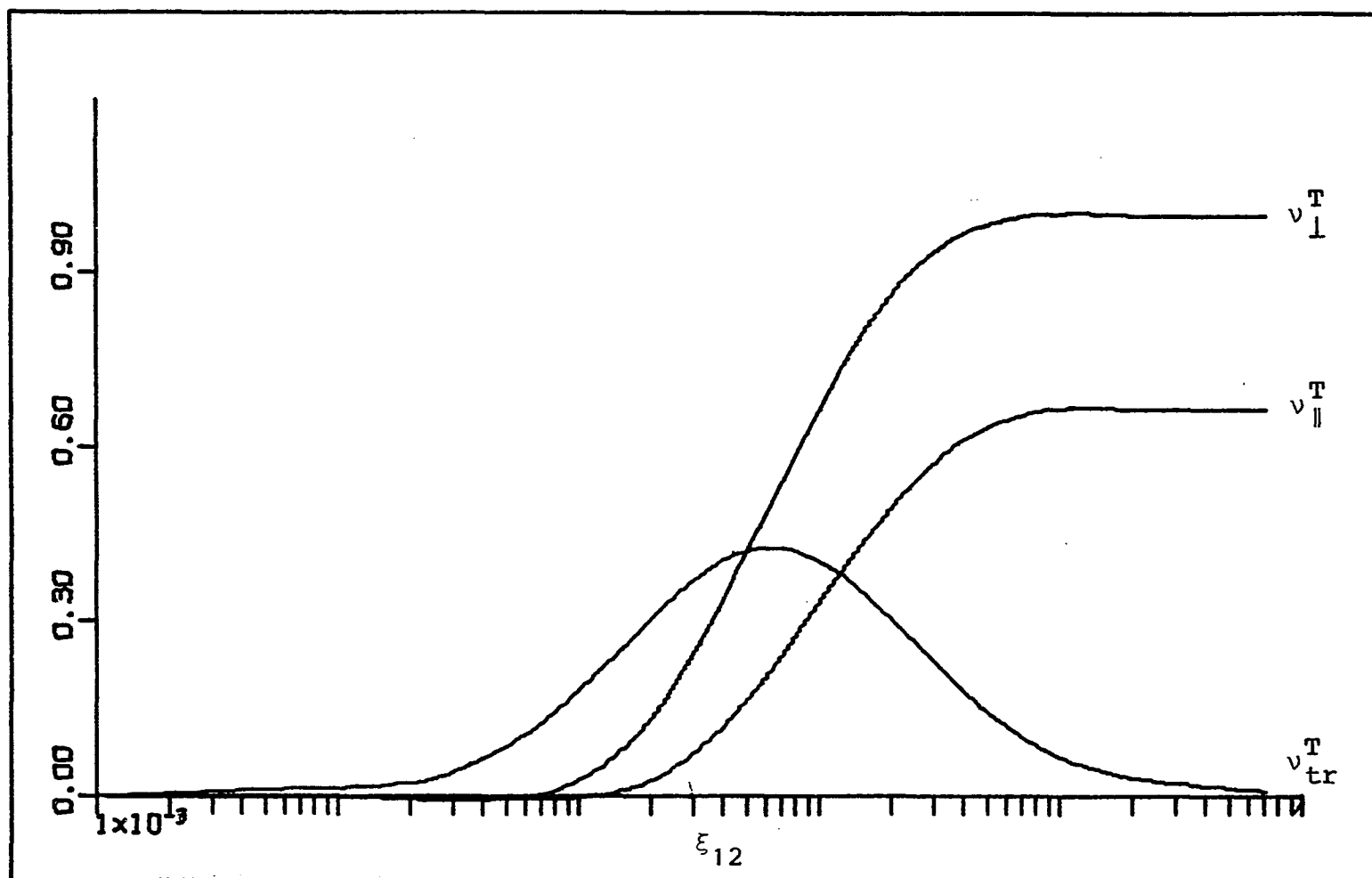
Fig. 5.1.  Senftleben-Beenakker Effects Characteristic of a Dilute Atom-Diatom Mixture

diatom mixture which is infinitely dilute in the diatomic
species is given by the formula,

$$\frac{H}{P}^{crit} = \frac{\hbar \xi_{crit}}{g_{\beta} \mu_N kT} \bar{v}_{\alpha\beta} G(\begin{smallmatrix} 1200 & | & \beta \\ 1200 & | & \beta \end{smallmatrix})_{\alpha\beta} \qquad (5.1-5)$$

where $g_{\beta}$ is the diatom rotational g-factor and $\mu_N$ is the nu-
clear magneton. The constant, $\xi_{crit}$, is a dimensionless num-
ber which to six decimal places has a value of 0.615795. In
the case of systems considered in this work, the inclusion of
$W\underline{\Omega}$ and/or other polarizations changes the preceding values at
most by only a few percent.

In order to assess the rate of convergence of the
nonsphericity perturbation expansion, the collision operator
was directly inverted. This result was compared to the first
few low order (up to fifth) results obtained using the
perturbation approach. The perpendicular component of the
thermal diffusion coefficient for an Ar- $CO_2$ system at $300°K$
is plotted versus $\xi_{12}$ in Fig. 5.2. The parallel and trans-
verse components exhibit similar behavior. As can be seen,
there is a significant deviation in second order which is
markedly improved in third order. Curves for orders higher
than third are indistinguishable from the exact inversion.
It should be noted that the Ar-$CO_2$ system at $300°K$ is given
here because it involves the most anisotropic interaction
dealt with in this work. In contrast, if one considers an
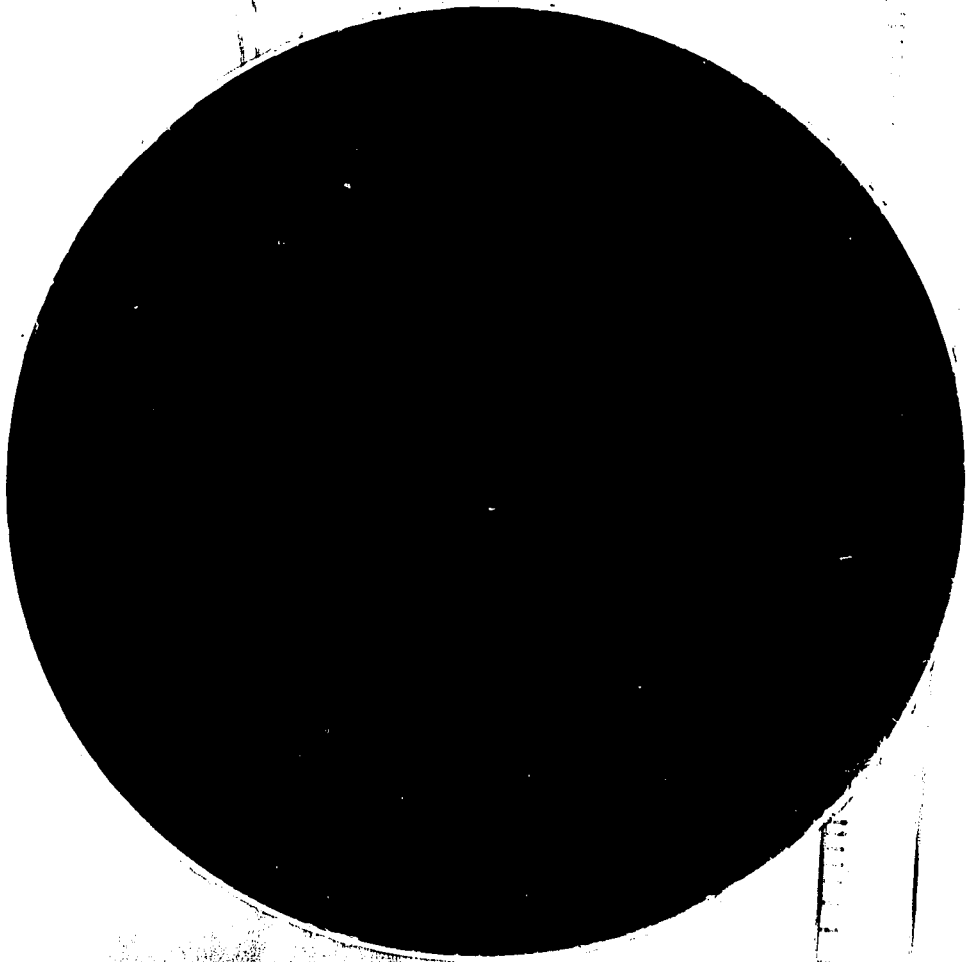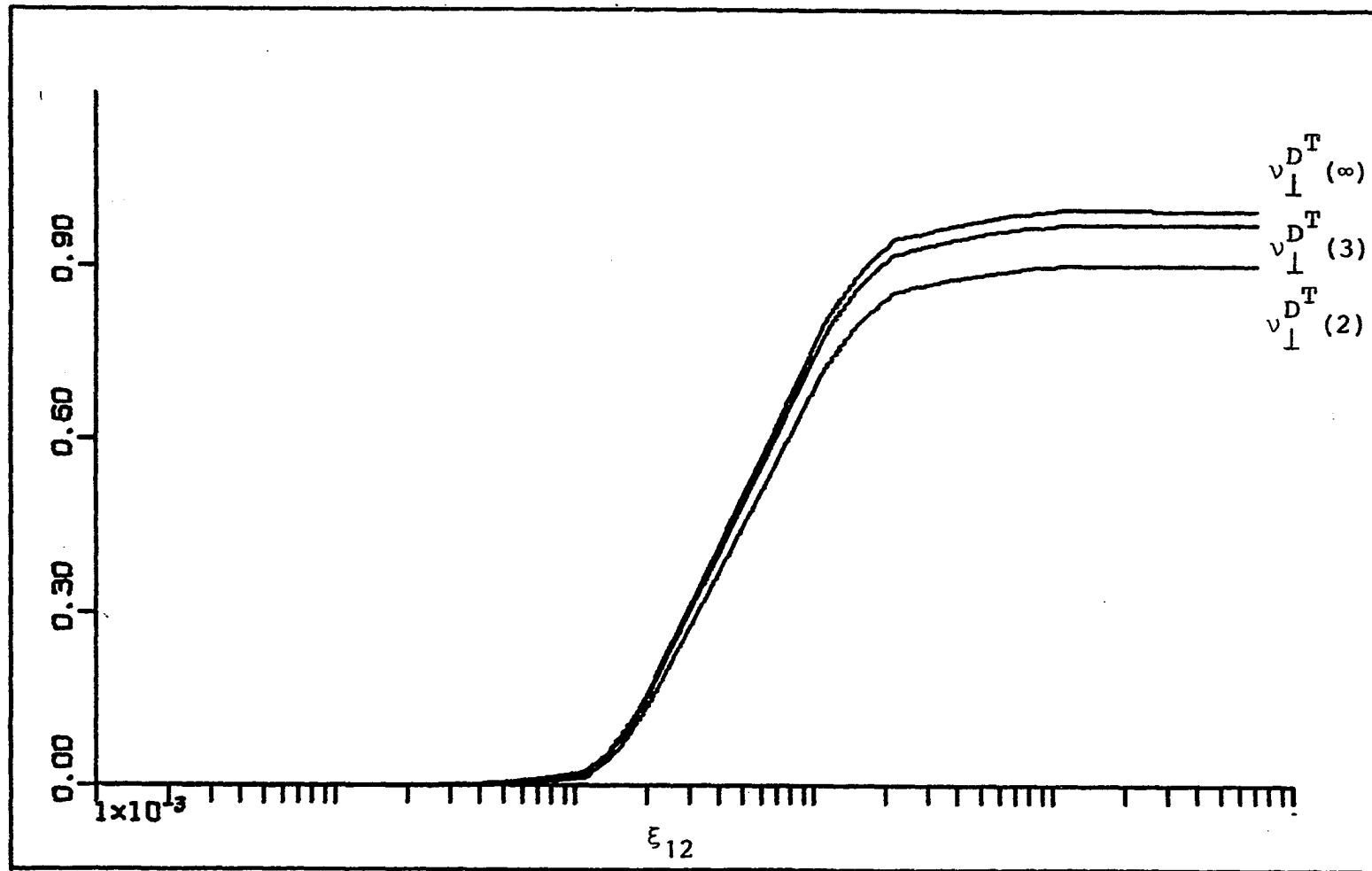
Fig. 5.2.   Convergence of $\nu_{\perp}^{D^T}$ in the Nonsphericity

$Ar-N_2$ system (i.e., the least anisotropic interaction investigated), one finds that even the second order results do not differ significantly from exact results.

In Chapter 3, expressions for various transport coefficients of interest are given in terms of effective collision cross sections. Thus, comparison of the various theoretical approaches taken in this work with each other and with experiment is conveniently made in terms of these cross sections themselves rather than in terms of actual transport coefficients. Furthermore, the effective cross sections are expressed in Chapter 4 as averages of energy dependent phenomenological cross sections over a Maxwellian energy distribution. Comparison of the unaveraged phenomenological cross sections obtained from the various methods is thus an even more rigorous test of the efficacy of the theoretical approaches developed in the preceding chapters.

The remainder of this chapter consists of five sections. The first is a presentation of results obtained for some specific model systems using the techniques of Chapter 4. The second is a comparative discussion of various numerical values of generalized phenomenological cross sections. The third section is a comparative discussion of various numerical values of effective collision cross sections. The fourth section is a presentation and discussion of results obtained using the Kihara model methods previously employed by Verlin

et al.(64) and the last section is a brief survey of future
areas of study related to the present work.


## 5.2. A Presentation of Monte Carlo and IOS Results

The Monte Carlo methodology was applied to four specific
molecular potential energy surfaces. These included two dif-
ferent $Ar-CO_2$ interactions due to Parker, Snow and Pack(65)
(denoted by I and II), an $He-CO_2$ interaction due to the same
authors, and an $Ar-N_2$ potential surface due to Pattengill, La
Budde, Bernstein, and Curtiss(66). The $Ar-CO_2(I)$ surface and
the $He-CO_2$ surface were employed in the calculation of effec-
tive cross sections for these systems at $300°$, $900°$, and $1800°$
K. The $Ar-CO_2(II)$ surface was used to calculate effective
cross sections at $300°K$ only (for comparison with the $Ar-CO_2$
(I) results). Finally, the $Ar-N_2$ surface was employed to
calculate effective cross sections at $300°K$ and
phenomenological (energy-dependent) cross sections at three
different initial relative translational energies (0.00500
eV, 0.02585 eV, and 0.05000 eV) and a single initial
rotational energy (0.0105 eV). The rotational energy chosen
corresponds to a rotor quantum number of six. The author was
greatly aided in this work by Dr. R. K. Preston(67), (cf.
Goldflam et al. (68)), formerly of Lawrence Livermore Labora-
tory, Livermore, California, who generated the original 11

sets of classical trajectories appropriate to the 11 cases listed above. He used a very efficient Adams-Moulton predictor-corrector algorithm in conjunction with a CDC 7600 computer to perform the necessary integrations of the classical equations of motion with randomly chosen initial conditions.

The precollisional conditions appearing in the original sets of classical trajectories (appropriate to the thermally averaged cross sections) were used by the author to generate control variate trajectory data as discussed in Chapter 4 (i.e., based on a Lennard-Jones 6-12 interaction with optimized force constants). These trajectories were combined with the original trajectories (via Eq. (4.5-1)) to obtain the values of the effective collision cross sections which appear in Tables 5.1 and 5.2. These quantities are reported in squared angstroms along with estimates of the relative standard deviation (in percent) which appear in parentheses. These data (especially for the $Ar-CO_2$ and $Ar-N_2$ surfaces) will be compared subsequently to corresponding IOS and Kihara model results. The reader should also note that effective cross sections at $300°K$ are given for the two $Ar-CO_2$ potential surfaces in the first two columns of Table 5.1. One can conclude from comparison of corresponding quantities that the $Ar-CO_2(I)$ potential surface is more anisotropic than the $Ar-CO_2(II)$ potential surface.

Table 5.1.  Monte Carlo Estimates of Effective Collision Cross Sections for $Ar\text{-}CO_2$ [a]

| Cross Section | $Ar\text{-}CO_2(I)$ $300°K$ | $Ar\text{-}CO_2(II)$ $300°K$ | $Ar\text{-}CO_2(I)$ $900°K$ | $Ar\text{-}CO_2(I)$ $1800°K$ |
|---|---|---|---|---|
| $G\left(\genfrac{}{}{0pt}{}{1000\,\beta}{1000\,\beta}\right)_{\alpha\beta}$ | 26.2(1.0) | 26.2(1.3) | 19.6(1.6) | 17.4(1.6) |
| $G\left(\genfrac{}{}{0pt}{}{1010\,\beta}{1010\,\beta}\right)_{\alpha\beta}$ | 43.8(2.0) | 44.0(2.8) | 32.6(3.5) | 28.8(3.5) |
| $G\left(\genfrac{}{}{0pt}{}{1010\,\alpha}{1010\,\alpha}\right)_{\alpha\beta}$ | 45.8(2.0) | 45.8(2.8) | 34.1(3.5) | 30.0(3.5) |
| $G\left(\genfrac{}{}{0pt}{}{1001\,\beta}{1001\,\beta}\right)_{\alpha\beta}$ | 57.2(2.6) | 63.1(2.5) | 36.5(4.0) | 30.5(3.8) |
| $G\left(\genfrac{}{}{0pt}{}{1100\,\beta}{1100\,\beta}\right)_{\alpha\beta}$ | 23.2(2.3) | 23.7(2.1) | 16.4(3.0) | 14.4(3.0) |
| $G\left(\genfrac{}{}{0pt}{}{1200\,\beta}{1200\,\beta}\right)_{\alpha\beta}$ | 103.5(3.4) | 86.2(3.0) | 61.3(4.8) | 48.6(4.7) |
| $G\left(\genfrac{}{}{0pt}{}{0200\,\beta}{0200\,\beta}\right)_{\alpha\beta}$ | 50.5(4.2) | 36.2(3.6) | 26.2(6.6) | 19.3(7.1) |
| $G\left(\genfrac{}{}{0pt}{}{1000\,\beta}{1010\,\beta}\right)_{\alpha\beta}$ , $G\left(\genfrac{}{}{0pt}{}{1010\,\beta}{1000\,\beta}\right)_{\alpha\beta}$ | -1.13(1.4) | -0.658(1.9) | -1.69(2.4) | -1.36(2.4) |
| $G\left(\genfrac{}{}{0pt}{}{1000\,\beta}{1001\,\beta}\right)_{\alpha\beta}$ , $G\left(\genfrac{}{}{0pt}{}{1001\,\beta}{1000\,\beta}\right)_{\alpha\beta}$ | 0.359(2.0) | -1.92(1.8) | -0.120(2.8) | 0.0974(2.7) |
| $G\left(\genfrac{}{}{0pt}{}{1010\,\beta}{1001\,\beta}\right)_{\alpha\beta}$ , $G\left(\genfrac{}{}{0pt}{}{1001\,\beta}{1010\,\beta}\right)_{\alpha\beta}$ | -7.57(4.3) | -7.84(3.0) | -4.25(5.0) | -3.31(4.8) |

[a] Cross sections are in square angstroms and the quantity in parentheses is percent relative standard deviation.

Table 5.1. (continued)

| Cross Section | $Ar\text{-}CO_2(I)$ $300°K$ | $Ar\text{-}CO_2(II)$ $300°K$ | $Ar\text{-}CO_2(I)$ $900°K$ | $Ar\text{-}CO_2(I)$ $1800°K$ |
|---|---|---|---|---|
| $G\left(\begin{smallmatrix}1010\\1000\end{smallmatrix}\middle\vert\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1000\\1010\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\alpha\end{smallmatrix}\right)_{\alpha\beta}$ | $-1.30(1.4)$ | $-0.76(1.9)$ | $-1.95(2.4)$ | $-1.57(2.4)$ |
| $G\left(\begin{smallmatrix}1010\\1010\end{smallmatrix}\middle\vert\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1010\\1010\end{smallmatrix}\middle\vert\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $-13.0(2.0)$ | $-11.2(2.8)$ | $-10.0(3.5)$ | $-9.01(3.5)$ |
| $G\left(\begin{smallmatrix}1010\\1001\end{smallmatrix}\middle\vert\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1001\\1010\end{smallmatrix}\middle\vert\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $-4.49(4.3)$ | $-7.70(3.0)$ | $-2.84(5.0)$ | $-2.31(4.8)$ |
| $G\left(\begin{smallmatrix}1000\\1200\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1000\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $0.958(14.2)$ | $0.554(24.6)$ | $0.614(16.6)$ | $0.606(14.9)$ |
| $G\left(\begin{smallmatrix}1010\\1200\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1010\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $-2.62(6.3)$ | $-2.12(7.7)$ | $-0.838(14.7)$ | $-0.579(18.8)$ |
| $G\left(\begin{smallmatrix}1001\\1200\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1001\end{smallmatrix}\middle\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $-3.13(11.0)$ | $-3.52(9.8)$ | $-1.77(14.6)$ | $-1.79(12.8)$ |

## Table 5.2. Monte Carlo Estimates of Effective Collision Cross Sections for $He-CO_2$ and $Ar-N_2$[a]

| Cross Section | $He-CO_2$ 300°K | $He-CO_2$ 900°K | $He-CO_2$ 1800°K | $Ar-N_2$ 300°K |
|---|---|---|---|---|
| $G\left(\begin{smallmatrix}1000\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 3.08(2.0) | 2.58(1.7) | 2.27(1.7) | 29.1(1.8) |
| $G\left(\begin{smallmatrix}1010\\1010\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 8.25(3.6) | 6.92(3.6) | 6.09(3.8) | 39.7(5.9) |
| $G\left(\begin{smallmatrix}1010\\1010\end{smallmatrix}\Big\vert\begin{smallmatrix}\alpha\\\alpha\end{smallmatrix}\right)_{\alpha\beta}$ | 39.4(3.6) | 32.6(3.6) | 28.8(3.8) | 34.4(5.9) |
| $G\left(\begin{smallmatrix}1001\\1001\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 17.8(5.8) | 12.4(3.4) | 10.3(3.7) | 35.0(8.6) |
| $G\left(\begin{smallmatrix}1100\\1100\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 2.13(3.2) | 2.03(2.7) | 1.83(2.8) | 28.1(3.4) |
| $G\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 18.3(5.8) | 13.0(3.9) | 10.8(4.2) | 53.8(8.6) |
| $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 7.31(7.0) | 4.71(7.7) | 3.80(8.5) | 7.12(3.7) |
| $G\left(\begin{smallmatrix}1000\\1010\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1010\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -0.0551(2.5) | -0.0453(2.5) | -0.0395(2.6) | -1.66(3.2) |
| $G\left(\begin{smallmatrix}1000\\1001\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1001\\1000\end{smallmatrix}\Big\vert\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -0.134(2.9) | -0.153(2.4) | -0.129(2.5) | -0.653(2.9) |

[a] Cross sections are in squared angstroms and the quantity in parentheses is percent relative standard deviation.

# Table 5.2. (continued)

| Cross Section | He-CO$_2$ 300°K | He-CO$_2$ 900°K | He-CO$_2$ 1800°K | Ar-N$_2$ 300°K |
|---|---|---|---|---|
| $G\left(\begin{smallmatrix}1010 & \beta\\1001 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1001 & \beta\\1010 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ | -0.615(3.8) | -0.401(3.7) | -0.326(3.9) | -1.16(4.9) |
| $G\left(\begin{smallmatrix}1010 & \alpha\\1000 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1000 & \beta\\1010 & \alpha\end{smallmatrix}\right)_{\alpha\beta}$ | -2.01(2.5) | -1.65(2.5) | -1.44(2.6) | -0.974(3.2) |
| $G\left(\begin{smallmatrix}1010 & \alpha\\1010 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1010 & \beta\\1010 & \alpha\end{smallmatrix}\right)_{\alpha\beta}$ | -1.67(3.6) | -1.39(3.6) | -1.21(3.8) | -14.0(5.9) |
| $G\left(\begin{smallmatrix}1010 & \alpha\\1001 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1001 & \beta\\1010 & \alpha\end{smallmatrix}\right)_{\alpha\beta}$ | -3.32(3.8) | -2.22(3.7) | -1.79(3.9) | -1.02(4.9) |
| $G\left(\begin{smallmatrix}1000 & \alpha\\1200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1200 & \beta\\1000 & \alpha\end{smallmatrix}\right)_{\alpha\beta}$ | 0.0890(18.0) | 0.0661(20.2) | 0.0632(18.6) | 0.111(56.6) |
| $G\left(\begin{smallmatrix}1010 & \beta\\1000 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1000 & \beta\\1010 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ | -0.281(6.9) | -0.184(8.8) | -0.148(9.6) | 0.292(44.2) |
| $G\left(\begin{smallmatrix}1001 & \beta\\1200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ , $G\left(\begin{smallmatrix}1200 & \beta\\1001 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ | -0.306(13.2) | -0.176(19.3) | -0.156(19.1) | 0.0264(1400.) |

The three remaining sets of classical trajectories (which are appropriate to energy-dependent cross sections) were used to generate estimates of quantum mechanical generalized phenomenological cross sections. These quantities are not rigorously defined in a classical sense owing to the continuous nature of the classical rotational energy spectrum. However, one obtains good high energy estimates of the quantal values by means of the following modified form of Eq. (4.4-27),

$$Q(\overline{\Psi}_v' \bullet \overline{\Psi}_\eta | \ j' \rightarrow j) =$$
$$\frac{2\pi}{\gamma^{s+s'}} \ b_{max} \int_0^1 - \int_0^1 d\underline{\xi}^{(7)} \ \delta_{jj^\star b \overline{\Psi}_v' \bullet (\overline{\Psi}_\eta - \overline{\Psi}_\eta^\star)} \ (-1)^n \qquad (5.2-1)$$

where for a homonuclear diatomic molecule,

$$j^\star = 2\{ |\frac{\Omega^\star}{2\hbar} \sqrt{2I_\beta kT} + \frac{1}{4}| \}. \qquad (5.2-2)$$

Here, the curly brackets denote the "greatest integer" function. It is clear that the role of the Kronecker delta is to divide the postcollisional domain of $\Omega^\star$ into subdomains or "bins" which correspond in an average sense to rotational quantum states. Similarly, the precollisional domain of can be divided into a similar set of "bins" (i.e. $j^\star$ and $\Omega^\star$ are replaced by $j'$ and $\Omega$ in Eq. (5.2-2)). Finally, it should be noted that the subdomains have been defined so as to be centered on $j^\star + \frac{1}{2}$. This formulation has been adopted because $j^\star + \frac{1}{2}$ corresponds more closely to $[j^\star(j^\star+1)]^{\frac{1}{2}}$ than either $j^\star$

or $j^*+1$. Thus, from Eq. (5.2-1), one obtains the result,

$$Q(\overline{\Psi}_\nu' \odot \overline{\Psi}_\eta) = \sum_j Q(\overline{\Psi}_\nu' \odot \overline{\Psi}_\eta | j' \rightarrow j) \qquad (5.2-3)$$

It is clear that $Q(\overline{\Psi}_\nu' \odot \overline{\Psi}_\eta | j' \rightarrow j)$ is easily evaluted as a Monte Carlo estimate.

One then obtains an expression for the scalar collision integrals in terms of the "binned" Q-cross sections as follows,

$$\{\overline{\Psi}_\nu' \odot \overline{\Psi}_\eta\}_{\nu\omega} =$$

$$[\frac{kT}{2\pi\mu}]_{\nu\omega}^{\frac{1}{2}} 16 \int \Omega d\Omega e^{-\Omega^2} \int_0^\infty d\gamma\ \gamma^{s+s'+3}\ e^{-\gamma^2} \sum_j Q(\overline{\Psi}_\nu' \odot \overline{\Psi}_\eta | j' \rightarrow j) \qquad (5.2-4)$$

This expression follows from the substitution of Eqs. (5.2-3) and (4.4-11) into Eq. (4.4-10). Finally, a classical estimate of the generalized phenomenological cross section can be written,

$$\sigma_{j\ j;j'j'}^{K_\ell K_j;K_\ell' K_j'}(K) = [\frac{8(2K+1)}{(j'+\frac{1}{2})}\ K_\ell! K_\ell'! [\frac{2^{K_\ell+K_\ell'}}{(2K_\ell)!(2K_\ell')!}]^{\frac{1}{2}} \gamma\ 's\ \gamma^{-s}$$

$$<j||S_q^{(t)}(\hat{\Omega}^2)[\hat{\Omega}]^{(K_j)}||j><j'||S_{q'}^{(t')}(\hat{\Omega}^2)[\hat{\Omega}]^{(K_j')}||j'>]^{-1} \qquad (5.2-5)$$

$$Q^{(K)}\begin{pmatrix} K_\ell & K_j;M \\ K_\ell' & K_j';M \end{pmatrix} j' \rightarrow j)$$

This expression is obtained by equating the integrands appearing on the right hand sides of Eq. (5.2-4) and Eq. (4.6-21) where $\overline{\Psi}_\nu'$ is $\gamma^s S_q^{(t)}(\hat{\Omega}^2)[\underline{\gamma}]^{(K_\ell)}[\underline{\hat{\Omega}}]^{(K_j)}$ and $\overline{\Psi}_\nu$ is $\gamma^{s'} S_{q'}^{(t')}(\hat{\Omega}^2)[\underline{\gamma}]^{(K_\ell')}[\hat{\Omega}]^{(K_j')}$. Monte Carlo estimates of these quantities appear in Tables 5.3, 5.4, and 5.5. These data

Table 5.3. Classical Estimates of the Generalized Phenomeno-
logical Cross Sections[a]

| Cross Section indices | | | | | Final Rotor State | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6[b] | j=8[c] |
| 0 | 0 | 0 | 0 | 0 | -9.20 | -21.3 | -35.7 | 51.5 | -4.83 |
| 1 | 0 | 1 | 0 | 1 | 0.40 | -1.59 | -4.01 | 46.9 | -0.38 |
| 0 | 1 | 0 | 1 | 1 | -3.27 | -5.47 | -10.5 | 74.9. | -1.07 |
| 2 | 0 | 2 | 0 | 2 | 0.11. | -0.62 | -1.88 | 29.6 | -0.17 |
| 0 | 2 | 0 | 2 | 2 | -0.17 | -2.10 | -4.61 | 15.9 | -0.45 |
| 1 | 1 | 1 | 1 | 0 | -0.74 | -0.86 | -0.85 | 20.4 | -0.01 |
| 1 | 1 | 1 | 1 | 1 | -0.03 | -0.51 | -1.46 | 13.4 | -0.16 |
| 1 | 1 | 1 | 1 | 2 | -0.35 | -0.69 | -1.15 | 16.3 | -0.10 |
| 1 | 2 | 1 | 2 | 1 | -0.68 | -0.40 | -0.54 | 10.9 | -0.02 |
| 1 | 2 | 1 | 2 | 2 | -0.10 | -0.37 | -0.72 | 8.46 | -0.07 |
| 1 | 2 | 1 | 2 | 3 | -0.44 | -0.43 | -0.53 | 10.1 | -0.05 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.00500 eV. Cross sections are in squared angstroms. The 6 6 cross sections are accurate to within 10%. All others are accurate to within a sign and an order of magnitude.

