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BAKER, WILLIAM MEBANE. A Quantum Mechanical Boltzmann Equation for a Polyatomic Gas in Magnetic and Electric Fields. (1972) Directed by: Dr. Francis J. McCormack.

The purpose of this thesis is to examine the development of a quantum mechanical Boltzmann equation for a general polyatomic gas. To formulate such an equation the method used was the development of a density matrix to describe the ensemble and then the equation of motion various operators have been formulated in as general a manner as possible to include explicit time dependence and effects of magnetic and electric fields, and yet not sacrificing the basic assumption of molecular independence. In the process of generating these operators it was discovered that because of the employment of the formal theory of scattering, the operators were time independent. We obtain an equation of motion for the density matrix in terms of the time dependent density matrix and interaction potential, and the time independent wave operators. To put this equation of motion for the density matrix into a form more recognizable as the Boltzmann transport equation required the development of a Wigner type distribution function. An illustrative example of the necessary procedure is then given, and a more familiar Boltzmann equation results.

A QUANTUM MECHANICAL BOLTZMANN EQUATION

"

FOR A POLYATOMIC GAS IN

MAGNETIC AND ELECTRIC

FIELDS

by

William Mebane Baker

"

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TABLE OF CONTENTS

	Page
CHAPTER 1. INTRODUCTION.....	1
CHAPTER 2. REPRESENTATION OF A QUANTIZED SYSTEM.....	4
CHAPTER 3. DEVELOPMENT OF THE DENSITY MATRIX.....	10
CHAPTER 4. TIME EVOLUTION OF THE DENSITY MATRIX.....	15
CHAPTER 5. APPLICATION OF FORMAL SCATTERING THEORY TO THE BOLTZMANN EQUATION.....	25
CHAPTER 6. DISTRIBUTION FUNCTIONS.....	52
SUMMARY.....	59
BIBLIOGRAPHY.....	61
APPENDIX.....	62

CHAPTER 1
INTRODUCTION

This paper proposes to examine the process by which a quantum mechanical Boltzmann equation for a dilute polyatomic gas, involving only binary collisions, is developed. The method employed parallels the work of R. F. Snider (Journal of Chemical Physics, April, 1960.), which is referenced throughout the text. Snider's procedure is extended to the case of a polyatomic gas in the presence of magnetic and electric fields, which may be time variant.

Chapter 2 is devoted to describing a quantized system by use of the concepts of state vectors and state functions. The state vectors and functions are then used to develop the idea of system averaging; specifically the concept of expectation values.

Chapter 3 extends the work of Chapter 2 in developing ensemble averaging from expectation values. The density matrix is then defined by its relationship to the ensemble average for the operator, and the operator itself.

In Chapter 4, the equation of motion for the density matrix is derived by employing the definition of the density matrix, developed in Chapter 3. The dilute nature of the gas is then used (i.e., use of the Boltzmann property) to rewrite the equation of motion in terms of the one and two particle density matrices. The problem is, thereby, greatly simplified. It then becomes necessary to solve the equation of motion

for the two particle density matrix, the inherent problem of binary collisions included.

Chapter 5 deals with solving the two particle density matrix equation of motion. In dealing with this problem, we will first determine the appropriate form of the Hamiltonian, bearing in mind that this form necessarily must account for the effects of fields. Applying this Hamiltonian to the Schrödinger equation, we develop the eigenfunctions, and, subsequently, the density matrix. The Hamiltonian also appears in sets of equations which are used to solve the actual two particle equations of motion. The implied explicit time dependence of the Hamiltonian complicates the solution and requires a non-explicit time dependence assumption. This assumption effects a meaningful solution of the equations of motion in terms of formal scattering theory procedure. It should be noted that formal scattering theory is required to describe the collision effects.

Chapter 6 discusses the use of Wigner type distribution functions. These functions are necessitated by the fact the momentum and position can not be simultaneously determined. Further, the Wigner type distribution functions must be employed in placing the final equation of motion for the density matrix into a more recognizable form of the Boltzmann integrodifferential equation.

Concluding, the results of this study indicate that while the method of developing the Boltzmann equation in terms of quantum mechanics is sound, the required use of Wigner type distributions renders this problem most difficult. It is suggested in the summary that a procedure

which does not include the Wigner type distribution functions should be employed to complete the quantum analog to the Boltzmann equation.

CHAPTER 2

REPRESENTATION OF A QUANTIZED SYSTEM

The intent of this section is to develop the basic concepts underlying the density matrix. To do so one must first understand how, in as general a manner as possible, to formulate a quantum mechanical description of the ensemble. This is accomplished by use of a state vector¹ to describe a state of the system.

A state vector is an element of Hilbert space upon which act the operators corresponding to an observable. To determine what state a system is in one must make a measurement, or set of measurements by acting on the system with the appropriate operator. Actual measurement of a physical observable carries the state vector of the system into an eigenvector belonging to the observed eigenvalue of the observable. In actuality a system can be in more than one possible eigenstate, represented by an eigenvector; and we will assume that there is a set of j possible eigenvectors. Then by the principle of superposition, or the linear nature of Hilbert space, we have

$$1) \quad \Phi = \sum_j c_j \phi_j \quad ,$$

Or, in other words, any vector Φ may be expanded in terms of the eigenvectors ϕ_j . Note that ϕ_j 's are eigenvectors and Φ is a

¹"The State of a Quantized System," Advanced Quantum Mechanics, Paul Roman, 1st ed. (1 vol. Reading, Massachusetts, Addison-Wesley Publishing Company), 1965, p. 11.

state vector. Or rewording slightly, an arbitrary physical state can be considered as a linear superposition of some suitably chosen states (eigenstates). However, the converse of the above statement, viz., an arbitrary superposition of physical states is again a possible physical state, is not true, unconditionally, (which deals with the phenomenon of selection rules.) So, in summary, one may consider a state, represented by a state vector, before a measurement is made, to be some superposition, such as

$$2) \quad \Psi = \sum_{j=a,b,\dots} c_j \phi_j \quad .$$

After a measurement has established ω_α , for example, as the eigenvalue corresponding to the operator A , the state becomes ϕ_α , or the state vector is determined to be ϕ_α , or

$$3) \quad A \phi_\alpha = \omega_\alpha \phi_\alpha \quad .$$

The c_j will be shown to behave as probability weight factors.

It should be noted that a complete description of the state vector requires the simultaneous measurement of the maximal set of commuting operators, i.e., momentum, position, spin et cetera. It is the common eigenvector of the members of the maximal set into which the state is projected by the maximal measurement; hence this eigenvector is the state vector. Again the state vector can be represented by a superposition of the eigenvectors of the operators of the maximal set, and we expect an expression such as that of equation 2.

For the purpose of continuing this work we now replace the c_j 's of equation 2 by $\Psi(\omega_j)$ which results in;

$$4) \quad \Psi = \sum_j \Psi(\omega_j) \phi_j \quad .$$

If one is involved with continuous as well as discrete eigenvalues, then the state vector is;

$$5) \quad \underline{\Psi} = \int_{\omega_j} \sum_n \Psi(n, \omega_j) \phi_{n,j} d\omega_j,$$

where $\Psi(n, \omega_j)$ is commonly called a state function, N refers to discrete, and ω_j refers to continuous variables. In summary it is apparent that a state is represented by a state vector, Ψ_i is a superposition of eigenvectors, or a maximal set, appropriately chosen to result in .

Denoting Ψ_i by

$$\Psi_i = \sum_j c_j \phi_j,$$

where $\Psi(\omega_j) \equiv c_j$, the $\Psi(\omega_j)$'s are state functions, and only discrete states are considered. In a more general notation

$$6) \quad \Psi_i = \sum_n \int \Psi_i(n, \bar{x}, t) \phi_n(\bar{x}) d\bar{x},$$

where N are the discrete and X the continuous variables for the i th state.

Before going further a discussion of the state function may be instructive. A state function is determined by the inner product

$$7) \quad \Psi_i(n, \bar{x}, t) = (\phi_n(\bar{x}), \Psi_i),$$

where the set of $\phi_m(\bar{x})$ is orthogonal and $\phi_n(\bar{x})$ is a member. Since the eigenvector set is known the state vector, Ψ_i , is exhaustively characterized by the set of coefficients, i.e., the state functions $\Psi_i(m, \bar{x}, t)$, which makes the role of the state function as a probability weighting factor more evident. In the following development the importance of our state function to observables and ultimately the density matrix will become apparent.

Interpretation of the state functions is facilitated by consideration of the following. We know that at a specific time a

state is represented by a state vector of Hilbert space; the mathematical formulation of this state vector has already been discussed. However, the concept of probability associated with this representation has not been considered. If a measurement is made on a state, i.e., acted upon by a Hermitian operator, one knows that the measurement can produce only one of the set of eigenvalues (corresponding to the eigenvector of that specific time and state) associated with that operator from the maximal set. The probabilities, the incidents of measurement, of a specific measurement is connected to the state function, as will be shown.

In general, the measurement of a physical observable does not lead with certainty to a specific value. Any one of the possible eigenvalues may be obtained, but with different probabilities. The average value, or expectation value of the result of the measurement of A is given axiomatically by the expression

$$8) \quad \langle A \rangle = (\Psi_i, A \Psi_i) \quad ,$$

where Ψ_i is the state vector of the system at a particular moment.

So much for the method of calculation of the expectation value. To more clearly understand what is meant by the expectation value the following example should be considered.

If a large number of identical systems exist such that they are exactly in the same state, and one measures a certain common physical quantity, one will always obtain a definite eigenvalue corresponding to one of the eigenvectors, but not the same eigenvalue for each state, or measurement. The weighted mean value of all measured values is

what one then calls the expectation value of the physical quantity or observable. The same procedure can be applied to one system by time averaging the results, always being sure to return the system to the original state, since as we have stated before measurement is a means of preparing a system in a specific state. If a state Ψ_i happens to be an eigenstate ϕ_i of the operator A , then

$$9) \quad \langle A \rangle = (\phi_i, A\phi_i) = (\phi_i, \omega_i \phi_i) = \omega_i,$$

as is expected. But the basic question is, what is the probability of obtaining, in a single measurement of a definite state, a specific eigenvalue of a given physical observable? In general a state vector, as noted previously, is represented by

$$10) \quad \Psi_i = \sum_m \int \psi_i(m, \vec{x}, t) \phi_m(\vec{x}) d\vec{x}.$$

So for our problem our definite state is Ψ_i .

The expectation value is then given as,

$$11) \quad \langle A \rangle_i = \left(\sum_m \int \psi_i(m, \vec{x}, t) \phi_m(\vec{x}) d\vec{x}, A \sum_n \int \psi_i(n, \vec{x}, t) \phi_n(\vec{x}) d\vec{x} \right),$$

or

$$12) \quad \langle A \rangle_i = \sum_m \sum_n \int_{\vec{x}} \int_{\vec{x}'} \psi_i^*(m, \vec{x}, t) \psi_i(n, \vec{x}', t) (\phi_m(\vec{x}'), A \phi_n(\vec{x})) d\vec{x} d\vec{x}'.$$

Since $A\phi_n(\vec{x}) = \omega_n \phi_n(\vec{x})$, where ω_n is the eigenvalue of $\phi_n(\vec{x})$ corresponding to A , we have

$$13) \quad \langle A \rangle_i = \sum_m \sum_n \int_{\vec{x}} \int_{\vec{x}'} \psi_i^*(m, \vec{x}, t) \psi_i(n, \vec{x}', t) (\phi_m(\vec{x}'), \omega_n \phi_n(\vec{x})) d\vec{x} d\vec{x}'.$$

Since the eigenvectors are orthogonal, then

$$14) \quad (\phi_m(\vec{x}'), \phi_n(\vec{x})) = \delta_{mn} \delta(\vec{x}' - \vec{x}),$$

so that,

$$15) \quad \langle A \rangle_i = \sum_m \int_{\vec{x}} \psi_i^*(m, \vec{x}, t) \psi_i(m, \vec{x}, t) \omega_n d\vec{x} .$$

The last expression demonstrates that the expectation value for the ith state is the weighted average of the eigenvalues and the probability weight factor $\psi_i^*(m, \vec{x}, t) \psi_i(m, \vec{x}, t)$.

The quantity $\iint_{\vec{x} \vec{x}'} \psi_i^*(m, \vec{x}', t) \psi_i(m, \vec{x}, t) d\vec{x} d\vec{x}'$ is the probability of the occurrence of $\phi_m(\vec{x})$ in the measurement.

Now that we have described what is meant by a state vector and function, and eigenvector and function, and the physical arguments behind them, we can proceed to a discussion and development of the density matrix.

CHAPTER 3
DEVELOPMENT OF THE DENSITY
MATRIX

It has been shown that a state vector can describe a quantized system. The state vector acts as a condensed symbol for the result of a maximal measurement. In other words it collects the maximum information that can be obtained by measurement.

In some cases, however, a maximal measurement either has not been made or cannot be made. Yet some predictions can still be made concerning the system behavior. Such may be the case of an ensemble, or system of mixed states. In such cases it is possible, with some basic knowledge of the system, to construct a probability distribution function.² For example, the symbol $\omega(\vec{p})$ means that the probability of finding a particle with momentum \vec{p} to $\vec{p} + d\vec{p}$ is $\omega(\vec{p}) d\vec{p}$. $\omega(\vec{p})$ is a distribution function of the system with respect to momentum. By use of such distribution functions the classical Boltzmann equation was developed. Hence, although no definite state vector can be assigned to the system, it is possible to determine, in a statistical mechanical sense, the outcome of any observation. One must form the usual quantum theoretical expectation value (for that observable) for all possible situations and

²"The Density Matrix", Advanced Quantum Mechanics, Paul Roman, 1st ed. (1 vol. Reading, Massachusetts, Addison-Wesley Publishing Company), 1965, p. 90.

add them incoherently, or take the ensemble average of the expectation values weighted with the known probability factors, as given by the distribution functions.

So when considering an ensemble, one is dealing with two different average concepts. First the quantum mechanical average, as already discussed in the expectation value calculation, calculated in a pure state; and second the ensemble average of these numbers with the weighting factors $\omega^{(i)}$, as previously described. The first average is inherent in the nature of quantized systems, and the second closely resembles the case of statistical mechanics and is introduced because of our lack of complete information. All this information is carried by the density matrix.

Since pure and mixed states have been mentioned, a distinction between them should be made. Systems completely specified by a single state vector are said to be in a pure state. Mixed states, however, are a set of possible states represented by a set of state vectors and the probability of occurrence of each. By measurement, a mixed state may be carried over into a pure state. In usage of the density matrix one treats pure and mixed states on the same footing.

