In the kinetic theory of dense fluids the many-particle collision bracket integral is given in terms of a classical collision operator defined in the phase space. To find an algorithm to compute the collision bracket integrals, we revisit the eigenvalue problem of the Liouville operator and re-examine the method previously reported [Chem. Phys. 1977, 20, 93]. Then we apply the notion and concept of the eigenfunctions of the Liouville operator and knowledge acquired in the study of the eigenfunctions to cast collision bracket integrals into more convenient and suitable forms for numerical simulations. One of the alternative forms is given in the form of time correlation function. This form, on a further manipulation, assumes a form reminiscent of the Chapman-Enskog collision bracket integrals, but for dense gases and liquids as well as solids. In the dilute gas limit it would give rise precisely to the Chapman-Enskog collision bracket integrals for two-particle collision. The alternative forms obtained are more readily amenable to numerical simulation methods than the collision bracket integrals expressed in terms of a classical collision operator, which requires solution of classical Lippmann-Schwinger integral equations. This way, the aforementioned kinetic theory of dense fluids is made fully accessible by numerical computation/simulation methods, and the transport coefficients thereof are made computationally as accessible as those in the linear response theory.

Key Words: Liouville operator, Eigenfunctions, Classical scattering, Collision bracket integrals, Transport coefficients

Introduction

Classical collision operators\(^1,3\) defined in the phase space are classical mechanical analogs of quantum mechanical collision operators defined in terms of Liouville-von Neumann operators and the classical limits of the latter. They appear in the statistical mechanical formulas of transport coefficients in kinetic theory of matter and present an important problem to resolve in the final stage of implementing the dense fluid kinetic theory to make it connect with experiments. Although practical methods of computing the classical collision operators are essential to making the kinetic theory a useful molecular theory of matter, they have not been given much attention beyond the formal theory level in contrast to their quantum mechanical analogs in the literature,\(^4,6\) and computation of them and related expressions appearing in the kinetic theory of dense fluids still poses a theoretical and computational challenge in nonequilibrium statistical mechanics. In this paper, we would like to take up the subject for study and make an attempt to mitigate the situation.

Classical collision operators are generally defined in formal analogy\(^7,8\) to quantum mechanical collision operators in Hilbert space, but their definitions have been made without much attention paid to the space of functions in which the operators live. Clearly, study of classical collision operators would require a space of eigenfunctions for the underlying Liouville operator in the phase space. However, the eigenfunctions of the Liouville operator are little known except for free particles. Here we first consider the classical eigenvalue problems for Liouville operators, especially when the spectrum is continuous, and then apply the eigenfunctions to recast many-particle collision bracket integrals, which are given in terms of classical collision operators and appear in the kinetic theory of dense fluids. In Ref. (9), the present author made a study of eigenvalue problems for Liouville operators from the perspective of scattering theory of few particle systems. In the present paper, we revisit the problem and improve upon the method of calculating eigenfunctions before applying the notion and existence of eigenfunctions to examine a way to calculate the collision bracket integrals in the context of the kinetic theory of transport processes, particularly, in liquids. We will examine the eigenfunctions for classical scattering of particles in phase space and make use of the acquired results to cast the collision bracket integral given in terms of a classical collision operator into a form more readily amenable to numerical computation/simulation methods. Since the many-body problems involved in such a theory do not allow simple analytic forms for the collision cross sections and transition probabilities for physically realistic dynamical events and hence pose a barrier to overcome and thereby make it practicable in kinetic theory in general, it is imperative to devise alternative forms of transport coefficients...
expressed in terms of classical collision operators, so that efficient numerical algorithms can be found for them. Therefore, this line of study is quite relevant to implementing the classical kinetic theory of matter to understand transport properties of dense gases and liquids studied in the laboratory.