[b] The average of mixed cross sections appears in parentheses.

[c] At this energy, the 6→8 channel is closed. However, the structure of the "bins" includes a small contribution to the 6 8 cross sections for an energy less than the classical cutoff.

Table 5.3.   (continued)

<table>
<tr><th colspan="5">Cross Section<br>Indices</th><th colspan="5">Final Rotor State</th></tr>
<tr><th>$K_\ell$</th><th>$K_j$</th><th>$K'_\ell$</th><th>$K'_j$</th><th>$K$</th><th>j=0</th><th>j=2</th><th>j=4</th><th>j=6</th><th>j=8</th></tr>
<tr><td>1</td><td>0</td><td>1</td><td>2</td><td>1</td><td>0.65</td><td>1.13</td><td>0.32</td><td>-3.91<br>(-3.94)</td><td>-0.11</td></tr>
<tr><td>1</td><td>2</td><td>1</td><td>0</td><td>1</td><td>0.56</td><td>-0.19</td><td>-0.42</td><td>-3.97</td><td>-0.07</td></tr>
<tr><td>2</td><td>0</td><td>0</td><td>2</td><td>2</td><td>-0.56</td><td>-0.59</td><td>-0.19</td><td>-0.05<br>(0.09)</td><td>-0.006</td></tr>
<tr><td>0</td><td>2</td><td>2</td><td>0</td><td>2</td><td>0.15</td><td>1.39</td><td>-0.06</td><td>0.22</td><td>-0.02</td></tr>
<tr><td>1</td><td>0</td><td>1</td><td>1</td><td>1</td><td>0.39i</td><td>-0.04i</td><td>-0.70i</td><td>-0.05i<br>(-0.13i)</td><td>0.004i</td></tr>
<tr><td>1</td><td>1</td><td>1</td><td>0</td><td>1</td><td>0.17i</td><td>-0.21i</td><td>-0.66i</td><td>-0.21i</td><td>0.05i</td></tr>
<tr><td>1</td><td>2</td><td>1</td><td>1</td><td>1</td><td>-1.40i</td><td>-0.85i</td><td>-1.13i</td><td>-1.13i<br>(-1.28i)</td><td>-0.03i</td></tr>
<tr><td>1</td><td>1</td><td>1</td><td>2</td><td>1</td><td>-0.11i</td><td>-0.04i</td><td>-0.88i</td><td>-1.42i</td><td>-0.02i</td></tr>
<tr><td>1</td><td>2</td><td>1</td><td>1</td><td>2</td><td>0.92i</td><td>0.25i</td><td>0.23i</td><td>0.68i<br>(0.60i)</td><td>0.02i</td></tr>
<tr><td>1</td><td>1</td><td>1</td><td>2</td><td>2</td><td>0.15i</td><td>0.05i</td><td>0.08i</td><td>0.52i</td><td>0.008i</td></tr>
</table>

Table 5.4. Classical Estimates of the Generalized Phenomenological Cross Sections[a]

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6[b] | j=8 | j=10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | -5.98 | -10.1 | -14.7 | 36.5 | -11.5 | -3.20 |
| 1 | 0 | 1 | 0 | 1 | -0.21 | -0.56 | -1.89 | 19.5 | -1.50 | 0.09 |
| 0 | 1 | 0 | 1 | 1 | -1.06 | -1.50 | -3.70 | 13.2 | -3.17 | -0.80 |
| 2 | 0 | 2 | 0 | 2 | 0.12 | -0.15 | -0.93 | 17.7 | -0.65 | 0.09 |
| 0 | 2 | 0 | 2 | 2 | -0.97 | -0.80 | -1.57 | 8.81 | -1.47 | -0.41 |
| 1 | 1 | 1 | 1 | 0 | -0.17 | -0.41 | -0.44 | 8.02 | -0.37 | -0.09 |
| 1 | 1 | 1 | 1 | 1 | -0.06 | -0.33 | -0.78 | 5.69 | -0.54 | 0.09 |
| 1 | 1 | 1 | 1 | 2 | -0.21 | -0.34 | -0.62 | 6.73 | -0.45 | 0.007 |
| 1 | 2 | 1 | 2 | 1 | -0.49 | -0.21 | -0.32 | 4.32 | -0.24 | -0.02 |
| 1 | 2 | 1 | 2 | 2 | 0.06 | 0.33 | -0.34 | 3.57 | -0.28 | 0.04 |
| 1 | 2 | 1 | 2 | 3 | -0.17 | -0.16 | -0.33 | 4.16 | -0.24 | 0.001 |
| 1 | 0 | 1 | 2 | 1 | 0.38 | 0.68 | 0.35 | -1.26 (-1.23) | -0.16 | 0.03 |
| 1 | 2 | 1 | 0 | 1 | 0.12 | 0.07 | -0.26 | -1.20 | 0.10 | 0.16 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.025E5 eV. Cross sections are square angstroms. The 6→6 cross sections are accurate to within 10%. All others are accurate to within a sign and an order of magnitude.

[b] The average of mixed cross sections appears in parentheses.

Table 5.4. (continued)

| Cross Section Indices | | | | | Final Rotor State | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6 | j=8 | j=10 |
| 2 | 0 | 0 | 2 | 2 | 0.22 | 0.14 | -0.03 | 0.03 | -0.04 | 0.005 |
|   |   |   |   |   |   |   |   | (0.05) |   |   |
| 0 | 2 | 2 | 0 | 2 | -0.14 | -0.13 | -0.20 | 0.07 | 0.008 | 0.10 |
|   |   |   |   |   |   |   |   |   |   |   |
| 1 | 0 | 1 | 1 | 1 | 0.09i | 0.19i | 0.02i | -0.29i | -0.07i | 0.05i |
|   |   |   |   |   |   |   |   | (-0.30i) |   |   |
| 1 | 1 | 1 | 0 | 1 | -0.09i | -0.12i | -0.09i | -0.31i | 0.05i | 0.07i |
|   |   |   |   |   |   |   |   |   |   |   |
| 1 | 2 | 1 | 1 | 1 | -1.01i | -0.12i | -0.15i | -0.19i | -0.06i | -0.004 |
|   |   |   |   |   |   |   |   | (-0.21i) |   |   |
| 1 | 1 | 1 | 2 | 1 | -0.05i | -0.06i | -0.11i | -0.23i | -0.10i | -0.01i |
|   |   |   |   |   |   |   |   |   |   |   |
| 1 | 2 | 1 | 1 | 2 | 1.35i | 0.64i | 0.05i | 0.032i | 0.04i | 0.02i |
|   |   |   |   |   |   |   |   | (0.035i |   |   |
| 1 | 1 | 1 | 2 | 2 | -0.03i | 0.02i | 0.05i | 0.037i | 0.03i | 0.01i |

Table 5.5. Classical Estimates of the Generalized Phenomenological Cross Sections[a]

| Cross Section Indices | | | | | Final Rotor State | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_\ell$ | $K_j$ | $K_\ell'$ | $K_j'$ | $K$ | j=0 | j=2 | j=4 | j=6[b] | j=8 | j=10 | j=12 |
| 0 | 0 | 0 | 0 | 0 | -3.82 | -7.60 | -14.1 | 37.1 | -11.2 | -4.32 | -0.96 |
| 1 | 0 | 1 | 0 | 1 | -0.17 | -0.62 | -2.00 | 16.5 | -1.43 | -0.08 | 0.15 |
| 0 | 1 | 0 | 1 | 1 | -0.15 | -1.03 | -3.25 | 13.3 | -3.06 | -1.24 | -0.26 |
| 2 | 0 | 2 | 0 | 2 | 0.C01 | -0.09 | -1.01 | 11.2 | -0.56 | 0.06 | -0.005 |
| 0 | 2 | 0 | 2 | 2 | -1.18 | -0.60 | -1.64 | 6.91 | -1.34 | -0.58 | -0.13 |
| 1 | 1 | 1 | 1 | 0 | 0.05 | -0.11 | -0.50 | 6.60 | -0.34 | -0.12 | -0.02 |
| 1 | 1 | 1 | 1 | 1 | -0.04 | -0.26 | -0.89 | 4.E6 | -0.58 | 0.02 | 0.08 |
| 1 | 1 | 1 | 1 | 2 | -0.02 | -0.27 | -0.73 | 5.66 | -0.44 | -0.05 | 0.04 |
| 1 | 2 | 1 | 2 | 1 | -0.16 | -0.094 | -0.39 | 3.57 | -0.27 | -0.04 | 0.006 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.05000 eV. Cross sections are in square angstroms. The 6→6 cross sections are accurate to within 10%. All others are accurate to within a sign and an order of magnitude.

[b] The average of mixed cross sections appears in parentheses.

Table 5.5. (continued)

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | $j=0$ | $j=2$ | $j=4$ | $j=6$ | $j=8$ | $j=10$ | $j=12$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **Final Rotor State** | | | |
| 1 | 2 | 1 | 2 | 2 | 0.09 | -0.0006 | -0.36 | 3.54 | -0.30 | -0.004 | 0.04 |
| 1 | 2 | 1 | 2 | 3 | -0.04 | -0.10 | -0.37 | 3.66 | -0.25 | -0.04 | 0.02 |
| 1 | 0 | 1 | 2 | 1 | 0.29 | 0.46 | 0.42 | -0.849 (-0.86) | -0.25 | 0.04 | -0.04 |
| 1 | 2 | 1 | 0 | 1 | -0.36 | -0.02 | -0.24 | -0.871 | 0.15 | 0.19 | 0.07 |
| 2 | 0 | 0 | 2 | 2 | 0.08 | 0.12 | -0.10 | 0.040 (0.12) | -0.09 | 0.007 | 0.03 |
| 0 | 2 | 2 | 0 | 2 | 0.38 | 0.04 | 0.09 | 0.201 | -0.07 | 0.10 | 0.05 |
| 1 | 0 | 1 | 1 | 1 | 0.08i | 0.09i | 0.07i | -0.07i (-0.085i) | -0.09i | 0.11i | 0.02i |
| 1 | 1 | 1 | 0 | 1 | 0.06i | 0.04i | -0.16i | -0.10i | -0.04i | 0.15i | 0.03i |
| 1 | 2 | 1 | 1 | 1 | -0.22i | -0.23i | -0.41i | -0.319i (-0.32i) | -0.23i | -0.02i | 0.002i |
| 1 | 1 | 1 | 2 | 1 | -0.22i | -0.03i | -0.30i | -0.322i | -0.32i | -0.09i | -0.008i |
| 1 | 2 | 1 | 1 | 2 | 0.25i | 0.17i | 0.10i | 0.09i (0.090i) | 0.10i | 0.10i | 0.01i |
| 1 | 1 | 1 | 2 | 1 | 0.02i | 0.02i | 0.12i | 0.09i | 0.10i | 0.08i | 0.01i |

will be discussed in detail in Section 5.3.

Quantum mechanical calculation of generalized phenomenological cross sections and selected effective cross sections was carried out within the IOS (infinite order sudden) approximation for the $Ar-N_2$ potential surface mentioned previously. Calculations were not attempted for the $Ar-CO_2$ and $He-CO_2$ surfaces because of the large number of open scattering channels possessed by these systems. Also, the author had hoped to include CS (coupled states) and CC (close coupling) calculations in the present work, However, limitations of time and computational resources made this impossible. It is hoped that the IOS results presented will provide a convenient reference point appropriate to future work involving CS and CC approaches.

As with the classical trajectory work, the author received invaluable aid from a collaborator, namely Dr. Dale E. Fitz of the University of Houston, who provided a series of computer programs appropriate to IOS L-average calculations.

Values of L-average, L-initial, and L-final generalized phenomenological cross sections appear in Tables 5.6, 5.7, 5.8, and 5.9. As in the classical trajectory calculations, the initial rotor energy was chosen to correspond to a rotational quantum number of six. Similarly, three initial values of the relative translational kinetic energy were

Table 5.6. ICS L-average Values of the Generalized Phenomenological Cross Sections[a]

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6[b] | j=8 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | -3.44 | -9.69 | -18.5 | 60.5 | -18.0 |
| 1 | 0 | 1 | 0 | 1 | 0.0365 | -0.540 | -3.22 | 30.2 | -3.21 |
| 0 | 1 | 0 | 1 | 1 | 0.0 | -1.98 | -5.06 | 21.0 | -5.4 |
| 2 | 0 | 2 | 0 | 2 | -0.0102 | -0.157 | -1.21 | 22.5 | -1.20 |
| 0 | 2 | 0 | 2 | 2 | 0.0 | -0.812 | -2.30 | 13.4 | -2.79 |
| 1 | 1 | 1 | 1 | 0 | 0.0 | -0.324 | -0.996 | 11.4 | -1.06 |
| 1 | 1 | 1 | 1 | 1 | 0.0 | -0.124 | -1.05 | 9.49 | -1.04 |
| 1 | 1 | 1 | 1 | 2 | 0.0 | -0.204 | -1.03 | 10.3 | -1.05 |
| 1 | 2 | 1 | 2 | 1 | 0.0 | -0.193 | -0.611 | 6.47 | -0.632 |
| 1 | 2 | 1 | 2 | 2 | 0.0 | 0.0331 | -0.482 | 5.84 | -0.552 |
| 1 | 2 | 1 | 2 | 3 | 0.0 | -0.112 | -0.565 | 6.25 | -0.604 |
| 1 | 0 | 1 | 2 | 1 | 0.0 | -0.0688 | -0.224 | -1.04 | -0.189 |
| 1 | 2 | 1 | 0 | 1 | 0.0 | 0.617 | -0.217 | -1.04 | 0.380 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.01550 eV. All cross sections are in square angstroms.

[b] This is a rigorously closed channel.

Table 5.6.　(continued)

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6 | j=8 |
|----|----|----|----|----|------|------|------|------|------|
| | | | | | | | Final Rotor State | | |
| 2 | 0 | 0 | 2 | 2 | 0.0 | -0.0540 | -0.164 | 0.178 | -0.199 |
| 0 | 2 | 2 | 0 | 2 | 0.0936 | 0.0947 | -0.217 | 0.178 | -0.230 |
| 1 | 0 | 1 | 1 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 0 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 2 | 1 | 1 | 1 | 0.0 | -0.106i | -0.249i | -0.108i | -0.203i |
| 1 | 1 | 1 | 2 | 1 | 0.0 | -0.297i | -0.364i | -0.108i | -0.266i |
| 1 | 2 | 1 | 1 | 2 | 0.0 | -0.0474i | 0.111i | 0.0514i | 0.0906i |
| 1 | 1 | 1 | 2 | 2 | 0.0 | 0.133i | 0.163i | 0.0514i | 0.119i |

Table 5.7. IOS L-initial/L-final Values of the Generalized Phenomenological Cross Sections[a]

| $K_\ell$ $K_j$ $K'_\ell$ $K'_j$ $K$ | Final Rotor State | | | | |
|---|---|---|---|---|---|
| | $j=0$ | $j=2$ | $j=4$ | $j=6$ | $j=8$ [b] |
| 0  0  0  0  0 | -3.46 | -9.72 | -18.5 | 60.5 | -18.0 |
| 1  0  1  0  1 | 0.0336 | -0.547 | -3.22 | 30.2 | -3.21 |
| 0  1  0  1  1 | 0.0 | -1.98 | -5.06 | 21.0 | -5.48 |
| 2  0  2  0  2 | -0.0116 | -0.161 | -1.21 | 22.5 | -1.21 |
| 0  2  0  2  2 | 0.0 | -0.813 | -2.30 | 13.4 | -2.79 |
| 1  1  1  1  0 | 0.0 | -0.0617 | -0.660 | 9.21 | -0.668 |
| 1  1  1  1  1 | 0.0 | -0.257 | -1.22 | 10.6 | -1.23 |
| 1  1  1  1  2 | 0.0 | -0.179 | -0.994 | 10.0 | -1.01 |

Cross Section Indices

[a] Initial rotor state = 6; initial translational kinetic energy = 0.01550 eV. All cross sections are in squared angstroms.

[b] This is a rigorously closed channel.

[c] 0220(2) and 2002(2) have different L-initial and L-final values. The L-initial results appear first followed by the L-final results.

Table 5.7.   (continued)

| Cross Section Indices | | | | | Final Rotor State | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | K | j=0 | j=2 | j=4 | j=6 | j=8 |
| 1 | 2 | 1 | 2 | 1 | 0.0 | -0.0442 | -0.427 | 5.90 | -0.474 |
| 1 | 2 | 1 | 2 | 2 | 0.0 | -0.117 | -0.667 | 6.41 | -0.712 |
| 1 | 2 | 1 | 2 | 3 | 0.0 | -0.0702 | -0.513 | 6.08 | -0.559 |
| 1 | 2 | 1 | 0 | 1 | 0.0107 | -0.152 | -0.593 | 0.860 | -0.188 |
| 1 | 0 | 1 | 2 | 1 | 0.0 | -0.0194 | -0.114 | 0.830 | -0.535 |
| 0 | 2 | 2 | 0 | 2 c | 0.349 / 0.0058 | 0.834 / 0.070 | 0.882 / 0.360 | -1.55 / -0.512 | -0.142 / 0.120 |
| 2 | 0 | 0 | 2 | 2 | 0.0058 / 0.0 | 0.0032 / 0.0434 | 0.0834 / -0.207 | -0.512 / -1.55 | 0.322 / 0.673 |
| 1 | 0 | 1 | 1 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 0 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 2 | 1 | 0.0 | 0.0135i | 0.147i | -0.0910i | 0.0759i |
| 1 | 2 | 1 | 1 | 1 | 0.0 | 0.0481i | 0.101i | -0.0910i | 9.979(-2)i |
| 1 | 1 | 1 | 2 | 2 | 0.0 | -0.0060i | -0.0660i | 0.0407i | -0.0340i |
| 1 | 2 | 1 | 1 | 2 | 0.0 | -0.0022i | -0.045i | 0.0407i | -0.0446i |

Table 5.8. IOS L-initial/L-final Values of the Generalized Phenomenological Cross Sections[a]

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | Final Rotor State | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $j=0$ | $j=2$ | $j=4$ | $j=6$ | $j=8$ | $j=10$ |
| 0 | 0 | 0 | 0 | 0 | -3.53 | -8.50 | -14.1 | 53.2 | -13.6 | -7.51 |
| 1 | 0 | 1 | 0 | 1 | 0.032 | -0.518 | -2.61 | 23.8 | -2.61 | -0.531 |
| 0 | 1 | 0 | 1 | 1 | 0.0 | -1.48 | -3.75 | 18.6 | -4.25 | -2.39 |
| 2 | 0 | 2 | 0 | 2 | -0.024 | -0.101 | -1.08 | 16.7 | -1.07 | -0.105 |
| 0 | 2 | 0 | 2 | 2 | 0.0 | -0.635 | -1.67 | 11.6 | -2.01 | -1.13 |
| 1 | 1 | 1 | 1 | 0 | 0.0 | -0.058 | -0.555 | 6.94 | -0.563 | -0.039 |
| 1 | 1 | 1 | 1 | 1 | 0.0 | -0.270 | -0.998 | 8.20 | -1.02 | -0.249 |
| 1 | 1 | 1 | 1 | 2 | 0.0 | -0.181 | -0.827 | 7.70 | -0.827 | -0.165 |
| 1 | 2 | 1 | 2 | 1 | 0.0 | -0.045 | -0.362 | 4.62 | -0.415 | -0.069 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.02585 eV. All cross sections are in squared angstroms.

[b] 0220(2) and 2002(2) have different L-initial and L-final values. The L-initial results appear first followed by the L-final results.

Table 5.8. (continued)

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | $j=0$ | $j=2$ | $j=4$ | $j=6$ | $j=8$ | $j=10$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **Final Rotor State** | | | |
| 1 | 2 | 1 | 2 | 2 | 0.0 | -0.116 | -0.557 | 5.04 | -0.605 | -0.14 |
| 1 | 2 | 1 | 2 | 3 | 0.0 | -0.064 | -0.425 | 4.78 | -0.470 | -0.094 |
| 1 | 2 | 1 | 0 | 1 | -0.080 | -0.150 | -0.474 | 0.742 | -0.141 | -0.075 |
| 1 | 0 | 1 | 2 | 1 | 0.0 | -0.018 | -0.075 | 0.742 | -0.427 | -0.142 |
| 0 | 2 | 2 | 0 | 2[b] | 0.360 / -0.017 | 0.729 / 0.130 | 0.683 / 0.326 | -1.22 / -0.472 | -0.170 / 0.131 | -0.055 / 0.021 |
| 2 | 0 | 0 | 2 | 2 | 0.0 / 0.0 | 0.009 / -0.005 | 0.096 / -0.182 | -0.472 / -1.22 | 0.319 / 0.489 | 0.026 / 0.524 |
| 1 | 0 | 1 | 1 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 0 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 2 | 1 | 0.0 | 0.017i | 0.132i | -0.103i | 0.065i | -0.003i |
| 1 | 2 | 1 | 1 | 1 | 0.0 | 0.003i | 0.090i | -0.103i | 0.086i | -0.004i |
| 1 | 1 | 1 | 2 | 2 | 0.0 | -0.008i | -0.059i | 0.0485i | -0.029i | 0.001i |
| 1 | 2 | 1 | 1 | 1 | 0.0 | -0.001i | -0.004i | 0.0485i | -0.039i | 0.020i |

232

Table 5.9. IOS L-initial/L-final Values of the Generalized Phenomenological
Cross Sections[a]

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6 | j=8 | j=10 | j=12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cross Section Indices | | | | Final Rotor State | | | | | | |
| 0 | 0 | 0 | 0 | 0 | -3.30 | -6.62 | -10.6 | 42.5 | -10.0 | -6.81 | -3.68 |
| 1 | 0 | 1 | 0 | 1 | -0.056 | -0.532 | -1.79 | 16.8 | -1.79 | -0.541 | 0.049 |
| 0 | 1 | 0 | 1 | 1 | 0.0 | -0.892 | -2.39 | 15.7 | -2.85 | -1.64 | -1.25 |
| 2 | 0 | 2 | 0 | 2 | 0.049 | -0.060 | -0.879 | 11.4 | -0.881 | -0.085 | 0.072 |
| 0 | 2 | 0 | 2 | 2 | 0.0 | -0.399 | -1.04 | 9.58 | -1.32 | -0.938 | -0.580 |
| 1 | 1 | 1 | 1 | 0 | 0.0 | -0.051 | -0.415 | 5.06 | -0.413 | -0.041 | -0.025 |
| 1 | 1 | 1 | 1 | 1 | 0.0 | -0.286 | -0.714 | 6.01 | -0.712 | -0.261 | -0.056 |
| 1 | 1 | 1 | 1 | 2 | 0.C | -0.197 | -0.588 | 5.64 | -0.591 | -0.180 | -0.058 |
| 1 | 2 | 1 | 2 | 1 | 0.0 | -0.040 | -0.247 | 3.24 | -0.285 | -0.72 | -0.007 |

[a] Initial rotor state = 6; initial translational kinetic energy = 0.050 eV.
All cross sections are in squared angstroms.

[b] 0220(2) and 2002(2) have different L-initial and L-final values. The
L-initial results appear first followed by the L-final results.

Table 5.9. (continued)

| Cross Section Indices | | | | | Final Rotor State | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | j=0 | j=2 | j=4 | j=6 | j=8 | j=10 | j=12 |
| 1 | 2 | 1 | 2 | 2 | 0.0 | -0.091 | -0.346 | 3.34 | -0.394 | -0.141 | -0.023 |
| 1 | 2 | 1 | 2 | 3 | 0.0 | -0.065 | -0.279 | 3.57 | -0.323 | -0.101 | -0.012 |
| 1 | 2 | 1 | 0 | 1 | -0.030 | -0.151 | -0.301 | 0.609 | -0.047 | -0.071 | -0.040 |
| 1 | 0 | 1 | 2 | 1 | 0.0 | -0.009 | 0.001 | 0.609 | -0.275 | -0.142 | -0.085 |
| 0 | 2 | 2 | 0 | 2[b] | 0.327 / 0.026 | 0.582 / 0.026 | 0.509 / 0.272 | -0.847 / -0.429 | -0.159 / 0.125 | -0.060 / 0.035 | 0.040 / -0.100 |
| 2 | 0 | 0 | 2 | 2 | 0.0 / 0.0 | 0.019 / -0.040 | 0.093 / -0.120 | -0.429 / -0.847 | 0.251 / 0.331 | 0.040 / 0.320 | -0.025 / 0.280 |
| 1 | 0 | 1 | 1 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 0 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 1 | 2 | 1 | 0.0 | 0.048i | 0.119i | -0.089i | 0.056i | -0.002i | -0.010i |
| 1 | 2 | 1 | 1 | 1 | 0.0 | 0.018i | 0.081i | -0.089i | 0.073i | 0.001i | -0.020i |
| 1 | 1 | 1 | 2 | 2 | 0.0 | -0.021i | -0.052i | 0.0432i | -0.026i | -0.001i | 0.005i |
| 1 | 2 | 1 | 1 | 2 | 0.0 | -0.013i | -0.037i | 0.0432i | -0.034i | -0.011i | 0.100i |

chosen as 0.01550 eV, 0.02585 eV, and 0.0500 eV. It should
be noted that the lowest energy, 0.01550 eV, was used in this
case intead of 0.00500 eV as in the classical case. The
reason for this is twofold. First, the WKB phase shifts cal-
culated using Pack's method(69) cannot be obtained since
0.00500 eV falls near an extremum of the potential for some
partial waves. Second and more importantly, the IOS approach
is likely to be greatly in error for this energy anyway,
since the collisional rotational energy change is a large
fraction of the relative translational energy. A detailed
comparison of IOS and classical trajectory results will be
given in the next section.

Values of selected effective cross sections within the
IOS approximation were obtained via the following equation,

$$\{ [\Phi_M^{K_\ell,K_j}]_Q^K, [\Phi_{M'}^{K'_\ell,K'_j}]_Q^K \}_{v,\omega} =$$

$$[\frac{8kT}{\pi\mu_{v\omega}}]^{\frac{1}{2}} K_\ell ! K'_\ell ! [\frac{2^{K_\ell+K'_\ell}}{(2K_\ell)!(2K'_\ell)!}]^{\frac{1}{2}} \sum_{jj'} \exp[-\frac{\theta_r}{T} j'(j'+1)]$$

$$<j||S_q^{(t)}(\bar{\Omega}^2)[\underline{\Omega}]^{(K_j)}||j><j'||S_{q'}^{(t')}(\bar{\Omega}^2)[\underline{\Omega}]^{(K'_j)}||j'> \quad (5.2-6)$$

$$\int_0^\infty d\epsilon' \, e^{-\epsilon'} \epsilon'^{\frac{1}{2}s'} \, \epsilon^{\frac{1}{2}s} \, \sigma_{jj;j'j'}^{K_\ell K_j;K'_\ell K'_j}(K)$$

This expression follows directly from Eq. (4.6-21) where one
notes that $\epsilon = \gamma^2$ and $\epsilon' = \gamma'^2$ and one drops superfluous sub-

scripts, "i" and "f." The integral over the translational

energy is easily evaluated as a Gauss-Laguerre quadrature.

Values of the generalized phenomenological cross sections at

the appropriate quadrature points were obtained by graphical

interpolation between values obtained at the three test

translational energies. A three point quadrature was found

to converge sufficiently for the purposes of this work.

These results will be presented and discussed in Section 5.4.

### 5.3. Comparison of the Numerical Values of the Generalized
### Phencmenological Cross Sections

The generalized phenomenological cross sections appro-

priate to the kinetic theory of gases (i.e. spectroscopic

subscripts "i" and "f" are ignored) can be classified as

"unmixed," "mixed real," and "mixed imaginary." The unmixed

cross sections are characterized by $K_\ell = K_\ell'$ and $K_j = K_j'$, the

mixed real cross sections are characterized by $K_\ell + K_\ell'$ and $K_j$

$+K_j'$, both even, and the mixed imaginary cross sections are

characterized by $K_\ell + K_\ell'$ even and $K_j + K_j'$ odd. Only the unmixed

cross sections have nonvanishing spherical limits.

To begin detailed comparison of the numerical values,

one should investigate IOS values of the cross sections ob-

tained using each of the three labeling schemes (i.e. L-

average, L-initial, and L-final). Appropriate data has been

presented in Tables 5.6, 5.7, 5.8, and 5.9.

At the outset, one should note that L-initial and L-final results are identical if $K_\ell = K'_\ell$. (This point is discussed in Section 4.7.) Thus, of the quantities evaluated, only the 2002(2) and 0220(2) mixed real cross sections can have different L-initial and L-final values. The results given in Tables 5.7, 5.8, and 5.9 show these values to be in very poor agreement.

It is more profitable to compare L-average with L-initial/L-final results. One finds excellent agreement (to three decimal places) between values of the 0000(0), 1010(1), 0101(1), 2020(2), and 0202(2) cross sections. Only fair agreement is found between the remaining unmixed cross sections (1111(K) and 1212(K)). Finally, the mixed cross sections (both real and imaginary) show very poor agreement (disregarding the 1011(1) and 1110(1) cross sections for which all IOS values trivially vanish).

Digressing briefly, it is possible in general to relate the usual degeneracy averaged integral cross section to the 0000(0) cross section via the expression,

$$\sigma_{jj;j'j'}^{00;00}(0) = -[\frac{2j'+1}{2j+1}]^{\frac{1}{2}}\sigma(j'\to j) + \delta_{jj'}\sum_{j''}[\frac{2j'+1}{2j''+1}]^{\frac{1}{2}}\sigma(j'\to j'') \qquad (5.3-1)$$

Equation (5.3-1) is easily obtained from Eq. (4.6-22) by sub-

stitution of the appropriate tensor indices and rotor quantum
numbers followed by use of the optical theorem. The
degeneracy averaged integral cross section has the explicit
form,

$$\sigma(j' \to j) = \frac{\pi}{K_{j'}^2} \sum_{J=0}^{\infty} \left(\frac{2J+1}{2j'+1}\right) \sum_{\ell \ell'} |T^J(j\ell|j'\ell')|^2 \qquad (5.3-2)$$

where $T^J(j\ell|j'\ell')$ is an Arthurs and Dalgarno T-matrix ele-
ment.