Mathematically the density matrix can be developed by considering the determination of the expectation value again. Corresponding to the ith state the expectation value of a physical observable A is given

by

$$16) \quad \langle A \rangle_i = (\Psi_i, A \Psi_i) \quad ,$$

where one assumes the state vector, for simplicity, is normalized such that $(\Psi_i, \Psi_i) = 1$. Expanding equation 16, we obtain

$$17) \quad \langle A \rangle_i = \left(\sum_m \int_{\bar{x}} \Psi_i(m, \bar{x}; t) \phi_m(\bar{x}') d\bar{x}', \sum_n \int_{\bar{x}} \Psi_i(m, \bar{x}; t) \phi_n(\bar{x}) d\bar{x} \right).$$

Regrouping equation 17 we now have,

$$18) \quad \langle A \rangle_i = \sum_m \sum_n \int_{\bar{x}} \int_{\bar{x}'} \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t) (\phi_m(\bar{x}'), A \phi_n(\bar{x})) d\bar{x}' d\bar{x}.$$

Defining the inner product in the above integral as a matrix element

$$19) \quad A_{mn}(\bar{x}; \bar{x}') = (\phi_m(\bar{x}'), A \phi_n(\bar{x}))$$

we can rewrite equation 18 as

$$20) \quad \langle A \rangle_i = \sum_m \sum_n \int_{\bar{x}} \int_{\bar{x}'} \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t) A_{mn}(\bar{x}; \bar{x}') d\bar{x}' d\bar{x}$$

which is the expectation value of A acting on the ith system. The ensemble average can be generated by summing over all possible states and considering the weighting factor of each, which will be represented by $\omega^{(i)}$ for the ith system, of N_0 system.

$$21) \quad \langle A \rangle_e = \sum_{i=1}^{N_0} \sum_m \sum_n \int_{\bar{x}} \int_{\bar{x}'} \omega^{(i)} \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t) A_{mn}(\bar{x}; \bar{x}') d\bar{x}' d\bar{x}$$

or

$$22) \quad \langle A \rangle_e = \sum_m \sum_n \int_{\bar{x}} \int_{\bar{x}'} \left\{ \sum_{i=1}^{N_0} \omega^{(i)} \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t) \right\} A_{mn}(\bar{x}; \bar{x}') d\bar{x}' d\bar{x}$$

where one now defines

$$23) \quad \rho_{mn}(\bar{x}; \bar{x}') = \sum_{i=1}^{N_0} \omega^{(i)} \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t)$$

as the element of the density matrix. And so the ensemble average is given by

$$24) \quad \langle A \rangle_e = \sum_m \sum_n \int_{\bar{x}} \int_{\bar{x}'} \rho_{mn}(\bar{x}; \bar{x}') A_{mn}(\bar{x}; \bar{x}') d\bar{x}' d\bar{x}.$$

To overcome a slight notational problem let us consider matrix multiplication of the following example. If one multiplies matrices A and B of a type functionally similar to the density matrix and

operator matrix A above, then the matrix element of the product of A and B is given by,

$$25) \quad [AB]_{ns}(\bar{x}, \bar{x}') = \sum_k \int A_{rk}(\bar{x}, \bar{x}'') B_{ks}(\bar{x}'', \bar{x}') d\bar{x}'' ,$$

where \bar{x} is used as a general coordinate. Rewriting the penultimated expression for the ensemble average as

$$26) \quad \langle A \rangle_e = \sum_n \left(\sum_m \int_{\bar{x}} \int_{\bar{x}'} P_{nm}(\bar{x}, \bar{x}') A_{mn}(\bar{x}', \bar{x}) d\bar{x} d\bar{x}' \right) ,$$

and considering only diagonal elements of the product of A and B above

$$27) \quad [AB]_{nn}(\bar{x}, \bar{x}) = \sum_k \int A_{rk}(\bar{x}, \bar{x}') B_{kn}(\bar{x}', \bar{x}) d\bar{x}' ,$$

then the ensemble average above is the sum of diagonal elements of the matrix product,

$$28) \quad \langle A \rangle_e = \sum_n \int_{\bar{x}} \left(\sum_m \int_{\bar{x}'} P_{nm}(\bar{x}, \bar{x}') A_{mn}(\bar{x}', \bar{x}) d\bar{x}' \right) d\bar{x} ,$$

or

$$29) \quad \langle A \rangle_e = \sum_n \int_{\bar{x}} \left[\rho(\bar{x}, \bar{x}) A(\bar{x}, \bar{x}) \right]_{nn} d\bar{x} .$$

The diagonal summation is usually referred to as the trace, so we have

$$30) \quad \langle A \rangle_e = \text{Tr} \left[\rho(\bar{x}, \bar{x}; t) A(\bar{x}, \bar{x}; t) \right] .$$

The advantage of the density matrix in application to other operators is obvious. The density matrix provides an alternate characterization of states of an arbitrary quantized system, whether pure or mixed. Since every representation can be formulated in terms of the density matrix, there is no need for the state vector concept to describe a physical system. In fact, if one takes equation 30 as the definition of the density matrix, by operation of ρ on as many

independent operators as there are independent parameters in ρ , then ρ can be computed from that equation. Once ρ is known it may be applied to any other operator. In a sense the density matrix formalism is more general than the state vector formalism, since one may deal with all systems, without regard to the completeness or incompleteness of one's knowledge of the systems.

CHAPTER 4

TIME EVOLUTION OF THE DENSITY MATRIX

From the previous discussion the density matrix element was defined in the following manner;

$$23) \quad \rho_{mn} = \sum_{i=1}^{N_0} \omega(i) \Psi_i^*(m, \bar{x}; t) \Psi_i(n, \bar{x}; t) .$$

To consider its change with respect to time, one takes the first derivative, assuming the weight factor is not a function of time.

Following the work of McCormack³ we have

$$31) \quad \frac{d}{dt} \rho_{mn} = \sum_{i=1}^{N_0} \omega(i) \left\{ \frac{\partial \Psi_i^*(m, \bar{x}; t)}{\partial t} \Psi_i(n, \bar{x}; t) + \Psi_i^*(m, \bar{x}; t) \frac{\partial \Psi_i(n, \bar{x}; t)}{\partial t} \right\} .$$

where, from earlier work, Ψ is given by equation 7, and

$$32) \quad \Psi_i^*(m, \bar{x}; t) = (\phi_m(\bar{x}'), \Psi_i)^* ,$$

where

$$\Psi_i = \sum_n \int_{\bar{x}'} \Psi_i(n, \bar{x}'; t) \phi_n(\bar{x}') d\bar{x}' .$$

We now have by differentiating with respect to time

$$33) \text{ a) } \quad \frac{\partial \Psi_i^*(m, \bar{x}; t)}{\partial t} = (\phi_m(\bar{x}'), \frac{\partial \Psi_i}{\partial t})^*$$

$$\text{b) } \quad \frac{\partial \Psi_i(n, \bar{x}; t)}{\partial t} = (\phi_n(\bar{x}), \frac{\partial \Psi_i}{\partial t}) .$$

From the equation of motion for the state vector one obtains

$$34) \text{ a) } \quad H \Psi_i = i\hbar \frac{\partial \Psi_i}{\partial t}$$

$$\text{b) } \quad -i/\hbar H \Psi_i = \frac{\partial \Psi_i}{\partial t} .$$

³Unpublished work by F. J. McCormack, 1972.

To first consider the

$\frac{d}{dt} \psi_i^*(m, \bar{x}', t)$ term of the equation of motion of ρ , one

develops, from equation 33a, the following;

$$\left[\frac{d}{dt} \psi_i(m, \bar{x}', t) \right]^* = \left[\phi_m(\bar{x}') \frac{d}{dt} \psi_i \right]^*$$

or

$$35) \quad \left[\phi_m(\bar{x}'), -i/\hbar \sum_j \int_{\bar{x}''} \psi_i(j, \bar{x}'', t) H \phi_j(\bar{x}'') d\bar{x}'' \right]^* = \\ \sum_j \int_{\bar{x}''} \left[-i/\hbar \psi_i(j, \bar{x}'', t) H_{mj}(\bar{x}', \bar{x}'') \right]^* d\bar{x}''.$$

By use of the Hermitian property of H equation 35 becomes

$$36) \quad \sum_j \int_{\bar{x}''} i/\hbar \psi_i^*(j, \bar{x}'', t) H_{jm}(\bar{x}', \bar{x}'') d\bar{x}''.$$

Similarly, we have

$$37) \quad \frac{d}{dt} \psi_i(n, \bar{x}, t) = \left[\phi_n(\bar{x}), -i/\hbar \sum_k \int_{\bar{x}''} \psi_i(k, \bar{x}'', t) H \phi_k(\bar{x}'') d\bar{x}'' \right] \\ = -i/\hbar \sum_k \int_{\bar{x}''} \psi_i(k, \bar{x}'', t) H_{nk}(\bar{x}, \bar{x}'') d\bar{x}''.$$

The equation of motion can now be written as

$$38) \quad \frac{d}{dt} \rho = \sum_{i=1}^{N_0} \omega^{(i)} \left\{ \sum_j \int_{\bar{x}''} i/\hbar \psi_i^*(j, \bar{x}'', t) \psi_i(m, \bar{x}, t) H_{jm}(\bar{x}', \bar{x}'') d\bar{x}'' - \right. \\ \left. \sum_k \int_{\bar{x}''} i/\hbar \psi_i^*(m, \bar{x}, t) \psi_i(k, \bar{x}'', t) H_{nk}(\bar{x}, \bar{x}'') d\bar{x}'' \right\}.$$

Relabeling indices $j=k$ we obtain from equation 38

$$39) \quad \frac{d\rho}{dt} = i/\hbar \sum_k \int_{\bar{x}''} \left\{ \sum_{i=1}^{N_0} \omega^{(i)} \psi_i^*(k, \bar{x}'', t) \psi_i(m, \bar{x}, t) H_{km}(\bar{x}', \bar{x}'') - \right. \\ \left. \sum_{i=1}^{N_0} \omega^{(i)} \psi_i^*(m, \bar{x}, t) \psi_i(k, \bar{x}'', t) H_{nk}(\bar{x}, \bar{x}'') \right\} d\bar{x}''.$$

and applying the definition of the density matrix 39 becomes

$$40) \quad \frac{\partial \rho_{mn}(\bar{x}, \bar{x}')}{\partial t} = i/\hbar \sum_k \int_{\bar{x}''} \left\{ \rho_{nk}(\bar{x}, \bar{x}'') H_{km}(\bar{x}', \bar{x}'') - \rho_{mk}(\bar{x}, \bar{x}'') H_{kn}(\bar{x}, \bar{x}'') \right\} d\bar{x}''.$$

Noting the matrix multiplication in the last expression, it is then

written as

$$41) \quad \frac{\partial \rho}{\partial t} = i/\hbar \{ \rho H - H \rho \} = i/\hbar [\rho, H] .$$

We now have an expression for the variation of the density matrix as a function of time under action of the Hamiltonian, H .

It might be well to recall at this point that the intent of this work is to derive as general a Boltzmann equation for polyatomic gases as possible and to consider the effect of external electric and magnetic fields on the gas. With this in mind it is simply noted that the general form of the Hamiltonian, since we are dealing with neutral polyatomic molecules, can be expressed as⁴

$$42) \quad H^{(N)} = \sum_{i=1}^N H_i^{(1)} + \frac{1}{2} \sum_{i \neq j} V_{ij} .$$

In this expression N denotes the number of particles involved, $H_i^{(1)}$ is the one-particle Hamiltonian (in this case the kinetic energy plus other energy terms that might be due to the existence of fields), and V_{ij} is the intermolecular potential between molecules denoted by i and j .

Having made the assumption that the polyatomic gas is dilute it is well to consider what this means in terms of our density matrix. Because of the dilute nature of the gas the polyatomic molecules spend most of the time far apart and are in general independent of each other. The mathematical relationship that expresses this is the Boltzmann property⁵,

⁴"Quantum-Mechanical Modified Boltzmann Equation for Degenerate Internal States," Journal of Chemical Physics, R. F. Snider, Vol. 32, No. 4, April, 1960, p. 1051.

⁵R. F. Snider, Journal of Chemical Physics, Vol. 32, No. 4, April 1960, p. 1052.

viz.,

$$43) \quad \rho^{(N)} = \prod_{i=1}^N \rho_i^{(1)},$$

which simply says that the N particle density matrix is a product of one particle density matrices. The N particle density matrix is the density matrix which contains the information about the entire system of molecules. Reference has not been made before to this N particle matrix, but it is the matrix to be considered in the density matrix.

If one treats each particle as a "system" of the ensemble then the state vectors can be written as done before in the derivations of the density matrix, and its associated equation of motion, as

$$44) \quad \Psi_i = \sum_K \int_{\bar{x}} \Psi_i(K, \bar{x}, t) \phi_K(\bar{x}) d\bar{x},$$

where as before the K denotes discrete indices of that individual particle and the \bar{x} the continuous variable associated with that particle. However, when one considers a system consisting of the entire ensemble one would represent it by a state vector of the form;

$$45) \quad \Psi_i = \sum_{n_1 n_2 \dots n_N} \int_{\bar{x}_1 \bar{x}_2 \dots \bar{x}_N} \Psi_i(n_1 n_2 \dots n_N; \bar{x}_1 \bar{x}_2 \dots \bar{x}_N; t) \phi_{n_1 n_2 \dots n_N}(\bar{x}_1 \bar{x}_2 \dots \bar{x}_N) d\bar{x}_1 d\bar{x}_2 \dots d\bar{x}_N.$$

And being consistent with our definition of the density matrix,

$$46) \quad \rho^{(N)} = \sum_{i=1}^{N_0} \omega^{(i)} \Psi_i^*(n_1 n_2 \dots n_N; \bar{x}_1 \bar{x}_2 \dots \bar{x}_N; t) \Psi_i(n_1 n_2 \dots n_N; \bar{x}_1 \bar{x}_2 \dots \bar{x}_N; t).$$

Now if the particles are all independent we may use a form of separation variables so that;

$$47) \quad \Psi_i(n_1 n_2 \dots n_N; \bar{x}_1 \bar{x}_2 \dots \bar{x}_N; t) = \prod_K \Psi_i^K(n_K, \bar{x}_K; t),$$

where the notation $\Psi_i^K(n_K, \bar{x}_K; t)$ refers to the k th particle of the i th system. The density matrix is now written as

$$48) \quad \rho^{(N)} = \sum_{i=1}^{N_0} \omega^{(i)} \prod_K \psi_i^{k*}(n_k, \bar{x}_k; t) \psi_i^k(m_k, \bar{x}'_k; t) .$$

Rewriting equation 48, we have

$$49) \quad \rho_{nm}^{(N)}(\bar{x}, \bar{x}') = \prod_K \left\{ \sum_{i=1}^{N_0} \omega^{(i)} \psi_i^{k*}(n_k, \bar{x}_k; t) \psi_i^k(m_k, \bar{x}'_k; t) \right\} .$$

$$50) \quad \rho_{nm}^{(N)}(\bar{x}, \bar{x}') = \sum_{i=1}^{N_0} \omega^{(i)} \prod_{k=1}^N \left[\rho_{n_k m_k}^k(\bar{x}_k, \bar{x}'_k) \right]_i$$

which is simply the Boltzmann property.

Since it is now possible to express the density matrix as a product of singlet density matrices one needs to consider the implications of this fact in terms of an ensemble average and the writing of the density matrix itself.