In Section II, we re-examine the eigenvalue problem for classical Liouville operator and obtain the eigenfunctions in terms of a generating function for canonical transformation in a more concise manner than in the previous work. The associated scattering theory in phase space is considered in Section III. The results, at least the basic concept, obtained in Section II will be used to cast the classical collision operator in a numerically convenient form in Section IV. The new form of the collision bracket integral will be shown to yield its low density limiting form in the same form as the Chapman-Enskog results for the transport coefficients for dilute gases. A form of collision bracket integrals involving a three-body collision operator is also presented to indicate the general idea of the method in the case of many-particle situations. Concluding remarks are given in Section V.

The Eigenvalue Problem for the Classical Liouville Operator

In the kinetic theory of matter, the formalism is usually formulated in terms of the Liouville operator, and associated classical collision operators appear in close analogy to quantum scattering theory. Formal theory of quantum scattering has been studied in depth from the mathematical standpoint and the mathematical properties of quantum scattering has been studied in depth from the mathematical nature of the function space for quantum scattering operators, such as the Hilbert space for the operators, are well understood at present. On the other hand, it cannot be said the same of the classical scattering theory based on the classical Liouville operator, and even the mathematical nature of the function space for the classical Liouville operator is not well clarified at present, almost all of mathematical operations involving the classical Liouville operators being performed by simple analogy to the quantum counterparts; see, for example, Refs. (2), (3), (7)-(11). Here in this section we will consider an aspect of the problem, limiting our study to construction of eigenfunctions, which may be given in terms of the Hamilton-Jacobi characteristic function. The eigenfunctions are \( L \) functions normalizable to unity and have a closure in phase space. If the Hamilton-Jacobi equation is separable, then the eigenfunctions can be given in terms of quadratures. Otherwise, a numerical solution method is the only way left to treat the problem adequately. Nevertheless, the eigenfunctions can be used to formulate formal classical scattering theory in analogy to quantum scattering theory, and the theory thus formulated can provide a mathematically transparent and practicable computational algorithm for the classical collision problems associated with transport coefficients of both gases and liquids.

The particles are assumed to interact by the pair potentials \( V_{jk}(r_{jk}) \), where \( r_{jk} \) is the relative coordinate vector between the two particles \( j \) and \( k \). Let \( p=(p_1, \cdots, p_m) \) and \( r=(r_1, \cdots, r_N) \) denote momenta and positions of particles with \( f \) standing for the number of degrees of freedom. The Hamiltonian in the relative coordinate system will be denoted by \( H(p, r) \):

\[
H(p, r) = \sum_{j<} \frac{p_j^2}{2m_j} + \sum_{j<k} V_{jk}(r_{jk})
\]

under the assumption that the interaction potential energies are pairwise additive. There is no problem to include many-particle potentials in the Hamiltonian. The Liouville operator is then defined by the Poisson brackets times \( -i \) where \( i = \sqrt{-1} \):

\[
\mathbf{L} = -i[H, \rho] = -i \sum_{k} \left( \frac{\partial H}{\partial p_k} \frac{\partial}{\partial r_k} - \frac{\partial H}{\partial r_k} \frac{\partial}{\partial p_k} \right).
\]

With \( -i \) multiplied, the Liouville operator becomes self-adjoint. The subscript \( k \) denotes Cartesian components of vectors \( p \) and \( r \). With this definition of Liouville operator the Liouville equation can be written as

\[
\frac{\partial \rho}{\partial t} = \mathbf{L} \rho(x,t),
\]

where \( x \) is the abbreviation for the phase \( x=(p, r) \) and \( \rho \) is the probability distribution function. Since it is possible to expand \( \rho \) into Fourier components as in the integral

\[
\rho(x,t) = \int x \, dx \exp(-iA x) \psi_{\lambda}(x),
\]

we arrive at an eigenvalue problem \(^1\) of \( \mathbf{L} \):

\[
\mathbf{L}(x) \, \psi_{\lambda}(x) = \lambda \psi_{\lambda}(x),
\]