Pack(70) has used the same $Ar-N_2$ potential as used in
this work to calculate CC and IOS values of $\sigma(j' \to j)$. Direct
comparison of Pack's IOS results to this work via Eq. (5.3-1)
for an initial relative translational energy of 0.02585 eV
results in virtually exact agreement. Pack's data appear in
Table V of the above reference. Furthermore, Pack has found
that classical trajectory and CC degeneracy averaged integral
cross sections exhibit excellent agreement for an initial
translational energy of 0.03878 eV. Thus, it is the opinion
of this worker that quantal corrections are negligible for
the cases considered and that the Monte Carlo results are
good estimates of the rigorous cross sections.

Detailed numerical comparisons will now be drawn between
the classical trajectory and IOS data. Here it is important
that the reader take notice of the inherent random error as-
sociated with Monte Carlo methods and the low frequency of
strongly inelastic collisions for this $Ar-N_2$ potential

surface. It follows that Monte Carlo values of the rotationally "off-diagonal" (i.e. $j \neq j'$) cross sections should be regarded as providing estimates only good to within an order of magnitude and as having the correct sign. The Monte Carlo values of the rotationally "diagonal" cross sections (i.e. $j=j$) are much more accurate (within 10 percent) owing to the larger number of trajectories used to construct the estimate. Table 5.10 presents Monte Carlo and IOS values of $\sigma_{66;66}^{K_\ell K_j; \; K'_\ell K'_j}(K)$ for comparison. It is evident that the agreement between Monte Carlo and IOS results improves with increasing energy. This is, of course, the expected result. More importantly, it is clear that the L-average labeling scheme gives better agreement with the Monte Carlo results than does the L-initial/L-final results differ in sign from the L-average and Monte Carlo results. Also, the L-average results show better agreement with Monte Carlo results than do the L-initial/L-final results for unmixed cross sections, 1111(K) and 1212(K). One also observes that diagonal values of unmixed cross sections with $K_\ell = 0$ are systematically too large. In contrast, for unmixed cross sections with $K_j = 0$ and $K_\ell \neq 0$, there is very good agreement between the classical trajectory and IOS results.

The reader should note that nonzero values of the 1110(1) and 1011(1) cross sections are given by Monte Carlo methods. A plot of the Monte Carlo contribution to the "di-

Table 5.10. Comparison of Monte Carlo and IOS Values of the $6 \to 6$ Generalized Phenomenological Cross Sections[a]

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | $K$ | CT ($0.0155$ eV $= E_k$) | IOS | ICS $\bar{L}$ | CT ($0.02585$) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 42.4 | 60.5 | 60.5 | 36.5 |
| 1 | 0 | 1 | 0 | 1 | 27.2 | 30.2 | 30.2 | 19.5 |
| 0 | 1 | 0 | 1 | 1 | 20.1 | 21.0 | 21.0 | 13.2 |
| 2 | 0 | 2 | 0 | 2 | 25.1 | 22.5 | 22.5 | 17.7 |
| 0 | 2 | 0 | 2 | 2 | 11.4 | 13.4 | 13.4 | 8.81 |
| 1 | 1 | 1 | 1 | 0 | 11.2 | 9.21 | 11.4 | 8.02 |
| 1 | 1 | 1 | 1 | 1 | 8.25 | 10.6 | 9.49 | 5.69 |
| 1 | 1 | 1 | 1 | 2 | 9.95 | 10.0 | 10.3 | 6.73 |
| 1 | 2 | 1 | 2 | 1 | 6.40 | 5.90 | 6.47 | 4.32 |
| 1 | 2 | 1 | 2 | 2 | 4.77 | 6.41 | 5.84 | 3.57 |
| 1 | 2 | 1 | 2 | 3 | 5.89 | 6.08 | 6.25 | 4.16 |
| 1 | 0 | 1 | 2 | 1 | -2.25 | 0.830 | -1.04 | -1.23 |
| 1 | 2 | 1 | 0 | 1 | -2.25 | 0.830 | -1.04 | -1.23 |
| 2 | 0 | 0 | 2 | 2 | 0.055 | -1.551 -0.512 | 0.178 | 0.050 |
| 0 | 2 | 2 | 0 | 2 | 0.055 | -0.512 -1.551 | 0.178 | 0.050 |
| 1 | 0 | 1 | 1 | 1 | -0.266i | 0.0 | 0.0 | -0.300i |
| 1 | 1 | 1 | 0 | 1 | -0.266i | 0.0 | 0.0 | -0.300i |

a  All cross sections are in squared angstroms and the values are accurate to within 10%.

| eV = $E_k$ | | 0.0500 eV = $E_k$ | | |
| --- | --- | --- | --- | --- |
| IOS | IOS $\bar{L}$ | CT | IOS | IOS $\bar{L}$ |
| 53.2 | 53.2 | 37.1 | 42.5 | 42.5 |
| 23.8 | 23.8 | 16.5 | 16.8 | 16.8 |
| 18.6 | 18.6 | 13.3 | 15.7 | 15.7 |
| 16.7 | 16.7 | 11.2 | 11.4 | 11.4 |
| 11.6 | 11.6 | 6.91 | 9.58 | 9.58 |
| 6.94 | 8.70 | 6.60 | 5.06 | 6.48 |
| 8.20 | 7.32 | 4.86 | 6.01 | 5.31 |
| 7.70 | 7.93 | 5.66 | 5.64 | 5.79 |
| 4.62 | 5.06 | 3.57 | 3.24 | 3.61 |
| 5.04 | 4.57 | 3.54 | 3.34 | 3.30 |
| 4.78 | 4.82 | 3.66 | 3.57 | 3.47 |
| | | | | |
| 0.742 | -0.764 | -0.860 | 0.609 | -0.442 |
| 0.742 | -0.764 | -0.860 | 0.609 | -0.442 |
| -1.22 / -0.472 | 0.195 | 0.120 | -0.847 / -0.429 | 0.196 |
| -0.472 / -1.22 | 0.195 | 0.120 | -0.429 / -0.847 | 0.196 |
| 0.0 | 0.0 | -0.0851 | 0.0 | 0.0 |
| 0.0 | 0.0 | -0.0851 | 0.0 | 0.0 |

Table 5.10 (continued)

| $K_\ell$ | $K_j$ | $K'_\ell$ | $K'_j$ | K | CT | IOS | IOS L | CT |
|---|---|---|---|---|---|---|---|---|
| Cross Section Indices | | | | | 0.0155 eV = $E_k$ | | | 0.02585 |
| 1 | 2 | 1 | 1 | 1 | -0.511i | -0.0910i | -0.108i | -0.210i |
| 1 | 1 | 1 | 2 | 1 | -0.511i | -0.0910i | -0.108i | -0.210i |
| 1 | 2 | 1 | 1 | 2 | 0.201i | 0.0407i | 0.0514i | 0.035i |
| 1 | 1 | 1 | 2 | 2 | C.201i | 0.04C7i | 0.0514i | 0.035i |

| eV = $E_k$ | | 0.0500 eV = $E_k$ | | |
|---|---|---|---|---|
| ICS | ICS $\bar{L}$ | CT | IOS | IOS $\bar{L}$ |
| -0.103i | -0.104i | -0.320i | -0.C89i | -0.108i |
| -0.103i | -0.104i | -0.320i | -0.089i | -0.108i |
| C.0485 | 0.0500i | 0.090i | 0.0452i | 0.0535i |
| 0.0485 | 0.0500i | 0.090i | 0.0452i | 0.0535i |

agonal" 1110(1) cross section versus impact parameter appears in Fig. 5.3. From this plot, it is clear that the "diagonal" 1110(1) cross section is the difference of two nearly equal contributions (which are exactly equal within the IOS approximation).

In conclusion, it should be mentioned that the magnitudes of IOS values of cross sections which involve an increase in rotational energy (i.e. j'→j where j>j') are systematically too large. In fact, the IOS approach gives nonvanishing contributions in energetically closed channels. This obviously incorrect behavior is characteristic of the IOS approximation and is also observed in IOS calculations of degeneracy averaged integral cross sections. Thus, if one makes use of IOS results to evaluate physical quantities (e.g. transport coefficients), one should ignore such unphysical cross sections.

This section can be summarized by the following conclusions. First, the L-average IOS calculations are in better agreement with the Monte Carlo results than the IOS L-initial/L-final calculations. This is not surprising because L-average labeling preserves time reversal invariance while L-initial/L-final labeling does not. Second, the IOS approximation gives poor results for cross sections which are most sensitive to angular momentum reorientation (i.e. the mixed cross sections). This is especially true for
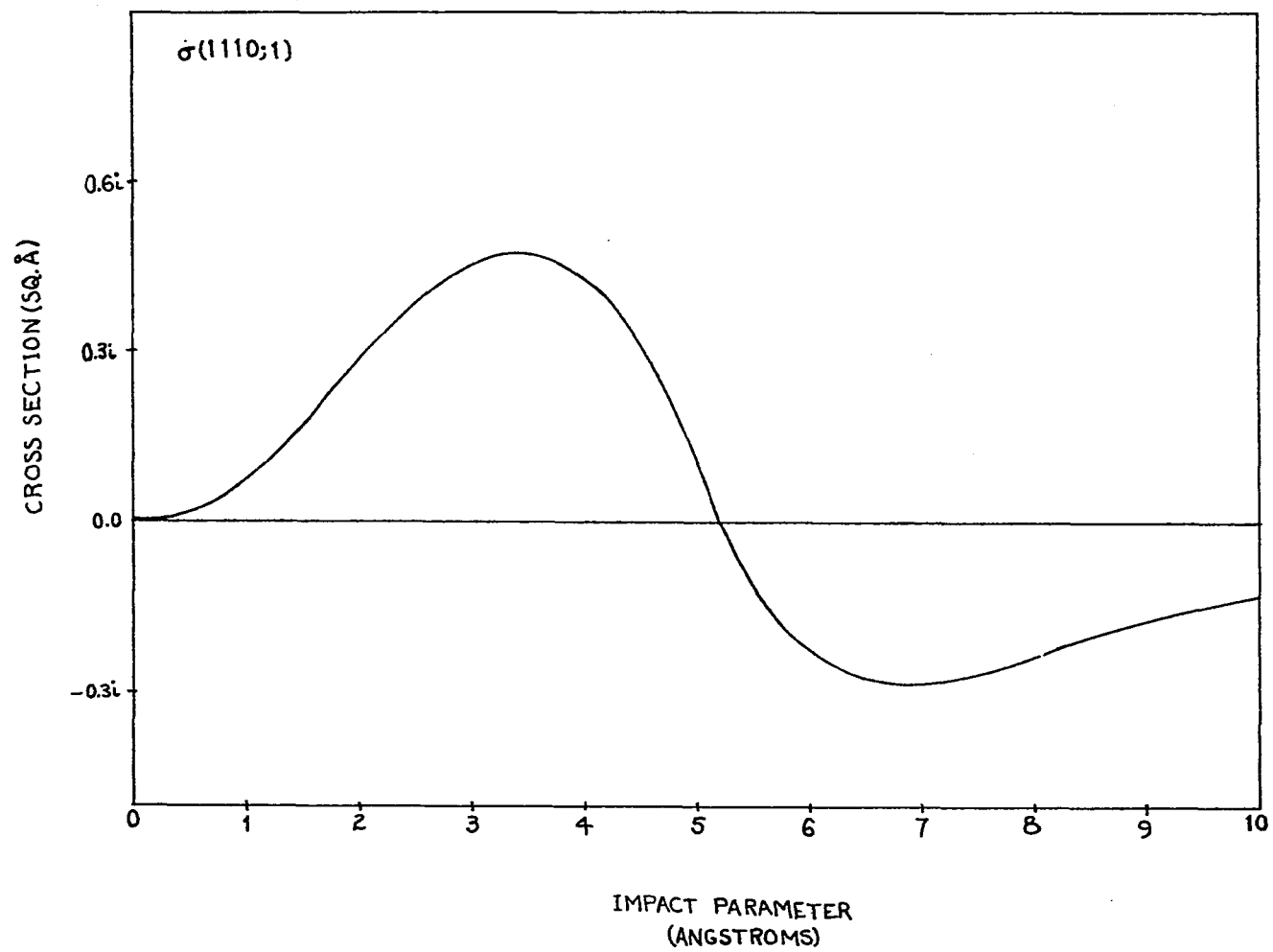
Fig. 5.3. Convergence of $\sigma(1110;1)$ as a Function of Impact Parameters

L-initial/L-final labeling. Finally, material disagreement between IOS and classical trajectory results in the cases considered are overwhelmingly due to the approximate nature of IOS dynamics rather than to quantum effects. Complete verification of this last conclusion must await accurate CC calculations.

### 5.4. Comparison of the Numerical Values of the Effective Collision Cross Sections

As stated previously, it is convenient to compare theoretical and experimental results at the level of the effective collision cross sections rather than that of the actual transport coefficients. In fact, results of experimental studies of gas phase transport processes are now customarily reported in terms of effective cross sections.

One source of experimental data which can be used for comparison with theoretical results is embodied in published values of Lennard-Jones force constants which are then used to evaluate the appropriate Chapman-Cowling integrals. Such data, of course, can only be profitably applied to effective cross sections which possess a dominant spherical contribution. Table 5.11 gives Lennard-Jones values in squared angstroms for the predominantly spherical cross section, $G\left(\begin{smallmatrix} 1000\,\beta \\ 1000\,\beta \end{smallmatrix}\right)_{\alpha\beta}$ . These values agree well with the Monte Carlo

results. Thus, one can conclude that the theoretical poten-

tial surfaces considered in this work are realistic in a

spherical sense (at least).

Table 5.11. Comparison of Values of $G\begin{pmatrix} 1000,\beta \\ 1000'\beta \end{pmatrix}_{\alpha\beta}$

| Potential Surface | $Ar-CO_2$ 300°K | $Ar-CO_2$ 900°K | $Ar-CO_2$ 1800°K | $He-CO_2$ 300°K | $He-CO_2$ 900°K | $He-CO_2$ 1800°K | $Ar-N_2$ 300°K |
|---|---|---|---|---|---|---|---|
| Lennard[a] Jones 6-12 | 29.3 | 22.1 | 19.5 | 2.96 | 2.47 | 2.22 | 29.8 |
| Realistic[b] | 26.2[c] | 19.6 | 17.4 | 3.08 | 2.58 | 2.27 | 29.1 |

[a] Force constants obtained from data given by Hirschfelder, Curtiss, and Bird(40) via the usual combination rules.

[b] Monte Carlo estimates from Table 5.1.

[c] Both $Ar-CO_2$(I) and $Ar-CO_2$(II) give the same value.

However, the nonspherical contribution to a molecular

interaction is much more difficult to investigate than the

spherical contribution. As stated in Chapter 1, analysis of

Senftleben-Beenakker effects (on the thermal diffusion coef-

ficient in particular) is one means of obtaining rather

direct information of this kind. t'Hooft(51) has given ex-

perimental values of depolarization cross sections obtained

from measurements of thermal diffusion Senftleben-Beenakker

effects in an $Ar-N_2$ mixture at 300°K. Specifically, experi-

mental values of $G\left(\begin{smallmatrix}1000 & \beta \\ 1200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ and $G\left(\begin{smallmatrix}1010 & \beta \\ 1200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ of $0.66$ $A^2$ and

$-5.4$ $A^2$ respectively, have been given. These values do not

at all agree with the theoretical values of $0.111$ $\overset{\circ}{A}{}^2$ and $0.292$

$\overset{\circ}{A}{}^2$ (given in Table 5.1). In contrast, experimental values of

the diagonal cross sections, $G\left(\begin{smallmatrix}1100 & \beta \\ 1100 & \beta\end{smallmatrix}\right)_{\alpha\beta} = 26.0$ $\overset{\circ}{A}{}^2$ and

$G\left(\begin{smallmatrix}1200 & \beta \\ 1010 & \beta\end{smallmatrix}\right)_{\alpha\beta} = 46.7$ $\overset{\circ}{A}{}^2$ are in much better agreement with the

theoretical results ($28.1$ $\overset{\circ}{A}{}^2$ and $53.8$ $\overset{\circ}{A}{}^2$, respectively).

These cross sections, however, have a significant spherical

contribution which makes this agreement not surprising. Fi-

nally, t'Hooft observes a value of $24.0$ $\overset{\circ}{A}{}^2$ for the cross sec-

tion $G\left(\begin{smallmatrix}0200 & \beta \\ 0200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$. The theoretical value is $7.12$ $\overset{\circ}{A}{}^2$. The

reader should note that $G\left(\begin{smallmatrix}0200 & \beta \\ 0200 & \beta\end{smallmatrix}\right)_{\alpha\beta}$ is highly sensitive to

the gross anisotropy of the potential surface in the direc-

tion parallel to the symmetry axis of the diatom. Comparison

of the theoretical and experimental results suggests that the

$Ar-N_2$ surface considered in this work is much too spherical

and not at all realistic.

Unfortunately, it appears that no experimental measure-

ments of Senftleben-Beenakker effects appropriate to $Ar-CO_2$

and $He-CO_2$ systems have been made to date. This makes it im-

possible to determine if the $Ar-CO_2$(I) surface or

$Ar-CO_2$(II) is more realistic.

Table 5.12 presents IOS values of selected effective

collision cross sections. In agreement with results given

previously for the generalized phenomenological cross sec-

Table 5.12. Values of Effective Cross Sections:
IOS and Classical Trajectory Results for
the Pattengill et al. Ar-N$_2$ Potential Surface

| Cross Section[a] | Classical Trajectory[b] | IOS | Percent Deviation | GPCS[c] used |
|---|---|---|---|---|
| $G\left({}^{1000}_{1000}\Big|{}^{\beta}_{\beta}\right)_{\alpha\beta}$ | 29.1(1.8) | 30.1 | 3.4 | 1010(0) |
| $G\left({}^{1010}_{1010}\Big|{}^{\beta}_{\beta}\right)_{\alpha\beta}$ | 39.7(5.9) | 43.1 | 8.6 | 2020(2) 1010(1) 0000(0) |
| $G\left({}^{1001}_{1001}\Big|{}^{\beta}_{\beta}\right)_{\alpha\beta}$ | 35.0(8.6) | 49.8 | 42.3 | 1010(1) 0000(0) |
| $G\left({}^{0200}_{0200}\Big|{}^{\beta}_{\beta}\right)_{\alpha\beta}$ | 7.12(3.7) | 35.6 | 400. | 0202(2) |
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 159.9(3.4) | 144.4 | -9.7 | 2020(2) |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | -4.68(3.7) | -22.1 | 372. | 0000(0) |

[a]  All cross sections are given in units of squared angstroms.

[b]  An estimate of the percent relative standard deviation
appears in the parentheses.

[c]  Generalized phenomenological cross section.

tions, one finds that the effective cross sections which contain thermal averages over the 0000(0) or 0202(0) cross sections show a significant positive deviation. Conversely, those which depend on thermal averages over the 1010(1) and/or 2020(2) cross sections but not the previously mentioned ones, agree well with the Monte Carlo results.

## 5.5. Comparison of Hard and Soft Spherocylinder Models to Classical Trajectory Results

Expressions for scalar collision integrals appropriate to hard convex ovaloid interactions were given in Section 4.3. Verlin, Matzen, and Hoffman(64) have extended this approach to an approximate treatment of soft nonspherical molecular models. The essence of this technique involves the modification of Eq. (4.3-7) to obtain a collision kernel appropriate to convex core soft interactions. It has the following form,

$$\langle \underline{p}_1 \underline{\ell}_1 \underline{p}_2 | \Theta | \underline{p}_1' \underline{\ell}_1' \underline{p}_2' \rangle =$$

$$\frac{\ell_1'}{\pi} \int_0^{2\pi} d\eta \{ \int_{\hat{k}\cdot\underline{g}\leqslant 0 \atop \text{unit} \atop \text{hemisphere}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) K \,\hat{k}\cdot\underline{g}\delta(\underline{p}'-\underline{p})\delta(\underline{\ell}_1'-\underline{\ell}_1) +$$

$$\int_{\hat{k}\cdot\underline{g}>0 \atop \text{unit} \atop \text{hemisphere}} d\hat{k} S_{\sigma_{1,2}}(\hat{k}) K\hat{k}\cdot\underline{g}\delta(\underline{p}'-\underline{p}+\frac{2\mu_{\alpha\beta}}{D}\underline{g}\cdot\hat{k}\hat{k})\delta(\underline{\ell}_1'-\underline{\ell}_1-\frac{2\mu_{\alpha\beta}}{D}\underline{g}\cdot\hat{k}\underline{a})\}\delta(\underline{P}-\underline{P}')$$

$$(5.5-1)$$

Here, a dimensionless scaling factor, $K$, has been included within the integrand and the surface, $\sigma_{1,2}$, is given a more general definition than in Section 4.3. Thus, $\sigma_{1,2}$ is identified as the convex equipotential surface upon which the molecular interaction energy vanishes. In the limiting case of a "hard" interaction it becomes the surface containing the "excluded volume." All other quantities appearing in Eq. (5.5-1) retain the same definitions as given earlier.

If one carries through with the operator method given by Eqs. (4.3-9) through (4.3-17), one obtains an expression identical to Eq. (4.3-18) where the tensor quantity $(u,v)_n$ has the form,

$$(u,v)_n =$$

$$\int_{E^{n-1}} d\underline{c}\, e^{-c^2} \int_0^\infty d\varepsilon_K\, e^{-\varepsilon_K^2} K[(\underline{c}-\varepsilon_K\hat{\kappa})^u - (\underline{c}+\varepsilon_K\hat{\kappa})^u](\underline{c}-\varepsilon_K\hat{\kappa})^v \varepsilon_K \quad (5.5-2)$$

Equation (5.5-2) is identical to Eq. (4.3-19) except for the appearance of $K$ in the integrand.

Following Verlin, Matzen, and Hoffman(64), one can argue that since the component of the generalized momentum, $\underline{\varepsilon}$, along the generalized apse vector, $\hat{\kappa}$, ($\hat{\kappa} = (\hat{R}_1 - \underline{a})/D$) changes sign on collision, it follows that $\underline{\varepsilon}$ is orthogonal to $\hat{\kappa}$ for an odd number of times during a molecular encounter. The

temporally central perpendicular configuration defines the apse point of the collision.

In general, $K$ is a very complicated function of orientation and momenta and the integrals indicated in Eq. (5.5-2) cannot be carried out analytically. However, one class of models exists for which $K$ can be simplified approximately. These are designated as "Kihara models" after Kihara who introduced them in 1951(71). A Kihara interaction potential models molecular interactions as impenetrable hard cores which interact via a potential, $\phi$, which is solely a function of the shortest distance, $\delta$, between the cores (i.e. $\phi(\delta)$ is of spherical form). Thus, molecular forces are directed along a vector connecting points of closest approach of the cores and molecular torques can be thought of as arising from the application of the force on a given molecule at the closest approach point on its core. It follows that the direction of forces and "moment arms" for the torques are independent of the magnitude of the molecular separation and depend only on molecular orientations and the direction of the unit vector, $\hat{k}$, which is perpendicular to the surface of each core at its point of closest approach. Examples of a Kihara interaction are afforded by soft spherical potential models and rigid ovaloids.

Again, following Verlin, Matzen, and Hoffman, it is assumed that for a Kihara interaction, the generalized force

(defined as $\underline{f} = \frac{d\varepsilon}{dt}$) is parallel to the apse vector at the apse point of a collision. Such an assumption is rigorously valid for both soft spherical models and rigid ovaloids under the assumption that chattering collisions can be neglected. One further assumes that for a Kihara potential, the scaling factor has the explicit form,

$$K = \frac{J_\phi}{r_m^2} . \qquad (5.5\text{-}3)$$

Here $J_\phi$ is the spherical differential cross section appropriate to the intercore potential, $\phi$. The distance, $r_m$, is characterized by $\phi(r_m) = 0$. This form of $K$ depends on $\tilde{\kappa}$ solely through the quantity $\tilde{\kappa} \cdot \underline{\varepsilon}$ and reduces to the soft spherical and rigid ovaloid expressions in the appropriate limits. Physically, the assumed momentum dependence of $\kappa$ is that appropriate to a spherical model but with a sphere radius and sphere center which depend on the molecular orientations and the closest approach surface normal at the apse point.

These assumptions allow the "u,v tensors" to be evaluated, when u+v is even, in terms of the usual reduced Chapman-Cowling omega integrals appropriate to the intercore potential, $\phi$. If u+v is odd, the spherical integrals obtained can be thought of as a generalization of $\Omega^{(\ell,\Delta)\star}$ to half-integer values of s. Substitution of these forms into Eq. (4.3-23)

yields expressions for the scalar collision integrals which involve the Chapman-Cowling omega integrals and the surface integrals, $\chi^{(n)}$, $T^{(n,m)}$, and G which are defined in Eqs. (4.3-26), (4.3-27), and (4.3-28).

For several reasons within the context of this analysis a spherocylinder proves to be an advantageous choice of core shape appropriate to the linear species, $\beta$. First and foremost, the shapes of the inner repulsive parts of potential surfaces, $Ar-CO_2(I)$ and $Ar-CO_2(II)$, are closely approximated by a spherocylinder. (Here one notes that the excluded volume appropriate to a rigid spherocylinder-sphere collision is also a spherocylinder.) Second, surface area integrals for spherocylindrical excluded volumes can be evaluated analytically. Last, a large body of literature exists which details the evaluation of transport properties using spherocylindrical models(72,73).

It should be noted here that a spherocylinder is not convex (i.e. surface points and normal unit vectors cannot be uniquely associated). This presents no problem (as expected since convexity was assumed just for mathematical convenience) and thus spherocylinder surface integrals can be performed in a piecewise fashion over spherical and cylindrical regions. The basic surface integrals, $\chi^{(n)}$, $T^{(n,m)}$, and G take the spherocylinder forms,

$$\chi^{(n)} = \frac{2A^n}{R^n}\{r_o^2\int_0^1 dz\,[\frac{A^2}{R^2}+1-z^2]^{-n/2} + r_o R\int_0^1 dz\,[\frac{A^2}{R^2}+z^2]^{-n/2}\} \quad (5.5-4)$$

$$T^{(n,m)} = \frac{2A^n r_o^2}{R^n}\int_0^1 dz\,z^m[\frac{A^2}{R^2}+1-z^2]^{-n/2} \quad (5.5-5)$$

$$G = \frac{2A^{3/2}}{R^{3/2}}r_o^2\int_0^1 dz\,z(1-z^2)\,[\frac{A^2}{R^2}+1-z^2]^{-1} \quad (5.5-6)$$

where A is a length defined by $[I_\beta/\mu_{\alpha\beta}]^{\frac{1}{2}}$, $r_o$ is the spherical radius and R is the cylindrical dimension. Figure 5.4 illustrates the geometry of spherocylindrical molecular models. For this work, explicit expressions for $\chi^{(-1)}$, $\chi^{(1)}$, $\chi^{(3)}$, $\chi^{(5)}$, $\chi^{(1,2)}$, $\chi^{(3,2)}$, and G are needed. These are given below in terms of the dimensionless parameter $\eta$ (equal to arc $\sin(R/\sqrt{A^2+R^2})$ which ranges from 0 to $\pi/2$.

$$\chi^{(-1)} = r_o^2\{\{1+\frac{\eta}{\sin\eta\cos\eta}\} + \frac{R}{r_o}\{\frac{1}{\cos\eta}+\frac{1}{\tan\eta}\ell n(\tan\eta+\frac{1}{\cos\eta})\}\}(5.5-7)$$

$$\chi^{(1)} = \frac{2r_o^2}{\tan\eta}\{\eta + \frac{R}{r_o}\ell n(\tan\eta + \frac{1}{\cos\eta})\} \quad (5.5-8)$$

$$\chi^{(3)} = 2r_o^2\cos\eta\{\cos\eta + \frac{R}{r_o}\} \quad (5.5-9)$$

$$\chi^{(5)} = \frac{2r_o^2}{3}\{(\cos\eta)^2(1+2(\cos\eta)^2)+\frac{R}{r_o}\cos\eta((\cos\eta)^2+2)\}(5.5-10)$$
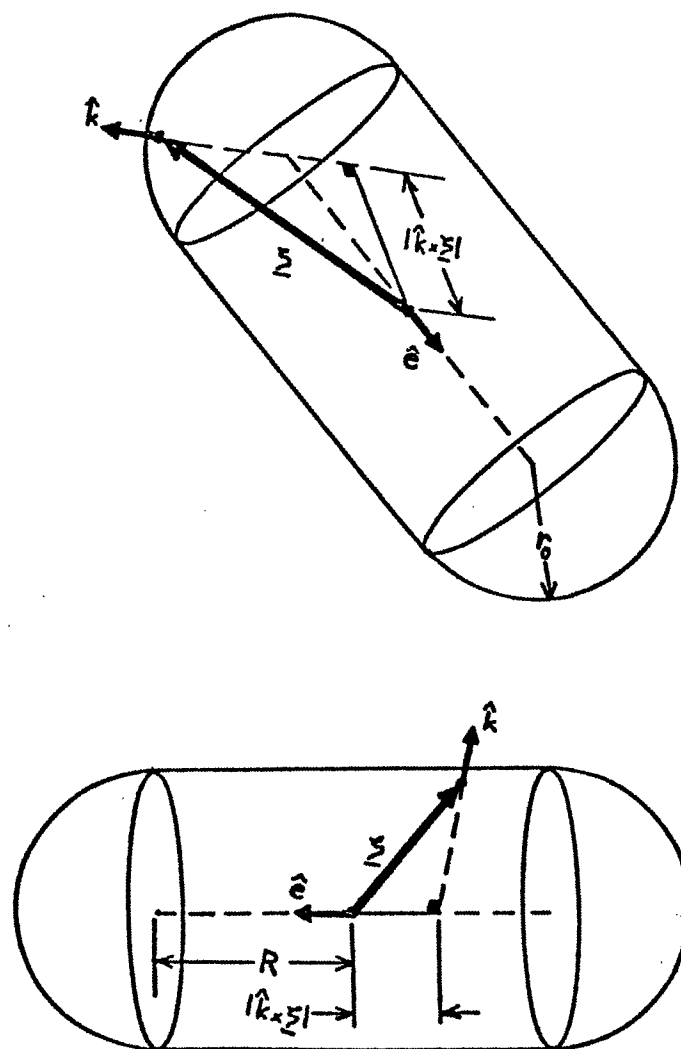
$$T^{(1,2)} = \frac{r_o^2}{\tan\eta}\{\frac{\eta}{(\sin\eta)^2} - \frac{1}{\tan\eta}\} \quad (5.5-11)$$

Fig. 5.4. Geometry of a Spherocylinder

$$T^{(3,2)} = \frac{2r_o^2}{(\tan\eta)^2} \{1 - \frac{\eta}{\tan\eta}\} \qquad (5.5\text{-}12)$$

$$G = \frac{r_o^2}{(\tan\eta)^{3/2}} \{1 + \frac{2}{(\tan\eta)^2} \ln(\cos\eta)\} \qquad (5.5\text{-}13)$$

These are easily evaluated by means of a hand calculator.