Previously the density matrix for N particles had been written, from equation 48, in the form

$$48) \quad \rho^{(N)} = \sum_{i=1}^{N_0} \omega^{(i)} \prod_{k=1}^N \psi_i^{k*}(n_k, \bar{x}_k; t) \psi_i^k(m_k, \bar{x}'_k; t) .$$

Here summation over i refers to sums over possible states of the system where the k denotes particle numbers of that state. However, it is more convenient to attribute to each particle the characteristics of a state. Making the assumption that the states are equally probable

$\omega^{(i)}$ is replaced by $1/N_0$. Therefore, we can write

$$51) \quad a) \quad \rho_{nm}^{(N)} = 1/N_0 \prod_{k=1}^N \psi_i^{k*}(n_k, \bar{x}_k; t) \psi_i^k(m_k, \bar{x}'_k; t)$$

$$b) \quad \rho_{nm}^{(N)} = \prod_{k=1}^N 1/N_0 \rho_{n_k m_k}^k(\bar{x}_k, \bar{x}'_k) \quad \text{or absorbing } 1/N_0 \text{ results in,}$$

$$52) \quad \rho_{nm}^{(N)} = \prod_{k=1}^N \rho_{n_k m_k}^k(\bar{x}_k, \bar{x}'_k) .$$

One now needs to examine the operator properties of the density matrix with consideration of the singlet density matrices previously

discussed.

Again taking the expectation value of an operator which we define as A , for the system, we have $\langle A \rangle_i = (\Psi_i, A \Psi_i)$

$$53) \quad \langle A \rangle_i = \sum_{m_1, m_2, \dots, m_N} \sum_{n_1, n_2, \dots, n_N} \int_{\bar{x}_1, \bar{x}_2} \int_{\bar{x}'_1, \bar{x}'_2} \Psi_i^*(m_1, m_2, \dots, m_N; \bar{x}_1, \bar{x}_2) \Psi_i(n_1, n_2, \dots, n_N; \bar{x}'_1, \bar{x}'_2) (\phi_{m_1}(\bar{x}_1), A \phi_{n_1}(\bar{x}'_1)) d\bar{x}_1 d\bar{x}'_1 \dots$$

The n 's and m 's denote discrete states and the \bar{x} 's and \bar{x}' 's continuous variables for each molecule. Taking the ensemble average and using the Boltzmann property, we obtain,

$$54) \quad \langle A \rangle_e = \sum_i \omega^{(i)} \langle A \rangle_i = \sum_i \omega^{(i)} \sum_{m's, n's} \int_{\bar{x}, \bar{x}'} \Psi_i^*(m_1, \bar{x}_1) \Psi_i^*(m_2, \bar{x}_2) \dots \Psi_i(n_1, \bar{x}'_1) \Psi_i(n_2, \bar{x}'_2) \dots (\phi_{m_1}, \phi_{m_2}, \dots, A \phi_{n_1}, \phi_{n_2}, \dots) d\bar{x}_1 \dots$$

We now consider one of two operators classes, viz., operators A such that

$$A = A(\bar{x}_i, n_i) \quad , \text{ and an operator of the form } V_{ij}(n_i, \bar{x}_i; n_j, \bar{x}_j)$$

Having chosen our operators as above we may now expand the ensemble average, noting that

$$55) \quad (\phi_{m_1}, \phi_{m_2}, \dots, A(\bar{x}_i, n_i) \phi_{n_1}, \phi_{n_2}, \dots) = A_{m_1 n_1}(\bar{x}'_i, \bar{x}_i) \prod_{i=2}^N \delta_{m_i n_i} \delta(\bar{x}'_i - \bar{x}_i)$$

and

$$56) \quad (\phi_{m_1}, \phi_{m_2}, \dots, V_{12}(n_1, \bar{x}_1; n_2, \bar{x}_2) \phi_{n_1}, \phi_{n_2}, \dots) = V_{12}(\bar{x}_1, \bar{x}_2; \bar{x}'_1, \bar{x}'_2) \prod_{i=3}^N \delta_{m_i n_i} \delta(\bar{x}'_i - \bar{x}_i) .$$

We then obtain

$$57) \quad a) \quad \langle A \rangle_e = \sum_i \omega^{(i)} \langle A \rangle_i = \sum_{i=1}^{N_0} \omega^{(i)} \sum_{m's, n's} \int_{\bar{x}, \bar{x}'} \Psi_i^*(m_1, \bar{x}_1) \Psi_i^*(m_2, \bar{x}_2) \dots \times \Psi_i(n_1, \bar{x}'_1) \Psi_i(n_2, \bar{x}'_2) \dots A_{m_1 n_1}(\bar{x}'_i, \bar{x}_i) \prod_{i=2}^N \delta_{m_i n_i} \delta(\bar{x}'_i - \bar{x}_i) d\bar{x}_1 d\bar{x}'_1 \dots,$$

which becomes

$$b) \quad \langle A \rangle_e = \sum_{i=1}^{N_0} \sum_{m_1, n_1, m_2, \dots} \int_{\bar{x}_1, \bar{x}'_1} \omega^{(i)} \Psi_i^*(m_1, \bar{x}_1) \Psi_i(n_1, \bar{x}'_1) \Psi_i^*(m_2, \bar{x}_2) \Psi_i(n_2, \bar{x}'_2) \dots A_{m_1 n_1}(\bar{x}'_i, \bar{x}_i) d\bar{x}_1 d\bar{x}'_1 \dots d\bar{x}_2 \dots d\bar{x}'_2 \dots$$

From before we had $\langle A \rangle_e = \text{Tr}(\rho A)$, and the same is true here if one requires the singlet matrix to be defined as:

$$58) \rho_{n_1 m_1, \bar{x}_1 \bar{x}'_1}^{(1)} = \sum_{i=1}^{N_0} \sum_{m_2} \int_{\bar{x}} \omega^{(i)} \psi_{i_1}(m_1 \bar{x}_1) \psi_{i_2}(m_2 \bar{x}'_1) \psi_{i_3}(m_2 \bar{x}_2) \psi_{i_4}(m_2 \bar{x}_2) \dots d\bar{x}_2 \dots d\bar{x}_N.$$

Then upon substituting equation 58 into 57 we obtain

$$59) \langle A \rangle_e = \sum_{m_1} \left\{ \sum_{n_1} \int_{\bar{x}_1} \int_{\bar{x}'_1} \rho_{n_1 m_1}^{(1)}(\bar{x}_1, \bar{x}'_1) A_{m_1 n_1}(\bar{x}_1, \bar{x}'_1) d\bar{x}_1 d\bar{x}'_1 \right\},$$

or

$$60) \langle A \rangle_e = \text{Tr}_{m=1 \dots N} (\rho^{(1)} A).$$

Suppose now that we consider our other operator, $V_{ij}(n_i \bar{x}_i, j n_j \bar{x}_j)$.

The ensemble average of this operator can then be constructed as

$$61) a) \langle V \rangle_e = \sum_i \omega^{(i)} \langle V_i \rangle = \sum_{i=1}^{N_0} \omega^{(i)} \sum_{m_1 m_2 \dots n_1 n_2 \dots} \int_{\bar{x}} \int_{\bar{x}'} \psi_{i_1}^*(m_1 \bar{x}_1) \psi_{i_2}^*(m_2 \bar{x}_2) \times \\ \psi_{i_3}(n_1 \bar{x}_1) \psi_{i_4}(n_2 \bar{x}_2) \dots V_{12}(n_1 \bar{x}_1, j n_2 \bar{x}_2) \prod_{i=3}^N \int_{m_i n_i} \times \\ \delta(\bar{x}_i - \bar{x}'_i) d\bar{x}_1 d\bar{x}_2 \dots d\bar{x}_N \dots d\bar{x}'_N,$$

which reduces, although not simply, to

$$b) \sum_{i=1}^{N_0} \sum_{m_1 m_2} \sum_{n_1 n_2} \sum_{m_3 \dots \bar{x}} \int_{\bar{x}'} \psi_{i_1}^*(m_1 \bar{x}_1) \psi_{i_2}^*(m_2 \bar{x}_2) \psi_{i_3}(n_1 \bar{x}_1) \psi_{i_4}(n_2 \bar{x}_2) \psi_{i_5}^*(m_3 \bar{x}_3) \psi_{i_6}^*(m_3 \bar{x}_3) \dots \times \\ V_{12}(n_1 \bar{x}_1, j n_2 \bar{x}_2) d\bar{x}_1 d\bar{x}_2 d\bar{x}_3 d\bar{x}_3 \dots d\bar{x}_N.$$

Which as before can be forced into the form of

$$62) \langle V \rangle_e = \text{Tr}(\rho V) \quad \text{if one defines } \rho \text{ as}$$

$$\rho = \rho_{m_1 m_2, n_1 n_2}^{(1)}(\bar{x}_1, \bar{x}'_1; \bar{x}_2, \bar{x}'_2) = \sum_{i=1}^{N_0} \sum_{m_3} \int_{\bar{x}_3 \dots} \psi_{i_1}^*(m_1 \bar{x}_1) \psi_{i_2}^*(m_2 \bar{x}_2) \psi_{i_3}(n_1 \bar{x}'_1) \psi_{i_4}(n_2 \bar{x}'_2) \times \\ \psi_{i_5}^*(m_3 \bar{x}_3) \psi_{i_6}(m_3 \bar{x}_3) \dots d\bar{x}_3 \dots d\bar{x}_N.$$

So that one now has

$$63) a) \langle V \rangle_e = \sum_{i=1}^{N_0} \omega^{(i)} \sum_{m_1 m_2 n_1 n_2} \int_{\bar{x}_1 \bar{x}'_1 \bar{x}_2 \bar{x}'_2} \rho_{m_1 m_2, n_1 n_2}^{(1)}(\bar{x}_1, \bar{x}'_1; \bar{x}_2, \bar{x}'_2) V_{12}(n_1 \bar{x}_1, j n_2 \bar{x}_2) d\bar{x}_1 d\bar{x}'_1 d\bar{x}_2 d\bar{x}'_2$$

or

$$b \quad \langle V \rangle_e = \text{Tr}(\rho^{(2)} V) .$$

Now what has been accomplished in the last section? First, by examining operators of the form of A and V , we have defined density matrices for the singlet and two particle cases, and because of the clever choice of the independent variables on which the operator is dependent, we have dealt with the singlet Hamiltonian of the form A and the encounter term for 2 particles of the form V . Secondly, it is now possible to express both the singlet and doublet density matrix in terms of the N particle matrices, as will be shown below.

Since the N particle matrix is given by

$$64) \quad \rho^N = \sum_{i=1}^{N_0} \omega^{(i)} \sum_{m_1 \dots m_i} \sum_{n_1 \dots n_i} \psi_i^*(m_1 \bar{x}_1) \psi_i^*(m_2 \bar{x}_2) \dots \psi_i(n_1 \bar{x}'_1) \psi_i(n_2 \bar{x}'_2) \dots ,$$

we can rewrite the singlet density matrix as

$$65) \quad \rho_{n_1 m_1}^{(1)}(\bar{x}_1, \bar{x}'_1) = \sum_{i=1}^N \omega^{(i)} \psi_i^*(m_1 \bar{x}_1) \psi_i(n_1 \bar{x}'_1) \times$$

$$\sum_{m_2 \dots m_N} \int_{\bar{x}_2 \dots \bar{x}_N} \psi_i^*(m_2 \bar{x}_2) \psi_i(m_2 \bar{x}_2) \dots \psi_i^*(m_N \bar{x}_N) \psi_i(m_N \bar{x}_N) \dots d\bar{x}_N ,$$

or

$$66) \quad \rho_{n_1 m_1}^{(1)}(\bar{x}_1, \bar{x}'_1) = \text{Tr}_{2 \dots N} \rho^N .$$

Similarly, we have

$$67) \quad \rho_{m_1 m_2 n_1 n_2}^{(2)}(\bar{x}_1 \bar{x}_2, \bar{x}'_1 \bar{x}'_2) = \text{Tr}_{3 \dots N} \rho^N , \quad \rho_{m_1 m_2 m_3 n_1 n_2 n_3}^{(3)}(\bar{x}_1 \bar{x}_2 \bar{x}_3, \bar{x}'_1 \bar{x}'_2 \bar{x}'_3) = \text{Tr}_{4 \dots N} \rho^N$$

and further

$$68) \quad \rho^{(1)} = \text{Tr}_2 \rho^{(2)} , \quad \rho^2 = \text{Tr}_3 \rho^3 .$$

The utility of the above identities can be seen when one

takes the trace 2 of the N particle equation of motion⁶

$$68) \quad \frac{d\rho^N}{dt} = i/\hbar [\rho^N, H^N] \quad , \quad \text{where,}$$

recalling

$$H^N = \sum_{i=1}^N H_i^{(1)} + \frac{1}{2} \sum_{i \neq j} V_{ij} .$$

Doing this, we obtain

$$69) \quad \frac{d}{dt} (\text{Tr}_{2, \dots, N} \rho^N) = i/\hbar \text{Tr}_{2, \dots, N} [\rho^N, H^N] .$$

Dropping some inconvenient notation, we can write

$$\begin{aligned} 70) \text{ a} \quad & \frac{d\rho^{(1)}}{dt} = \text{Tr}_{2, \dots, N} i/\hbar [\rho^N, H^N] \\ \text{b} \quad & = i/\hbar [\rho^{(1)}, H^{(1)}] + i/\hbar \text{Tr}_{2, \dots, N} [\rho^N, V_{ij}] \\ \text{c} \quad & = i/\hbar [\rho^{(1)}, H^{(1)}] + i/\hbar \text{Tr}_2 \left\{ \text{Tr}_{3, \dots, N} [\rho^N, V_{ij}] \right\} \\ \text{d} \quad & = i/\hbar \left\{ [\rho^{(1)}, H^{(1)}] + \text{Tr}_2 [\rho^{(2)}, V_{12}] \right\} . \end{aligned}$$

In the last term we encounter the doublet density matrix, which is to be expected since, physically, the interaction term requires two molecules for its expression. However, the equation of $\rho^{(1)}$ requires some knowledge of $\rho^{(2)}$ so that the equation of motion for $\rho^{(2)}$ is needed. By the same procedures as above the equation of motion for $\rho^{(2)}$ is

found by taking the trace over all but two molecules:

$$\begin{aligned} 71) \text{ a} \quad & \frac{d\rho^{(2)}}{dt} = \frac{d}{dt} (\text{Tr}_{3, \dots, N} \rho^N) = i/\hbar \text{Tr}_{3, \dots, N} [\rho^N, H^N] \\ \text{b} \quad & = i/\hbar [\rho^{(2)}, H^{(2)}] + i/\hbar \text{Tr}_3 \left\{ \text{Tr}_{4, \dots, N} [\rho^N, \frac{1}{2} V^N] \right\} \\ \text{c} \quad & = i/\hbar \left\{ [\rho^{(2)}, H^{(2)}] + \text{Tr}_3 [\rho^{(3)}, V_{13} + V_{23}] \right\} \end{aligned}$$

⁶R. F. Snider, Journal of Chemical Physics, Vol. 32, No. 4, April 1960, p. 1052.

where $H^{(2)} = H_1^{(1)} + H_2^{(1)} + V(1,2)$, and the indices 1 and 2 represent molecule numbers. The T_3 term above represents 3 molecule interactions and will hereafter be neglected since they are an extremely rare occurrence in a dilute gas. Therefore the equation for $\rho^{(2)}$ reduces to

$$72) \quad \frac{d\rho^{(2)}}{dt} = i/\hbar [\rho^{(2)}, H^{(2)}]$$

All that remains to be accomplished is to obtain the solution for $\rho^{(2)}$ and use that in the expression for $\rho^{(1)}$.