where \( \lambda \) is an eigenvalue and \( \psi_{\lambda} \) the eigenfunction belonging to \( \lambda \). This eigenvalue problem is subject to appropriate boundary conditions. It is intimately related to the Hamilton-Jacobi theory in classical mechanics as will be shown below. Let us consider the eigenvalue problem, Eq. (5), in another form, which appears to be more insightful. The Liouville operator \( \mathbf{L} \) is Hermitian in the space of square-integrable functions \( \psi_{\lambda} \), which are generally complex. Therefore, if \( \psi_{\lambda}(x) \) is written in the form

\[
\psi_{\lambda}(x) = A(x) \exp[i\Gamma(x)],
\]

then the eigenvalue problem can be cast in the pair of equations

\[
[H, A]_{pr} = \lambda, \quad [H, \Gamma]_{pr} = 0.
\]

Eq. (8) indicates that the amplitude \( A(x) \) is a function of canonical invariants. Therefore the amplitude \( A(x) \) is a function of the basic invariants of \( H \); for example, a function of the Hamiltonian and the total momentum. However, the precise form for the function is not obvious at this point of development.

Since the Liouville operator is invariant to canonical transformation \((p, r) \rightarrow (P, Q)\) where \( P \) and \( Q \) are the new canonical momentum and coordinate preserving the forms of Hamilton's canonical equations of motion, the eigenvalue problem takes the form in the new canonical variable system
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\[ L(X) \psi_\alpha(X) = \lambda \psi_\alpha(X), \]  
where \( X = (P, Q) \) and

\[ L(X) = -i[H, \rho_0] = -i \sum \frac{\partial H}{\partial P_k} \frac{\partial}{\partial Q_k} - i \sum \frac{\partial H}{\partial Q_k} \frac{\partial}{\partial P_k} \]  

Here \( H \) is the new Hamiltonian \( H = H(P, Q) \). If the new Hamiltonian is independent of \( Q \), then we have

\[ L(X) = -i[H, \rho_0] = -i \sum \frac{\partial H}{\partial P_k} \frac{\partial}{\partial Q_k}. \]

We will return to this form for \( L \) presently. Other mathematical properties of \( L \) and aspects of the eigenvalue problem in hand are discussed in Appendix A. They are collected in Appendix A for completeness and also to make this article self-contained.

Let us assume \( S(P, r, t) \) to be the generating function \(^{13}\) of canonical transformation such that

\[ p_k = \frac{\partial S}{\partial Q_k}, \quad Q_k = \frac{\partial S}{\partial P_k}. \]

The generating function \( S \) obeys the Hamilton-Jacobi equation

\[ \frac{\partial S}{\partial t} + H\{ S, P \} = 0. \]

Under this canonical transformation the amplitude function is given by

\[ A(x) = \delta( \alpha - \frac{\partial S}{\partial r} ) = \delta(\alpha - (\alpha_1, \dots, \alpha_j)), \]

where \( \alpha_1, \cdots, \alpha_j \) are the values of \( P_1, \cdots, P_j \), respectively, with \( j \) denoting the degrees of freedom. It is sufficient to take this form because the Hamilton-Jacobi equation is subject to a constant energy for a conservative system. It is easily shown that the expression for \( A \) given above satisfies Eq. (8).

To find the phase function \( \Gamma \), we observe that Eq. (7), upon canonical transformation, can be written as

\[ [H, \Gamma] \rho_0 = \lambda. \]

Explicitly written out, Eq. (15) has the form

\[ \lambda = \sum \frac{\partial H}{\partial P_k} \frac{\partial \Gamma}{\partial Q_k}. \]

It is useful to define

\[ \omega_k = \frac{\partial H}{\partial P_k}, \]

which is independent of \( Q \) since \( H = H(P) \) is independent of \( Q \). Then, Eq. (16) is readily solved, and we find

\[ \Gamma = \sum \lambda_k Q_k + \Gamma_0, \]

where \( \Gamma_0 \) is a constant, which can be absorbed into the normalization factor, and constants (eigenvalues) \( \lambda_k \) are such that

\[ \Lambda = \sum \lambda_k. \]

They will be more precisely determined on imposing suitable boundary conditions on the eigenfunctions \( \psi_\alpha \). It should be noted that \( Q_k = Q(r, \alpha) \).