It is stated in Chapter 1 of this dissertation that one of the motivations for this work is the assessment of strengths and weaknesses of model calculations in the light of rigorous trajectory studies. In particular, since the Kihara model approach just developed represents the greatest sophistication achieved using the "projection" operator techniques, the assessment of its applicability is of particular interest.

The primary deficiency characteristic of model calculations can be summarized as an oversimplification of the relevant molecular dynamics. This oversimplification is embodied in the choice of an inherently unrealistic interaction potential for which rigorous dynamics are easily considered and/or the application of an approximation which results in a simplification of the dynamics appropriate to a more realistic interaction. Examples of the former case are afforded by the application of soft spherical or rigid ovaloid models to the description of atom-linear molecule in-

teractions. As previously noted in Chapter 4, the
"projection" operator techniques, when used in conjunction
with the rigid ovaloid models, introduce an approximate
simplification in the rigorous impulsive dynamics
characterized by the neglect of "chattering." The term
"chattering" can be generalized to soft nonspherical interac-
tions in which case it denotes collisions in which the
strongly repulsive region of the interaction is encountered
more than once. One expects that the application of
projection operator techniques to Kihara models neglects
chattering as defined in this more general sense. In addi-
tion, the form of the differential cross section embodied in
Eq. (5.5-3) is approximate and is correct only in the sense
that it gives the appropriate limiting forms.

The usual procedure employed in model calculations is to
fit the model parameters to known experimental values of
transport coefficients. One then supposes that the resulting
optimal values reflect the true nature of the intermolecular
interaction. The degree to which optimal values of the model
parameters obtained by consideration of different transport
properties are commensurate allows one to make a critical
appraisal of the model. Indeed, Verlin, Hoffman, and
Matzen(64) have found that within the context of the Kihara
approach (employing a Lennard-Jones 6-12 interaction) the
values of the optimal model parameters appropriate to the

thermal conductivity and shear viscosity differ widely. This is unsatisfying since the same intermolecular potential must describe both kinds of transport.

A more stringent test of the Kihara model approach is afforded by fitting the Kihara effective cross sections to the effective cross sections obtained from the Monte Carlo calculations. Here, the model parameters can be compared directly to the realistic potential surfaces. The following three figures (Figs. 5.5, 5.6, and 5.7) on the right half show the realistic potential surfaces and on the left half show spherocylindrical Kihara interactions. In this work, has been chosen to be of a Lennard-Jones 6-12 form. The energy contours are in hartree units (1 hartree = 27.212 eV).

Values of Ar-$CO_2$ effective cross sections appropriate for comparison with the Monte Carlo control variate results for Ar-$CO_2$(I), Ar-$CO_2$(II), and Ar-$N_2$ at $300°$K have been obtained by fitting Kihara model results (spherocylinder core) to classical trajectory results. These quantities appear in Tables 5.13, 5.14, and 5.15.

The quantities, $\Delta G \binom{ijkl}{pqst} \big| ^\beta_\beta \big)_{\alpha\beta}$, which are collected in Table 5.16, give the number of standard deviations of the Monte Carlo estimate $\big( G \binom{ijkl}{pqst} \big| ^\beta_\beta \big)_{\alpha\beta} \big)$ which are contained in the magnitude of the difference between the Kihara model and classical trajectory values. Thus, if $\Delta G \binom{ijkl}{pqst} \big| ^\beta_\beta \big)_{\alpha\beta}$ is less than unity, the Kihara model value of $G \binom{ijkl}{pqst} \big| ^\beta_\beta \big)_{\alpha\beta}$ lies within
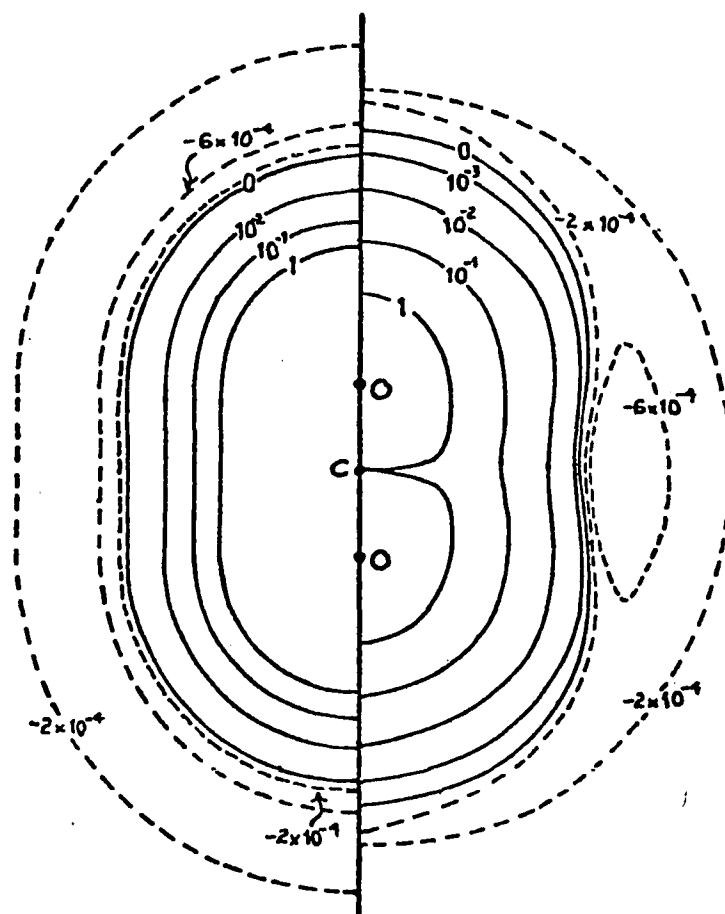
Fig. 5.5. Kihara and "Realistic" Ar-CO$_2$(I) Potential Surfaces
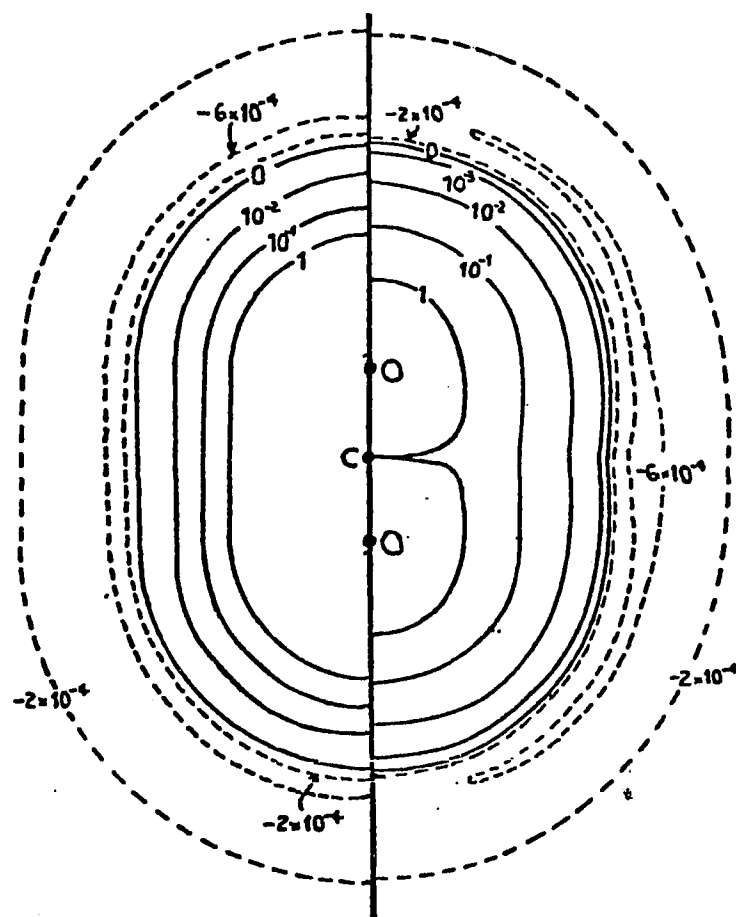
Fig. 5.6. Kihara and "Realistic" Ar-CC$_2$(II) Potential
Surfaces
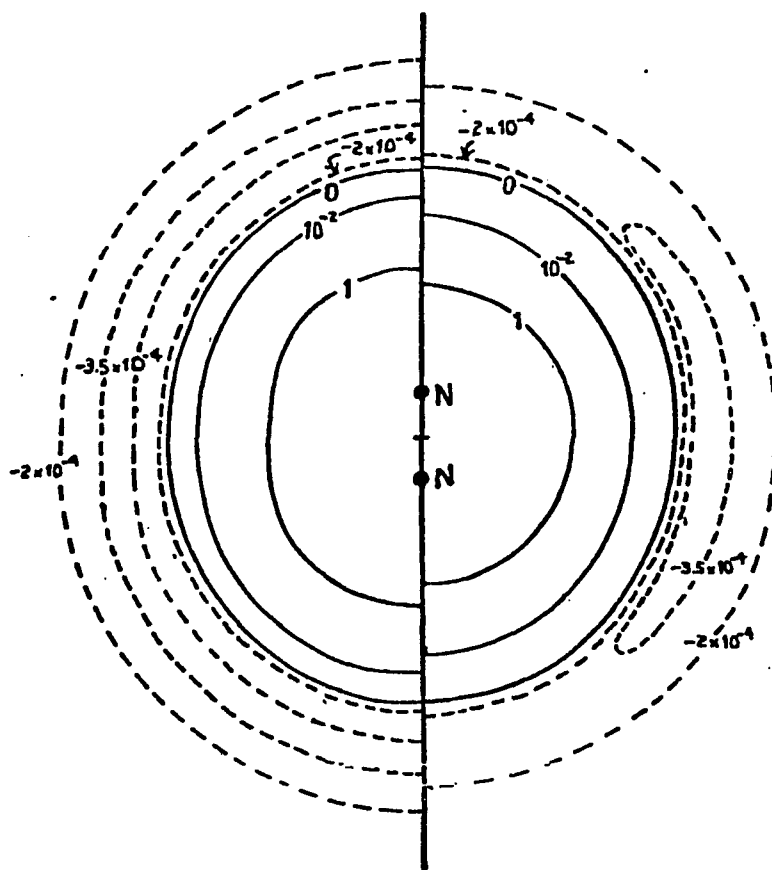
Fig. 5.7. Kihara and "Realistic" Ar-N$_2$ Potential Surfaces

Table 5.13. Values of Effective Cross Sections:  Comparison
of Classical Trajectory and Kihara Model
Results for Ar-$CO_2$(I)

| Cross section[a] | Classical Trajectory[b] | Kihara Model[c] | Percent Deviation |
|---|---|---|---|
| $G(^{1000}_{1000}|^{\beta}_{\beta})_{\alpha\beta}$ | 26.2(1.0) | 26.1 | -0.4 |
| $G(^{1100}_{1100}|^{\beta}_{\beta})_{\alpha\beta}$ | 23.2(2.3) | 21.1 | -9.1 |
| $G(^{1200}_{1200}|^{\beta}_{\beta})_{\alpha\beta}$ | 103.5(3.4) | 90.7 | -12.4 |
| $G(^{0200}_{0200}|^{\beta}_{\beta})_{\alpha\beta}$ | 50.5(4.2) | 40.9 | -19.0 |
| $G(^{1000}_{1200}|^{\beta}_{\beta})_{\alpha\beta}$ $G(^{1200}_{1000}|^{\beta}_{\beta})_{\alpha\beta}$ | 0.958(14.2) | 1.09 | 13.8 |
| $G(^{1010}_{1200}|^{\beta}_{\beta})_{\alpha\beta}$ $G(^{1200}_{1010}|^{\beta}_{\beta})_{\alpha\beta}$ | -2.62(6.3) | -3.65 | 39.3 |
| $G(^{1001}_{1200}|^{\beta}_{\beta})_{\alpha\beta}$ $G(^{1200}_{1001}|^{\beta}_{\beta})_{\alpha\beta}$ | -3.13(11.0) | -4.28 | 36.8 |

[a]  All cross sections given in units of squared angstroms.

[b]  Percent relative standard deviation appears in parentheses.

[c]  Potential Parameters:  $T^* = 1.60$,  $r_o = 3.07$Å,  R = 1.19Å.

Table 5.13.  (continued)

| Cross section | Classical Trajectory | Kihara Model | Percent Deviation |
|---|---|---|---|
| $G(\underline{\gamma};\underline{\gamma})_{\alpha\beta}$ | 82.5(1.0) | 82.1 | -0.4 |
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 190.7(1.5) | 209.9 | 10.1 |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | -22.9(4.2) | -44.8 | 95.6 |
| $G(\underline{\gamma\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma\Omega})_{\alpha\beta}$ | -9.17(10.9) 9.17(10.9) | -8.30 8.30 | -9.5 -9.5 |

Table 5.14. Values of Effective Cross Sections: Comparison of Classical Trajectory and Kihara Model Results for $Ar-CO_2(II)$

| Cross section[a] | Classical Trajectory[b] | Kihara Model[c] | Percent Deviation |
|---|---|---|---|
| $G\left(\begin{smallmatrix}1000\\1000\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 26.2(1.0) | 25.8 | -1.5 |
| $G\left(\begin{smallmatrix}1100\\1100\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 23.7(2.1) | 20.9 | -11.8 |
| $G\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 86.2(3.0) | 74.2 | -13.9 |
| $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 36.2(3.6) | 30.5 | -16.4 |
| $G\left(\begin{smallmatrix}1000\\1200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1000\\1200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | 0.554(24.6) | 0.920 | 66.1 |
| $G\left(\begin{smallmatrix}1010\\1200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1010\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -2.12(7.7) | -2.56 | 20.8 |
| $G\left(\begin{smallmatrix}1001\\1200\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ $G\left(\begin{smallmatrix}1200\\1001\end{smallmatrix}\middle|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | -3.52(9.8) | -4.10 | 15.8 |

[a] All cross sections given in units of squared angstroms.

[b] Percent relative standard deviation appears in parentheses.

[c] $T^* = 1.60$, $r_o = 3.07$Å, $R = 0.938$Å.

Table 5.14.  (continued)

| Cross section | Classical Trajectory | Kihara Model | Percent Deviation |
|---|---|---|---|
| $G(\underline{\gamma};\underline{\gamma})$ | 82.6(1.0) | 81.3 | -1.5 |
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 192.5(1.6) | 201.6 | 4.7 |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | -28.9(3.6) | -35.0 | 21.1 |
| $G(\underline{\gamma}\underline{\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma}\underline{\Omega})_{\alpha\beta}$ | -9.15(9.9) 9.15(9.9) | -8.33 8.33 | -9.0 -9.0 |

Table 5.15. Values of Effective Cross Sections: Comparison of Classical Trajectory and Kihara Model Results for Ar-$N_2$

| Cross section[a] | Classical Trajectory[b] | Kihara Model[c] | Percent Deviation |
|---|---|---|---|
| $G(^{1000}_{1000}|^\beta_\beta)_{\alpha\beta}$ | 29.1(1.8) | 28.3 | -2.8 |
| $G(^{1010}_{1010}|^\beta_\beta)_{\alpha\beta}$ | 39.7(5.9) | 40.4 | 1.8 |
| $G(^{1001}_{1001}|^\beta_\beta)_{\alpha\beta}$ | 35.0(8.6) | 37.9 | 8.3 |
| $G(^{1100}_{1100}|^\beta_\beta)_{\alpha\beta}$ | 28.1(3.4) | 25.8 | 8.2 |
| $G(^{1200}_{1200}|^\beta_\beta)_{\alpha\beta}$ | 53.8(8.6) | 50.9 | -5.4 |
| $G(^{0200}_{0200}|^\beta_\beta)_{\alpha\beta}$ | 7.12(2.7) | 10.4 | 46.1 |
| $G(\underline{\gamma};\underline{\gamma})_{\alpha\beta}$ | 74.4(1.8) | 72.2 | -2.8 |
| $G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 159.9(3.4) | 166.6 | 4.2 |
| $G(\gamma^2,\Omega^2)_{\alpha\beta}$ $G(\Omega^2,\gamma^2)_{\alpha\beta}$ | -4.68(3.7) | -12.8 | 174.0 |
| $G(\underline{\gamma\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ | -8.05(6.1) | -9.52 | 18.3 |
| $G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma\Omega})_{\alpha\beta}$ | 8.05(6.1) | 9.52 | 18.3 |

[a] All cross sections given in units of squared angstroms.

[b] Percent relative standard deviation appears in parentheses.

[c] $T^* = 3.50$, $r_o = 3.49$ Å, $R = 0.269$ Å.

Table 5.16. Deviations of Classical Trajectory and Kihara Model Results

| Cross Section Deviation[a] | Ar-$CO_2$ (I) to Kihara | Ar-$CC_2$ (II) to Kihara | Ar-$N_2$ to Kihara |
|---|---|---|---|
| $\Delta G \left( {}^{1000}_{1000} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $-0.40$ | $-1.5$ | $-1.6$ |
| $\Delta G \left( {}^{1100}_{1100} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $-4.0$ | $-5.6$ | $2.4$ |
| $\Delta G \left( {}^{1200}_{1200} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $-3.7$ | $-4.6$ | $-0.63$ |
| $\Delta G \left( {}^{0200}_{0200} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $-4.5$ | $-4.6$ | $12.5$ |
| $\Delta G \left( {}^{1000}_{1200} {}^{\beta}_{\beta} \right)_{\alpha\beta}$<br>$\Delta G \left( {}^{1200}_{1000} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $12.7$ | $2.7$ | $--$ |
| $\Delta G \left( {}^{1010}_{1200} {}^{\beta}_{\beta} \right)_{\alpha\beta}$<br>$\Delta G \left( {}^{1200}_{1010} {}^{\beta}_{\beta} \right)_{\alpha\beta}$ | $10.8$ | $2.7$ | $--$ |
| $\Delta G \left( {}^{1001}_{1200} {}^{\beta}_{\beta} \right)_{\alpha\beta}$<br>$\Delta G \left( {}^{1200}_{1001} {}^{\beta}_{\beta} \right)$ | $8.6$ | $1.6$ | $--$ |
| $\Delta G \left( \underline{\gamma} ; \underline{\gamma} \right)_{\alpha\beta}$ | $-0.40$ | $-1.5$ | $-1.6$ |

[a] Deviations are expressed in terms of the number of Monte Carlo standard deviations.

Table 5.16. (continued)

| Cross Section Deviation | $Ar-CO_2$ (I) to Kihara | $Ar-CO_2$ (II) to Kihara | $Ar-N_2$ to Kihara |
|---|---|---|---|
| $\Delta G ([\underline{\gamma}]^{(2)}; [\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 6.7 | 2.9 | 1.2 |
| $\Delta G (\gamma^2, \Omega^2)_{\alpha\beta}$ $\Delta G (\Omega^2, \gamma^2)_{\alpha\beta}$ | 22.8 | 5.9 | 47.0 |
| $\Delta G (\underline{\gamma\Omega}; \underline{\gamma} \times [\underline{\Omega}]^{(2)})_{\alpha\beta}$ $\Delta G (\underline{\gamma} \times [\underline{\Omega}]^{(2)}; \underline{\gamma\Omega})_{\alpha\beta}$ | $-0.87$ | $-0.91$ | 3.0 |

one standard deviation of the "realistic" Monte Carlo estimate.

One can consider errors in the Kihara model approach as having one or more of the following four sources. The first is the neglect of "chattering." This point has been discussed extensively with regard to rigid ovaloids in Section 4.5. A second source is embodied in the ad hoc assumption of a factorized form for the differential cross section as is implied by Eqs. (5.5-1) and (5.5-3). Third, the "realistic" potential surfaces are only approximated by a Kihara potential form, and finally, the statistical nature of Monte Carlo methodology introduces a source of random errors. Of these four sources of error, only the last can be quantitively appraised. To see this, one recalls from statistical theory that an isolated observation of a quantity subject to random fluctuations has a probability of 0.843 of being within one standard deviation of its mean value. Thus, random error contributes on the order of one standard deviation to $\Delta G(\begin{smallmatrix} ijkl \\ pqst \end{smallmatrix}|\begin{smallmatrix}\beta\\\beta\end{smallmatrix})_{\alpha\beta}$.

If one averages the values of $\Delta G(\begin{smallmatrix} ijkl \\ pqst \end{smallmatrix}|\begin{smallmatrix}\beta\\\beta\end{smallmatrix})_{\alpha\beta}$ "columnwise" with respect to Table 5.16, one finds that the $Ar-CO_2$ (I) data gives 6.9, the $Ar-CO_2$ (II) data gives 3.1 and the $Ar-N_2$ data gives 8.7. This "average deviation" can be interpreted as a crude measure of the closeness of the "fit" between the Kihara surface and the "realistic" surface. It is evident

that the $Ar-CO_2(II)$ interaction is best approximated by a Kihara interaction. This conclusion is also indicated by the close correspondence of the shapes of the Kihara and $Ar-CO_2(II)$ equipotential contours shown in Fig. 5.6.

Digressing briefly, one should recall that in Chapter 4, it was observed that some rigid ellipsoid-rigid sphere effective cross sections are more strongly influenced by the neglect of multiple collisions than others. This is summarized in Table 5.17 which presents values of $\Delta G \left( {ijkl \atop pqst} \Big| {\beta \atop \beta} \right)_{\alpha\beta}$ appropriate to the comparison of Monte Carlo and projection operator cross sections based on rigid ellipsoid-rigid sphere interactions. (The corresponding effective cross section values were given previously in Section 4.6.) It is evident that the energy exchange cross sections, $G(\gamma^2, \Omega^2)_{\alpha\beta}$ and $G(\Omega^2, \gamma^2)_{\alpha\beta}$, are the ones most strongly affected (always overestimated) by the neglect of chattering. The cross sections, $G\left( {1010 \atop 1200} \Big| {\beta \atop \beta} \right)_{\alpha\beta}$, $G\left( {1200 \atop 1010} \Big| {\beta \atop \beta} \right)_{\alpha\beta}$, $G\left( {0200 \atop 0200} \Big| {\beta \atop \beta} \right)_{\alpha\beta}$, and $G\left( {1200 \atop 1200} \Big| {\beta \atop \beta} \right)_{\alpha\beta}$ are also affected, though not as strongly as the energy exchange cross sections. In addition, the energy exchange cross sections do not depend on angular momentum polarization and are thus likely to be more sensitive to the gross anisotropy of the potential surface rather than its detailed nature. The other "chattering sensitive cross sections" do depend on angular momentum polarization.

Table 5.17. Deviations Between Monte Carlo Estimates and Projection Operator Values of Effective Collision Cross Sections for Hard Sphere-Hard Ellipsoid Models[a]

| Cross Section Difference[b] | Semiminor axis = 4.02 Å | Semiminor axis = 3.06 Å | Semiminor axis = 2.12 Å |
|---|---|---|---|
| $\Delta G \left( \begin{smallmatrix} 1000 \\ 1000 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 1.8 | -0.63 | -5.3 |
| $\Delta G \left( \begin{smallmatrix} 1100 \\ 1100 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 0.97 | 0.061 | 4.1 |
| $\Delta G \left( \begin{smallmatrix} 1200 \\ 1200 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 1.3 | 3.6 | 10.5 |
| $\Delta G \left( \begin{smallmatrix} 0200 \\ 0200 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 0.87 | 6.4 | 15.0 |
| $\Delta G \left( \begin{smallmatrix} 1000 \\ 1200 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ $\Delta G \left( \begin{smallmatrix} 1200 \\ 1000 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | -1.7 | -2.4 | -5.3 |
| $\Delta G \left( \begin{smallmatrix} 1010 \\ 1200 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ $\Delta G \left( \begin{smallmatrix} 1200 \\ 1010 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | -0.96 | 6.7 | 25.9 |
| $\Delta G \left( \begin{smallmatrix} 1001 \\ 1200 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ $\Delta G \left( \begin{smallmatrix} 1200 \\ 1001 \end{smallmatrix} \middle\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | -1.4 | -0.81 | -2.8 |

[a] Sphere radius = 1.90505 Å ; ellipsoid semimajor axis = 4.23344 Å

[b] Deviations are expressed in terms of the number of Monte Carlo standard deviations.

Table 5.17.  (continued)

| Cross Section Difference | Semiminor axis = 4.02 Å | Semiminor axis = 3.06 Å | Semiminor axis = 2.12 Å |
|---|---|---|---|
| $\Delta G([\underline{\gamma}]^{(2)};[\underline{\gamma}]^{(2)})_{\alpha\beta}$ | 1.2 | 0.43 | -0.19 |
| $\Delta G(\gamma^2,\Omega^2)_{\alpha\beta}$ $\Delta G(\Omega^2,\gamma^2)_{\alpha\beta}$ | 0.60 | 9.8 | 38.9 |
| $\Delta G(\underline{\gamma}\underline{\Omega};\underline{\gamma}\times[\underline{\Omega}]^{(2)})_{\alpha\beta}$ $\Delta G(\underline{\gamma}\times[\underline{\Omega}]^{(2)};\underline{\gamma}\underline{\Omega})_{\alpha\beta}$ | 0.89 | -1.2 | -0.42 |

Continuing to digress, it is of interest to speculate as to the reason why the energy exchange effective cross sections are strongly affected by the neglect of chattering. If one visualizes a collision between a rigid ellipsoid (i.e. diatom) and a rigid sphere (i.e. atom), chattering can occur if nearly all of the relative translational energy is transferred by the initial impulse to the rotational degrees of freedom of the rotor. In such a case, the atom "hovers" within the spherical volume swept out by the rotor and receives a second impulse. When this occurs, much of the energy originally transferred to rotation is transferred back to translation. Thus, the neglect of chattering overestimates the rate at which rotational and translational energies can be exchanged and thus leads to overestimation of the energy exchange effective cross sections.

Returning to the previous discussion, one notes that the Kihara methodology systematically overestimates the energy exchange cross sections relative to "realistic" Monte Carlo estimates. In addition, the cross section $G\left(\begin{smallmatrix} 0200 & \beta \\ 0200 & \beta \end{smallmatrix}\right)_{\alpha\beta}$ is overestimated. It seems likely that this behavior is due to the neglect of chattering in the Kihara approach.

In this work, the spherical potential, $\phi(\delta)$, used to construct the Kihara surface was chosen as the usual Lennard-Jones 6-12 interaction. This choice of $\phi(\delta)$ was convenient due to the availability of the necessary omega integrals.

However, it is evident from Figs. 5.5, 5.6, and 5.7 that the Lennard-Jones-Kihara potential surfaces have more repulsive cores and much simpler well structure than the corresponding "realistic" surfaces. It appears, however, that these differences are not too critical since it is possible to attribute a significant part of the deviation in the results to the neglect of chattering. Also, and perhaps more importantly, the Kihara values of the effective collision cross sections which give rise to the Senftleben-Beenakker effects are reasonably close to the Monte Carlo values.

It is of interest, however, to investigate how one might go about obtaining the "best fit" of a Kihara potential to a "realistic" potential surface. To begin, one should note that any potential surface appropriate to an atom-diatom interaction can be written as a series of Legendre polynomials,

$$V = \sum_{j=0}^{\infty} v_j(r)P_j(\cos\theta) \qquad (5.5-14)$$

If $\underline{r}$ is defined as the vector distance between molecular centers and e is defined as a unit vector parallel to the internuclear axis, then r is $|\underline{r}|$ and $\theta$ is arc $\cos(r^{-1}\underline{r}\cdot\hat{e})$. One is at liberty to define a reference convex surface, $\sigma_h$, described by a supporting function, h(z), and a scale factor, $\rho$, so that $\underline{r}$ has the form,

$$\underline{r} = \rho[(h-zh')\hat{k}+h'\hat{e}] \qquad (5.5-15)$$

Here, one notes that $\rho^{-1}\underline{r}$ has its endpoint on $\sigma_h$ and that $\hat{k}$ is the unit vector normal to $\sigma_h$ at that point. The quantity z is defined as $\hat{k}\cdot\hat{e}$. This immediately yields,

$$r = \rho[(h-zh')^2+2zh'(h-zh')+h'^2]^{\frac{1}{2}} \qquad (5.5-16)$$

$$\cos\theta = \frac{(h-zh')z+h'}{[(h-zh')^2+2zh'(h-zh')+h'^2]^{\frac{1}{2}}} \qquad (5.5-17)$$

where h and h' (derivative of h) are understood to be functions of cosz.

Now, the "realistic" potential can be written in the alternate form,

$$V = \sum_{j=0}^{\infty} w_j(\rho)P_j(\cos\phi) . \qquad (5.5-18)$$

where $\phi$ = arc cos z. It is clear that the Kihara potential can be identified as $w_0(\rho)$. From this, one obtains,

$$w_0(\rho) = \frac{1}{2}\int_{-1}^{1}d(\cos\phi) \sum_{j=0}^{\infty} v_j(r(\rho,\phi))P_j(\cos\theta(\rho,\phi)) . \qquad (5.5-19)$$

This integral can be evaluated via Gauss-Legendre quadrature. Finally, it should be noted that for "best" results, should be chosen so as to closely correspond with an equipotential surface of the "realistic" potential.

In conclusion, it is interesting to note that the IOS and Kihara calculations show interesting correspondences. In particular, values of $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\Big|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$, $G(\gamma^2,\Omega^2)_{\alpha\beta}$, and $G(\Omega^2,\gamma^2)_{\alpha\beta}$ are strongly overestimated relative to the Monte Carlo results. The appropriate values of $\Delta G\left(\begin{smallmatrix}ijkl\\pqst\end{smallmatrix}\Big|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ appear in Table 5.18. It will be left to future study to determine how or if dynamical approximations characteristic of the Kihara and IOS methodologies are related.