We have obtained the equation of motion for the two particle density matrix of the form

$$72) \quad \frac{d\rho^{(2)}}{dt} = i/\hbar [\rho^{(2)}, H^{(2)}],$$

which is valid only during collisions between two molecules. Still, as noted in the last section, our primary objective is to solve the equation of motion for the singlet density matrix.

Since the above equation involves scattering of molecules, examination of that theory, although the development will be incomplete, is necessary.

CHAPTER 5
APPLICATION OF FORMAL SCATTERING THEORY
TO THE BOLTZMANN EQUATION

In the last section two equations were derived, viz.,

$$69) \quad \frac{d\rho^{(1)}}{dt} = \frac{i}{\hbar} \left\{ [\rho^{(1)}, H^{(1)}] + \text{Tr}_2 [\rho^{(2)}, V_{12}] \right\}$$

and

$$72) \quad \frac{d\rho^{(2)}}{dt} = \frac{i}{\hbar} [\rho^{(2)}, H^{(2)}] .$$

Where $H^{(1)}$ and $H^{(2)}$ represent kinetic energies, K , of molecules 1 and 2 and $H^{(2)}$ represents the kinetic energies and the interaction potentials energies of the 2 molecules, i.e.,

$$73) \quad H^{(2)} = H^{(1)} + H^{(2)} + V_{(1,2)} \quad ; \quad H = K + V .$$

Up to this point the operator $H^{(2)}$ has been of little consequence; it has simply been assumed to be an Hermitian operator. Now, however, for generality we will assume that it is at least time dependent. This assumption is necessary to include such notions as time varying fields, and the following developments will proceed along these lines. Foregoing any long discussion of the Schrodinger or Heisenberg formulations of quantum mechanics we will simply assume, based on previous work, that we may separate the time dependence of $\rho^{(2)}(t)$ by use of unitary transformations as follows:

$$74) \quad \rho^{(2)}(t) = U(t, t_0) \rho^{(2)}(t_0) U^\dagger(t, t_0)$$

where $U(t, t_0)$ is a unitary operator which takes the system from time

t_0 to t . Equation 74 is a solution of equation 72 if the following conditions apply:

$$75) \quad \frac{\partial p^{(2)}}{\partial t} = \frac{\partial U}{\partial t} p^{(2)}(t_0) U^* + U p^{(2)}(t_0) \frac{\partial U^*}{\partial t} = \frac{i}{\hbar} [p^{(2)}(t), H^{(2)}(t)],$$

$$\text{or} \quad \frac{\partial U}{\partial t} p^{(2)}(t_0) U^* + U p^{(2)}(t_0) \frac{\partial U^*}{\partial t} = \frac{i}{\hbar} U p^{(2)}(t_0) U^* H^{(2)}(t) - \frac{i}{\hbar} H U p^{(2)}(t_0) U^*,$$

$$76) \quad \frac{\partial U}{\partial t} p^{(2)}(t_0) U^* = -\frac{i}{\hbar} H^{(2)}(t) U p^{(2)}(t_0) U^*,$$

and

$$77) \quad \frac{\partial U^*}{\partial t} = \frac{i}{\hbar} U p^{(2)}(t_0) U^* H^{(2)}(t),$$

which may be further reduced to

$$78) \quad \frac{\partial U}{\partial t} = -\frac{i}{\hbar} H^{(2)}(t) U,$$

and

$$79) \quad \frac{\partial U}{\partial t} = \frac{i}{\hbar} U^* H^{(2)}(t).$$

Since equation 79 is the adjoint of 78, one need only solve one of these equations. Equation 78 is formally solved by

$$80) \quad U(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^{(2)}(t') U(t', t_0) dt'$$

where I is the unitary operator. This is a Volterra type integral equation.⁷ A Neumann-Liouville series expansion of the Volterra equation will always be convergent. Since it is convergent it is not unreasonable to formulate a series solution by successive approximations as follows.

$$81) \text{ Let } U_{(0)}(t, t_0) = I.$$

⁷Advanced Quantum Mechanics, p. 311.

Then the first approximation is given by;

$$82) \quad U_{(1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^{(2)}(t') dt' ;$$

and the second is given by;

$$U_{(2)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^{(2)}(t') dt' + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t \int_{t_0}^{t'} H^{(2)}(t') H^{(2)}(t'') dt'' dt' .$$

Continuing in the above manner one generates a series solution of the

form;

$$84) \quad U(t, t_0) = \sum_{n=0}^{\infty} U_n(t, t_0) ,$$

where

$$85) \quad U_n(t, t_0) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t \dots \int_{t_0}^{t^{n-1}} H^{(2)}(t) H^{(2)}(t^{n-1}) \dots H^{(2)}(t^n) dt^n \dots dt' .$$

A considerable problem is uncovered when one realizes that $H^{(2)}(t)$ does not necessarily commute with $H^{(2)}(t^n)$, and this problem is due to the differences in times t', t'', t''', \dots et cetera. In fact by arrangement of the intergral, the following ordering is required:

$$86) \quad t_0 \leq t^n \leq t^{n-1} \leq \dots \leq t' \leq t .$$

The operators $H^{(2)}(t) H^{(2)}(t^n)$ etc. are time ordered from the right in equation 85. Solution of the integral would be greatly facilitated if the upper limits were all equal. This is achieved by the invention of Dyson⁸. By use of the Dyson method a chronological time ordering operator is introduced, represented here by P, whose properties are summarized in the following relations

$$87) \quad P(H(t') H(t'')) = \begin{cases} H(t') H(t'') & t' > t'' \\ H(t'') H(t') & t' < t'' \end{cases} .$$

⁸Advanced Quantum Mechanics, pp. 311-314

In the case of equation 85, we have

$$88) \quad P(H^2(t') H^2(t'') \dots H^2(t^n)) = H^2(t') H^2(t'') \dots H^2(t^n)$$

where 88) a $t' \geq t'' \geq \dots t^n$,

and the equality signs of expression 88) a are the result of all being equal at the same time. It should be noted that for any ordering of the H^2 , the operation of P on the set has the same results, that is

$$89) \quad P(H^2(t^n), H^2(t'), H^2(t'') \dots H^2(t^{n-1})) = \\ H^2(t') H^2(t'') \dots H^2(t^{n-1}) H^2(t^n).$$

Since there are $n!$ ways of ordering the Hamiltonian operators corresponding to different times then the following relationship

holds:

$$90) \quad \int_{t_0}^t \dots \int_{t_0}^t P(H^2(t') \dots H^2(t^n)) dt^n \dots dt' = \\ n! \int_{t_0}^t \int_{t_0}^{t'} \dots \int_{t_0}^{t^{n-1}} H^2(t') H^2(t'') \dots H^2(t^n) dt^n \dots dt'.$$

Using the ordering operator, P, equation 85 may now be rewritten as

$$91) \quad U_n(t, t_0) = \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t \dots \int_{t_0}^t P[H^2(t') H^2(t'') \dots H^2(t^n)] dt' \dots dt^n.$$

P can be evaluated if the commutator relations between the H 's are known. That is if $D(t', t'')$ represents the commutator of $H^2(t')$ and $H^2(t'')$ i.e.,

$$92) \quad [H^2(t'), H^2(t'')] \equiv D(t', t''),$$

$$93) \text{ then } P(H^2(t') H^2(t'')) = H^2(t') H^2(t'') - \Delta(t'' - t') D(t', t''),$$

where

$$\Delta(t'' - t') = \begin{cases} 1 & t'' \neq t' \\ 0 & t'' = t' \end{cases}.$$

For the case of 91 we have

$$94) \quad P(H^{(1)}(t') H^{(2)}(t') \dots H^{(n)}(t')) = H^{(1)}(t') H^{(2)}(t') \dots \Delta(t^{(n)} - t^{(n-1)}) D(t^{(n)} - t^{(n-1)}).$$

However for our purposes, to find a general solution of equation 72, we need only, the result

$$95) \quad U(t, t_0) = U_0(t, t_0) + U_1(t, t_0) + U_2(t, t_0) + \dots \\ = 1 + \frac{1}{i\hbar} (-i\hbar) \int_{t_0}^t H^{(1)}(t') dt' + \frac{1}{2!} (-i\hbar)^2 \int_{t_0}^t \int_{t_0}^t P H^{(2)}(t') H^{(1)}(t'') dt' dt'' + \dots$$

or

$$96) \quad U(t, t_0) = P \exp \left[(-i/\hbar) \int_{t_0}^t H^{(1)}(t') dt' \right].$$

In summary we have obtained a solution of equation 72 by use of equation 74, and the required form of the unitary operator is given by equation 96. If the Hamiltonian were time independent, the unitary operators would take the form;

$$97) \quad U(t, t_0) = \exp \left[-i/\hbar H^{(1)}(t - t_0) \right].$$

However, since we are considering fields, in general, time variation must be included. In order to properly treat the above, an expression for $H^{(1)}$ must be developed.

As noted previously we now need an expression for the two particle Hamiltonian. To do so, we must first write the Hamiltonian for the single polyatomic molecule, then we must consider electron degrees of freedom and finally intermolecular forces and general external conservative forces. Also while we are developing the Hamiltonian it will be appropriate to consider the resulting eigenfunction and density matrix.

For this problem the Hamiltonian will be written as (for N molecules);

$$98) \quad H^{(N)} = \sum_{\mu=1}^N H_{\mu}^{(1)} + \frac{1}{2} \sum_{\mu \neq \lambda} V_{\mu\lambda}$$

(Greek letters indicate molecule number throughout) where $H_{\mu}^{(1)}$ denotes single molecule energy and $V_{\mu\lambda}$ denotes molecular collisions.

The single molecule Hamiltonian can be further separated into the following form:

$$99) \quad H_{\mu}^{(1)} = \phi_{\mu} + \frac{P_{\mu}^2}{2M} + \frac{P_{\mu}^2}{2\bar{m}} + V(r_{ij}, r_{ik}, \dots)_{\mu} + \sum_{k=1}^A H_k.$$

Term one, of this very general expression, is due to all possible external conservative forces acting on the molecule μ and is in general given by

$$100) \quad \phi_{\mu} = \phi_{\mu} [\bar{R}_{\mu}, \bar{r}_{\mu}],$$

where the center of mass coordinate for the molecule is given by

$$101) \quad \bar{R}_{\mu} = \frac{1}{\sum_{i=1}^A m_i} [m_1 \bar{R}_{1\mu} + m_2 \bar{R}_{2\mu} + \dots + m_A \bar{R}_{A\mu}], \text{ where } M = \sum_{i=1}^A m_i.$$

In this expression, $\bar{R}_1, \bar{R}_2, \dots, \bar{R}_A$ locate individual atoms in the molecule.

Momentum is given by the time derivative of equation 101 or

$$102) \quad \bar{P}_{\mu} = \bar{P}_{1\mu} + \bar{P}_{2\mu} + \dots + \bar{P}_{A\mu}.$$

Term two and three of equation 99 are translation and rotation-vibrational energy terms, respectively, and the momentum operators are given by

$$103) \quad \frac{P_{\mu}^2}{2M} = -\frac{\hbar^2}{2M} \frac{\partial}{\partial \bar{R}_{\mu}} \cdot \frac{\partial}{\partial \bar{R}_{\mu}},$$

$$104) \quad \frac{P_{\mu}^2}{2\bar{m}} = -\frac{\hbar^2}{2\bar{m}} \cdot \frac{1}{2} \sum_{i \neq j=1}^A \frac{\partial}{\partial \bar{r}_{ij\mu}} \cdot \frac{\partial}{\partial \bar{r}_{ij\mu}}$$

105) In equation 103 and 104

$$\bar{r}_{ij,u} = \bar{R}_{iu} - \bar{R}_{ju}$$

is the interatomic separation of atoms in the molecule and \bar{m} is the reduced mass of the atoms of the molecule. The momentum for a rotation and vibration state of two atoms is given by,

$$106) \quad \bar{p}_{ij,u} = \frac{1}{m_i + m_j} [m_i \bar{p}_{iu} - m_j \bar{p}_{ju}]$$

Term four of equation 99 is the interaction potential of the individual atoms in the molecule. Term five encompasses the effects of the electric and magnetic fields (time dependence of these fields is not ruled out). Before dealing with the fifth term it is instructive to discuss the Hamiltonian without the presence of the fields.

Without term five the single molecule Hamiltonian (molecule u)

is,

$$107) \quad H_u^{(1)} \Phi_u + \frac{\bar{P}_u^2}{2M} + \frac{\bar{P}_u^2}{2m} + V(\bar{r}_{ij}, \bar{r}_{in}, \dots)_u$$

Further reducing by eliminating the external conservative forces, which may be carried with the \bar{P}_u^2 in some cases, we have

$$108) \quad H_u^{(1)} = \frac{p_u^2}{2m} + \frac{p_u^2}{2\bar{m}} + V(\bar{r}_{ij}, \bar{r}_{in}, \dots)_u$$

Substituting equations 103 and 104 into 108, one obtains

$$H_u^{(1)} = -\frac{\hbar^2}{2m} \frac{\partial}{\partial \bar{R}_u} \cdot \frac{\partial}{\partial \bar{R}_u} - \frac{\hbar^2}{4m} \sum_{i,j=1}^N \left(\frac{\partial}{\partial \bar{r}_{ij}} \cdot \frac{\partial}{\partial \bar{r}_{ij}} \right)_u + V(\bar{r}_{ij}, \bar{r}_{in}, \dots)_u$$

The eigenfunction corresponding to the Hamiltonian is derived from the following equations:

$$109) \quad H_u^{(1)} \Psi = E \Psi$$

$$110) \quad [H_u^{(1)}(\bar{R}_u) + H_u^{(1)}(\bar{r}_{ij,u})] \Psi(\bar{R}_u, \bar{r}_{ij,u}) = E \Psi(\bar{R}_u, \bar{r}_{ij,u})$$

The eigenfunction can be developed by use of the separation of variables

method, resulting in

$$111) \quad \Psi(\bar{R}_u, \bar{r}_{ij, \mu j t}) = \Psi(\bar{R}_u, t) \Psi_T(r_{ij, \mu j t}).$$

In the absence of external forces acting on the molecules, we have

$$112) \quad \Psi(\bar{R}_u, t) = \sum_n c_n(t) e^{i \bar{K}_n \cdot \bar{R}_u}$$

and

$$113) \quad \Psi(r_{ij, \mu j t}) = \frac{1}{|r_{ij}|} Z_{(n\ell)ij}(r_{ij}) Y_{(\ell m)ij}(\theta_{ij}, \phi_{ij}),$$

where $Y_{(\ell m)ij}(\theta_{ij}, \phi_{ij})$ is a spherical harmonic for an atomic pair (ij) in the molecule and $Z_{(n\ell)ij}$ is a radial function that is the solution of the following expression:⁹

$$114) \quad \frac{d^2 Z_{(n\ell)ij}}{d|r_{ij}|^2} + \frac{2\bar{m}_{ij}}{\hbar^2} \left[E_{(n\ell)ij} - V(r_{ij}) - \frac{\hbar^2}{2\mu(r_{ij})} \ell(\ell+1) \right] Z_{(n\ell)ij} = 0.$$

Note that in the above discussion it is assumed that the atomic coupling term is basically of the form, or can be made to fit an expansion of the form

$$115) \quad V(r_{ij}, r_{in}, \dots) = V(r_{ij}) + \alpha_1 V(r_{in}) + \dots$$

If equation 115 is valid, and subsequently 114, the term $\Psi_T(r_{ij, \mu j t})$ of equation 111 can be written as

$$116) \quad \Psi_T(r_{ij, \mu j t}) = \Psi(r_{ij, \mu j t}) \Psi(r_{in, \mu j t}) \dots$$

In the above, and in what will follow, the molecular collision term is not involved since we "rotate" to the collision time from times before the collision, precisely when we solve equation 111.