In summary of the results up to this point, under the canonical transformation (12) the eigenfunctions are in the form

\[ \psi_\alpha = A_0 \delta(\alpha - \frac{\partial S}{\partial r}) \exp(i \sum \frac{\lambda_k}{\omega_k} \frac{\partial \psi}{\partial \alpha_k}), \]

where \( A_0 \) is the normalization factor, and \( p_k \) and \( Q_k \) are used for the second equality of Eq. (20). Since the generating function \( S \) can be written for a conservative system in terms of the characteristic function \( W \) defined by

\[ S = W - Et, \]

where \( E \) is a constant (energy), the eigenfunction can be also written as

\[ \psi_\alpha = A_0 \delta(\alpha - P) \exp(i \sum \frac{\lambda_k}{\omega_k} \frac{\partial W}{\partial \alpha_k}). \]

This result shows that the eigenfunction will be explicitly found if the Hamilton-Jacobi equation is solved, given the initial conditions for \( (P, r) \).

This function \( \psi_\alpha = \psi(r, P, \alpha, \lambda) \) may be regarded as an eigenfunction with two sets of eigenvalues \( (\alpha, \lambda) \). This set of eigenfunctions can be easily shown orthogonal and normalizable. For this proof we simply note that under the canonical transformation and subject to \( \delta(\alpha - P) \)

\[ \frac{\partial (Q_1, \cdots, Q_j)}{\partial (r_1, \cdots, r_j)} = \frac{\partial (p_1, \cdots, p_j)}{\partial (\alpha_1, \cdots, \alpha_j)} = 1. \]

Before proceeding further, it is interesting to note the following. Recalling that the generating function \( S \) can be expressed in terms of the action integral

\[ S(t) = -\int_{t_0}^t ds L(p, r, s), \]

where \( L(p, r, s) \) is the Lagrangian, the eigenfunctions, e.g., Eq. (22), may be expressed in the form

\[ \psi(r, P, \alpha, \lambda) = \frac{A_0}{(2\pi)^{j/2}} \delta(\alpha - \frac{\partial \psi}{\partial \alpha}) \int_{t_0}^t ds L(p, r, s) \times \exp\left[-i \sum \frac{\lambda_j}{\omega_j} \frac{\partial \psi}{\partial \alpha_j} \right], \]

which reminds us of the Feynman path integral \(^{14}\) in quantum mechanics in that it is given in terms of the action integral. It is useful to note

\[ \int_{t_0}^t ds L(p, r, s) = \sum \int_{t_0}^{t_s} ds p \left| \frac{ds}{ds} - E(t - t_0) \right| = \sum \int_{t_0}^{t_s} ds p \left| E(t - t_0) \right| \]

\[ \frac{\partial \psi}{\partial \alpha_j} \]

A comment on Eq. (25) for the eigenfunction \( \psi(r, P, \alpha, \lambda):\)
The present classical action integral form suggests that the eigenfunctions can be numerically obtained by running a molecular dynamic simulation method in which the Hamilton-Jacobi equations are numerically solved from a set of initial conditions to the final state desired. This possibility seems extremely attractive for chemical dynamic studies of complex systems in the classical mechanical formalism. However, we will not dwell on this aspect here in this article, but will leave it to future study on the subject.