## 5.6. Some Proposals for Future Work

It is commonly the case in the course of scholarly research for one to produce more questions than one is able to answer. This work falls in that category. However, out of the many possible proposals for future work that could be put forward, the author will give only the following three. First, the lack of CC and CS calculations are obvious gaps that need filling. This work is straightforward and can be pursued as resources are made available. Second, it would be interesting to know if factorization formulae for the IOS generalized phenomenological cross sections can be developed. Although this subject is not the province of the author, it is his opinion that such formulae hold the promise of producing more economical computation methods which would allow more ambitious problems to be attacked. Third, it appears to

Table 5.18. Deviations Between Monte Carlo Estimates and IOS Values of the Effective Collision Cross Section for the Pattengill $\underline{et}$ $\underline{al.}$ Ar-N$_2$ Potential Surface

| Cross Section Deviation[a] | Ar-N$_2$ Classical Trajectory to Kihara | Ar-N$_2$ Classical Trajectory to IOS |
|---|---|---|
| $\Delta G \left( \begin{smallmatrix} 1000 \\ 1000 \end{smallmatrix} \Big\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | -1.6 | 1.9 |
| $\Delta G \left( \begin{smallmatrix} 1010 \\ 1010 \end{smallmatrix} \Big\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 0.30 | 1.5 |
| $\Delta G \left( \begin{smallmatrix} 1001 \\ 1001 \end{smallmatrix} \Big\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 0.97 | 4.9 |
| $\Delta G \left( \begin{smallmatrix} 0200 \\ 0200 \end{smallmatrix} \Big\vert \begin{smallmatrix} \beta \\ \beta \end{smallmatrix} \right)_{\alpha\beta}$ | 12.5 | 108.2 |
| $\Delta G \left( [\underline{\gamma}]^{(2)} ; [\underline{\gamma}]^{(2)} \right)$ | 1.2 | -2.9 |
| $\Delta G \left( \gamma^2 , \Omega^2 \right)_{\alpha\beta}$ $\Delta G \left( \Omega^2 , \gamma^2 \right)_{\alpha\beta}$ | 47.0 | 100.5 |

[a] Deviations are expressed in terms of the number of Monte Carlo standard deviations.

the author that the IOS and Kihara model methodologies are related in some fundamental way. It would be satisfying to know the nature and extent of such a connection. It is the author's opinion that this connection is involved with the neglect of chattering. It would then be interesting to try to devise some means of explicitly treating multiple impulse collisions. If this could be achieved, these methodologies (the IOS and Kihara model) might even become of practical use in an engineering context since grossly unrealistic rigid rough sphere models are currently applied for such purposes.

## 6. LITERATURE CITED

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# 7. ACKNOWLEDGEMENTS

"And further, by these my son, be admonished:

of making many books there is no end;

and much study is a weariness of the flesh."

Ecc. 12:12

## 8. APPENDIX A: IRREDUCIBLE TENSORS

The irreducible tensors used in this work can be defined by considering a Taylor series expansion of a general function, G, of a three dimensional vector, $\underline{x}$

$$G(\underline{x}) = \sum_{j=0}^{\infty} (\underline{x})^j \underset{\overline{j!}}{\otimes} \underline{\nabla}^j_{\underline{x}} G(\underline{x}) \big|_{\underline{x}=0} \qquad (8-1)$$

Clearly, the polyads, $(\underline{x})^j$, form a nonorthogonal complete basis under the norm,

$$(G,G') = \int d\hat{x} \; G(\underline{x})G(\underline{x}') \qquad (8-2)$$

If one orthogonalizes the polyads under the above norm, one obtains the irreducible tensors

$$[\underline{x}]^{(n)} = (\underline{x})^n + \sum_{s=1}^{\{n/2\}} \frac{(-1)^s \nleq (\underline{x})^{n-2s} (\underline{U})^s \nleq x^{2s}}{\prod_{j=1}^{s} (2(n-j)+1)} \qquad (8-3)$$

Here, the notation $\nleq A \nleq$ means "the tensor formed by the sum of all distinguishable perturbations of the tensor indices of $\underline{\underline{A}}$" (e.g. $\nleq xyy \nleq = xyy+yxy+yyx$) and the notation $\{n/2\}$ means "the greatest integer contained in $n/2$." If one "traces" any pair of indices of $[\underline{x}]^{(n)}$ it follows directly from Eq. (8-3) that the result is zero. Thus, $[\underline{x}]^{(n)}$ is the n-rank "traceless and symmetric" component $(\underline{x})^n$.

It can be shown by direct substitution that $[\underline{x}]^{(n)}$ obeys the following differential equation,

$$\frac{\partial}{\partial \hat{x}}\bigg|_x \cdot \frac{\partial}{\partial \hat{x}}\bigg|_x [\underline{x}]^{(n)} = -n(n+1)[\underline{x}]^{(n)} \qquad (8-4)$$

which is immediately recognizable as the angular part of the Helmholtz equation. Thus, the cartesian components of $[\underline{x}]^{(n)}$ are linear combinations of the spherical harmonics, $Y_n^n(\hat{x})$, $Y_n^{n-1}(\hat{x})$, ... $Y_n^{-n}(\hat{x})$ multiplied by $x^n$. Like the spherical harmonics, the tensors, $[\underline{x}]^{(n)}$, form irreducible representations of the rotation group, $O^+(3)$, which leads to the designation of the $[\underline{x}]^{(n)}$ as irreducible tensors.

The spherical harmonics have the conventional orthonormal definition,

$$Y_n^m(\hat{x}) = (-1)^{\frac{m+|m|}{2}} \frac{(2n)!}{2^n n!} \left[\frac{2n+1}{4\pi}\right]^{\frac{1}{2}} \left[\frac{(n-|m|)!}{(n+|m|)!}\right]^{\frac{1}{2}} e^{im\phi} (\sin\theta)^{|m|}$$

$$\left\{ (\cos\theta)^{n-|m|} + \sum_{s=1}^{\{\frac{n-|m|}{2}\}} \frac{(-1)^s (\cos\theta)^{n-|m|-2s}}{2^s s!(n-|m|-2s)! \prod_{j=1}^{s}(2(n-j)+1)} \right\} \qquad (8-5)$$

where $\theta$ and $\phi$ are the angles of $\hat{x}$ (i.e., $\hat{x} = \hat{i}\sin\theta\cos\phi + \hat{j}\sin\theta \sin\phi + \hat{k}\cos\theta$). Also, the associated Legendre function, $P_n^{(m)}(\cos\theta)$, has been explicitly written as a series. Now, if one evaluates the "zz...z" cartesian component of $[\underline{x}]^{(n)}$, one finds,

$$[\underline{x}]_{zz \cdots z}^{(n)} = x^n \frac{(n!)^2 2^n}{(2n)!} \left[\frac{4\pi}{2n+1}\right]^{\frac{1}{2}} Y_n^0 (\hat{x}) \qquad (8\text{-}6)$$

In evaluating $[\underline{x}]_{zz \cdots z}^{(n)}$, one must note that $\hat{k} \cdot \hat{x} = \cos\theta$ and that $\mp(\underline{x})^{n-2s}(\underline{u})^s \mp$ has $n!/2^s s! (n-2s)!$ terms.

It follows from Eq. (8-3) that the scalar product $[\underline{x}]^{(n)} \underset{n}{\odot} [\underline{x}]^{(n)}$ is,

$$[\underline{x}]^{(n)} \underset{n}{\odot} [\underline{x}]^{(n)} = \frac{(n!)^2}{(2n)!} \sum_{s=0}^{2\{n/2\}} (-1)^s \frac{(2n-2s)!}{s!(n-2s)!(n-s)!}$$

$$= \frac{(n!)^2 2^n}{(2n)!} \qquad (8\text{-}7)$$

One can define a standard spherical component, $[\underline{x}]_m^n$, of the irreducible tensor, $[\underline{x}]^{(n)}$, such that

$$[\underline{x}]^{(n)} \underset{n}{\odot} [\underline{x}]^{(n)} = \sum_{m=-n}^{n} [\underline{x}]_m^{n*} [\underline{x}]_m^n \qquad (8\text{-}8)$$

where it follows that $[\underline{x}]_m^n$ can be given the explicit form in terms of spherical harmonics,

$$[\underline{x}]_m^n = 2^{3/2} \pi^{\frac{1}{2}} \left[\frac{n!(n+1)!2^n}{(2n+2)!}\right]^{\frac{1}{2}} x^n Y_n^m(\hat{x}) . \qquad (8\text{-}9)$$

One can show that Eq. (8-7) is satisfied by the above definition of $[\underline{x}]_m^n$ if one notes that $Y_n^{m*}(\hat{x})$ equals $(-1)^m Y_n^{-m}(\hat{x})$ and makes use of the addition theorem for spherical harmonics (i.e., $2n+1/4\pi = \sum_{m=-n}^{n} (-1)^m Y_n^{-m}(\hat{x}) Y_n^m(\hat{x})$).

If one uses the standard definition of the Wigner 3j coefficients and the expression for the integration of three spherical harmonics as given by Edmonds(60), it is possible to obtain an expression for a spherical component, $[\underline{x}]_{n_0}^{J}$, in terms of the cartesian components, x, y, and z,

$$[\underline{x}]_{n_0}^{J} = \prod_{s=1}^{J} \left( \sum_{n_s=-J+s}^{J-s} E(J,s) \left\{ \frac{x}{\sqrt{2}} \left[ \begin{pmatrix} 1 & J-s & J-s+1 \\ -1 & n_s & -n_{s-1} \end{pmatrix} - \begin{pmatrix} 1 & J-s & J-s+1 \\ 1 & n_s & -n_{s-1} \end{pmatrix} \right] \frac{-iy}{\sqrt{2}} \left[ \begin{pmatrix} 1 & J-s & J-s+1 \\ -1 & n_s & -n_{s-1} \end{pmatrix} + \begin{pmatrix} 1 & J-s & J-s+1 \\ 1 & n_s & -n_{s-1} \end{pmatrix} \right] + z \begin{pmatrix} 1 & J-s & J-s+1 \\ 0 & n_s & -n_{s-1} \end{pmatrix} \right\} \right) \tag{8-10}$$

where,

$$E(J,s) = \left[ \frac{2(2J-2s)!}{(2J-2s+2)!} \right]^{\frac{1}{2}} \frac{(J-s+1)!}{(J-s)!} \left[ \begin{pmatrix} 1 & J-s & J-s+1 \\ 0 & 0 & 0 \end{pmatrix} \right]^{-1} \tag{8-11}$$

In conclusion, some useful identities are listed.

$$[\underline{x}]^{(0)} = 1 \tag{8-12}$$

$$[\underline{x}]^{(1)} = \underline{x} \tag{8-13}$$

$$[\underline{x}]^{(2)} = \underline{x}\underline{x} - \frac{1}{3}x^2\underline{\underline{U}} \tag{8-14}$$

$$[\underline{x}\underline{y}]^{(0)} = \frac{1}{\sqrt{3}} \underline{x}\cdot\underline{y} \tag{8-15}$$

$$[\underline{x}\underline{y}]^{(1)} = \frac{i}{\sqrt{2}} \underline{x}\times\underline{y} \tag{8-16}$$

$$[\underline{x}\underline{y}]^{(2)} = \frac{1}{2}(\underline{x}\underline{y}+\underline{y}\underline{x}) - \frac{1}{3}\underline{x}\cdot\underline{y}\ \underline{\underline{U}} \qquad (8-17)$$

$$[\underline{x}[\underline{y}]^{(2)}]^{(1)} = -\sqrt{\frac{3}{5}}\ (\underline{x}\cdot\underline{y}\underline{y}-\frac{1}{3}\underline{x}y^2) \qquad (8-18)$$

$$[\underline{x}[\underline{y}]^{(2)}]^{(2)} = \frac{i}{\sqrt{6}}\ (\underline{x}\times\underline{y}\underline{y}-\underline{y}\underline{y}\times\underline{x}) \qquad (8-19)$$

$$[\underline{x}[\underline{y}]^{(2)}]^{(3)} = \frac{1}{3}(\underline{x}\underline{y}\underline{y}+\underline{y}\underline{x}\underline{y}+\underline{y}\underline{y}\underline{x}) - \frac{y^2}{15}\ (\underline{x}\underline{\underline{U}}+ \lfloor\underline{x}\rfloor +\underline{\underline{U}}\underline{x}) - \qquad (8-20)$$

$$\frac{2}{15}\ \underline{x}\cdot\underline{y}(\underline{y}\underline{\underline{U}}+ \lfloor\underline{y}\rfloor +\underline{\underline{U}}\underline{y})$$

## 9. APPENDIX B: ISOTROPIC TENSORS

An isotropic tensor, by definition, is totally symmetric with respect to $O^+(3)$ and thus must consist of direct products of the unit tensor, $\underline{U}$, and the Levi-Civita density, $\underline{\varepsilon}$. Since this admits a great many possibilities, the present discussion will be limited to the presentation of results which are useful within the scope of this work.

Two particularly useful identities are,

$$\int d\hat{x}(\underline{x})^{2n} = \frac{2^{n+3}\pi^{3/2}}{\Gamma(n+3/2)} \not= (U)^{2n} \downdownarrows x^{2n} \tag{9-1}$$

and,

$$\int d\hat{x}[\underline{x}]^{(n)}[\underline{x}]^{(n)} = \frac{2^{n+3}\pi^{3/2}}{\Gamma(n+3/2)} \Delta^{(n)} x^{2n} \tag{9-2}$$

where an explicit expression for $\Delta^{(n)}$ follows immediately from Eq. (8-3) via Eq. (9-1).

$$\Delta^{(n)} = \frac{1}{(n!)^2} \not= \left\lfloor \frac{\not=\not=}{:\underline{n}} \right\rfloor \downdownarrows + \sum_{s=1}^{\{n/2\}} \frac{(-1)^s}{2^s s! [(n-s)!]^2 \prod_{j=1}^{s}(2(n-j)+1)} \tag{9-3}$$

$$\not= (\underline{U})^s \left\lfloor \frac{\not=\not=}{:\overline{n-2s}} \right\rfloor (\underline{U})^s$$

Here, is constructed by an n-fold nesting of $\underline{U}$'s (i.e.

$_{1\cdots2n} = \delta_{1,2n}\delta_{2,2n-1}\cdots\delta_{n,n-1})$. Some specific examples are,

$$\Delta^{(0)} = 1 \tag{9-4}$$

$$\Delta^{(1)} = \underline{U} \tag{9-5}$$

$$\Delta^{(2)} = \frac{1}{2}(\underline{\underline{UU}} + \underline{\underline{U}}) - \frac{1}{3}\underline{UU} \tag{9-6}$$

$$\Delta^{(1,1)} = \underline{\underline{U}} \tag{9-7}$$

$$\Delta^{(1,2)} = \frac{1}{2}(\underline{\underline{U}} + \underline{\underline{U}}) - \frac{1}{3}\underline{UUU} \tag{9-8}$$

Cooper(46) has given explicit expressions for $\Delta^{(3)}$, $\Delta^{(1,3)}$, $\Delta^{(2,2)}$, and $\Delta^{(2,1)}$.

In Chapter 3, the inverse collision operator is written in terms of tensors which are isotropic with respect to the group of two dimensional rotations about the direction of the field. Following Cooper(46) one can define the linearly independent tensors,

$$B_m^{(+)}(q) = (\hat{k})^{q-m} \underline{\underline{U}}_{\vdots m}^{(2)} {}^{(2)} (\hat{k})^{q-m} \tag{9-9}$$

$$B_m^{(-)}(q) = (\hat{k})^{q-m} \, \underline{v} \cdot \underline{\underline{U}}_{\vdots m}^{(2)} {}^{(2)} (\hat{k})^{q-m} \tag{9-10}$$

where $\hat{k}$ is a unit vector parallel to the field, $\underline{H}$, and

$$\underline{U}^{(2)} = \underline{U} - \hat{k}\hat{k} \tag{9-11}$$

$$\underline{V} = -\hat{k} \times \underline{U} \qquad (9\text{-}12)$$

The tensors $B_m^{(+)}(q)$ and $B_m^{(-)}(q)$ can be used to construct tensors $\mathring{B}_m^{(+)}(q)$ and $\mathring{B}_m^{(-)}(q)$ which are symmetric and traceless on the first and last q indices.

$$\mathring{B}_m^{(+)}(q) = \qquad (9\text{-}13)$$

$$N_{qm}[\pm(\hat{h})^{q-m} \underbrace{\left[\,\underline{\pm\hat{+}}\,\right]^{(2)}}_{:\,\underline{\overline{m}}} {}^{(2)}(\hat{h})^{q-m}\pm - \text{trace terms}]$$

$$\mathring{B}_m^{(-)}(q) = \qquad (9\text{-}14)$$

$$N_{qm}[\ (\hat{h})^{q-m}\underline{V}\cdot \underbrace{\left[\,\underline{\pm\hat{+}}\,\right]^{(2)}}_{:\,m^{\equiv}} {}^{(2)}(\hat{h})^{q-m} - \text{trace terms}]$$

where,

$$N_{qm} = \frac{2^{q-m}(q+m)!\,(q-m)!}{m!\,(2q)!} \qquad (9\text{-}15)$$

The tensors defined in Eqs. (9-13) and (9-14) satisfy the relations,

$$\mathring{B}_m^{(+)}(q) \overset{\circ}{\underset{q}{\odot}} \mathring{B}_{m'}^{(+)}(q) = \mathring{B}_m^{(+)}\delta_{mm'} \qquad (9\text{-}16)$$

$$\mathring{B}_m^{(-)}(q) \overset{\circ}{\underset{q}{\odot}} \mathring{B}_{m'}^{(-)}(q) = -\mathring{B}_m^{(-)}\delta_{mm'} \qquad (9\text{-}17)$$

$$\mathring{B}_m^{(+)}(q) \overset{\circ}{\underset{q}{\odot}} \mathring{B}_{m'}^{(-)}(q) = \mathring{B}_m^{(-)}\delta_{mm'} \qquad (9\text{-}18)$$

Using these relations, Matzen(45) has defined a linearly independent set of tensors here denoted by $y_m^{(q)}$, as follows,

$$y_{\pm m}^{(q)} = \frac{1}{\sqrt{2}}(\overset{\circ}{B}_m^{(+)}(q) \pm i\overset{\circ}{B}_m^{(-)}(q)) \tag{9-19}$$

where,

$$\Delta^{(q)} = \sum_{m=0}^{q} \overset{\circ}{B}_m^{(+)}(q) = \sum_{m=-q}^{q} y_m^{(0)} \tag{9-20}$$

$$\Delta^{(q)} \times_q \hat{h} = -\sum_{m=1}^{q} m\overset{\circ}{B}_m^{(-)}(q) = -\sum_{m=-q}^{q} imy_m^{(q)} \tag{9-21}$$

Specific examples of $y_m^{(q)}$ pertinent to this work are,

$$\overset{\circ}{B}_0^{(+)}(0) = 1 \tag{9-22}$$

$$\overset{\circ}{B}_1^{(+)}(1) = \underline{U}^{(2)} \tag{9-23}$$

$$\overset{\circ}{B}_0^{(+)}(1) = \hat{k}\hat{k} \tag{9-24}$$

$$\overset{\circ}{B}_1^{(-)}(1) = \underline{U} \tag{9-25}$$

$$B_2^{(+)}(2) = \frac{1}{2}(\ \underbrace{\ \ }^{(2)}\ \underbrace{\ \ }^{(2)} + \underbrace{\ \ }^{(2)}\ \underbrace{\ \ }^{(2)^-} - \underline{U}^{(2)}\underline{U}^{(2)}) \tag{9-26}$$

$$B_1^{(+)}(2) = \frac{1}{2}(\hat{k}\underline{U}^{(2)}\hat{k} + \hat{k}\lfloor\hat{k}\rfloor^{(2)} + \lfloor\hat{k}\rfloor^{(2)}\hat{k} + \lfloor\hat{k}\hat{k}\rfloor^{(2)}) \tag{9-27}$$

$$B_0^{(+)}(2) = \frac{2}{3}(\hat{k}\hat{k}\hat{k}\hat{k} - \frac{1}{2}\hat{k}\hat{k}\underline{U}^{(2)} - \frac{1}{2}\underline{U}^{(2)}\hat{k}\hat{k} + \frac{1}{4}\underline{U}^{(2)}\underline{U}^{(2)}) \tag{9-28}$$

$$\tag{9-29}$$

$$B_1^{(-)}(2) = \frac{1}{2}(\hat{k}\underline{v}\hat{k} + \hat{k}\underline{\widetilde{k}} + \underline{\hat{k}}\hat{k} + \underline{\widetilde{kk}}) \qquad (9\text{-}29)$$

$$B_2^{(-)}(2) = \frac{1}{2}(\underline{\underline{v}}^{(2)} + \underline{v}^{(2)} + \underline{v}^{(2)} + \underline{u}^{(2)}) \qquad (9\text{-}30)$$

## 10.  APPENDIX C:  HARD SPHERE-HARD ELLIPSOID ALGORITHM

An efficient hard sphere-hard ellipsoid trajectory algorithm was developed by this worker only after a considerable number of approaches were tried and discarded. For this reason, this appendix is included here so that future workers can benefit from the experience of this author.

A complete description of a "hard" interaction is obtained if one locates both temporally and spatially the "point of impact" (or "points of impact" for chattering collisions). The most efficient algorithm found by the author for doing this is summarized in the following steps:

1. The atom (sphere) and molecule (ellipsoid) are advanced via free flight dynamics from the initial configuration to a configuration in which the center of the sphere is the distance of $r_o$+b from the center of the ellipsoid.

2. The interval necessary for the atom to traverse a "collision" sphere of radius $r_o$+b about the center of the molecule is calculated under the assumption that no interaction occurs (i.e. the sphere and ellipsoid are able to "penetrate" each other).

3. The time interval in step 2 is divided into an integral number of subintervals. A convenient number was found to be 50.

4. The atom is advanced via free flight dynamics through the first subinterval.

5. Using an appropriate criterion (this will be discussed later) the algorithm checks to determine if an impact occurs during this interval. If none occurs the atom is advanced to the second interval and step 5 is repeated. If the atom is advanced outside of the collision sphere (i.e. after 50 repetitions with no impact) it is obvious that no collision has occurred. Thus, the postcollisional values of the dynamical parameters follow trivially from the

precollisional values.

6. If an impact is found to occur, the subinterval is partitioned (four partitions are found to be optimal) and the searching process is repeated on these finer divisions.

7. When the impact point is determined to within a predefined tolerance, postimpact values of the dynamical parameters are determined from the preimpact values.

8. The interval necessary for the atom to escape from the collision sphere after impact is calculated via free flight dynamics assuming no subsequent impacts.

9. This new interval is divided into subintervals. (Twenty was found to be appropriate.) The entire process is repeated to check for subsequent or "chattering" impacts.

10. The process is repeated until the atom finally escapes from the collision sphere.

The above procedure is easily generalized to more complicated "hard" interactions. The criterion used in step 5 can take several forms but basically follows frcm the nature of the geometry of the sphere and ellipsoid when in contact. Defining $\hat{k}$ as the unit vector normal to the surfaces at the point of contact, $\hat{e}$ as the unit vector along the symmetry axis of the ellipsoid, and $\hat{r}$ as the unit vector parallel to the relative position vector, $\underline{r}$, between the sphere and ellipsoid centers, one finds that $\hat{k} \cdot \hat{e}$ is an analytic function of $\hat{r} \cdot \hat{e}$ when the sphere and ellipsoid are in contact. Using this fact, at any point along the trajectory, one can calculate a hypothetical value of $\hat{k} \cdot \hat{e}$ from the current value of $\hat{r} \cdot \hat{e}$. Now, it is also true that the distance, $h$, between the centers of the sphere and ellipsoid when in contact is an analytic function of $\hat{k} \cdot \hat{e}$. Thus, a hypothetical

value of $h$ can be computed from the value of $\hat{k}\cdot\hat{e}$. If one
compares this computed value of $h$ to the current value of
$|\underline{r}|$, one finds $|\underline{r}|>h$ implies that there is no contact, $|\underline{r}|<h$,
implies that the sphere and ellipsoid have penetrated each
other, and $|\underline{r}|=h$ implies that the surfaces just touch. Thus,
an impact point can be located using the preceding condi-
tions.

## 11. APPENDIX D: TABLES OF NUMERICAL DATA APPROPRIATE TO THE SPHERE-SPHEROCYLINDER KIHARA CROSS SECTIONS

The scalar collision integral appropriate to a sphere-spherocylinder Kihara interaction can be written in terms of the quantities given explicitly in Eq. (5.5-7) through (5.5-13). These can be decomposed into the dimensionless quantities, $\overline{\chi}_s^{(i)}$, $\overline{\chi}_c^{(i)}$, $\overline{T}_{sc}^{(i,j)}$, and $\overline{G}_{sc}$ where,

$$\chi^{(i)} = r_o^2 [\overline{\chi}_s^{(i)} + \frac{R}{r_o} \overline{\chi}_c^{(i)}] \qquad (11-1)$$

$$T^{(i,j)} = \frac{1}{3} r_o^2 \overline{T}_{sc}^{(i,j)} \qquad (11-2)$$

$$G = r_o^2 \overline{G}_{sc} \qquad (11-3)$$

These quantities and necessary omega integrals are given in the following tables as functions of $\eta$ and $T^*$ (reduced temperature).

Table 11.1. Lennard-Jones 6-12 Chapman Cowling Omega Integrals

| $T^*$ | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 0.05 | 5.074 | 4.506 | 5.163 | 4.125 | 4.734 | 4.755 |
| 0.10 | 4.012 | 3.552 | 4.099 | 3.239 | 3.759 | 3.750 |
| 0.15 | 3.481 | 3.066 | 3.588 | 2.774 | 3.295 | 3.235 |
| 0.20 | 3.130 | 2.731 | 3.267 | 2.439 | 3.001 | 2.881 |
| 0.25 | 2.865 | 2.469 | 3.034 | 2.176 | 2.775 | 2.613 |
| 0.30 | 2.649 | 2.256 | 2.844 | 1.966 | 2.581 | 2.400 |
| 0.35 | 2.468 | 2.080 | 2.680 | 1.799 | 2.409 | 2.225 |
| 0.40 | 2.314 | 1.932 | 2.533 | 1.665 | 2.257 | 2.079 |
| 0.45 | 2.181 | 1.810 | 2.402 | 1.558 | 2.124 | 1.958 |

Table 11.1. (continued)

| $T^*$ | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 0.50 | 2.066 | 1.707 | 2.286 | 1.469 | 2.007 | 1.852 |
| 0.55 | 1.965 | 1.618 | 2.182 | 1.397 | 1.905 | 1.762 |
| 0.60 | 1.876 | 1.545 | 2.085 | 1.336 | 1.816 | 1.682 |
| 0.65 | 1.798 | 1.481 | 1.999 | 1.285 | 1.736 | 1.613 |
| 0.70 | 1.729 | 1.425 | 1.922 | 1.242 | 1.668 | 1.554 |
| 0.75 | 1.667 | 1.375 | 1.854 | 1.205 | 1.607 | 1.501 |
| 0.80 | 1.610 | 1.332 | 1.792 | 1.172 | 1.552 | 1.455 |
| 0.85 | 1.561 | 1.293 | 1.736 | 1.144 | 1.505 | 1.412 |
| 0.90 | 1.518 | 1.260 | 1.685 | 1.118 | 1.462 | 1.374 |
| 0.95 | 1.477 | 1.231 | 1.637 | 1.096 | 1.424 | 1.340 |
| 1.00 | 1.440 | 1.204 | 1.593 | 1.076 | 1.389 | 1.309 |
| 1.05 | 1.406 | 1.180 | 1.554 | 1.058 | 1.358 | 1.281 |
| 1.10 | 1.375 | 1.158 | 1.518 | 1.041 | 1.330 | 1.255 |
| 1.15 | 1.347 | 1.138 | 1.485 | 1.027 | 1.305 | 1.232 |
| 1.20 | 1.320 | 1.120 | 1.454 | 1.013 | 1.281 | 1.211 |
| 1.25 | 1.295 | 1.103 | 1.427 | 1.009 | 1.260 | 1.191 |
| 1.30 | 1.272 | 1.087 | 1.402 | 0.9895 | 1.240 | 1.173 |
| 1.35 | 1.252 | 1.072 | 1.378 | 0.9789 | 1.222 | 1.157 |
| 1.40 | 1.233 | 1.058 | 1.356 | 0.9691 | 1.205 | 1.141 |
| 1.45 | 1.216 | 1.046 | 1.335 | 0.9599 | 1.189 | 1.127 |
| 1.50 | 1.199 | 1.035 | 1.316 | 0.9514 | 1.175 | 1.113 |
| 1.55 | 1.183 | 1.024 | 1.297 | 0.9430 | 1.161 | 1.101 |
| 1.60 | 1.168 | 1.014 | 1.280 | 0.9359 | 1.149 | 1.089 |
| 1.65 | 1.154 | 1.005 | 1.264 | 0.9288 | 1.137 | 1.078 |
| 1.70 | 1.141 | 0.9958 | 1.249 | 0.9221 | 1.126 | 1.068 |
| 1.75 | 1.128 | 0.9870 | 1.235 | 0.9158 | 1.116 | 1.058 |
| 1.80 | 1.116 | 0.9790 | 1.222 | 0.9098 | 1.106 | 1.049 |
| 1.85 | 1.105 | 0.9715 | 1.210 | 0.9040 | 1.097 | 1.040 |
| 1.90 | 1.095 | 0.9644 | 1.198 | 0.8986 | 1.088 | 1.032 |
| 1.95 | 1.085 | 0.9580 | 1.187 | 0.8933 | 1.080 | 1.024 |
| 2.00 | 1.075 | 0.9513 | 1.176 | 0.8883 | 1.072 | 1.017 |
| 2.10 | 1.058 | 0.9394 | 1.156 | 0.8790 | 1.058 | 1.003 |
| 2.20 | 1.042 | 0.9285 | 1.138 | 0.8704 | 1.045 | 0.9903 |
| 2.30 | 1.027 | 0.9185 | 1.122 | 0.8625 | 1.033 | 0.9788 |
| 2.40 | 1.013 | 0.9092 | 1.107 | 0.8551 | 1.022 | 0.9683 |
| 2.50 | 1.001 | 0.9005 | 1.093 | 0.8481 | 1.011 | 0.9586 |
| 2.60 | 0.9889 | 0.8924 | 1.081 | 0.8417 | 1.002 | 0.9496 |
| 2.70 | 0.9781 | 0.8849 | 1.069 | 0.8356 | 0.9934 | 0.9412 |
| 2.80 | 0.9681 | 0.7780 | 1.058 | 0.8300 | 0.9853 | 0.9334 |
| 2.90 | 0.9587 | 0.8711 | 1.048 | 0.8245 | 0.9778 | 0.9261 |
| 3.00 | 0.9500 | 0.8649 | 1.039 | 0.8193 | 0.9706 | 0.9193 |
| 3.10 | 0.9418 | 0.8590 | 1.030 | 0.8145 | 0.9640 | 0.9129 |