⁹"Transport Phenomena in a Fluid Composed of Diatomic Molecules," Journal of Chemical Physics, John S. Dahler, Vol. 30, No. 6, June, 1959, p. 1462.

Term five of equation 99 has been omitted, but if arbitrary electric and magnetic fields are to be considered it must be included. To do so one must consider electron degrees of freedom. Nuclear spin interactions will be neglected in this consideration. The Hamiltonian

H_K , for each atom is written as follows.

$$117) \quad H_K = \sum_{i=1}^{n_e/A} \left\{ \frac{1}{2m_i} \left[p_i + \left(\frac{e}{c}\right) A(\vec{r}_i, t) \right]^2 + e \vec{E}(\vec{r}_i, t) \cdot \vec{r}_i + V(\vec{r}_i) + g(\vec{r}_i) \vec{L}(\vec{r}_i) \cdot \vec{S}_i + e/m_{ec} \vec{B}(\vec{r}_i, t) \cdot \vec{S}_i \right\},$$

where summation is made over the numbers of electrons per atom. In equation 117, for an electron with position vector \vec{r}_i , $A(\vec{r}_i, t)$ is the electromagnetic field vector potential; $\vec{E}(\vec{r}_i, t)$ the electric field; $V(\vec{r}_i)$ coulombic potential; $\vec{L}(\vec{r}_i)$ total angular momentum; and \vec{S}_i is spin. Possible time dependence of the fields is included.

Since H_K can be written as the sum of ith electron Hamiltonians, all functionally independent of each other, each of these operators commute and it is possible to write the eigenfunction for the total atom neglecting electron interactions, as

$$118) \quad \psi_K(\vec{r}, t) = \prod_{m=1}^{n_e} \psi_m(\vec{r}_m, t).$$

Equation 99 can be rewritten in the form

$$119) \quad H_{\mu}^{(1)} = H(\vec{R}_\mu)_{\text{mole.}} + H(\vec{r}_{ij, \mu})_{\text{Atom}} + H(\vec{r}_i)_{\text{Elect.}},$$

and since

$$120) \quad [H(\vec{R}_\mu), H(\vec{r}_{ij, \mu})] = [H(\vec{R}_\mu), H(\vec{r}_i)] = [H(\vec{r}_{ij, \mu}), H(\vec{r}_i)] = 0,$$

one may write the eigenfunction for a molecule as follows:

$$121) \quad \psi_{\mu}(\text{mole.}) = \psi(\vec{R}_\mu, t) \prod_{i \neq j=1}^A \psi(\vec{r}_{ij, \mu}, t) \prod_{k=1}^A \left[\prod_{m=1}^{n_e} \psi_m(\vec{r}_m, t) \right]_K$$

where $\{\vec{r}_{ij}, \mu\}$ means $(\vec{r}_{ij}, \mu, \eta, l, m)$ and $\{\vec{r}_m\}$ means
 (r_m, η, l, m, s) . The single molecule density matrix is given by
 122)
$$\rho_{\mu}^{(1)} = \Psi_{\mu}^* \Psi_{\mu},$$

and

123)
$$\rho^{(N)} = \prod_{\mu=1}^N \rho_{\mu}^{(1)}, \rho^{(N)}$$
 is the N molecule density matrix.

Noting from the form of equations 122 and 123 it is possible to write the density matrix for a molecule as the product of density matrices for the center of mass molecules, atoms of the molecules, and electrons of the atoms for each molecule. With this in mind, equation 112 can be written as

124)
$$\rho_{\mu}^{(1)} = \rho(\{\bar{R}_{\mu}, t\}) \rho(\{\vec{r}_{IJ}\}_{\mu}^A, t) \rho(\{\{r_i\}_A\}_{\mu}^{n_e}, t),$$

where \bar{R}_{μ} locates center of mass of the molecules. $\{\vec{r}_{IJ}\}_{\mu}^A$ locates pairs of A interacting atoms of molecule μ , $\{\{r_i\}_A\}_{\mu}^{n_e}$ are electron coordinates for n_e electrons for each A' atom pairs of the molecule μ . In general Greek letters, label molecules; capital English label atoms; small English letters label electrons.

From our development of the Hamiltonian for one molecule it is apparent that if explicit dependence of time is to be found it will be in the form of time varying fields, $\bar{E}(\vec{r}_i, t)$ and $\bar{B}(\vec{r}_i, t)$. It should be noted that we have assumed that, consistent with the notation applied in derivation of the Hamiltonian, the intermolecular interaction term is dependent only on $\bar{R}_{\mu\nu}, \bar{R}_{\mu}, \bar{R}_{\nu}$ and possibly explicitly on time, t . The two particle Hamiltonian $H^{(2)}$ can now be

written as

$$125) \quad H_{\mu\nu}^{(2)} = H_{\mu}^{(1)} + H_{\nu}^{(1)} + V(\mu, \nu) ,$$

where $V(\mu, \nu)$ is intermolecular potential dependent on $\bar{R}_{\mu\nu}, \bar{R}_{\mu}, \bar{R}_{\nu}, t$ and $H_{\mu}^{(1)}$ and $H_{\nu}^{(1)}$ are given by the expression that follows, differing only in subscript lettering

$$126) \quad H_{\mu}^{(1)} = \phi_{\mu}(\bar{R}_{\mu}, \bar{r}_{\mu}) + \frac{p_{\mu}^2}{2m} + \frac{p_{\mu}^2}{2\bar{m}} + V(\bar{r}_{\mu 1}, \bar{r}_{\mu 2}, \dots, \bar{r}_{\mu n})_{\mu} + \\ \left\{ \sum_{k=1}^{n_{\mu}/A} \left\{ \frac{1}{2m_k} \left[\bar{p}_k + \frac{e}{c} \bar{A}(\bar{r}_{\mu}, t) \right]^2 + e \bar{E}(\bar{r}_{\mu}, t) + V(\bar{r}_{\mu}) + \right. \right. \\ \left. \left. g(\bar{r}_{\mu}) \bar{L}(\bar{r}_{\mu}) \cdot \bar{S}_k + \frac{e}{m_k c} \bar{B}(\bar{r}_{\mu}, t) \cdot \bar{S}_k \right\} \right\}_{\mu} .$$

Rewriting the above expression so that time dependent terms are separated one obtains

$$127) \quad H_{\mu\nu}^{(2)} = H_{\mu}^{(1)} + \Lambda_{\mu}^{(1)}(t) + V(\mu, \nu) + H_{\nu}^{(1)} + \Lambda_{\nu}^{(1)}(t) ,$$

which for further convenience will be written as

$$128) \quad H^{(2)} = K + \Lambda^{(1)}(t) + V(1, 2; t) ,$$

where

$$\Lambda^{(1)}(t) = \Lambda^{(1)}(\bar{A}(\bar{r}_{\mu}, t), \bar{E}(\bar{r}_{\mu}, t), \bar{B}(\bar{r}_{\mu}, t))$$

From equations 95 and 96 of the previous section the operator \mathcal{U} can be written as

$$129) \quad \mathcal{U}(t, t_0) = P \exp \left[-\frac{i}{\hbar} K(t-t_0) - \frac{i}{\hbar} \int_{t_0}^t \Lambda^{(1)}(t') dt' - \frac{i}{\hbar} \int_{t_0}^t V(1, 2; t') dt' \right]$$

where P is the Dyson chronological time ordering operator. It should be noted that the exponential can not be separated since the operators do not necessarily commute with each other. It will be useful to show that $\mathcal{U}(t, t_0)$ in the form of equation 129 is a unitary operator (see Appendix A.) Because the operator is in fact unitary we may now use this

fact to obtain a more favorable representation in which to consider this problem. The physical significance of the operator is that it transforms the density matrix from time t_0 to t under the action of the Hamiltonian.

Suppose the Hamiltonian had no explicit time dependences and could instead be written as

$$130) \quad H^2 = K + V(1,2) \quad .$$

$U(t, t_0)$ would then be given by

$$131) \quad U(t, t_0) = e^{-i/\hbar H^2(t-t_0)} \quad .$$

With the aid of yet another unitary operation the density matrix could be transformed to an "interaction representation" where the density matrix changes are due only to the collision term. This transformation is attained as follows:

$$132) \quad \rho_v^{(2)}(t) = e^{ikt/\hbar} \rho(t) e^{-ikt/\hbar} \quad .$$

That this accomplishes the purpose stated above is shown by use of the 2 particle equation of motion in the derivative which follows.

Taking the time derivative of equation 132 we have,

$$133) \quad \frac{\partial \rho_v^{(2)}(t)}{\partial t} = i/\hbar k e^{ikt/\hbar} \rho^{(2)}(t) e^{-ikt/\hbar} + e^{ikt/\hbar} \frac{\partial \rho(t)}{\partial t} e^{-ikt/\hbar} \\ + e^{ikt/\hbar} \rho^{(2)}(t) (-i/\hbar) e^{-ikt/\hbar} \quad ,$$

or

$$\frac{\partial \rho_v^{(2)}(t)}{\partial t} = i/\hbar \left\{ e^{ikt/\hbar} k \rho^{(2)}(t) e^{-ikt/\hbar} - e^{ikt/\hbar} \rho^{(2)}(t) k e^{-ikt/\hbar} - e^{ikt/\hbar} i/\hbar [k w, \rho^{(2)}(t)] e^{-ikt/\hbar} \right\} \quad ,$$

so that

$$134) \quad \frac{\partial \rho_v^{(2)}(t)}{\partial t} = i/\hbar e^{ikt/\hbar} [\rho^{(2)}(t), V] e^{-ikt/\hbar} \quad .$$

Since the unitary operator $e^{\pm iKt/\hbar}$ represents, in this case, only kinetic energy terms, they have no effect on the collision operator V ; therefore the above equation may be rewritten as

$$135) \quad \frac{d\rho_V^{(2)}(t)}{dt} = i/\hbar e^{iKt/\hbar} [\rho^{(2)}(t_0), V] e^{-iKt/\hbar},$$

which is the equation of motion of the two particle Hamiltonian in the interaction representation.

This same type of operator used previously may now be used in this representation, that is

$$136) \quad \rho_V^{(2)}(t) = J(t, t_0) \rho_V(t_0) J^*(t, t_0).$$

In exactly the same manner as shown above, the time dependent case can be considered by use of the following unitary operators;

$$137) \quad \rho_V^{(2)}(t) = \lim_{\epsilon \rightarrow 0} I^*(t, \epsilon) \rho^{(2)}(t) I(t, \epsilon)$$

where

$$138) \quad I^*(t, \epsilon) = P^* \exp \left[i/\hbar k(t-\epsilon) + i/\hbar \int_{\epsilon}^t \Lambda(t') dt' \right].$$

$J(t, t_0)$ is evaluated as follows,

$$139) \quad \rho_V^{(2)}(t) = \lim_{\epsilon \rightarrow 0} I^*(t, \epsilon) [U(t, t_0) \rho^{(2)}(t_0) U^*(t, t_0)] I(t, \epsilon),$$

while

$$140) \quad \rho^{(2)}(t_0) = \lim_{\xi \rightarrow 0} I(t_0, \xi) \rho_V^{(2)}(t_0) I^*(t_0, \xi).$$

Combining equations 139 and 140, we obtain

$$141) \quad \rho_V^{(2)}(t) = \lim_{\epsilon \rightarrow 0} \lim_{\xi \rightarrow 0} I^*(t, \epsilon) U(t, t_0) I(t_0, \xi) \rho_V^{(2)}(t_0) I^*(t_0, \xi) U^*(t, t_0) I(t, \epsilon),$$

so that

$$142) \quad J(t, t_0) = \lim_{\epsilon \rightarrow 0} \lim_{\xi \rightarrow 0} I^*(t, \epsilon) U(t, t_0) I(t_0, \xi),$$

which can be rewritten as

$$143) \quad J(t, t_0) = \lim_{\epsilon \rightarrow 0} \lim_{\xi \rightarrow 0} I^*(t, \epsilon) U(t, t_0) I(t_0, \xi) I^*(t_0, \epsilon) I(t, \epsilon),$$

where a new operator has been derived, namely,

$$144) \quad U(t, t_0) = \lim_{\epsilon \rightarrow 0} \lim_{\xi \rightarrow 0} U(t, t_0) I(t_0, \xi) I^*(t, \epsilon).$$

Physical meaning maybe ascribed to the operator formulated in equation 144 if we consider again the time independent case. In that case

$$145) \quad U(t, t_0) = e^{-i/\hbar H^{(2)}(t-t_0)}$$

and

$$146) \quad I(t_0, \xi) = e^{i/\hbar \{K(\xi-t_0) + \Lambda(\xi-t_0)\}} = e^{i/\hbar K(\xi-t_0)},$$

Taking the inverse of 146, we have

$$147) \quad I^*(t, \epsilon) = e^{i/\hbar K(t-\epsilon)}.$$

Then

$$U(t, t_0) \rightarrow U(0, t_0-t) = \lim_{\epsilon \rightarrow 0} \lim_{\xi \rightarrow 0} U(t, t_0) I(t_0, \xi) I^*(t, \epsilon),$$

or

$$148) \quad U(0, t_0-t) = e^{i/\hbar H^{(2)}(t_0-t)} e^{-i/\hbar K(t_0-t)}.$$

The physical significance of the times t and t_0 is that at time t the molecules are in the middle of a collision. At time t_0 the molecules are before the collision, where the Boltzmann property is valid namely,

$$149) \quad \rho^{(2)}(t_0) = \rho^{(1)}(1, t_0) \rho^{(1)}(2, t_0).$$

The effect of the operator $U(0, t_0-t)$ is to transform a system in the interaction representation at time t_0-t before a collision to time t_0 in the middle of the collision. It should be noted that the operator $U(0, t_0-t)$ has no effect on the system until a collision has

occurred, and is for that reason insensitive to the length of times before the collision, even an infinitely long period. In fact it has been shown by Jauch¹⁰ that for the case of time independence one can write

$$150) \quad U(0, -\infty) = \lim_{\tau \rightarrow +\infty} e^{iH\tau/\hbar} e^{-iK\tau/\hbar} = \Omega^{(+)},$$

where $\Omega^{(+)}$ is a Møller wave operator to be discussed later.

Our Boltzmann equation is not, however, to be written in the interaction representation and we must return to the appropriate representation by yet another set of operators, all the while using the operator $U(0, t_0 - t)$ since it allows us to use the Boltzmann property at the very time it is not valid, i.e. during collision.

Using our newly derived operator, we have

$$151) \quad J(t, t_0) = \lim_{\epsilon \rightarrow 0} I^*(t, \epsilon) U(0, t_0 - t) I(t, \epsilon).$$

Recalling the following relationship

$$152) \quad \rho_v^2(t) = J(t, t_0) \rho_v^2(t_0) J^*(t, t_0),$$

and transforming from the interaction representation we obtain,

$$153) \quad \rho^2(t) = \lim_{\xi \rightarrow 0} I(t, \xi) \rho_v^2(t) I^*(t, \xi).$$

Substituting 152 into 153 produces the result

$$154) \quad \rho^2(t) = \lim_{\xi \rightarrow 0} I(t, \xi) J(t, t_0) \rho_v^2(t_0) J^*(t, t_0) I^*(t, \xi);$$

and using another interaction transformation, viz.,

$$155) \quad \rho_v^2(t_0) = \lim_{\xi \rightarrow 0} I^*(t_0, \xi) \rho^2(t_0) I(t_0, \xi),$$

¹⁰R. F. Snider, Journal of Chemical Physics, Vol. 32, No. 4, April 1960, p. 1054

one finally obtains

$$156) \quad \rho^2(t) = \lim_{\substack{\epsilon \rightarrow 0 \\ \xi \rightarrow 0}} I(t, \xi) J(t, t_0) I^*(t, \xi) \rho^2(t_0) I(t_0, \xi) J^*(t, t_0) I^*(t, \xi),$$

which expanded results in

$$157) \quad \rho^2(t) = \lim_{\substack{\epsilon \rightarrow 0 \\ \xi \rightarrow 0}} I(t, \xi) I^*(t, \xi) U(0, t_0 - t) I(t, \xi) I^*(t, \xi) \times \\ \rho^2(t_0) I(t_0, \xi) I^*(t, \xi) U^*(0, t_0 - t) I(t, \xi) I^*(t, \xi).$$

This very long expression may be simplified by use of the following expression:

$$\lim_{\substack{\epsilon \rightarrow 0 \\ \xi \rightarrow 0}} I(t, \xi) I^*(t, \xi) = 1, \quad \text{which holds by virtue of the}$$

definition of unitary operators and

$$158) \quad \lim_{\substack{\epsilon \rightarrow 0 \\ \xi \rightarrow 0}} I(t, \xi) I^*(t, \xi) \rightarrow \lim_{\substack{\xi \rightarrow 0 \\ \xi \rightarrow 0}} I(t, \xi) I(\xi, t_0) = I(t, t_0).$$

Then the expression becomes

$$159) \quad \rho^2(t) = U(0, t_0 - t) I(t, t_0) \rho^2(t_0) I^*(t, t_0) U^*(0, t_0 - t).$$

Once again if the time independence case is considered one obtains

$$160) \quad \rho^{(2)}(t) = U(0, t_0 - t) e^{-i/k K(t-t_0)} \rho^{(2)}(t_0) e^{i/k K(t-t_0)} U^*(0, t_0 - t).$$

In the preceding equation 159 the $I(t, t_0)$ operators serve to make the following modifications

$$161) \quad I(t, t_0) \rho^{(1)}(1; t_0) \rho^{(1)}(2; t_0) I^*(t, t_0) = \\ \rho^{(1)}(1; t_0; t) \rho^{(1)}(2; t_0; t).$$

The physical meaning of such a transformation is that the single particle matrices are transformed by the Hamiltonian, excluding collision terms, for time t_0 to t and assume coordinates, momenta, etc. due to the action of the Hamiltonian after $t - t_0$ time has passed. Substitution

of equation 161 into 166 now leaves us only,

$$162) \quad \rho^{(2)}(t) = U(0, t_0 - t) \rho^{(1)}(k_0, j; t) \rho^{(1)}(2 + k_0, j; t) U^*(0, t_0 - t).$$

As noted before $U(0, t_0 - t)$ is insensitive to large negative values of $t_0 - t$, in fact as large as $-\infty$. We will now use this fact to evaluate $U(0, -\infty)$ and establish relationships with the transition matrix associated with scattering phenomena.

It should be noted before dealing with the scattering problem that that procedure is warranted by the following. The equation of motion for the single particle matrix is now written as

$$163) \quad \frac{d\rho^{(1)}(1; t)}{dt} = \frac{i}{\hbar} \left\{ [\rho^{(1)}(1; t), H^0] + \text{Tr} \left[U(0, t_0 - t) \rho^{(1)}(k_0, j; t) \rho^{(1)}(2 + k_0, j; t) U^*(0, t_0 - t) V(1, 2; t) \right] \right\}$$

where in the low density limit, when the Boltzmann equation is valid,

$\rho^{(1)}(k_0, j; t)$ becomes, or is rather not measurably different from $\rho^{(1)}(1; t)$,

and for that reason the latter will hereafter be used. We invoke the scattering theory in order to eliminate the operator $U(0, t_0 - t)$ and along with it $V(1, 2; t)$ in favor of more physically pertinent quantities.

In the formal scattering theory incoming and outgoing (scattered) states are related to each other in the following manner:

$$164) \quad \Psi^{\text{out}}(t) = S \Psi^{\text{in}}(t) \quad , \text{ where } S \text{ is the scattering}$$

operator, or scattering "matrix." In the time-dependent approach, it is convenient, especially in our case, to treat the times t and t' as, respectively, very long after the collision and very long before the collision; and in this manner $t \rightarrow +\infty$ and $t' \rightarrow -\infty$, so that one is left with,

$$165) \quad \Psi^{\text{out}}(+\infty) = S \Psi^{\text{in}}(-\infty) \quad .$$

Physical meaning of S is derived by considering the following

example. Suppose the incoming state is a specific state ψ_i^{IN} which is transformed into a superposition of the members belonging to the specifying maximal set; that is

$$166) \quad \psi_i^{OUT} = \sum_j c_j \psi_j$$

The transition "amplitude" from state i to some state g of the maximal set is given by

$$167) \quad c_g = (\psi_g, \psi_i^{OUT}) = (\psi_g, S \psi_i^{IN}) = \langle g | S | i \rangle = S_{gi}$$

This, however, is not related, by $|S_{gi}|^2$, to the transition probability between state g and i . Since two eigenvectors of $H^{(A)}$ belonging to different energy eigenvalues are orthogonal, any scattering matrix is always diagonal with respect to the energy.¹¹ For that reason

$$168) \quad S_{gi} = \delta_{gi} + \delta(E_i - E_g) T_{gi}'$$

where T_{gi}' is the transition matrix between state g and i , and where there is no singularity in T_{gi}' when $E_i = E_g$. $|T_{gi}'|^2$ is related to the transition probability between states g and i . $\delta(E_i - E_g)$ serves as an energy conservation factor, since we are dealing with infinitely far removed initial and final states.

Since we have been working in the interaction representation, we must use that representation for a solution of the scattering matrix.

In this representation recall that

$$169) \quad \frac{\partial p_v^2(t)}{\partial t} = i/\hbar [p_v^2(t), V(t, t)]$$

¹¹"The Scattering Matrix", Quantum Mechanics, Eugen Merzbacher, 1st edition (1 vol. New York, John Wiley and Sons, Inc.), 1961, p. 495.

A solution, as noted before, was given by

$$170) \quad \rho_V^{(1)}(t) = J(t, t_0) \rho_V^{(1)}(t_0) J^*(t, t_0)$$

where

$$171) \quad J(t, t_0) = I - i/\hbar \int_{t_0}^t V(t') J(t', t_0) dt'$$

In view of our previous discussion, it follows that

$$172) \quad S = \lim_{\substack{t \rightarrow \infty \\ t_0 \rightarrow -\infty}} J(t, t_0) = J(+\infty, -\infty) .$$

The difficulties encountered in going through the integration of $t \rightarrow +\infty$,

$t_0 \rightarrow -\infty$ can be eliminated by use of the Møller wave operators. These operators, $\Omega^{(+)}$ and $\Omega^{(-)}$, are defined such that

$$173) \text{ a} \quad J(0, -\infty) = \Omega^{(+)}$$

$$\text{b} \quad J(0, +\infty) = \Omega^{(-)}$$

Noting that since J is unitary

$$174) \quad \begin{aligned} J(+\infty, -\infty) &= J^*(0, +\infty) J(0, -\infty) = \Omega^{*(-)} \Omega^{(+)} \\ &= J(+\infty, 0) J(0, -\infty), \end{aligned}$$

it follows that

$$175) \quad S = \Omega^{*(-)} \Omega^{(+)} .$$

It should be pointed out that, by such an arrangement, we have, by use of the Møller operators, eliminated time from consideration. That is

$$J(+\infty, t) J(t, -\infty) \equiv J(+\infty, 0) J(0, -\infty) .$$

What is now needed is to show that with the required limiting operation $J(0, -\infty)$ does exist and with it $\Omega^{(+)}$. To do so one must use integrals of the following form, which are defined to be;

$$176) \quad \lim_{t \rightarrow \pm\infty} f(t) = \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} f(t') dt'$$

and

$$177) \quad \lim_{t \rightarrow +\infty} f(t) = \lim_{\eta \rightarrow +0} \eta \int_0^{\infty} e^{-\eta t'} f(t') dt'$$

Integrating both expressions by parts and then taking the indicated limits one obtains,

$$178) \text{ a) } \quad \lim_{t \rightarrow -\infty} f(t) = \lim_{\eta \rightarrow +0} [f(t') e^{\eta t'}]_{-\infty}^0 - \lim_{\eta \rightarrow +0} \int_{-\infty}^0 e^{\eta t'} \frac{df}{dt'} dt'$$

$$\text{b) } \quad = \lim_{\eta \rightarrow +0} \left\{ f(0) - \int_{-\infty}^0 e^{\eta t'} \frac{df}{dt'} dt' \right\}$$

$$\text{c) } \quad = f(0) - \int_{-\infty}^0 \frac{df}{dt'} dt'$$

$$\text{d) } \quad = f(0) - f(0) + f(-\infty)$$

$$\text{e) } \quad \lim_{t \rightarrow -\infty} f(t) = f(-\infty)$$

By a similar procedure we also find

$$179) \quad \lim_{t \rightarrow +\infty} f(t) = f(+\infty)$$

Applying this procedure to the case of $J(t, t_0)$ when $t_0 \rightarrow -\infty$ we have,

$$180) \quad J(t, -\infty) = \lim_{\eta \rightarrow +0} \int_{-\infty}^0 e^{\eta t'} \left[I - (i/\hbar) \int_{t'}^t v(t'') J(t'', t') dt'' \right] dt'$$

Integrating, we obtain

$$181) \quad J(t, -\infty) = \lim_{\eta \rightarrow +0} [e^{\eta t}]_{-\infty}^0 I - (i/\hbar) \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 \int_{t'}^t e^{\eta t''} v(t'') J(t'', t') dt'' dt'$$

Because of the exponential convergence factor we may interchange the order of integration¹² and obtain

$$182) \quad J(t, -\infty) = I - (i/\hbar) \int_{-\infty}^t dt'' \left[v(t'') \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} J(t'', t') dt' \right] - (i/\hbar) \int_{t'}^{\infty} dt'' \left[v(t'') \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} J(t'', t') dt' \right].$$

¹²Advanced Quantum Mechanics, p. 317

Since $\int_{t_0}^0 e^{\eta t'} U(t, t') dt'$ is a proper integral,

then taking

$$\lim_{\eta \rightarrow +0} \eta \int_{t_0}^0 e^{\eta t'} U(t, t') dt' \rightarrow 0$$

so that

$$183) \quad J(t, -\infty) = I - (i/\hbar) \int_{-\infty}^t dt'' [v(t'') \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} J(t', t') dt']$$

Noting that in this expression

$$\lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} J(t'', t') dt'$$

is similar to

$$\lim_{t \rightarrow -\infty} f(t) = \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} f(t') dt'$$

then by comparison of the two previous expressions we find that

$$184) \quad \lim_{t' \rightarrow -\infty} J(t'', t') = \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t'} J(t'', t') dt';$$

so that substituting into equation 183, one has,

$$185) \quad J(t, -\infty) = I - (i/\hbar) \int_{-\infty}^t dt'' [v(t'') J(t'', -\infty)]$$

This result simply states that provided $J(t'', -\infty)$ exists, then J operators with finite arguments have the same form and properties of those with one infinite argument.

So in summary we now write the general expression for the Møller operator with our time dependent functions as

$$186) \quad \Omega^{(+)} = I - (i/\hbar) \int_{-\infty}^0 [v(t'') J(t'', -\infty)] dt''$$

and similarly

$$187) \quad \Omega^{(-)} = I + (i/\hbar) \int_0^{\infty} [v(t'') J(t'', +\infty)] dt''$$

From equations 143 and 144, coupled with the fact that $\Omega^{(+)} = J(0, -\infty)$,

we have

$$188) \quad \Omega^{(+)} = J(0, -\infty) = \lim_{\substack{t \rightarrow 0 \\ t_0 \rightarrow -\infty}} U(0, t_0 - t) = U(0, -\infty)$$

Now the Boltzmann equation, thanks to the limit insensitivity property of $M(t_0, t)$, can be written as;

$$189) \quad \frac{\partial \rho^{(i)}(1, t)}{\partial t} = i/\hbar \left\{ [\rho^{(i)}(1, t) H^{(i)}] + T_2 \left[\rho^{(i)}(1, t) \rho^{(i)}(2, t) \rho^{(i)}(2, t) \rho^{(i)}(1, t) V(1, 2, t) \right] \right\}$$

Up to this point our work has been very general and because of that we have kept time dependence in the general Hamiltonian. In the case of the above Boltzmann equation it is carried in the single particle density matrices, as expected, and in the collision potential term $V(1, 2, t)$. It is not explicitly found in $\rho^{(i)}$ which is time independent, (i.e. $t \rightarrow \infty$ by choice, which is of no real consequence since we are dealing with scattering theory concepts.) If we could eliminate explicit time dependence, the Boltzmann equation could then be written in a more simplified form in the sense that the collisional terms would not be present. The elimination could be accomplished by separation of $V(1, 2)$ or by some Fourier decomposition. In that case the time effects would appear as phase factors in the wave operators. For continuation of this work we will simply assume that it has been eliminated from consideration. With this assumption we now proceed to evaluate the Møller wave operator for the time independent case.