Table 11.1.    (continued)

| T* | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 3.20 | 0.9341 | 0.8534 | 1.022 | 0.8098 | 0.9576 | 0.9068 |
| 3.30 | 0.9267 | 0.8481 | 1.014 | 0.8054 | 0.9517 | 0.9010 |
| 3.40 | 0.9198 | 0.8430 | 1.007 | 0.8011 | 0.9460 | 0.8956 |
| 3.50 | 0.9132 | 0.8382 | 0.9998 | 0.7971 | 0.9406 | 0.8903 |
| 3.60 | 0.9069 | 0.8336 | 0.9932 | 0.7932 | 0.9355 | 0.8854 |
| 3.70 | 0.9009 | 0.8292 | 0.9870 | 0.7894 | 0.9306 | 0.8807 |
| 3.80 | 0.8952 | 0.8250 | 0.9810 | 0.7858 | 0.9260 | 0.8761 |
| 3.90 | 0.8898 | 0.8209 | 0.9754 | 0.7823 | 0.9215 | 0.8718 |
| 4.00 | 0.8846 | 0.8170 | 0.9700 | 0.7790 | 0.9172 | 0.8677 |
| 4.10 | 0.8797 | 0.8133 | 0.9649 | 0.7757 | 0.9131 | 0.8637 |
| 4.20 | 0.8748 | 0.8097 | 0.9600 | 0.7726 | 0.9092 | 0.8599 |
| 4.30 | 0.8703 | 0.8062 | 0.9552 | 0.7696 | 0.9054 | 0.8562 |
| 4.40 | 0.8659 | 0.8029 | 0.9507 | 0.7666 | 0.9018 | 0.8527 |
| 4.50 | 0.8617 | 0.7996 | 0.9463 | 0.7638 | 0.8982 | 0.8493 |
| 4.60 | 0.8576 | 0.7965 | 0.9421 | 0.7614 | 0.8948 | 0.8460 |
| 4.70 | 0.8537 | 0.7935 | 0.9381 | 0.7586 | 0.8915 | 0.8428 |
| 4.80 | 0.8499 | 0.7905 | 0.9342 | 0.7557 | 0.8880 | 0.8397 |
| 4.90 | 0.8463 | 0.7876 | 0.9304 | 0.7532 | 0.8853 | 0.8367 |
| 5.00 | 0.8427 | 0.7849 | 0.9268 | 0.7507 | 0.8820 | 0.8228 |
| 5.10 | 0.8393 | 0.7822 | 0.9233 | 0.7483 | 0.8794 | 0.8310 |
| 5.20 | 0.8360 | 0.7796 | 0.9199 | 0.7460 | 0.8766 | 0.8283 |
| 5.30 | 0.8328 | 0.7770 | 0.9166 | 0.7437 | 0.8728 | 0.8256 |
| 5.40 | 0.8297 | 0.7745 | 0.9134 | 0.7414 | 0.8712 | 0.8231 |
| 5.50 | 0.8267 | 0.7721 | 0.9103 | 0.7393 | 0.8686 | 0.8205 |
| 5.60 | 0.8238 | 0.7698 | 0.9073 | 0.7372 | 0.8660 | 0.8181 |
| 5.70 | 0.8210 | 0.7675 | 0.9044 | 0.7351 | 0.8636 | 0.8157 |
| 5.80 | 0.8182 | 0.7652 | 0.9016 | 0.7331 | 0.8612 | 0.8124 |
| 5.90 | 0.8155 | 0.7630 | 0.8988 | 0.7312 | 0.8588 | 0.8111 |
| 6.00 | 0.8127 | 0.7609 | 0.8962 | 0.7291 | 0.8565 | 0.8089 |
| 6.10 | 0.8103 | 0.7588 | 0.8936 | 0.7272 | 0.8543 | 0.8068 |
| 6.20 | 0.8078 | 0.7567 | 0.8910 | 0.7253 | 0.8521 | 0.8046 |
| 6.30 | 0.8054 | 0.7547 | 0.8886 | 0.7235 | 0.8500 | 0.8026 |
| 6.40 | 0.8030 | 0.7528 | 0.8861 | 0.7217 | 0.8479 | 0.8006 |
| 6.50 | 0.8006 | 0.7508 | 0.8838 | 0.7200 | 0.8459 | 0.7986 |
| 6.60 | 0.7984 | 0.7490 | 0.8815 | 0.7182 | 0.8439 | 0.7966 |
| 6.70 | 0.7962 | 0.7471 | 0.8792 | 0.7165 | 0.8419 | 0.7974 |
| 6.80 | 0.7940 | 0.7453 | 0.8770 | 0.7149 | 0.8400 | 0.7929 |
| 6.90 | 0.7919 | 0.7435 | 0.8748 | 0.7132 | 0.8381 | 0.7911 |
| 7.00 | 0.7900 | 0.7418 | 0.8727 | 0.7116 | 0.8362 | 0.7893 |
| 7.10 | 0.7877 | 0.7401 | 0.8707 | 0.7101 | 0.8344 | 0.7875 |
| 7.20 | 0.7857 | 0.7384 | 0.8686 | 0.7085 | 0.8326 | 0.7858 |
| 7.30 | 0.7838 | 0.7368 | 0.8666 | 0.7070 | 0.8309 | 0.7841 |

Table 11.1. (continued)

| $T^*$ | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 7.40 | 0.782 | 0.7351 | 0.8647 | 0.7058 | 0.8292 | 0.7825 |
| 7.50 | 0.7800 | 0.7336 | 0.8628 | 0.7040 | 0.8275 | 0.7308 |
| 7.60 | 0.7782 | 0.7320 | 0.8609 | 0.7026 | 0.8258 | 0.7792 |
| 7.70 | 0.7762 | 0.7305 | 0.8591 | 0.7011 | 0.8242 | 0.7777 |
| 7.80 | 097744 | 0.7289 | 0.8573 | 0.6997 | 0.8226 | 0.7761 |
| 7.90 | 0.7727 | 0.7275 | 0.8555 | 0.6983 | 0.8210 | 0.7746 |
| 8.00 | 0.7710 | 0.7260 | 0.8538 | 0.6970 | 0.8195 | 0.7731 |
| 8.10 | 0.7693 | 0.7246 | 0.8521 | 0.6956 | 0.8179 | 0.7716 |
| 8.20 | 0.7677 | 0.7231 | 0.8504 | 0.6943 | 0.8164 | 0.7702 |
| 8.30 | 0.7661 | 3.7217 | 0.8488 | 0.6930 | 0.8150 | 0.7687 |
| 8.40 | 0.7645 | 0.7204 | 0.8472 | 0.6917 | 0.8135 | 0.7673 |
| 8.50 | 0.7629 | 0.7190 | 0.8455 | 0.6904 | 0.8120 | 0.7659 |
| 8.60 | 0.7614 | 0.7177 | 0.8440 | 0.6891 | 0.8106 | 0.7645 |
| 8.70 | 0.7599 | 0.7164 | 0.8424 | 0.6879 | 0.8092 | 0.7632 |
| 8.80 | 0.7584 | 0.7151 | 0.8409 | 0.6867 | 0.8078 | 0.7618 |
| 8.90 | 0.7569 | 0.7138 | 0.8394 | 0.6855 | 0.8064 | 0.7605 |
| 9.00 | 0.7555 | 0.7125 | 0.8379 | 0.6843 | 0.8051 | 0.7593 |
| 9.10 | 0.7540 | 0.7113 | 0.8365 | 0.6832 | 0.8038 | 0.7598 |
| 9.20 | 097526 | 0.7100 | 0.8351 | 0.6820 | 0.8025 | 0.7567 |
| 9.30 | 0.7513 | 0.7088 | 0.8337 | 0.6809 | 0.8012 | 0.7555 |
| 9.40 | 0.7499 | 0.7076 | 0.8323 | 0.6798 | 0.7999 | 0.7543 |
| 9.50 | 0.7486 | 0.7065 | 0.8309 | 0.6786 | 0.7987 | 0.7531 |
| 9.60 | 0.7473 | 0.7053 | 0.8296 | 0.6775 | 0.7974 | 0.7519 |
| 9.70 | 0.7460 | 0.7042 | 0.8282 | 0.6765 | 0.7962 | 0.7507 |
| 9.80 | 0.7447 | 0.7030 | 0.8269 | 0.6754 | 0.7950 | 0.7495 |
| 9.90 | 0.7434 | 0.7019 | 0.8256 | 0.6743 | 0.7938 | 0.7484 |
| 10.00 | 0.7421 | 0.7008 | 0.8243 | 0.6733 | 0.7926 | 0.7472 |
| 10.20 | 0.7397 | 0.6986 | 0.8218 | 0.6712 | 0.7903 | 0.7456 |
| 10.40 | 0.7373 | 0.6965 | 0.8194 | 0.6692 | 0.7881 | 0.7429 |
| 10.60 | 0.7350 | 0.6944 | 0.8170 | 0.6673 | 0.7859 | 0.7408 |
| 10.80 | 0.7328 | 0.6924 | 0.8147 | 0.6654 | 0.7837 | 0.7387 |
| 11.00 | 0.7305 | 0.6904 | 0.8124 | 0.6635 | 0.7816 | 0.7367 |
| 11.20 | 0.7284 | 0.6885 | 0.8132 | 3.6616 | 0.7796 | 0.7347 |
| 11.40 | 0.7263 | 0.6866 | 0.8081 | 0.6598 | 0.7776 | 0.7328 |
| 11.60 | 0.7242 | 0.6848 | 0.8059 | 0.6581 | 0.7759 | 0.7309 |
| 11.80 | 0.7222 | 0.6829 | 0.8039 | 0.6564 | 0.7736 | 0.7290 |
| 12.00 | 0.7232 | 0.6811 | 0.8018 | 0.6547 | 0.7718 | 0.7272 |
| 12.20 | 0.7183 | 0.6794 | 0.7999 | 0.6530 | 0.7699 | 0.7254 |
| 12.40 | 0.7164 | 0.6777 | 0.7979 | 0.6514 | 0.7681 | 0.7237 |
| 12.60 | 0.7143 | 0.6760 | 0.7960 | 0.6498 | 0.7663 | 0.7220 |
| 12.80 | 0.7128 | 0.6743 | 0.7941 | 0.6482 | 0.7645 | 0.7203 |
| 13.00 | 0.7110 | 0.6727 | 0.7923 | 0.6467 | 0.7629 | 0.7187 |

Table 11.1. (continued)

| T* | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 13.20 | 0.7092 | 0.6711 | 0.7905 | 0.6451 | 0.7611 | 0.7170 |
| 13.40 | 0.7075 | 0.6696 | 0.7887 | 0.6437 | 0.7594 | 0.7154 |
| 13.60 | 0.7058 | 0.6680 | 0.7870 | 0.6422 | 0.7578 | 0.7138 |
| 13.80 | 0.7042 | 0.6665 | 0.7853 | 0.6408 | 0.7562 | 0.7123 |
| 14.00 | 0.7026 | 0.6620 | 0.7837 | 0.6393 | 0.7546 | 0.7108 |
| 14.20 | 0.7010 | 0.6636 | 0.7820 | 0.6379 | 0.7531 | 0.7093 |
| 14.40 | 0.6994 | 0.6622 | 0.7804 | 0.6366 | 0.7515 | 0.7078 |
| 14.60 | 0.6979 | 0.6607 | 0.7788 | 0.6352 | 0.7500 | 0.7064 |
| 14.80 | 0.6964 | 0.6594 | 0.7772 | 0.6339 | 0.7485 | 0.7050 |
| 15.00 | 0.6949 | 0.6580 | 0.7757 | 0.6326 | 0.7471 | 0.7036 |
| 15.50 | 0.6913 | 0.6547 | 0.7719 | 0.6294 | 0.7435 | 0.7002 |
| 16.00 | 0.6878 | 0.6515 | 0.7683 | 0.6263 | 0.7401 | 0.6969 |
| 16.50 | 0.6845 | 0.6484 | 0.7649 | 0.6234 | 0.7368 | 0.6937 |
| 17.00 | 0.6812 | 0.6454 | 0.7615 | 0.6205 | 0.7336 | 0.6907 |
| 17.50 | 0.6781 | 0.6425 | 0.7583 | 0.6178 | 0.7305 | 0.6877 |
| 18.00 | 0.6751 | 0.6397 | 0.7552 | 0.6151 | 0.7275 | 0.6849 |
| 18.50 | 0.6722 | 0.6370 | 0.7522 | 0.6125 | 0.7246 | 0.6821 |
| 19.00 | 0.6694 | 0.6344 | 0.7492 | 0.6100 | 0.7218 | 0.6794 |
| 19.50 | 0.6667 | 0.6319 | 0.7464 | 0.6076 | 0.7191 | 0.6768 |
| 20.00 | 0.6641 | 0.6294 | 0.7436 | 0.6052 | 0.7164 | 0.6743 |
| 21.00 | 0.6590 | 0.6247 | 0.7383 | 0.6007 | 0.7114 | 0.6694 |
| 22.00 | 0.6543 | 0.6203 | 0.7333 | 0.5964 | 0.7065 | 0.6648 |
| 23.00 | 0.6497 | 0.6160 | 0.7286 | 0.5923 | 0.7020 | 0.6605 |
| 24.00 | 0.6455 | 0.6120 | 0.7241 | 0.5884 | 0.6976 | 0.6563 |
| 25.00 | 0.6414 | 0.6082 | 0.7198 | 0.5847 | 0.6934 | 0.6524 |
| 26.00 | 0.6375 | 0.6045 | 0.7156 | 0.5811 | 0.6895 | 0.6486 |
| 27.00 | 0.6338 | 0.6010 | 0.7117 | 0.5778 | 0.6856 | 0.6449 |
| 28.00 | 0.6302 | 0.5976 | 0.7080 | 0.5745 | 0.6820 | 0.6415 |
| 29.00 | 0.6268 | 0.5944 | 0.7043 | 0.5714 | 0.6785 | 0.6381 |
| 30.00 | 0.6235 | 0.5913 | 0.7008 | 0.5684 | 0.6751 | 0.6349 |
| 35.00 | 0.6088 | 0.5773 | 0.6851 | 0.5549 | 0.6598 | 0.6204 |
| 40.00 | 0.5963 | 0.5654 | 0.6717 | 0.5435 | 0.6468 | 0.6081 |
| 45.00 | 0.5855 | 0.5552 | 0.6601 | 0.5335 | 0.6355 | 0.5973 |
| 50.00 | 0.5760 | 0.5461 | 0.6498 | 0.5248 | 0.6255 | 0.5879 |
| 55.00 | 0.5675 | 0.5380 | 0.6406 | 0.5170 | 0.6166 | 0.5794 |
| 60.00 | 0.5598 | 0.5300 | 0.6323 | 0.5099 | 0.6085 | 0.5718 |
| 65.00 | 0.5529 | 0.5241 | 0.6248 | 0.5035 | 0.6012 | 0.5648 |
| 70.00 | 0.5465 | 0.5180 | 0.6178 | 0.4976 | 0.5944 | 0.5584 |
| 75.00 | 0.5407 | 0.5124 | 0.6114 | 0.4922 | 0.5882 | 0.5525 |
| 80.00 | 0.5352 | 0.5072 | 0.6054 | 0.4872 | 0.5824 | 0.5470 |
| 85.00 | 0.5301 | 0.5024 | 0.5998 | 0.4828 | 0.5770 | 0.5419 |
| 90.00 | 0.5254 | 0.4979 | 0.5946 | 0.4782 | 0.5797 | 0.5372 |

Table 11.1.    (continued)

| $T^*$ | $\Omega^{(1,1)\star}$ | $\Omega^{(1,2)\star}$ | $\Omega^{(2,2)\star}$ | $\Omega^{(1,3)\star}$ | $\Omega^{(2,3)\star}$ | $\Omega^{(3,3)\star}$ |
|---|---|---|---|---|---|---|
| 95.00 | 0.5210 | 0.4936 | 0.5898 | 0.4741 | 0.5672 | 0.5327 |
| 100.00 | 0.5168 | 0.4897 | 0.5851 | 0.4702 | 0.5627 | 0.5285 |
| 150.00 | 0.4847 | 0.4590 | 0.5497 | 0.4407 | 0.5284 | 0.4960 |
| 200.00 | 0.4630 | 0.4383 | 0.5256 | 0.4207 | 0.5050 | 0.4740 |
| 300.00 | 0.4338 | 0.4106 | 0.4931 | 0.3940 | 0.4736 | 0.4444 |
| 400.00 | 0.4142 | 0.3919 | 0.4711 | 0.3760 | 0.4523 | 0.4244 |
| 500.00 | 0.3995 | 0.3779 | 0.4546 | 0.3626 | 0.4364 | 0.4094 |
| 600.00 | 0.3878 | 0.3669 | 0.4415 | 0.3519 | 0.4238 | 0.3975 |
| 700.00 | 0.3783 | 0.3578 | 0.4307 | 0.3432 | 0.4133 | 0.3877 |
| 800.00 | 0.3701 | 0.3500 | 0.4215 | 0.3357 | 0.4045 | 0.3794 |
| 900.00 | 0.3631 | 0.3434 | 0.4136 | 0.3293 | 0.3968 | 0.3722 |
| 1000.00 | 0.3569 | 0.3375 | 0.4066 | 0.3237 | 0.3901 | 0.3659 |

Table 11.2. A Compilation of Hard Spherocylinder Projection Operator Integrals

| $\eta$ | $\bar{X}_s^{(-1)}$ | $\bar{X}_c^{(-1)}$ | $\bar{X}_s^{(1)}$ | $\bar{X}_c^{(1)}$ | $\bar{X}_s^{(3)}$ |
|---|---|---|---|---|---|
| 0.00 | 2.00000 | 2.00000 | 2.00000 | 2.00000 | 2.00000 |
| 0.01 | 2.00007 | 2.00003 | 1.99993 | 1.99997 | 1.99980 |
| 0.02 | 2.00027 | 2.00013 | 1.99973 | 1.99987 | 1.99920 |
| 0.03 | 2.00060 | 2.00030 | 1.99940 | 1.99970 | 1.99820 |
| 0.04 | 2.00107 | 2.00053 | 1.99893 | 1.99947 | 1.99680 |
| 0.05 | 2.00167 | 2.00083 | 1.99833 | 1.99917 | 1.99500 |
| 0.06 | 2.00240 | 2.00120 | 1.99760 | 1.99880 | 1.99281 |
| 0.07 | 2.00327 | 2.00164 | 1.99673 | 1.99836 | 1.99022 |
| 0.08 | 2.00428 | 2.00214 | 1.99573 | 1.99786 | 1.98723 |
| 0.09 | 2.00542 | 2.00271 | 1.99460 | 1.99730 | 1.98384 |
| 0.10 | 2.00670 | 2.00335 | 1.99333 | 1.99666 | 1.98007 |
| 0.11 | 2.00811 | 2.00406 | 1.99193 | 1.99596 | 1.97590 |
| 0.12 | 2.00966 | 2.00484 | 1.99039 | 1.99518 | 1.97134 |
| 0.13 | 2.01136 | 2.00568 | 1.98872 | 1.99435 | 1.96639 |
| 0.14 | 2.01319 | 2.00660 | 1.98692 | 1.99344 | 1.96106 |
| 0.15 | 2.01516 | 2.00759 | 1.98498 | 1.99246 | 1.95534 |
| 0.16 | 2.01727 | 2.00865 | 1.98290 | 1.99142 | 1.94924 |
| 0.17 | 2.01953 | 2.00978 | 1.98070 | 1.99031 | 1.94275 |
| 0.18 | 2.02193 | 2.01098 | 1.97835 | 1.98912 | 1.93590 |
| 0.19 | 2.02448 | 2.01226 | 1.97588 | 1.98787 | 1.92866 |
| 0.20 | 2.02717 | 2.01361 | 1.97326 | 1.98655 | 1.92106 |
| 0.21 | 2.03002 | 2.01504 | 1.97051 | 1.98516 | 1.91309 |
| 0.22 | 2.03301 | 2.01655 | 1.96763 | 1.98370 | 1.90475 |
| 0.23 | 2.03616 | 2.01813 | 1.96461 | 1.98216 | 1.89605 |
| 0.24 | 2.03946 | 2.01979 | 1.96145 | 1.98056 | 1.88699 |
| 0.25 | 2.04291 | 2.02153 | 1.95816 | 1.97888 | 1.87758 |
| 0.26 | 2.04653 | 2.92334 | 1.95473 | 1.97713 | 1.86782 |
| 0.27 | 2.05031 | 2.02525 | 1.95116 | 1.97531 | 1.85771 |
| 0.28 | 2.05424 | 2.02723 | 1.94746 | 1.97342 | 1.84726 |
| 0.29 | 2.05835 | 2.02930 | 1.94362 | 1.97145 | 1.83646 |
| 0.30 | 2.06262 | 2.03145 | 1.93964 | 1.96940 | 1.82534 |
| 0.31 | 2.06706 | 2.03370 | 1.93552 | 1.96729 | 1.81388 |
| 0.32 | 2.07168 | 2.03603 | 1.93126 | 1.96509 | 1.80210 |
| 0.33 | 2.07647 | 2.03845 | 1.92687 | 1.96282 | 1.78999 |
| 0.34 | 2.08144 | 2.04096 | 1.92233 | 1.96048 | 1.77757 |
| 0.35 | 2.08659 | 2.04357 | 1.91766 | 1.95805 | 1.76484 |
| 0.36 | 2.09193 | 2.04627 | 1.91284 | 1.95555 | 1.75181 |
| 0.37 | 2.09745 | 2.04907 | 1.90789 | 1.95297 | 1.73847 |
| 0.38 | 2.10317 | 2.05197 | 1.90279 | 1.95031 | 1.72484 |
| 0.39 | 2.10909 | 2.05497 | 1.89756 | 1.94757 | 1.71091 |

| $\overline{X}_c^{(3)}$ | $\overline{X}_s^{(5)}$ | $\overline{X}_c^{(5)}$ | $\overline{T}_{sc}^{(1,2)}$ | $\overline{T}_{sc}^{(3,2)}$ | $\overline{G}_{sc}$ |
|---|---|---|---|---|---|
| 2.00000 | 2.00000 | 2.00000 | 2.00000 | 2.00000 | 0.00000 |
| 1.99990 | 1.99967 | 1.99963 | 1.99999 | 1.99978 | 0.05266 |
| 1.99960 | 1.99867 | 1.99933 | 1.99986 | 1.99947 | 0.07076 |
| 1.99910 | 1.99700 | 1.99850 | 1.99964 | 1.99891 | 0.08653 |
| 1.99840 | 1.99467 | 1.99733 | 1.99936 | 1.99807 | 0.09991 |
| 1.99750 | 1.99168 | 1.99584 | 1.99900 | 1.99700 | 0.11167 |
| 1.99640 | 1.98803 | 1.99401 | 1.99856 | 1.99568 | 0.12226 |
| 1.99510 | 1.98373 | 1.99185 | 1.99804 | 1.99412 | 0.13196 |
| 1.99360 | 1.97877 | 1.98936 | 1.99744 | 1.99232 | 0.14097 |
| 1.99191 | 1.97316 | 1.98654 | 1.99675 | 1.99023 | 0.14939 |
| 1.99001 | 1.96691 | 1.98340 | 1.99599 | 1.98801 | 0.15732 |
| 1.98791 | 1.96002 | 1.97993 | 1.99515 | 1.98549 | 0.16483 |
| 1.98562 | 1.95250 | 1.97613 | 1.99422 | 1.98273 | 0.17196 |
| 1.98312 | 1.94436 | 1.97201 | 1.99321 | 1.97974 | 0.17875 |
| 1.98043 | 1.93560 | 1.96758 | 1.99212 | 1.97650 | 0.18525 |
| 1.97754 | 1.92623 | 1.96268 | 1.99095 | 1.97303 | 0.19147 |
| 1.97445 | 1.91625 | 1.95775 | 1.98970 | 1.96932 | 0.19744 |
| 1.97117 | 1.90568 | 1.95236 | 1.98836 | 1.96537 | 0.20318 |
| 1.96769 | 1.89453 | 1.94666 | 1.98694 | 1.96118 | 0.20869 |
| 1.96401 | 1.88280 | 1.94066 | 1.98544 | 1.95676 | 0.21401 |
| 1.96013 | 1.87051 | 1.93434 | 1.98385 | 1.95209 | 0.21913 |
| 1.95606 | 1.85767 | 1.92773 | 1.98217 | 1.94719 | 0.22408 |
| 1.95179 | 1.84428 | 1.92081 | 1.98041 | 1.94206 | 0.22884 |
| 1.94733 | 1.83036 | 1.91360 | 1.97857 | 1.93668 | 0.23345 |
| 1.94268 | 1.81591 | 1.90609 | 1.97664 | 1.93107 | 0.23789 |
| 1.93782 | 1.80097 | 1.89829 | 1.97462 | 1.92523 | 0.24219 |
| 1.93278 | 1.78552 | 1.89020 | 1.97252 | 1.91915 | 0.24633 |
| 1.92754 | 1.76960 | 1.88183 | 1.97033 | 1.91283 | 0.25033 |
| 1.92211 | 1.75320 | 1.87318 | 1.96805 | 1.90628 | 0.25420 |
| 1.91649 | 1.73635 | 1.86425 | 1.96568 | 1.89950 | 0.25793 |
| 1.91067 | 1.71906 | 1.85505 | 1.96322 | 1.89248 | 0.26153 |
| 1.90467 | 1.70134 | 1.84558 | 1.96066 | 1.88523 | 0.26501 |
| 1.89847 | 1.68321 | 1.83585 | 1.95802 | 1.87774 | 0.26836 |
| 1.89208 | 1.66469 | 1.82586 | 1.95529 | 1.87003 | 0.27158 |
| 1.88551 | 1.64578 | 1.81561 | 1.95246 | 1.86208 | 0.27469 |
| 1.87875 | 1.62650 | 1.80511 | 1.94954 | 1.85390 | 0.27768 |
| 1.87179 | 1.60688 | 1.79437 | 1.94652 | 1.84549 | 0.28055 |
| 1.86465 | 1.58691 | 1.78338 | 1.94341 | 1.83685 | 0.28331 |
| 1.85733 | 1.56663 | 1.77215 | 1.94020 | 1.82798 | 0.28596 |
| 1.84982 | 1.54605 | 1.76069 | 1.93689 | 1.81888 | 0.28849 |

Table 11.2. (continued)

| $\eta$ | $\bar{X}^{(-1)}_s$ | $\bar{X}^{(-1)}_c$ | $\bar{X}^{(1)}_s$ | $\bar{X}^{(1)}_c$ | $\bar{X}^{(3)}_s$ |
|------|---------|---------|---------|---------|---------|
| 0.40 | 2.11521 | 2.05808 | 1.89218 | 1.94475 | 1.69571 |
| 0.41 | 2.12153 | 2.06129 | 1.88666 | 1.94185 | 1.68222 |
| 0.42 | 2.12806 | 2.06462 | 1.88099 | 1.93887 | 1.66746 |
| 0.43 | 2.13480 | 2.06805 | 1.87519 | 1.93580 | 1.65244 |
| 0.44 | 2.14176 | 2.07160 | 1.86924 | 1.93264 | 1.63715 |
| 0.45 | 2.14895 | 2.07526 | 1.86314 | 1.92941 | 1.62161 |
| 0.46 | 2.15636 | 2.07905 | 1.85690 | 1.92608 | 1.60582 |
| 0.47 | 2.16400 | 2.08295 | 1.85052 | 1.92267 | 1.58979 |
| 0.48 | 2.17189 | 2.08699 | 1.84399 | 1.91917 | 1.57352 |
| 0.49 | 2.18002 | 2.09115 | 1.83731 | 1.91558 | 1.55702 |
| 0.50 | 2.18840 | 2.09544 | 1.83049 | 1.91190 | 1.54030 |
| 0.51 | 2.19703 | 2.09988 | 1.82352 | 1.90813 | 1.52337 |
| 0.52 | 2.20593 | 2.10445 | 1.81640 | 1.90427 | 1.50622 |
| 0.53 | 2.21510 | 2.10916 | 1.80913 | 1.90031 | 1.48887 |
| 0.54 | 2.22455 | 2.11402 | 1.80171 | 1.89626 | 1.47133 |
| 0.55 | 2.23428 | 2.11904 | 1.79415 | 1.89211 | 1.45360 |
| 0.56 | 2.24431 | 2.12421 | 1.78643 | 1.88786 | 1.43568 |
| 0.57 | 2.25463 | 2.12954 | 1.77856 | 1.88351 | 1.41759 |
| 0.58 | 2.26527 | 2.13504 | 1.77054 | 1.87907 | 1.39934 |
| 0.59 | 2.27622 | 2.14071 | 1.76236 | 1.87452 | 1.38092 |
| 0.60 | 2.28750 | 2.14656 | 1.75404 | 1.86987 | 1.36236 |
| 0.61 | 2.29912 | 2.15259 | 1.74555 | 1.86511 | 1.34365 |
| 0.62 | 2.31108 | 2.15881 | 1.73692 | 1.86025 | 1.32480 |
| 0.63 | 2.32340 | 2.16522 | 1.72812 | 1.85528 | 1.30582 |
| 0.64 | 2.33609 | 2.17183 | 1.71917 | 1.85020 | 1.28672 |
| 0.65 | 2.34917 | 2.17865 | 1.71007 | 1.84501 | 1.26750 |
| 0.66 | 2.36263 | 2.18569 | 1.70080 | 1.83970 | 1.24818 |
| 0.67 | 2.37650 | 2.19294 | 1.69138 | 1.83428 | 1.22875 |
| 0.68 | 2.39078 | 2.20043 | 1.68179 | 1.82874 | 1.20924 |
| 0.69 | 2.40550 | 2.20815 | 1.67205 | 1.82309 | 1.18964 |
| 0.70 | 2.42067 | 2.21612 | 1.66214 | 1.81731 | 1.16997 |
| 0.71 | 2.43630 | 2.22434 | 1.65207 | 1.81141 | 1.15023 |
| 0.72 | 2.45241 | 2.23283 | 1.64183 | 1.80539 | 1.13042 |
| 0.73 | 2.46901 | 2.24159 | 1.63144 | 1.79924 | 1.11057 |
| 0.74 | 2.48612 | 2.25063 | 1.62087 | 1.79296 | 1.09067 |
| 0.75 | 2.50377 | 2.25997 | 1.61014 | 1.78654 | 1.07074 |
| 0.76 | 2.52196 | 2.26962 | 1.59924 | 1.78000 | 1.05077 |
| 0.77 | 2.54073 | 2.27959 | 1.58817 | 1.77331 | 1.03079 |
| 0.78 | 2.56001 | 2.28989 | 1.57693 | 1.76649 | 1.01080 |
| 0.79 | 2.58001 | 2.30053 | 1.56552 | 1.75952 | 0.99080 |

| $\overline{X}_c^{(3)}$ | $\overline{X}_s^{(5)}$ | $\overline{X}_c^{(5)}$ | $\overline{T}_{sc}^{(1,2)}$ | $\overline{T}_{sc}^{(3,2)}$ | $\overline{G}_{sc}$ |
|---|---|---|---|---|---|
| 1.84212 | 1.52517 | 1.74900 | 1.93349 | 1.80956 | 0.29092 |
| 1.83424 | 1.50403 | 1.73709 | 1.92938 | 1.80001 | 0.29323 |
| 1.82618 | 1.48263 | 1.72497 | 1.92638 | 1.79023 | 0.29544 |
| 1.81793 | 1.46100 | 1.71262 | 1.92267 | 1.78022 | 0.29754 |
| 1.80950 | 1.43914 | 1.70007 | 1.91886 | 1.76999 | 0.29954 |
| 1.80089 | 1.41708 | 1.68732 | 1.91494 | 1.75954 | 0.30143 |
| 1.79210 | 1.39483 | 1.67437 | 1.91092 | 1.74886 | 0.30322 |
| 1.78314 | 1.37240 | 1.66123 | 1.90679 | 1.73797 | 0.30490 |
| 1.77399 | 1.34983 | 1.64789 | 1.90256 | 1.72685 | 0.30648 |
| 1.76467 | 1.32711 | 1.63438 | 1.89821 | 1.71551 | 0.30796 |
| 1.75517 | 1.30428 | 1.62069 | 1.89376 | 1.70395 | 0.30934 |
| 1.74549 | 1.28134 | 1.60683 | 1.88919 | 1.69217 | 0.31061 |
| 1.73564 | 1.25831 | 1.59280 | 1.88451 | 1.68018 | 0.31179 |
| 1.72561 | 1.23520 | 1.57861 | 1.87971 | 1.66796 | 0.31286 |
| 1.71542 | 1.21205 | 1.56427 | 1.87480 | 1.65554 | 0.31384 |
| 1.70505 | 1.18885 | 1.54977 | 1.86977 | 1.64290 | 0.31471 |
| 1.69451 | 1.16562 | 1.53514 | 1.86462 | 1.63005 | 0.31548 |
| 1.68380 | 1.14239 | 1.52036 | 1.85934 | 1.61699 | 0.31616 |
| 1.67293 | 1.11916 | 1.50545 | 1.85395 | 1.60372 | 0.31673 |
| 1.66188 | 1.09596 | 1.49041 | 1.84843 | 1.59024 | 0.31721 |
| 1.65067 | 1.07279 | 1.47525 | 1.84278 | 1.57655 | 0.31759 |
| 1.63930 | 1.04968 | 1.45997 | 1.83700 | 1.56266 | 0.31787 |
| 1.62776 | 1.02663 | 1.44458 | 1.83109 | 1.54857 | 0.31805 |
| 1.61606 | 1.00366 | 1.42908 | 1.82505 | 1.53427 | 0.31813 |
| 1.60419 | 0.98078 | 1.41348 | 1.81887 | 1.51977 | 0.31811 |
| 1.59217 | 0.95802 | 1.39779 | 1.81256 | 1.50508 | 0.31800 |
| 1.57998 | 0.93537 | 1.38201 | 1.80611 | 1.49019 | 0.31779 |
| 1.56764 | 0.91286 | 1.36614 | 1.79951 | 1.47510 | 0.31748 |
| 1.55515 | 0.89050 | 1.35019 | 1.79278 | 1.45982 | 0.31707 |
| 1.54249 | 0.86830 | 1.33416 | 1.78589 | 1.44435 | 0.31656 |
| 1.52968 | 0.84626 | 1.31807 | 1.77886 | 1.42869 | 0.31596 |
| 1.51672 | 0.82441 | 1.30191 | 1.77168 | 1.41285 | 0.31526 |
| 1.50361 | 0.80276 | 1.28569 | 1.76434 | 1.39682 | 0.31446 |
| 1.49035 | 0.78131 | 1.26942 | 1.75685 | 1.38060 | 0.31357 |
| 1.47694 | 0.76008 | 1.25310 | 1.74920 | 1.36421 | 0.31257 |
| 1.46338 | 0.73907 | 1.23673 | 1.74139 | 1.34764 | 0.31144 |
| 1.44967 | 0.71830 | 1.22033 | 1.73341 | 1.33090 | 0.31030 |
| 1.43582 | 0.69777 | 1.20389 | 1.72526 | 1.31399 | 0.30902 |
| 1.42183 | 0.67750 | 1.18741 | 1.71695 | 1.29690 | 0.30764 |
| 1.40769 | 0.65749 | 1.17092 | 1.70856 | 1.27965 | 0.30616 |