Recall from equations 143, 147 and 148 that

$$190) \quad J(t, t_0) = e^{i/\hbar K t} e^{i/\hbar H^{(i)}(t_0 - t)} e^{-i/\hbar K(t_0 - t)} e^{-i/\hbar K t}$$

and from 171

$$191) \quad J(t, t_0) = I - i/\hbar \int_{t_0}^t V(t') e^{i/\hbar K t'} e^{i/\hbar H^{(i)}(t_0 - t')} e^{-i/\hbar K(t_0 - t')} e^{-i/\hbar K t'} dt'$$

To find $\rho^{(i)}$, one first needs $J(t, \infty)$ as seen from equation 186. To evaluate $J(t, \infty)$, we follow the same procedure as that used in equations 176 through 179, resulting in

$$192) \quad \lim_{t_0 \rightarrow -\infty} J(t, t_0) = \lim_{\eta \rightarrow +0} [J(t, t') e^{\eta t'}]_{-\infty}^0 - \lim_{\eta \rightarrow +0} \int_{-\infty}^0 e^{\eta t'} \frac{\partial J}{\partial t'} dt'$$

$$193) \quad \frac{\partial J}{\partial t'}(t, t') = (i/\hbar H^{(2)} - i/\hbar K) J(t, t') = i/\hbar V J(t, t')$$

where $H^{(2)} - K = V$, as must be the case from equation 191. Equation

192 then becomes

$$194) \text{ a) } \quad \lim_{t_0 \rightarrow -\infty} J(t, t_0) = \lim_{\eta \rightarrow +0} \left\{ J(t, 0) - \int_{-\infty}^0 e^{\eta t'} i/\hbar V J(t, t') dt' \right\}$$

$$\text{ b) } \quad J(t, -\infty) = \lim_{\eta \rightarrow +0} \left\{ J(t, 0) - \int_{-\infty}^0 e^{\eta t'} i/\hbar V e^{i/\hbar K t} e^{i/\hbar H^{(2)} t} e^{-i/\hbar K(t-t')} e^{-i/\hbar K t'} dt' \right\}$$

since $\Omega^{(+)} = J(0, -\infty)$ from 194 b we have

$$195) \text{ a) } \quad J(0, -\infty) = \lim_{\eta \rightarrow +0} \left\{ J(0, 0) - i/\hbar \int_{-\infty}^0 e^{\eta t'} V e^{i/\hbar H^{(2)} t'} e^{-i/\hbar K t'} dt' \right\}.$$

Since, from equation 190, it is obvious that $J(0, 0) = I$ equation

195) a becomes

$$195) \text{ b) } \quad \Omega^{(+)} = \lim_{\eta \rightarrow +0} \left\{ I - i/\hbar \int_{-\infty}^0 e^{\eta t'} e^{i/\hbar H^{(2)} t'} e^{-i/\hbar K t'} V dt' \right\}$$

Since $H^{(2)}$ and K do not necessarily commute, even in the time independent case, we must resort to two other relationships derived from the formal theory of scattering,^{13, 14}

$$196) \quad \Psi_i^+ = \Omega^+ \phi_i$$

and

$$197) \quad V(1, 2) \Omega^+ = T(1, 2)$$

Equation 196 simply means that for the time independent case the effect on the operator is to transform an eigenvector of K (no collisional effects; i.e. before collision) to a state vector Ψ_i^+ during the collision.

¹³Advanced Quantum Mechanics, p. 317

¹⁴Advanced Quantum Mechanics, p. 320

Equation 197 relates the transition matrix for transitions between states of particle 1 and 2. The commutation problem of H^2 and K is eliminated by use of

$$198) \quad K\phi_i = E_i\phi_i$$

By use of 196 and 198 we now have

$$199) a \quad \Psi_i^+ = \lim_{\eta \rightarrow +0} \left\{ I - i/k \int_{-\infty}^0 e^{\eta t'} e^{i/k H t'} e^{-i/k E_i t'} V dt' \right\} \phi_i$$

Adding exponents, we obtain

$$b \quad \Psi_i^+ = \lim_{\eta \rightarrow +0} \left\{ I - i/k \int_{-\infty}^0 e^{(\eta + i/k H - i/k E_i)t'} V(1,2) dt' \right\} \phi_i$$

$$c \quad \Psi_i^+ = \lim_{\eta \rightarrow +0} \left\{ I - i/k \frac{V(1,2)}{[\eta + i/k H - i/k E_i]} \right\} \phi_i$$

$$d \quad \Psi_i^+ = \lim_{\eta \rightarrow +0} \left\{ I - \frac{V(1,2)}{[-i/k \eta + H - E_i]} \right\} \phi_i$$

$$e \quad \Psi_i^+ = \phi_i + \lim_{\eta \rightarrow +0} [i/k \eta - H^{(2)} + E_i]^{-1} V(1,2) \phi_i$$

We can define still another operator by

$$200) \quad \Psi_i^+ = \phi_i + G_i^{(+)}(1,2) V(1,2) \Psi_i^+$$

where

$$G_i^{(+)}(1,2) \equiv \lim_{\eta \rightarrow +0} [i/k \eta - H^{(2)} + E_i]^{-1}$$

By use of equations 196 and 200, 200 maybe written as

$$201) \quad \Omega_i^{(+)} \phi_i = \phi_i + G_i^{(+)}(1,2) V(1,2) \Omega_i^{(+)} \phi_i$$

or

$$202) \quad \Omega_i^{(+)} = I + G_i^{(+)}(1,2) V(1,2) \Omega_i^{(+)}$$

Equation 202, with the results of 197, can now be written as

$$203) \quad \Omega_i^{(+)} = I + G_i^{(+)}(1,2) T(1,2)$$

By use of equation 203 the wave operator may be eliminated from the Boltzmann equation:

$$204) \quad \frac{\partial \rho^{(1)}(1;t)}{\partial t} = i/k \left\{ [\rho^{(1)}(1;t), H^{(1)}] + \text{Tr} \left[\rho^{(1)}(1) \rho^{(1)}(2) \rho^{(1)}(2) V(1,2) - V(1,2) \rho^{(1)}(1) \rho^{(1)}(2) \rho^{(1)}(2) \right] \right\}$$

or

$$205) \quad \frac{\partial \rho^{(1)}(1;t)}{\partial t} = i/k \left\{ [\rho^{(1)}(1;t), H^{(1)}] + \text{Tr} \left[(I + G^{(1)}(1,2) T(1,2)) \rho^{(1)}(1) \rho^{(1)}(2) T^{*}(1,2) - T(1,2) \rho^{(1)}(1) \rho^{(1)}(2) (I + G^{(1)}(1,2) T^{*}(1,2)) \right] \right\}$$

Then 205 becomes:

$$206) \quad \frac{\partial \rho^{(1)}(1)}{\partial t} = i/k [E^{(1)}, H^{(1)}] + i/k [\rho^{(1)}(1) \rho^{(1)}(2) T^{*}(1,2) - T(1,2) \rho^{(1)}(1) \rho^{(1)}(2)] + i/k [G^{(1)}(1,2) T(1,2) \rho^{(1)}(1) \rho^{(1)}(2) T^{*}(1,2) - T(1,2) \rho^{(1)}(1) \rho^{(1)}(2) T^{*}(1,2) G^{(1)}(1,2)].$$

We have already shown how to evaluate $G^{(1)}(1,2)$ for this case.

What is now needed is a formal evaluation of the $T_{(1,2)}^{(1)}$ matrix.

We recall that

$$207) \quad J(t, -\infty)^* J(t, +\infty) = S.$$

With the help of equation 171 we now have

$$208) \quad S = I - (i/k) \int_{-\infty}^{+\infty} V(t') J(t', -\infty) dt'.$$

In our theory developed so far the scattering matrix operator S

produced from the initial state vector $\psi_a(-\infty)$, the final state vector $\psi_a(+\infty)$,

where $\psi_a(+\infty) = S \psi_a(-\infty)$. It should be noted that the field effects must be

included already at $t = -\infty$, and thus the only additional effects to be

added by the S operator are the collisional effects. The probability

that a state represented by $\psi_b(+\infty)$ is included, but not noted hereafter)

will eventually become state ψ_b is given by

$$209) \quad W_{ba} = |\langle \psi_b, S \psi_a \rangle|^2 = |S_{ba}|^2$$

We define our transition matrix operator in the following manner,

$$210) \quad T = S - I$$

From equation 208, 209 and 210 we have

$$211) \quad S_{ba} = (\psi_b, S \psi_a),$$

$$212) \quad S_{ba} = (\psi_b, \psi_a) - i/\hbar \int_{-\infty}^{\infty} (\psi_b, V(t') J(t', -\infty) \psi_a) dt'$$

and

$$213) \quad T_{ba} = S_{ba} - (\psi_b, \psi_a)$$

$$214) \quad T_{ba} = -i/\hbar \int_{-\infty}^{\infty} (\psi_b, V(t') J(t', -\infty) \psi_a) dt'.$$

For the case of equation 206, b and a become references to molecules 1 and 2 respectively.

The intent of the preceding development was the establishment of a formal device to evaluate the matrix elements for the transition matrix. No evaluation will be made for this problem or any special case. The reason for this is that, in our case, the problem is greatly complicated by the presence of the electric and magnetic fields; and for this reason the energy levels are split. Calculation of transition probability between various times is possible only with exact expressions for the state vector, which necessarily involve time in the most general case.

A summary for the scattering theory section is now in order. We began with our basic equation of motion for the one particle density matrix. This was obtained by use of a unitary transformation, which produced a Volterra integral equation which was solved by employment

of Dyson time ordering operators. It then became necessary to develop a complete Hamiltonian to describe the polyatomic molecule in the presence of fields; this was done along with the eigenfunctions and density matrix. We found that collisional effects could be eliminated by completing the solution of the equation of motion for the two particle matrix in an interaction representation. Such a procedure produced a set of unitary operators transforming the system from one representation to another, the entire process being complicated by the presence of explicit time dependence of the Hamiltonian. However, out of this operator chaos rose an operator (ultimately connected to Møller wave operators) which was insensitive to time dependence and allowed transformations from times before collisions to times during collisions. This had the considerable advantage of providing justification for use of the Boltzmann property during the collision and made the final form of the equation of motion valid for all times.

Formal scattering theory was then used to relate the operators to a transition matrix formalism. However this was done for the special case when explicit time dependence is not included, and the result is equation 206. The most general equation of motion is equation 189, where no special assumptions are made concerning time dependence. Time dependence in 189 is abandoned so that we may more easily develop a quantum Boltzmann equation without special treatment of time dependent scattering.

CHAPTER 6

DISTRIBUTION FUNCTIONS

Equation 206 resembles the Boltzmann equation. However, in the classical problem the equation is given in terms of distribution functions and for the quantum mechanical problem in terms of the Wigner distribution function. From our work in developing the total Hamiltonian, (and from equation 121, the total eigenfunction for a molecule,) it is apparent that the distribution function must have many degrees of freedom. A Wigner distribution function can be generated in the following manner

215)
$$f^{(N)}(\{\bar{R}_0, \bar{P}_0, \{\bar{r}_{IJ}, \bar{p}_{IJ}\}_A, \{n_i, \eta_i\}_A, t) = \mathcal{T} \hbar^{-3nN} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} e^{i\hbar \sum_{\nu=1}^{N_m} (\bar{p}_0 \cdot \bar{y}_\nu)} \times$$

$$e^{i/\hbar \sum_{\nu=1}^{N_m} [\sum_A \bar{p}_{IJ} \bar{y}_{IJ}]} e^{(i/\hbar) \sum_{\nu=1}^N [\sum_A \{ \sum_{i=1}^{N_e} \bar{p}_i \cdot \eta_i \}_A]} \prod_{\nu=1}^N \rho_{\nu}^{(N)}(\bar{R}_0 - \bar{y}_\nu; \bar{R}_0 + \bar{y}_\nu; t)$$

$$\times \rho^{(N)}(\{\bar{r}_{IJ} - \bar{y}_{IJ}, \bar{r}_{IJ} + \bar{y}_{IJ}\}_A, \{n_i - \eta_i, n_i + \eta_i\}_A) \prod_{\nu=1}^N d\bar{y}_\nu (d\eta_i)_{\nu} \{ \{ \sigma_i \}_A \}^{\eta_i} / 2$$
 where \bar{y}_ν, η_i are vector integrating factors, integrated from $-\infty$ to ∞ , and

$Q = 1 + A(A-1)$, where $A = \frac{1}{2}A(A-1)$ is the number of pairs of atoms which may interact.

In equation 215 the notation has been kept consistent with the notation developed earlier. It also should be noted that N_m refers to molecule number, A , the number of atoms and N_e , the number of electrons per atom. We have also made use of the separation of the density matrix into independent parts developed earlier.

¹⁵"On the Quantum Correction For Thermodynamic Equilibrium," Physical Review, E. Wigner, Vol. 40, June 1, 1932, p. 250.

¹⁶J. S. Dahler, Journal of Chemical Physics, Vol. 30, No. 6, June, 1959, p. 1463.

There is an unfortunate difficulty inherent in this equation, which consists of the inability to associate each integrating factor with a physical quantity. This is especially true in the case of the internal momenta and coordinates, which are discrete observables in general. Evaluation of 215 is a thesis problem in itself; and to demonstrate what we ask the distribution function to do for us can be illustrated by considering point monatomic molecules, but including the necessary nondegenerate internal states. In that case our general density matrix will be written as

$$216) \quad \rho^{(1)}(1) = \rho^{(1)} \left(\begin{array}{c|c} KLM & K'L'M' \\ \hline n'lms & n'l'm's' \\ \bar{R}_1 & \bar{R}_1' \end{array} \right),$$

where KLM denotes molecular rotation and vibration states, $n'lms$ denotes electron states with their customary meanings, and \bar{R}_1 denotes the position of the point molecule number 1. The Wigner distribution for a single molecule is then taken to be, from 215,

$$217) \quad f_{KLM, n'lms}(\bar{R}, \bar{P}, t) = \frac{1}{(\pi \hbar)^3} \int_{-\infty}^{\infty} e^{i/\hbar \bar{P} \cdot \bar{Y}} \rho \left(\begin{array}{c|c} KLM & K'L'M' \\ \hline n'lms & n'l'm's' \\ \bar{R} + \bar{Y} & \bar{R} - \bar{Y} \end{array} \right) d\bar{Y}.$$

Having written equation 217, all that remains to make the distribution function usable is to evaluate the integration variable \bar{Y} . This is done by assuming, as Snider¹⁷ has done, a "periodic" lattice type structure of the gas. Since the gas is dilute it will be assumed that the distribution function varies very slowly inside the cell

¹⁷R. F. Snider, Journal of Chemical Physics, Vol. 32, No. 4, April, 1960, pp. 1055-1057.

which will be defined to be a volume of a^3 , where a is so chosen that f remains nearly constant. These cells will be located in space by the position vector $\vec{r}_a = \vec{n}a$. Where the vector \vec{n} is given by three coordinate values n_x, n_y, n_z , and where each n_{xy} value is an integer. Any point in the gas is further located by $\vec{R} = \vec{r}_a + \vec{r}_i$ where \vec{r}_i locates molecules in the cell relative to the center of the cell. Because we are dealing with averages, f now depends only on \vec{r}_a . Equation 217 may now be written as

$$218) \quad f_{klm, n'lm'}(\vec{R}, \vec{p}, t) = (\pi\hbar)^{-3} \int_{-\infty}^{\infty} e^{2i/\hbar \vec{p} \cdot \vec{r}_a} \rho^{(1)} \left(\begin{array}{c|c} klm & k'l'm' \\ n'lm's' & nlm's \end{array} \middle| \begin{array}{c} \vec{R} + \vec{r}_a \\ \vec{R} - \vec{r}_a \end{array} \right) d\vec{r}_a.$$

Since we are dealing with neutral molecules the presence of the fields should not alter basic conservation of momentum; and for this reason when dealing with collision problems, it is convenient to use the momentum representation. This may be arranged by taking the inverse Fourier transformation of equation 218 and using a delta function in momentum space. Doing this, we obtain

$$219) \quad \rho \left(\begin{array}{c|c} klm & k'l'm' \\ \vec{p} & \vec{p}' \end{array} \right) = \int e^{i/\hbar (\vec{p} - \vec{p}') \cdot \vec{R}} f_{klm, n'lm'}[\vec{R}, (\vec{p} + \vec{p}')/2, t] d\vec{R}$$

where

$$\delta(\vec{p} - \vec{p}') = \int e^{i/\hbar (\vec{p} - \vec{p}') \cdot \vec{R}} d\vec{R}.$$

Since $\vec{R} = \vec{r}_a + \vec{r}_i$ it follows that

$$220) \quad \rho \left(\begin{array}{c|c} klm & k'l'm' \\ \vec{p} & \vec{p}' \end{array} \right) = \int_{\vec{R}} e^{i/\hbar (\vec{p} - \vec{p}') \cdot \vec{r}_i} d\vec{r}_i \sum_{\vec{r}_a} e^{i/\hbar (\vec{p} - \vec{p}') \cdot \vec{r}_a} f_{klm, n'lm'}[\vec{r}_a, (\vec{p} + \vec{p}')/2, t]$$

The summation over \vec{r}_a is required since \vec{r}_a is periodic.