Table 11.2. (continued)

| $\eta$ | $\overline{X}^{(-1)}_s$ | $\overline{X}^{(-1)}_c$ | $\overline{X}^{(1)}_s$ | $\overline{X}^{(1)}_c$ | $\overline{X}^{(3)}_s$ |
|---|---|---|---|---|---|
| 0.80 | 2.60068 | 2.31153 | 1.55394 | 1.75241 | 0.97080 |
| 0.81 | 2.62196 | 2.32291 | 1.54219 | 1.74516 | 0.95082 |
| 0.82 | 2.64393 | 2.33467 | 1.53026 | 1.73775 | 0.93085 |
| 0.83 | 2.66663 | 2.34685 | 1.51815 | 1.73019 | 0.91091 |
| 0.84 | 2.69007 | 2.35945 | 1.50587 | 1.72247 | 0.89101 |
| 0.85 | 2.71429 | 2.37249 | 1.49341 | 1.71459 | 0.87116 |
| 0.86 | 2.73932 | 2.38599 | 1.48077 | 1.70655 | 0.85135 |
| 0.87 | 2.76521 | 2.39998 | 1.46795 | 1.69834 | 0.83160 |
| 0.88 | 2.79198 | 2.41447 | 1.45495 | 1.68997 | 0.81192 |
| 0.89 | 2.81968 | 2.42949 | 1.44176 | 1.68141 | 0.79232 |
| 0.90 | 2.84834 | 2.44507 | 1.42839 | 1.67268 | 0.77280 |
| 0.91 | 2.87801 | 2.46123 | 1.41483 | 1.66377 | 0.75337 |
| 0.92 | 2.90875 | 2.47799 | 1.40109 | 1.65467 | 0.73404 |
| 0.93 | 2.94059 | 2.49540 | 1.38716 | 1.64539 | 0.71481 |
| 0.94 | 2.97360 | 2.51348 | 1.37303 | 1.63591 | 0.69570 |
| 0.95 | 3.00782 | 2.53226 | 1.35871 | 1.62622 | 0.67671 |
| 0.96 | 3.04332 | 2.55179 | 1.34420 | 1.61634 | 0.65785 |
| 0.97 | 3.08017 | 2.57210 | 1.32949 | 1.60624 | 0.63913 |
| 0.98 | 3.11843 | 2.59323 | 1.31459 | 1.59594 | 0.62055 |
| 0.99 | 3.15818 | 2.61523 | 1.29949 | 1.58541 | 0.60212 |
| 1.00 | 3.19950 | 2.63814 | 1.28419 | 1.57466 | 0.58385 |
| 1.01 | 3.24247 | 2.66203 | 1.26868 | 1.56367 | 0.56575 |
| 1.02 | 3.28718 | 2.68694 | 1.25297 | 1.55245 | 0.54782 |
| 1.03 | 3.33373 | 2.71293 | 1.23706 | 1.54099 | 0.53008 |
| 1.04 | 3.38223 | 2.74006 | 1.22093 | 1.52928 | 0.51252 |
| 1.05 | 3.43278 | 2.76842 | 1.20460 | 1.51761 | 0.49515 |
| 1.06 | 3.48552 | 2.79807 | 1.18806 | 1.50508 | 0.47799 |
| 1.07 | 3.54057 | 2.82908 | 1.17130 | 1.49258 | 0.46104 |
| 1.08 | 3.59808 | 2.86156 | 1.15433 | 1.47980 | 0.44430 |
| 1.09 | 3.65820 | 2.89560 | 1.13714 | 1.46673 | 0.42779 |
| 1.10 | 3.72110 | 2.93129 | 1.11973 | 1.45337 | 0.41150 |
| 1.11 | 3.78696 | 2.96876 | 1.10210 | 1.43971 | 0.39545 |
| 1.12 | 3.85599 | 3.00812 | 1.08424 | 1.42573 | 0.37964 |
| 1.13 | 3.92840 | 3.04950 | 1.06616 | 1.41143 | 0.36408 |
| 1.14 | 4.00442 | 3.09307 | 1.04785 | 1.39680 | 0.34877 |
| 1.15 | 4.08433 | 3.13897 | 1.02931 | 1.38183 | 0.33372 |
| 1.16 | 4.16840 | 3.18738 | 1.01054 | 1.36650 | 0.31894 |
| 1.17 | 4.25694 | 3.23851 | 0.99153 | 1.35080 | 0.30444 |
| 1.18 | 4.35032 | 3.29256 | 0.97229 | 1.33473 | 0.29021 |
| 1.19 | 4.44890 | 3.34977 | 0.95280 | 1.31827 | 0.27626 |

| $\overline{X}_c^{(3)}$ | $\overline{X}_s^{(5)}$ | $\overline{X}_c^{(5)}$ | $\overline{T}_{sc}^{(1,2)}$ | $\overline{T}_{sc}^{(3,2)}$ | $\overline{G}_{sc}$ |
|---|---|---|---|---|---|
| 1.39341 | 0.63775 | 1.15440 | 1.69980 | 1.26224 | 0.30459 |
| 1.37900 | 0.61829 | 1.13786 | 1.69095 | 1.24467 | 0.30292 |
| 1.36444 | 0.59911 | 1.12131 | 1.68192 | 1.22694 | 0.30116 |
| 1.34975 | 0.58023 | 1.10475 | 1.67271 | 1.20905 | 0.29930 |
| 1.33493 | 0.56164 | 1.08819 | 1.66330 | 1.19102 | 0.29734 |
| 1.31997 | 0.54336 | 1.07163 | 1.65370 | 1.17284 | 0.29529 |
| 1.30487 | 0.52538 | 1.05507 | 1.64390 | 1.15451 | 0.29314 |
| 1.28965 | 0.50772 | 1.03852 | 1.63390 | 1.13605 | 0.29090 |
| 1.27430 | 0.49038 | 1.02197 | 1.62370 | 1.11745 | 0.28857 |
| 1.25882 | 0.47336 | 1.00545 | 1.61328 | 1.09872 | 0.28614 |
| 1.24322 | 0.45667 | 0.98894 | 1.60266 | 1.07986 | 0.28362 |
| 1.22749 | 0.44031 | 0.97245 | 1.59181 | 1.06089 | 0.28100 |
| 1.21164 | 0.42428 | 0.95599 | 1.58074 | 1.04179 | 0.27829 |
| 1.19567 | 0.40859 | 0.93956 | 1.56944 | 1.02258 | 0.27549 |
| 1.17958 | 0.39323 | 0.92316 | 1.55792 | 1.00326 | 0.27259 |
| 1.16337 | 0.37822 | 0.90679 | 1.54615 | 0.98383 | 0.26961 |
| 1.14704 | 0.36354 | 0.89046 | 1.53415 | 0.96431 | 0.26653 |
| 1.13060 | 0.34920 | 0.87417 | 1.52189 | 0.94470 | 0.26337 |
| 1.11405 | 0.33521 | 0.85792 | 1.50939 | 0.92500 | 0.26011 |
| 1.09738 | 0.32156 | 0.84171 | 1.49663 | 0.90521 | 0.25677 |
| 1.08060 | 0.30825 | 0.82556 | 1.48360 | 0.88535 | 0.25333 |
| 1.06372 | 0.29528 | 0.80945 | 1.47031 | 0.86543 | 0.24981 |
| 1.04673 | 0.28264 | 0.79339 | 1.45674 | 0.84544 | 0.24621 |
| 1.02964 | 0.27035 | 0.77739 | 1.44289 | 0.82539 | 0.24252 |
| 1.01244 | 0.25840 | 0.76144 | 1.42875 | 0.80529 | 0.23874 |
| 0.99514 | 0.24678 | 0.74555 | 1.41433 | 0.78515 | 0.23488 |
| 0.97774 | 0.23549 | 0.72972 | 1.39960 | 0.76498 | 0.23094 |
| 0.96025 | 0.22453 | 0.71395 | 1.38456 | 0.74478 | 0.22692 |
| 0.94266 | 0.21390 | 0.69824 | 1.36921 | 0.72456 | 0.22282 |
| 0.92497 | 0.20360 | 0.68260 | 1.35354 | 0.70433 | 0.21864 |
| 0.90719 | 0.19361 | 0.66701 | 1.33755 | 0.68410 | 0.21439 |
| 0.88932 | 0.18394 | 0.65150 | 1.32121 | 0.66387 | 0.21006 |
| 0.87136 | 0.17459 | 0.63604 | 1.30453 | 0.64366 | 0.20565 |
| 0.85332 | 0.16554 | 0.62066 | 1.28750 | 0.62348 | 0.20118 |
| 0.83519 | 0.15680 | 0.60534 | 1.27012 | 0.60333 | 0.19663 |
| 0.81697 | 0.14837 | 0.59009 | 1.25236 | 0.58323 | 0.19202 |
| 0.79868 | 0.14022 | 0.57491 | 1.23422 | 0.56319 | 0.18734 |
| 0.78030 | 0.13237 | 0.55979 | 1.21570 | 0.54321 | 0.18260 |
| 0.76185 | 0.12481 | 0.54475 | 1.19678 | 0.52331 | 0.17780 |
| 0.74332 | 0.11753 | 0.52977 | 1.17745 | 0.50350 | 0.17294 |

Table 11.2. (continued)

| $\eta$ | $\overline{X}_s^{(-1)}$ | $\overline{X}_c^{(-1)}$ | $\overline{X}_s^{(1)}$ | $\overline{X}_c^{(1)}$ | $\overline{X}_s^{(3)}$ |
|---|---|---|---|---|---|
| 1.20 | 4.55312 | 3.41040 | 0.93307 | 1.30140 | 0.26261 |
| 1.21 | 4.66344 | 3.47476 | 0.91310 | 1.28411 | 0.24925 |
| 1.22 | 4.78040 | 3.54317 | 0.89287 | 1.26639 | 0.23618 |
| 1.23 | 4.90457 | 3.61599 | 0.87240 | 1.24822 | 0.22343 |
| 1.24 | 5.03663 | 3.69364 | 0.85167 | 1.22958 | 0.21099 |
| 1.25 | 5.17730 | 3.77658 | 0.83068 | 1.21045 | 0.19886 |
| 1.26 | 5.32744 | 3.86534 | 0.80944 | 1.19082 | 0.18705 |
| 1.27 | 5.48798 | 3.96051 | 0.78793 | 1.17066 | 0.17556 |
| 1.28 | 5.66001 | 4.06276 | 0.76616 | 1.14995 | 0.16441 |
| 1.29 | 5.84475 | 4.17287 | 0.74412 | 1.12867 | 0.15349 |
| 1.30 | 6.04363 | 4.29173 | 0.72180 | 1.10680 | 0.14311 |
| 1.31 | 6.25828 | 4.42037 | 0.69921 | 1.08430 | 0.13297 |
| 1.32 | 6.49059 | 4.55998 | 0.67634 | 1.06114 | 0.12318 |
| 1.33 | 6.74277 | 4.71194 | 0.65319 | 1.03730 | 0.11374 |
| 1.34 | 7.01741 | 4.87790 | 0.62976 | 1.01274 | 0.10466 |
| 1.35 | 7.31756 | 5.05978 | 0.60603 | 0.98742 | 0.09593 |
| 1.36 | 7.64689 | 5.25988 | 0.58201 | 0.96130 | 0.08756 |
| 1.37 | 8.00974 | 5.48097 | 0.55770 | 0.93434 | 0.07956 |
| 1.38 | 8.41440 | 5.72637 | 0.53308 | 0.90649 | 0.07193 |
| 1.39 | 8.85834 | 6.00018 | 0.50816 | 0.87770 | 0.06467 |
| 1.40 | 9.35850 | 6.30744 | 0.48293 | 0.84789 | 0.05778 |
| 1.41 | 9.92185 | 6.65444 | 0.45739 | 0.81702 | 0.05127 |
| 1.42 | 10.5610 | 7.04916 | 0.43154 | 0.78500 | 0.04514 |
| 1.43 | 11.2920 | 7.50185 | 0.40536 | 0.75174 | 0.03939 |
| 1.44 | 12.1361 | 8.02589 | 0.37886 | 0.71715 | 0.03402 |
| 1.45 | 13.1212 | 8.63913 | 0.35202 | 0.68112 | 0.02904 |
| 1.46 | 14.2858 | 9.36582 | 0.32486 | 0.64352 | 0.02445 |
| 1.47 | 15.6831 | 10.2399 | 0.29735 | 0.60420 | 0.02025 |
| 1.48 | 17.3902 | 11.3103 | 0.26950 | 0.56296 | 0.01644 |
| 1.49 | 19.5219 | 12.6501 | 0.24130 | 0.51959 | 0.01303 |
| 1.50 | 22.2585 | 14.3737 | 0.21274 | 0.47381 | 0.01001 |
| 1.51 | 25.8983 | 16.6711 | 0.18383 | 0.42526 | 0.00738 |
| 1.52 | 30.9750 | 19.8817 | 0.15455 | 0.37346 | 0.00516 |
| 1.53 | 38.5450 | 24.6777 | 0.12491 | 0.31775 | 0.00333 |
| 1.54 | 51.0376 | 32.6051 | 0.09488 | 0.25713 | 0.00190 |
| 1.55 | 75.5539 | 48.1839 | 0.06448 | 0.18994 | 0.00086 |
| 1.56 | 145.505 | 92.6823 | 0.03369 | 0.11275 | 0.00023 |
| 1.57 | 1972.55 | 1255.77 | 0.00250 | 0.01247 | $1.3(10^{-6})$ |
| $\dfrac{\pi}{2}$ | $\infty$ | $\infty$ | 0.00000 | 0.00000 | 0.00000 |

| $\overline{X}_c^{(3)}$ | $\overline{X}_s^{(5)}$ | $\overline{X}_c^{(5)}$ | $\overline{T}_{sc}^{(1,2)}$ | $\overline{T}_{sc}^{(3,2)}$ | $\overline{G}_{sc}$ |
|---|---|---|---|---|---|
| 0.72472 | 0.11052 | 0.51486 | 1.15771 | 0.48380 | 0.16802 |
| 0.70604 | 0.10379 | 0.50002 | 1.13754 | 0.46421 | 0.16306 |
| 0.68729 | 0.09732 | 0.48525 | 1.11693 | 0.44475 | 0.15804 |
| 0.66848 | 0.09112 | 0.47054 | 1.09588 | 0.42544 | 0.15297 |
| 0.64959 | 0.08517 | 0.45590 | 1.07436 | 0.40628 | 0.14787 |
| 0.63064 | 0.07947 | 0.44133 | 1.05238 | 0.38730 | 0.14272 |
| 0.61163 | 0.07401 | 0.42682 | 1.02991 | 0.36850 | 0.13754 |
| 0.59256 | 0.06880 | 0.41238 | 1.00694 | 0.34991 | 0.13233 |
| 0.57343 | 0.06381 | 0.39800 | 0.98347 | 0.33154 | 0.12709 |
| 0.55424 | 0.05906 | 0.38368 | 0.95947 | 0.31341 | 0.12182 |
| 0.53500 | 0.05453 | 0.36943 | 0.93493 | 0.29553 | 0.11654 |
| 0.51570 | 0.05022 | 0.35523 | 0.90985 | 0.27793 | 0.11125 |
| 0.49635 | 0.04612 | 0.34109 | 0.88420 | 0.26063 | 0.10595 |
| 0.47695 | 0.04223 | 0.32701 | 0.85797 | 0.24364 | 0.10065 |
| 0.45751 | 0.03854 | 0.31298 | 0.83114 | 0.22698 | 0.09535 |
| 0.43801 | 0.03504 | 0.29901 | 0.80370 | 0.21069 | 0.09007 |
| 0.41848 | 0.03174 | 0.28509 | 0.77563 | 0.19477 | 0.08480 |
| 0.39890 | 0.02863 | 0.27122 | 0.74692 | 0.17926 | 0.07956 |
| 0.37928 | 0.02570 | 0.25740 | 0.71754 | 0.16417 | 0.07435 |
| 0.35963 | 0.02295 | 0.24363 | 0.68747 | 0.14954 | 0.06919 |
| 0.33993 | 0.02037 | 0.22990 | 0.65671 | 0.13539 | 0.06408 |
| 0.32021 | 0.01797 | 0.21621 | 0.62522 | 0.12175 | 0.05903 |
| 0.30045 | 0.01572 | 0.20256 | 0.59299 | 0.10864 | 0.05405 |
| 0.28066 | 0.01365 | 0.18895 | 0.55999 | 0.09610 | 0.04915 |
| 0.26085 | 0.01173 | 0.17538 | 0.52620 | 0.08416 | 0.04435 |
| 0.24101 | 0.00996 | 0.16184 | 0.49161 | 0.07285 | 0.03965 |
| 0.22114 | 0.00835 | 0.14833 | 0.45618 | 0.06220 | 0.03508 |
| 0.20125 | 0.00689 | 0.13485 | 0.41990 | 0.05225 | 0.03065 |
| 0.18134 | 0.00557 | 0.12139 | 0.38273 | 0.04303 | 0.02638 |
| 0.16142 | 0.00440 | 0.10796 | 0.34465 | 0.03459 | 0.02228 |
| 0.14147 | 0.00337 | 0.09455 | 0.30563 | 0.02696 | 0.01838 |
| 0.12152 | 0.00248 | 0.08116 | 0.26565 | 0.02019 | 0.01471 |
| 0.10155 | 0.00173 | 0.06779 | 0.22468 | 0.01431 | 0.01129 |
| 0.08157 | 0.00111 | 0.05443 | 0.18267 | 0.00937 | 0.00816 |
| 0.06158 | 0.00063 | 0.04107 | 0.13961 | 0.00542 | 0.00537 |
| 0.04159 | 0.00029 | 0.02773 | 0.09546 | 0.00251 | 0.00299 |
| 0.02159 | 0.00008 | 0.01440 | 0.05018 | 0.00069 | 0.00112 |
| 0.00159 | $4.2(10^{-7})$ | 0.00106 | 0.00375 | $3.8(10^{-6})$ | 0.00002 |
| 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |

## 12. APPENDIX E: SCALAR COLLISION INTEGRALS

Table 12.1. Central Potential Scalar Collision Integrals

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma};\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 4\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma};\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 12\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,2)\star}$ |
| $\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 48\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,3)\star}$ |
| $\{\underline{\gamma};\underline{\gamma}\Omega^2\}$ $\{\underline{\gamma}\Omega^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 4\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 12\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,2)\star}$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 8\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma};\underline{\Omega}(\underline{\gamma}\cdot\underline{\Omega})\}$ $\{(\underline{\gamma}\cdot\underline{\Omega})\underline{\Omega};\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} \dfrac{4}{3}\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma}\cdot\underline{\Omega},\underline{\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} \dfrac{4}{3}\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma}\times\underline{\Omega};\underline{\Omega}\underline{\gamma}\cdot\underline{\Omega}\}$ $\{\underline{\Omega}\cdot\underline{\gamma}\underline{\Omega};\underline{\gamma}\times\underline{\Omega}\}$ | $0$ |

a  $\mu$ is the atom-diatom reduced mass.

Table 12.1.　(continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma\Omega};\underline{\gamma}\times\underline{\Omega\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega\Omega};\underline{\gamma\Omega}\}$ | 0 |
| $\{\underline{\gamma\Omega};\underline{\gamma\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{4}{3}\pi^{\frac{1}{2}}\sigma^2\Omega^{(1,1)\star}$ |
| $\{\underline{\gamma\Omega};\underline{\Omega\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}\sigma^2\Omega^{(1,1)\star}$ |
| $\{\underline{\gamma\Omega\Omega};\underline{\Omega\Omega\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}8\pi^{\frac{1}{2}}\sigma^2\Omega^{(1,1)\star}$ |
| $\{\underline{\gamma\Omega\Omega};\underline{\gamma\Omega\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{8}{3}\pi^{\frac{1}{2}}\sigma^2\Omega^{(1,1)\star}$ |
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\Omega\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}\sigma^2\Omega^{(1,2)\star}$ |
| $\{\underline{\Omega};\underline{\Omega}\}$ | 0 |
| $\{\Omega^2,\Omega^2\}$ | 0 |
| $\{\underline{\Omega\Omega};\underline{\Omega\Omega}\}$ | 0 |
| $\{\gamma^2,\Omega^2\}$ $\{\Omega^2,\gamma^2\}$ | 0 |

Table 12.1. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\gamma^2, \gamma^2\}$ | 0 |
| $\{\underline{\gamma\gamma}; \underline{\gamma\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 8\pi^{\frac{1}{2}}\sigma^2 \Omega^{(2,2)\star}$ |
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega}, \underline{\Omega\Omega}\cdot\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{8}{3}\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma};\underline{\Omega\Omega};\underline{\gamma}\Omega^2\}$ <br> $\{\underline{\gamma}\Omega^2; \underline{\Omega\gamma}\dot{\cdot}\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{8}{3}\pi^{\frac{1}{2}}\sigma^2 \Omega^{(1,1)\star}$ |
| $\{\underline{\gamma};\underline{\gamma}\times\underline{\Omega}\}$ <br> $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\}$ | 0 |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\times\underline{\Omega}\}$ <br> $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\Omega^2\}$ | 0 |
| $\{\underline{\gamma}\gamma^2;\underline{\gamma}\times\underline{\Omega}\}$ <br> $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\gamma^2\}$ | 0 |
| $\{\underline{\gamma\gamma};\underline{\Omega\Omega}\}$ <br> $\{\underline{\Omega\Omega};\underline{\gamma\gamma}\}$ | 0 |
| $\{1,\gamma^2\}$ <br> $\{\gamma^2,1\}$ | 0 |

# Table 12.2. Selected "u,v" Tensors

| "u,v" Tensor | Explicit Form |
|---|---|
| (0,0) | $\dfrac{\pi}{2}^{\frac{1}{2}(q-1)}$ |
| (1,0) | $-\dfrac{\pi}{2}^{\frac{1}{2}q}\,\hat{\kappa}$ |
| (1,1) | $\pi^{\frac{1}{2}(q-1)}\,\hat{\kappa}\hat{\kappa}$ |
| (1,2) | $-\dfrac{\pi}{2}^{\frac{1}{2}q}\,(\tfrac{1}{2}\hat{\kappa}\underline{U} + \hat{\kappa}\hat{\kappa}\hat{\kappa})$ |
| (2,1) | $-\dfrac{\pi}{2}^{\frac{1}{2}q}\,(\tfrac{1}{2}\hat{\kappa}\underline{U} + \tfrac{1}{2}\underline{[\hat{\kappa}]} - \hat{\kappa}\hat{\kappa}\hat{\kappa})$ |
| (3,0) | $-\dfrac{\pi}{4}^{\frac{1}{2}q}\,(\hat{\kappa}\underline{U} + \tfrac{1}{2}\underline{[\hat{\kappa}]} + \underline{U}\hat{\kappa})$ |
| (2,2) | $\dfrac{\pi}{2}^{\frac{1}{2}(q-1)}\,(\hat{\kappa}\underline{U}\hat{\kappa} + \hat{\kappa}\underline{[\hat{\kappa}]} + \underline{[\hat{\kappa}]}\hat{\kappa} + \underline{[\hat{\kappa}\hat{\kappa}]} - 4\hat{\kappa}\hat{\kappa}\hat{\kappa}\hat{\kappa})$ |
| (3,1) | $\dfrac{\pi}{2}^{\frac{1}{2}(q-1)}\,(\hat{\kappa}\underline{U}\hat{\kappa} + \underline{[\hat{\kappa}]}\hat{\kappa} + \underline{U}\hat{\kappa}\hat{\kappa} + \hat{\kappa}\hat{\kappa}\hat{\kappa}\hat{\kappa})$ |
| (1,3) | $\dfrac{\pi}{2}^{\frac{1}{2}(q-1)}\,(\hat{\kappa}\underline{U}\hat{\kappa} + \hat{\kappa}\underline{[\hat{\kappa}]} + \hat{\kappa}\hat{\kappa}\underline{U} + \hat{\kappa}\hat{\kappa}\hat{\kappa}\hat{\kappa})$ |

Table 12.2. (continued)

| "u,v" Tensor | Explicit Form |
|---|---|

(3,2)

$$-\frac{\pi}{8}^{\frac{1}{2}q} [\text{R}\underset{=}{\text{U}}\underset{=}{\text{U}} + \text{R}\underset{=}{\text{U}} + \text{R}\underset{=}{\text{U}} + \underset{=}{\text{R}}\text{U} + \underset{=}{\text{RU}} + \underset{=}{\text{RU}} + \text{URU} + \underset{=}{\text{R}} + \underset{=}{\text{R}} + 2\hat{\text{R}}\underset{=}{\text{U}}\hat{\text{R}}\hat{\text{R}} -$$

$$2\text{RRUR} + 2\text{URRR} - 2\text{R}\underset{=}{\text{R}}\text{R} - 2\text{RR}\underset{=}{\text{R}} + 2\underset{=}{\text{R}}\text{RR} - 2\text{R}\underset{=}{\text{RR}} - 2\underset{=}{\text{RR}}\text{R} - 2\underset{=}{\text{RRR}} +$$

$$12\text{RRRRR}]$$

(2,3)

$$-\frac{\pi}{8}^{\frac{1}{2}q} [\text{R}\underset{=}{\text{U}}\underset{=}{\text{U}} + \text{R}\underset{=}{\text{U}} + \text{R}\underset{=}{\text{U}} + \underset{=}{\text{R}}\text{U} + \underset{=}{\text{RU}} + \hat{\text{R}}\underset{=}{\text{U}} - 2\text{RRRU} + 2\text{RURR} - 2\text{RRUR} +$$

$$2\text{R}\underset{=}{\text{R}}\text{R} - 2\text{RR}\underset{=}{\text{R}} + 2\underset{=}{\text{R}}\text{RR} + 2\text{R}\underset{=}{\text{RR}} + 2\underset{=}{\text{RR}}\text{R} + 2\underset{=}{\text{RRR}} - 12\text{RRRRR}]$$