To evaluate 220, we treat momentum space in exactly the same manner as position space by use of the following expression

$\bar{p} = \bar{p}_a + [\bar{p}]$ where $\bar{p}_a = \bar{k}(h/a)$ and $[\bar{p}] = \bar{g} \cdot \bar{v}_L \cdot \bar{k}$ and \bar{g} are vectors whose components are positive and negative integers similar to \bar{n} except that \bar{k} ranges from $-\infty$ to ∞ while \bar{g} is restricted as follows: $|g_i|_{i=x,y,z} < L/2a$. The above assumptions allow us to note the following relations

$$\bar{r}_a \cdot \bar{p}_a = 2\pi \bar{n} \cdot \bar{k} h = 2\pi h (\text{Integer})$$

so that

$$e^{i(\bar{r}_a \cdot \bar{p}_a)/h} = e^{i2\pi(\text{Integer})} = I.$$

With the above simplification we have

$$221) \quad \rho \left(\begin{matrix} KLM \\ \bar{p} \end{matrix} \middle| \begin{matrix} K'L'M' \\ \bar{p}' \end{matrix} \right) = \int e^{i/h(\bar{p}_a - \bar{p}'_a) \cdot \bar{r}_i} \frac{d\bar{r}_i}{\bar{r}_a} \sum_{\bar{r}_a} e^{i/h([\bar{p}] - [\bar{p}']) \cdot \bar{r}_a} f(\bar{r}_a, (\bar{p} + \bar{p}')/2t).$$

Noting in equation 221 that

$$\frac{1}{a^3} \int e^{i/h(\bar{p}_a - \bar{p}'_a) \cdot \bar{r}_i} d\bar{r}_i = \delta_{\bar{p}_a \bar{p}'_a} \approx \delta_{\bar{p} \bar{p}'}$$

since $\bar{p} \gg [\bar{p}]$, $\bar{p} \approx \bar{p}_a$, we can write 221 as

$$222) \quad \rho \left(\begin{matrix} KLM \\ \bar{p} \end{matrix} \middle| \begin{matrix} K'L'M' \\ \bar{p}' \end{matrix} \right) = a^3 \int \delta_{\bar{p} \bar{p}'} \sum_{\bar{r}_a} e^{i/h([\bar{p}] - [\bar{p}']) \cdot \bar{r}_a} f(\bar{r}_a; \bar{p} + \frac{1}{2}([\bar{p}] + [\bar{p}']), t).$$

Equation 222 indicates that ρ is nearly diagonal in \bar{p} since the right hand side is approximately $\delta_{\bar{p} \bar{p}'}$. It should be noted that in order to use equation 222 in our Boltzmann equation we need yet another Fourier type transformation (relating the density matrix of 222 to be distribution function) of the form

$$223) \quad f(\bar{r}, \bar{p}, t) = (h)^{-3} \int e^{i\bar{q} \cdot \bar{r}} \rho \left(\begin{matrix} KLM \\ \bar{p} + \frac{1}{2}\bar{q} \end{matrix} \middle| \begin{matrix} K'L'M' \\ \bar{p} - \frac{1}{2}\bar{q} \end{matrix} \right) d\bar{q},$$

where \bar{q} has the units of momentum and, in spite of the cell model of momentum space, we assume momentum to be a continuous variable. This assumption requires only that $L \rightarrow \infty$

Using the results of 222 and equation 223 we can obtain the necessary modification for use in the Boltzmann equation.

At the beginning of the section we saw that in order to make our Boltzmann equation 206 usable, or rather make it more like the Boltzmann equation, we need distribution functions of the form 215. These functions are very complex and contain the problem of how to treat internal states. We "got around" this problem by assuming structureless single molecules for the purpose of illustration, and assumed that the density matrix carried the information with it. In what follows we will complete the illustrative example of our, perhaps over simplified, case and then discuss a possible more satisfactory method of treating the problem. From equation 206, and by use of the results of 214, we have

$$\begin{aligned}
 224) \quad \frac{d\rho}{dt}(\bar{r}, \bar{p}, t) = & -i/\hbar \left[\rho^{(0)}(\bar{r}, \bar{p}, t), H^{(0)} \right] + i/\hbar \left[\rho^{(0)}(\bar{r}, \bar{p}, t), \rho^{(0)}(\bar{r}_2, \bar{p}_2, t) \left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| T \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle^* \right. \\
 & - \left. \left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| T \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle \rho^{(0)}(\bar{r}, \bar{p}, t) \rho^{(0)}(\bar{r}_2, \bar{p}_2, t) \right] + \\
 & i/\hbar \left[\left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| G^+ T \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle \rho^{(0)}(\bar{r}_1, \bar{p}_1, t) \left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| T \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle^* - \right. \\
 & \left. \left. \left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| T \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle \rho^{(0)}(\bar{r}_1, \bar{p}_1, t) \left\langle \frac{\Delta_1 \Delta_2}{\bar{p}_1 \bar{p}_2} \middle| T G^+ \middle| \frac{\Delta'_1 \Delta'_2}{\bar{p}'_1 \bar{p}'_2} \right\rangle \right].
 \end{aligned}$$

It should be noted here that application of 214 involves the usage of a two particle state vector, or the system (2 particles) before the interaction and afterwards. The $T, G^+ T$ refer to operators as previously defined. The reader should also recall that this expression is based

upon the same assumptions that allowed one to develop G^\dagger , that of explicit time independence of the Hamiltonian. Δ_1, Δ_2 refer to sets of quantum numbers before and Δ'_1, Δ'_2 refer to after the interaction quantum numbers. The conditions apply in the case of p, p_1 and p', p'_1 using the results of 222 with 223 (where (q, p_1) is treated as p) in 224 and the fact that $\bar{p} \cong \bar{p}_0$, we obtain

$$\begin{aligned}
 225) \quad & \frac{\partial f_1}{\partial t} + \frac{\bar{p}_1}{m_1} \frac{\partial f_1}{\partial \bar{R}_1} + \frac{\bar{F}_1}{m_1} \cdot \frac{\partial f_1}{\partial \bar{R}_1} = i/\hbar \frac{1}{h^3} \int \dots \int e^{i\bar{q} \cdot \bar{R}_1 / \hbar} \left[e^{-i/\hbar (\bar{R}'_1 - \bar{p}_1 + \frac{1}{2}\bar{q}) \cdot \bar{R}'_1} \right. \\
 & e^{-i/\hbar (\bar{p}'_2 - \bar{p}_2) \cdot \bar{R}_2} f_{\Delta_1, \Delta'_1} \left\{ \bar{R}'_1, \frac{1}{2}(\bar{p}'_1 + \bar{p}_1 - \frac{1}{2}\bar{q}) \right\} f_{\Delta_2, \Delta'_2} \left\{ \bar{R}_1, \frac{1}{2}(\bar{p}'_2 + \bar{p}_2) \right\} \right] \times \\
 & \left\langle \frac{\Delta_1, \Delta_2}{\bar{p}_1, \bar{p}_2} \middle| T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle - \left\langle \frac{\Delta_1, \Delta_2}{\bar{p}_1, \bar{p}_2} \middle| T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle e^{-i/\hbar (\bar{p}_1 - \bar{p}'_1 + \frac{1}{2}\bar{q}) \cdot \bar{R}'_1} \\
 & e^{-i/\hbar (\bar{p}_2 - \bar{p}'_2) \cdot \bar{R}_2} f_{\Delta_1, \Delta'_1} \left\{ \bar{R}_1, \frac{1}{2}(\bar{p}_1 + \bar{p}'_1 + \frac{1}{2}\bar{q}) \right\} \times f_{\Delta_2, \Delta'_2} \left\{ \bar{R}_1, \frac{1}{2}(\bar{p}_2 + \bar{p}'_2) \right\} \\
 & \times d\bar{q} d\bar{p}_1 d\bar{p}_2 d\bar{p}'_1 d\bar{p}'_2 d\bar{R}'_1 d\bar{R}_2 + i/\hbar \frac{1}{h^3} \int \dots \int e^{i\bar{q} \cdot \bar{R}_1} \left[\left\langle \frac{\Delta_1, \Delta_2}{\bar{p}_1, \bar{p}_2} \middle| G^\dagger T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle \right] \times \\
 & e^{-i/\hbar (\bar{p}'_1 + \bar{p}_1(-1) + \frac{1}{2}\bar{q}) \cdot \bar{R}'_1} e^{-i/\hbar (\bar{p}'_2 - \bar{p}_2) \cdot \bar{R}_2} f_{\Delta_1, \Delta'_1} \left\{ \bar{R}'_1, \frac{1}{2}(\bar{p}'_1 + \bar{p}_1 - \frac{1}{2}\bar{q}) \right\} \times \\
 & f_{\Delta_2, \Delta'_2} \left\{ \bar{R}'_1, \frac{1}{2}(\bar{p}'_2 + \bar{p}_2) \right\} \left\langle \frac{\Delta_1, \Delta_2}{\bar{p}_1, \bar{p}_2} \middle| T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle - \left\langle \frac{\Delta_1, \Delta_2}{\bar{p}_1, \bar{p}_2} \middle| T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle e^{-i/\hbar (\bar{p}_1 - \bar{p}'_1 + \frac{1}{2}\bar{q}) \cdot \bar{R}'_1} \\
 & e^{-i/\hbar (\bar{p}_2 - \bar{p}'_2) \cdot \bar{R}_2} f_{\Delta_1, \Delta'_1} \left\{ \bar{R}_1, \frac{1}{2}(\bar{p}_1 + \bar{p}'_1 + \frac{1}{2}\bar{q}) \right\} f_{\Delta_2, \Delta'_2} \left\{ \bar{R}_1, \frac{1}{2}(\bar{p}_2 + \bar{p}'_2) \right\} \left\langle \frac{\Delta_1, \Delta_2}{p, p_1} \middle| G^\dagger T \middle| \frac{\Delta'_1, \Delta'_2}{\bar{p}'_1, \bar{p}'_2} \right\rangle d\bar{q} d\bar{p}'_1 d\bar{p}'_2 d\bar{R}'_1 d\bar{R}_2.
 \end{aligned}$$

Equation 225 represents the quantum Boltzmann equation based on a Wigner distribution function. It is an equation for the change in the distribution function for particle 1. $\frac{\partial \bar{R}}{\partial t}$ and F/m_1 refer to changes in the distribution for molecule 1 due to momentum of 1 and net forces F_1 . Everything on the right hand side refers to the effects of collisions between our molecule 1 and molecule 2. The distribution functions are

derived from equation results of 222 and 223. Terms of the form

$$K f_{A_1 A_2}(\frac{1}{2}(\bar{p}_1 + \bar{p}_1 - \frac{1}{2}q) \bar{r}_1) f_{A_1 A_2}(\frac{1}{2}(\bar{p}_2' + \bar{p}_2), \bar{r}_1)$$

represent the distribution changes due to those molecules scattered

into the range $\bar{p}_1 + \bar{p}_1'$, while terms of the form

$$K f_{A_1 A_2}(\bar{r}_1, \frac{1}{2}(\bar{p}_1 + \bar{p}_1' + \frac{1}{2}q)) f_{A_1 A_2}(\bar{r}_1', \frac{1}{2}(\bar{p}_2 + \bar{p}_2'))$$

represent those scattered out of the range $\bar{p}_1 + \bar{p}_1'$.

SUMMARY

We have derived a quantum mechanical Boltzmann transport equation. This was done in as general a method as possible beginning with a density matrix describing the ensemble and using the equation of motion for that matrix. In order to maintain the Boltzmann property, and its obvious advantage of being able to describe the N particle density matrix as a set of single density matrix products, we developed Møller wave operator and unitary operators so that the effects of the collisional interactions were present while the Boltzmann property remained valid. This produced equation 189 which is the most general possible for this problem. The field effects are present in the Hamiltonian, and consequently in the Møller and unitary operators as well as the density matrix by way of the state function for the polyatomic molecule, equation 111.

In order to make equation 189 recognizable as the Boltzmann equation we made a number of simplifying assumptions, among them the elimination of explicit time dependence from the Hamiltonian. As a part of this procedure formal scattering theory was employed and we finally obtained equation 206. It was then necessary to use Wigner type distribution functions to relate the density matrix and statistical mechanical distribution functions. However, the Wigner functions which we employed dealt only with point molecules and the internal state information was carried in the density matrix itself.

In work on this thesis explicit time dependence of the Hamiltonian has been a problem, and we have seen that relating the density matrices

and distributions for polyatomic molecules in general, can not easily be handled by using Wigner distribution functions. Another approach to this problem might be the use of creation and annihilation operators to describe the density matrix, at least for the internal states. These operators would result in counting operators which might be used to actually count the number of molecules per state at a position in space and at a specific time.

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APPENDIX

To demonstrate that the operator $U(t, t_0)$ of equation 129 is unitary one should first note that by its nature

$$1) \quad e^{i/\hbar K(t-t_0)}$$

is a unitary operator. That operators of the form

$$2) \quad F(t, t_0) = P e^{-i/\hbar \int_{t_0}^+ X(t') dt'}$$

are also unitary is not so easily shown, but for generality it will be attempted.

Because of the definition of a unitary operator we have,

$$3) \quad F^*(t, t_0) F(t, t_0) \equiv 1$$

where * is used to denote the adjoint. Using equation 2 in 3 one obtains,

$$4) \quad e^{i/\hbar \int_{t_0}^+ X(t') dt'} P^* P e^{-i/\hbar \int_{t_0}^+ X(t') dt'} \equiv 1.$$

Therefore, if $P^* P \equiv 1$, then $F(t, t_0)$ is unitary.

Suppose we choose two unitary operators $A(t_1)$ and $B(t_2)$.

By definition of the chronological time operator

$$5) \quad P(A(t_1) B(t_2)) = \begin{cases} A(t_1) B(t_2) & t_1 > t_2 \\ B(t_2) A(t_1) & t_2 > t_1 \end{cases}.$$

Suppose we now form the product and assume $t_1 > t_2$. We then obtain

$$6) \quad \begin{aligned} P(B(t_2) A(t_1))^* P(B(t_2) A(t_1)) &= (A(t_1) B(t_2))^* (A(t_1) B(t_2)) \\ &= B^*(t_2) A^*(t_1) A(t_1) B(t_2) \\ &= B^*(t_2) B(t_2) \\ &= 1. \end{aligned}$$

Rewriting equation 6 we have by use of adjoint property,

$$7) \quad A^*(t_1) B^*(t_2) P^* P B(t_2) A(t_1) = I.$$

If the results of equations 6 and 7 are to be consistent, then

$P^* P = I$, which demonstrates the $F(t, t_0)$ is unitary.