(3,3)

$$\frac{\pi}{4}^{\frac{1}{2}(q-1)} [\text{R}\underset{=}{\text{U}}\underset{=}{\text{U}}\text{R} + \underset{=}{\text{R}}\text{UR} + \text{URUR} + \text{RU}\underset{=}{\text{R}} + \underset{=}{\text{R}}\underset{=}{\text{R}} + \text{UR}\underset{=}{\text{R}} + \text{RURU} + \underset{=}{\text{R}}\text{RU} +$$

$$\text{URRU} + \text{R}\underset{=}{\text{U}}\text{R} + \underset{=}{\text{U}}\text{R} + \underset{=}{\text{R}}\text{R} + \text{R}\underset{=}{\text{U}}\underset{=}{\text{R}} + \underset{=}{\text{R}}\underset{=}{\text{R}} + \text{R}\underset{=}{\text{U}} + \underset{=}{\text{R}}\underset{=}{\text{R}} +$$

$$\underset{=}{\text{RR}} + \text{R}\underset{=}{\text{U}}\text{R} + \underset{=}{\text{R}}\text{U}\text{R} + \underset{=}{\text{U}}\text{R} + \underset{=}{\text{RR}} + \text{R}\underset{=}{\text{UR}} + \underset{=}{\text{R}}\text{UR} + \underset{=}{\text{R}} +$$

$$\text{R}\underset{=}{\text{U}} + \underset{=}{\text{R}}\underset{=}{\text{R}} + \underset{=}{\text{RR}} + \text{R}\text{U}\text{RR} + \underset{=}{\text{R}}\text{RR} + \text{U}\text{RRR} + \text{RRU}\text{R} + \text{RRR}\underset{=}{\text{R}} +$$

$$\text{RRRU} - 4\text{R}\underset{=}{\text{U}}\text{RR} - 4\text{R}\underset{=}{\text{RR}}\text{R} - 4\underset{=}{\text{RR}}\text{RR} - 4\underset{=}{\text{RRR}}\text{R} - 4\text{RR}\underset{=}{\text{U}}\text{R} - 4\text{RR}\underset{=}{\text{RR}} -$$

$$4\text{R}\underset{=}{\text{RRR}} - 4\text{RRU}\text{RR} - 4\underset{=}{\text{RRRR}} + 27\text{RRRRRR}]$$

Table 12.3.  Rigid Sphere-Rigid Ovaloid Scalar Collision
Integrals

| Scalar Collision Integral | Explicit Form |
| --- | --- |
| $\{\underline{\gamma};\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}2\pi^{\frac{1}{2}}\chi^{(1)}$ |
| $\{\underline{\gamma};\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(5\chi^{(1)}+\chi^{(3)})$ |
| $\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(55\chi^{(1)}-34^{(3)}+27\chi^{(5)})$ |
| $\{\underline{\gamma};\underline{\gamma}\Omega^2\}$ $\{\underline{\gamma}\Omega^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(3\chi^{(1)}-\chi^{(3)})$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(-5\chi^{(1)}+44\chi^{(3)}-27\chi^{(5)})$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(35\chi^{(1)}-54\chi^{(3)}+27\chi^{(5)})$ |
| $\{\underline{\gamma};\underline{\Omega}(\underline{\gamma}\cdot\underline{\Omega})\}$ $\{(\underline{\gamma}\cdot\underline{\Omega})\underline{\Omega};\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(\chi^{(1)}-T^{(1,2)})$ |
| $\{\underline{\gamma}\cdot\underline{\Omega},\underline{\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(\chi^{(-1)}-T^{(1,2)})$ |
| $\{\underline{\gamma}\Omega;\underline{\gamma}\Omega\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(\chi^{(-1)}-T^{(1,2)})$ |
| $\{\underline{\gamma}\Omega;\underline{\Omega}\gamma\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(3\chi^{(-1)}-5\chi^{(1)}+4\chi^{(3)})$ |

**Table 12.3.** (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma\Omega\Omega};\underline{\Omega\Omega\gamma}\}$ $\{\underline{\Omega\Omega\gamma};\underline{\gamma\Omega\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(6\chi^{(-1)} + 9\chi^{(1)} - 44\chi^{(3)} + 27\chi^{(5)})$ |
| $\{\underline{\gamma\Omega\Omega};\underline{\gamma\Omega\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(-2\chi^{(1)} + 10\chi^{(1)} - 4\chi^{(3)} - 4T^{(3,2)})$ |
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma\gamma}^2\}$ $\{\underline{\gamma\gamma}^2;\underline{\Omega\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(\chi^{(1)} + 5\chi^{(3)} - 5T^{(1,2)} - T^{(3,2)})$ |
| $\{\underline{\Omega};\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}2\pi^{\frac{1}{2}}(\chi^{(-1)} - \chi^{(1)})$ |
| $\{\Omega^2,\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}(\chi^{(1)} - \chi^{(3)})$ |
| $\{\underline{\Omega\Omega};\underline{\Omega\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}2\pi^{\frac{1}{2}}(\chi^{(-1)} + \chi^{(1)} - 2\chi^{(3)})$ |
| $\{\gamma^2,\Omega^2\}$ $\{\Omega^2,\gamma^2\}$ | $-\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}(\chi^{(1)} - \chi^{(3)})$ |
| $\{\underline{\gamma\gamma};\underline{\Omega\Omega}\}$ $\{\underline{\Omega\Omega};\underline{\gamma\gamma}\}$ | $0$ |
| $\{\gamma^2,\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}(\chi^{(1)} - \chi^{(3)})$ |
| $\{\underline{\gamma\gamma};\underline{\gamma\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}(2\chi^{(1)} - \chi^{(3)})$ |

Table 12.3.  (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\Omega}\underline{\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(\chi^{(-1)}+3\chi^{(1)}-4T^{(3,2)})$ |
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\Omega^2\}$ $\{\Omega^2\underline{\gamma};\underline{\Omega}\underline{\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}(9\chi^{(1)}-5\chi^{(3)}-5T^{(1,2)}+T^{(3,2)})$ |
| $\{\underline{\gamma};\underline{\gamma}\times\underline{\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\}$ | $0$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\times\underline{\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\Omega^2\}$ | $0$ |
| $\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\times\underline{\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega};\underline{\Omega\Omega}\cdot\underline{\gamma}\}$ | $\mp\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi G$ |
| $\{\underline{\gamma}\Omega;\underline{\Omega}\underline{\gamma}\times\underline{\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega\Omega};\underline{\Omega}\underline{\gamma}\}$ | $0$ |
| $\{\underline{\gamma}\Omega;\underline{\gamma}\times\underline{\Omega\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega\Omega};\underline{\gamma}\Omega\}$ | $\mp\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi G$ |
| $\{\underline{\gamma}\gamma^2;\underline{\gamma}\times\underline{\Omega}\}$ $\{\underline{\gamma}\times\underline{\Omega};\underline{\gamma}\gamma^2\}$ | $0$ |

Table 12.4. Kihara Model Scalar Collision Integrals

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma};\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 2\pi^{\frac{1}{2}}\Omega^{(1,1)\star}\chi^{(1)}$ |
| $\{\underline{\gamma};\underline{\gamma}\gamma^2\}$ $\{\underline{\gamma}\gamma^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}}\left[5\Omega^{(2,2)\star}\chi^{(1)} + (6\Omega^{(1,2)\star} - 5\Omega^{(2,2)\star})\chi^{(3)}\right]$ |
| $\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} \dfrac{\pi^{\frac{1}{2}}}{2}\left[(-\dfrac{165}{2}\Omega^{(1,3)\star} + 55\Omega^{(2,3)\star} + \dfrac{165}{2}\Omega^{(3,3)\star})\chi^{(1)} +\right.$ $(171\Omega^{(1,3)\star} - 34\Omega^{(2,3)\star} - 171\Omega^{(3,3)\star})\chi^{(3)} + (-\dfrac{81}{2}\Omega^{(1,3)\star} -$ $\left. 21\Omega^{(2,3)\star} + \dfrac{177}{2}\Omega^{(3,3)\star})\chi^{(5)}\right]$ |
| $\{\underline{\gamma};\underline{\gamma}\Omega^2\}$ $\{\underline{\gamma}\Omega^2;\underline{\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}}\left[(2\Omega^{(1,1)\star} + 6\Omega^{(1,2)\star} - 5\Omega^{(2,2)\star})\chi^{(1)} + (-6\Omega^{(1,2)\star} +\right.$ $\left. 5\Omega^{(2,2)\star})\chi^{(3)}\right]$ |

[a] Note that in the spherical limit, $\chi^{(n)} = 2\sigma^2$ and $T^{(1,n)} = \dfrac{2}{3}\sigma^2$ where $\sigma$ is a reference hard sphere radius and also in the rigid limit, $\Omega^{(1,s)\star} = 1$.

Table 12.4. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}$ <br> $\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}\Big[(10\Omega^{(2,2)\star} + \dfrac{165}{2}\Omega^{(1,3)\star} - 15\Omega^{(2,3)\star} - \dfrac{165}{2}\Omega^{(3,3)\star})$ <br><br> $\chi^{(1)} + (12\Omega^{(1,2)\star} - 10\Omega^{(2,2)\star} - 123\Omega^{(1,3)\star} - 6\Omega^{(2,3)\star} +$ <br><br> $171\Omega^{(3,3)\star})\chi^{(3)} + (\dfrac{81}{2}\Omega^{(1,3)\star} + 21\Omega^{(2,3)\star} - \dfrac{177}{2}\Omega^{(3,3)\star})\chi^{(5)}\Big]$ |
| $\{\underline{\gamma}\Omega^2;\underline{\gamma}\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\dfrac{\pi^{\frac{1}{2}}}{2}\Big[(12\Omega^{(2,2)\star} + 18\Omega^{(1,3)\star} - 12\Omega^{(2,3)\star} - 18\Omega^{(3,3)\star})$ <br><br> $\chi^{(-1)} + (8\Omega^{(1,1)\star} + 24\Omega^{(1,2)\star} - \dfrac{153}{2}\Omega^{(1,3)\star} + 3\Omega^{(2,3)\star} +$ <br><br> $\dfrac{249}{2}\Omega^{(3,3)\star})\chi^{(1)} + (-24\Omega^{(1,2)\star} + 36\Omega^{(2,2)\star} + 99\Omega^{(1,3)\star} +$ <br><br> $30\Omega^{(2,3)\star} - 195\Omega^{(3,3)\star})\chi^{(3)} + (-\dfrac{81}{2}\Omega^{(1,3)\star} - 21\Omega^{(2,3)\star} +$ <br><br> $\dfrac{177}{2}\Omega^{(3,3)\star})\chi^{(5)}\Big]$ |

Table 12.4. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|

$\{\underline{\gamma};\underline{\Omega}(\underline{\gamma}\cdot\underline{\Omega})\}$

$\{\underline{\gamma}\cdot\underline{\Omega}\underline{\Omega};\underline{\gamma}\}$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\Omega^{(1,1)\star}(\chi^{(1)}-T^{(1,2)})$$

$\{\underline{\gamma}\cdot\underline{\Omega},\underline{\gamma}\cdot\underline{\Omega}\}$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\left[\Omega^{(2,2)\star}\chi^{(-1)} + (\Omega^{(1,1)\star} - \Omega^{(2,2)\star})\chi^{(1)} - \Omega^{(1,1)\star}T^{(1,2)}\right]$$

$\{\underline{\gamma}\underline{\Omega};\underline{\gamma}\underline{\tilde{\Omega}}\}$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\left[\Omega^{(2,2)\star}\chi^{(-1)} + (\Omega^{(1,1)\star} - \Omega^{(2,2)\star})\chi^{(1)} - \Omega^{(1,1)\star}T^{(1,2)}\right]$$

$\{\underline{\gamma}\underline{\Omega};\underline{\Omega}\underline{\gamma}\}$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\left[3\Omega^{(2,2)\star}\chi^{(-1)} + (2\Omega^{(1,1)\star} - 7\Omega^{(2,2)\star})\chi^{(1)} + 4\Omega^{(2,2)\star}\chi^{(3)}\right]$$

$\{\underline{\gamma}\underline{\Omega}\underline{\Omega};\underline{\Omega}\underline{\Omega}\underline{\gamma}\}$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\frac{\pi^{\frac{1}{2}}}{2}\left[(18\Omega^{(2,2)\star} + 18\Omega^{(1,3)\star} - 12\Omega^{(2,3)\star} - 18\Omega^{(3,3)\star})\right.$$

$$\chi^{(-1)} + (8\Omega^{(1,1)\star} + 12\Omega^{(1,2)\star} - 52\Omega^{(2,2)\star} - \frac{153}{2}\Omega^{(1,3)\star} +$$

$$3\Omega^{(2,3)\star} + \frac{249}{2}\Omega^{(3,3)\star})\chi^{(1)} + (-12\Omega^{(1,2)\star} + 34\Omega^{(2,2)\star} +$$

$$99\Omega^{(1,3)\star} + 30\Omega^{(2,3)\star} - 195\Omega^{(3,3)\star})\chi^{(3)} + (-\frac{81}{2}\Omega^{(1,3)\star} -$$

Table 12.4. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| | $21\Omega^{(2,3)\star} + \dfrac{177}{2}\Omega^{(3,3)\star})\chi^{(5)}]$ |
| $\{\underline{\gamma}\underline{\Omega}\underline{\Omega};\underline{\gamma}\underline{\Omega}\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\dfrac{1}{2}\Big[(2\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star})\chi^{(-1)} +$ |
| | $(4\Omega^{(1,1)\star} - 2\Omega^{(2,2)\star} - 12\Omega^{(1,3)\star} + 8\Omega^{(2,3)\star} + 12\Omega^{(3,3)\star})\chi^{(1)} +$ |
| | $(6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star})\chi^{(3)} + (-4\Omega^{(1,1)\star} + 4\Omega^{(2,2)\star})$ |
| | $T^{(1,2)} - 4\Omega^{(2,2)\star}T^{(3,2)}]$ |
| $\{\underline{\gamma}\cdot\underline{\Omega}\underline{\Omega};\underline{\gamma}\gamma^{2}\}$ $\{\underline{\gamma}\gamma^{2};\underline{\Omega}\underline{\gamma}\cdot\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}\pi^{\frac{1}{2}}\dfrac{1}{2}\Big[(5\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star})\chi^{(1)} +$ |
| | $(6\Omega^{(1,2)\star} - 5\Omega^{(2,2)\star} - 6\Omega^{(1,3)\star} + 4\Omega^{(2,3)\star} + 6\Omega^{(3,3)\star})\chi^{(3)} +$ |
| | $-5\Omega^{(2,2)\star}T^{(1,2)} + (-6\Omega^{(1,2)\star} + 5\Omega^{(2,2)\star})T^{(3,2)}]$ |

Table 12.4. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\Omega};\underline{\Omega}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 2\pi^{\frac{1}{2}}\Omega^{(1,1)\star}(\chi^{(-1)} - \chi^{(1)})$ |
| $\{\Omega^2,\Omega^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}} 4\pi^{\frac{1}{2}}\Omega^{(2,2)\star}(\chi^{(1)} - \chi^{(3)})$ |
| $\{\underline{\underline{\Omega\Omega}};\underline{\underline{\Omega\Omega}}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}2\pi^{\frac{1}{2}}\Big[(3\Omega^{(1,1)\star} - 2\Omega^{(2,2)\star})\chi^{(-1)} + (-3\Omega^{(1,1)\star} + 4\Omega^{(2,2)\star})\chi^{(1)} + -2\Omega^{(2,2)\star}\chi^{(3)}\Big]$ |
| $\{\gamma^2,\Omega^2\}$ $\{\Omega^2,\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}\Omega^{(2,2)\star}(-\chi^{(1)} + \chi^{(3)})$ |
| $\{\underline{\gamma\gamma};\underline{\underline{\Omega\Omega}}\}$ $\{\underline{\underline{\Omega\Omega}};\underline{\gamma\gamma}\}$ | $0$ |
| $\{\gamma^2,\gamma^2\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}\Omega^{(2,2)\star}(2\chi^{(1)} - \chi^{(3)})$ |

Table 12.4. (continued)

| Scalar Collision Integral | Explicit Form |
|---|---|
| $\{\underline{\gamma\gamma};\underline{\gamma\gamma}\}$ | $\left(\dfrac{2kT}{\mu}\right)^{\frac{1}{2}}4\pi^{\frac{1}{2}}\Omega^{(2,2)\star}(2\chi^{(1)} - \chi^{(3)})$ |

$$\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\Omega\gamma}\cdot\underline{\Omega}\}$$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\frac{\pi^{\frac{1}{2}}}{2}\left[\left(6\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star}\right)\chi^{(-1)} + \right.$$

$$\left(4\Omega^{(1,1)\star} - 10\Omega^{(2,2)\star} - 12\Omega^{(1,3)\star} + 8\Omega^{(2,3)\star} + 12\Omega^{(3,3)\star}\right)\chi^{(1)} +$$

$$\left(4\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star}\right)\chi^{(3)} + \left(-4\Omega^{(1,1)\star} + \right.$$

$$\left. 4\Omega^{(2,2)\star}\right)T^{(1,2)} + - \Omega^{(2,2)\star}T^{(3,2)}\right]$$

$$\begin{aligned}&\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\Omega^2\}\\ &\{\underline{\gamma}\Omega^2;\underline{\Omega\gamma}\cdot\underline{\Omega}\}\end{aligned}$$

$$\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\frac{\pi^{\frac{1}{2}}}{2}\left[\left(4\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - 6\Omega^{(3,3)\star}\right)\chi^{(-1)} + \right.$$

$$\left(4\Omega^{(1,1)\star} + 6\Omega^{(1,2)\star} - 9\Omega^{(2,2)\star} - 12\Omega^{(1,3)\star} + 8\Omega^{(2,3)\star} + \right.$$

$$12\Omega^{(3,3)\star}\right)\chi^{(1)} + \left(-6\Omega^{(1,2)\star} + 5\Omega^{(2,2)\star} + 6\Omega^{(1,3)\star} - 4\Omega^{(2,3)\star} - \right.$$

$$6\Omega^{(3,3)\star}\right)\chi^{(3)} + \left(-4\Omega^{(1,1)\star} - 6\Omega^{(1,2)\star} + 5\Omega^{(2,2)\star}\right)T^{(1,2)} +$$

$$\left. \left(6\Omega^{(1,2)\star} - 5\Omega^{(2,2)\star}\right)T^{(3,2)}\right]$$

Table 12.5. Effective Cross Sections in Terms of Scalar Collision Integrals (Field-Free Transport Coefficients)

| Effective Cross Section | Explicit Form[a] |
|---|---|
| $G\left({1000 \atop 1000}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ | $\dfrac{2\xi_\alpha^2}{3\bar{v}_{\alpha\beta}}\{\underline{\gamma};\underline{\gamma}\}$ |
| $G\left({1000 \atop 1010}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ $G\left({1010 \atop 1000}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ | $\dfrac{2}{3}\sqrt{\dfrac{2}{5}}\,\dfrac{\xi_\alpha^4}{\bar{v}_{\alpha\beta}}\left[\dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\} - {\{\underline{\gamma};\underline{\gamma}\gamma^2\} \atop \{\underline{\gamma}\gamma^2;\underline{\gamma}\}}\right]$ |
| $G\left({1000 \atop 1001}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ $G\left({1001 \atop 1000}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ | $\dfrac{2\xi_\alpha^2}{3\bar{v}_{\alpha\beta}}\left[\{\underline{\gamma};\underline{\gamma}\} - {\{\underline{\gamma};\underline{\gamma}\Omega^2\} \atop \{\underline{\gamma}\Omega^2;\underline{\gamma}\}}\right]$ |
| $G\left({1010 \atop 1010}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ | $\dfrac{4\xi_\alpha^6}{15\bar{v}_{\alpha\beta}}\left[\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma}\gamma^2;\underline{\gamma}\}\right.$ $\left. + \left(\dfrac{25}{4} + \dfrac{15\xi_\beta^6}{2\xi_\alpha^4}\right)\{\underline{\gamma};\underline{\gamma}\} + \dfrac{\xi_\beta^2}{\xi_\alpha^2}\left(\dfrac{7}{2}\{\gamma^2,\gamma^2\} + 2\{\underline{\gamma}\gamma;\underline{\gamma}\gamma\}\right)\right]$ |
| $G\left({1010 \atop 1001}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ $G\left({1001 \atop 1010}\Big|{\beta \atop \beta}\right)_{\alpha\beta}$ | $\dfrac{2}{3}\sqrt{\dfrac{2}{5}}\,\dfrac{\xi_\alpha}{3\bar{v}_{\alpha\beta}}\left[{\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\} \atop \{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}} - {\{\underline{\gamma}\gamma^2;\underline{\gamma}\} \atop \{\underline{\gamma};\underline{\gamma}\gamma^2\}} - \right.$ $\left.\dfrac{5}{2}{\{\underline{\gamma};\underline{\gamma}\Omega^2\} \atop \{\underline{\gamma}\Omega^2;\underline{\gamma}\}} + \dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\} + \dfrac{5\xi_\beta^2}{2\xi_\alpha^2}{\{\gamma^2,\Omega^2\} \atop \{\Omega^2,\gamma^2\}}\right]$ |

[a] $\xi_\eta = \sqrt{\dfrac{M_\eta}{(M_\alpha + M_\beta)}}$

Table 12.5.  (continued)

| Effective Cross Section | Explicit Form |
|---|---|
| $G\left(\begin{matrix}1001\\1001\end{matrix}\bigg\vert\begin{matrix}\beta\\\beta\end{matrix}\right)_{\alpha\beta}$ | $\dfrac{2\xi_\alpha^2}{3\nabla_{\alpha\beta}}\left[\{\underline{\gamma}\Omega^2;\underline{\gamma}\Omega^2\} - \{\underline{\gamma};\underline{\gamma}\Omega^2\} - \{\underline{\gamma}\Omega^2;\underline{\gamma}\} + \{\underline{\gamma};\underline{\gamma}\}\right.$ $\left. + \dfrac{3\xi_\beta^2}{\xi_\alpha^2}\{\Omega^2,\Omega^2\}\right]$ |
| $G\left(\begin{matrix}1010\\1000\end{matrix}\bigg\vert\begin{matrix}\alpha\\\beta\end{matrix}\right)_{\alpha\beta}$ $G\left(\begin{matrix}1000\\1010\end{matrix}\bigg\vert\begin{matrix}\beta\\\alpha\end{matrix}\right)_{\alpha\beta}$ | $\dfrac{2}{3}\sqrt{\dfrac{2}{5}}\,\dfrac{\xi_\alpha^3\xi_\beta^3}{\nabla_{\alpha\beta}}\left[\dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\} - \dfrac{\{\underline{\gamma}\gamma^2;\underline{\gamma}\}}{\{\underline{\gamma};\underline{\gamma}\gamma^2\}}\right]$ |
| $G\left(\begin{matrix}1010\\10\ 0\end{matrix}\bigg\vert\begin{matrix}\alpha\\\beta\end{matrix}\right)_{\alpha\beta}$ $G\left(\begin{matrix}1010\\1010\end{matrix}\bigg\vert\begin{matrix}\beta\\\alpha\end{matrix}\right)_{\alpha\beta}$ | $\dfrac{-4\xi_\alpha^3\xi_\beta^3}{15\nabla_{\alpha\beta}}\left[\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma}\gamma^2;\underline{\gamma}\}\right.$ $\left. + \dfrac{55}{4}\{\underline{\gamma};\underline{\gamma}\} - \dfrac{7}{2}\{\gamma^2,\gamma^2\} - 2\{\underline{\gamma}\underline{\gamma};\underline{\gamma}\underline{\gamma}\}\right]$ |
| $G\left(\begin{matrix}1010\\1001\end{matrix}\bigg\vert\begin{matrix}\alpha\\\beta\end{matrix}\right)_{\alpha\beta}$ $G\left(\begin{matrix}1001\\1010\end{matrix}\bigg\vert\begin{matrix}\alpha\\\beta\end{matrix}\right)_{\alpha\beta}$ | $-\dfrac{2}{3}\cdot\sqrt{\dfrac{2}{5}}\,\dfrac{\xi_\alpha\xi_\beta^3}{\nabla_{\alpha\beta}}\left[\begin{matrix}\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\}\\\{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}\end{matrix} - \dfrac{5}{2}\begin{matrix}\{\underline{\gamma};\underline{\gamma}\Omega^2\}\\\{\underline{\gamma}\Omega^2;\underline{\gamma}\}\end{matrix} + \begin{matrix}\{\underline{\gamma}\gamma^2;\underline{\gamma}\}\\\{\underline{\gamma};\underline{\gamma}\gamma^2\}\end{matrix}\right.$ $\left. - \dfrac{5}{2}\begin{matrix}\{\gamma^2,\Omega^2\}\\\{\Omega^2,\gamma^2\}\end{matrix}\right]$ |
| $G\left(\begin{matrix}1010\\1010\end{matrix}\bigg\vert\begin{matrix}\alpha\\\alpha\end{matrix}\right)_{\alpha\beta}$ | $\dfrac{4\xi_\beta^6}{15\nabla_{\alpha\beta}}\left[\{\underline{\gamma}\gamma^2;\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma};\underline{\gamma}\gamma^2\} - \dfrac{5}{2}\{\underline{\gamma}\gamma^2;\underline{\gamma}\} + \right.$ $\left. \left(\dfrac{25}{4} + \dfrac{15\xi_\alpha^4}{2\xi_\beta^4}\right)\{\underline{\gamma};\underline{\gamma}\} + \dfrac{\xi_\alpha^2}{\xi_\beta^2}\left(\dfrac{7}{2}\{\gamma^2,\gamma^2\} + 2\{\underline{\gamma}\underline{\gamma};\underline{\gamma}\underline{\gamma}\}\right)\right]$ |

Table 12.6. Effective Cross Sections in Terms of Scalar Collision Integrals (Senftleben-Beenakker Effects--Critical Field)

| Effective Cross Section | Explicit Form |
|---|---|
| $G\left(\begin{smallmatrix}1100\\1100\end{smallmatrix}\bigg|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $\dfrac{\xi_\alpha^2}{5\bar{v}_{\alpha\beta}}\Big[-\{\underline{\gamma\Omega};\underline{\gamma\Omega}\} + 4\{\underline{\gamma\Omega};\underline{\Omega\gamma}\} - \{\underline{\gamma}\cdot\underline{\Omega},\underline{\gamma}\cdot\underline{\Omega}\} - \dfrac{\xi_\beta^2}{\xi_\alpha^2}\{\underline{\Omega};\underline{\Omega}\}\Big]$ |
| $G\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\bigg|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $\dfrac{3\xi_\alpha^2}{2\bar{v}_{\alpha\beta}}\Big[\dfrac{\xi_\beta^2}{\xi_\alpha^2}(\{\underline{\Omega\Omega};\underline{\Omega\Omega}\} - \tfrac{1}{3}\{\Omega^2,\Omega^2\}) - \tfrac{2}{7}\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\Omega\gamma}\cdot\underline{\Omega}\} - \tfrac{2}{7}\{\underline{\gamma\Omega\Omega};\underline{\gamma\Omega\Omega}\} + \tfrac{11}{21}\{\underline{\gamma\Omega\Omega};\underline{\Omega\Omega\gamma}\} + \tfrac{4}{21}\{\underline{\gamma\gamma}^2;\underline{\Omega\Omega}\cdot\underline{\gamma}\} + \tfrac{4}{21}\{\underline{\gamma}\cdot\underline{\Omega\Omega};\gamma\gamma^2\} - \tfrac{1}{9}\{\underline{\gamma\Omega}^2;\underline{\gamma\Omega}^2\}\Big]$ |
| $G\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\bigg|\begin{smallmatrix}\beta\\\beta\end{smallmatrix}\right)_{\alpha\beta}$ | $\dfrac{3}{4\bar{v}_{\alpha\beta}}\Big[\{\underline{\Omega\Omega};\underline{\Omega\Omega}\} - \tfrac{1}{3}\{\Omega^2,\Omega^2\}\Big]$ |

Table 12.7. Effective Cross Sections in Terms of Scalar Collision Integrals (Senftleben-Beenakker Effects-Saturation Values)

| Effective Cross Section | Explicit Form |
|---|---|
| $G\begin{pmatrix}1000 & \beta\\1200 & \beta\end{pmatrix}_{\alpha\beta}$ $G\begin{pmatrix}1200 & \beta\\1000 & \beta\end{pmatrix}_{\alpha\beta}$ | $\dfrac{\sqrt{7}\,\xi_\alpha^2}{5\bar{v}_{\alpha\beta}}\left[\dfrac{\{\underline{\gamma};\underline{\Omega\gamma}\cdot\underline{\Omega}\}}{\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\}} - \dfrac{1}{3}\dfrac{\{\underline{\gamma};\underline{\gamma}\Omega^2\}}{\{\underline{\gamma}\Omega^2;\underline{\gamma}\}}\right]$ |
| $G\begin{pmatrix}1010 & \beta\\1200 & \beta\end{pmatrix}_{\alpha\beta}$ $G\begin{pmatrix}1200 & \beta\\1010 & \beta\end{pmatrix}_{\alpha\beta}$ | $\dfrac{\sqrt{6}\,\xi_\alpha^2}{5\bar{v}_{\alpha\beta}}\left[\dfrac{5}{2}\dfrac{\{\underline{\gamma};\underline{\Omega\gamma}\ \underline{\Omega}\}}{\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\}} - \dfrac{5}{6}\dfrac{\{\underline{\gamma};\underline{\gamma}\Omega^2\}}{\{\underline{\gamma}\Omega^2;\underline{\gamma}\}} - \dfrac{\{\underline{\gamma}\gamma^2;\underline{\Omega\gamma}\cdot\underline{\Omega}\}}{\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\gamma^2\}}\right.$ $\left. + \dfrac{1}{3}\dfrac{\{\underline{\gamma}\gamma^2;\underline{\gamma}\Omega^2\}}{\{\underline{\gamma}\Omega^2;\underline{\gamma}\gamma^2\}} + \dfrac{\xi_\beta^2}{\xi_\beta^2}\dfrac{\{\gamma^2,\Omega^2\}}{\{\Omega^2,\gamma^2\}}\right]$ |
| $G\begin{pmatrix}1001 & \beta\\1200 & \beta\end{pmatrix}_{\alpha\beta}$ $G\begin{pmatrix}1200 & \beta\\1010 & \beta\end{pmatrix}_{\alpha\beta}$ | $\dfrac{\sqrt{7}\,\xi_\alpha^2}{5\bar{v}_{\alpha\beta}}\left[\dfrac{\{\underline{\gamma};\underline{\Omega\gamma}\cdot\underline{\Omega}\}}{\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\}} - \dfrac{\{\underline{\gamma}\Omega^2;\underline{\Omega\gamma}\cdot\underline{\Omega}\}}{\{\underline{\gamma}\cdot\underline{\Omega\Omega};\underline{\gamma}\Omega^2\}} - \dfrac{1}{3}\dfrac{\{\underline{\gamma};\underline{\gamma}\Omega^2\}}{\{\underline{\gamma}\Omega^2;\underline{\gamma}\}}\right.$ $\left. + \dfrac{1}{3}\{\underline{\gamma}\Omega^2;\underline{\gamma}\Omega^2\}\right]$ |