We now consider periodic boundary conditions on the eigenfunctions. Let \( \Omega \) be the dimension of the cubic box enclosing the system. Then the eigenfunctions must obey the condition

\[
\psi_j(r + \Omega) = \psi_j(r).
\]

(27)

It follows

\[
\frac{\lambda_j}{\omega_j} [Q_j(r + \Omega) - Q_j(r)] = 2\pi l_j.
\]

(28)

Here \( l_j \) is an integer. Since \( Q_j(r + \Omega) - Q_j(r) = \Omega \) it follows that

\[
\lambda_j = \frac{2\pi l_j \omega_j}{\Omega}.
\]

(29)

Define the wave number \( k_j \)

\[
k_j = \frac{2\pi l_j}{\Omega}, \quad (l_j = 0, \pm 1, \pm 2, \ldots).
\]

(30)

Hence the eigenfunctions are:

\[
\psi_j(r,p,\alpha,\lambda) = \frac{A_0}{(2\pi)^{1/2}} \delta(\alpha - p) \exp(i \sum_j k_j r_j).
\]

(31)

Since the characteristic function \( W \) is a surface in the phase space and the trajectories of \( l_j \neq 0 \) are on the family of surfaces, the eigenfunctions represent waves propagating perpendicularly to the surface of the characteristic function \( W \) with the phase

\[
\Gamma = \sum_j \frac{\lambda_j}{\omega_j} \frac{\partial W}{\partial \alpha_j} = k_j \frac{\partial W}{\partial \alpha_j} = \sum_j k_j Q_j(r,\alpha).
\]

(32)

Eqs. (22) and (32) represent the formal solution of the eigenvalue problem in terms of the Hamilton-Jacobi characteristic function \( W \). This method of constructing the eigenfunctions is not only somewhat different from, but also more insightful than that obtained in the previous work.\(^9\) by the present author.

For noninteracting particles we easily obtain

\[
\psi_j = A_0 \delta(\alpha - p) \exp(i \sum_j k_j r_j),
\]

(33)

in agreement with the known result in the literature.\(^1\)

It is an interesting exercise to construct the eigenfunctions for separable bound-state problems in the case of two interacting particles. Such examples are given for a few cases in Ref. (9). Such eigenfunctions can be used for calculations of few-body dynamics problems related to bound states or scattering of isolated two-particle systems in a classical approximation to quantum dynamics.

### Classical Scattering Theory in Phase Space

Collision bracket integrals appear in the formulas\(^3,15,16\) of transport processes when dynamic processes are treated for gases and liquids in kinetic theory. If we wish to achieve a molecular theory of such processes in fluids it is essential to calculate them in terms of molecular information on the basis of mechanical laws. Since it wouldn't be possible to expect to evaluate them in analytic form for a realistic potential model, it would be essential to develop numerical computational algorithms for them.

As a preparation for expressing collision bracket integrals involving classical collision operators in an equivalent but computationally more practical form and also to make this work self-contained, we briefly review classical scattering theory in the phase space. Formal classical theory of scattering\(^1,3,7,9\) can be formulated in the phase space in a manner parallel to the quantum mechanical scattering theory, and it holds some advantages for statistical mechanics and, especially, for kinetic theory as has been frequently demonstrated in kinetic theory investigations\(^1,3,11,12\) in which classical collision operators are used in a formalism analogous to quantum scattering theory. Nevertheless, the meanings of such collision operators have not been studied beyond the formal definition level. Since they are often used in such investigations but without their computational methods sufficiently well discussed, it is all the more important to try to comprehend their mathematical basis, so that one can perform computations, for example, of the collision integrals appearing in the theory of transport processes in a rational manner. Our aim here, however, is not in developing classical scattering theory in depth, but rather in exposing the essential features that may be relevant to mathematical treatments of and developing computational algorithms and suitable approximations for them which one might use in future calculations of transport properties. For this purpose the eigenfunctions presented in the previous section provide valuable mathematical tools and the conceptual framework as well as the methodology for such efforts.

Consider a scattering situation where particles (beams) at infinite separation converge toward each other and interact and then separate to infinite relative distance from each other. In classical mechanics, there is no concept of waves for particle motion. However, when the collision problem is formulated in the phase space, there appears a notion of waves as we have seen in the previous section where the eigenfunctions are calculated for continuous spectra of the Liouville operator. The Liouville equation (3) governs this scattering process of waves in the phase space. We describe the basic aspects of the theory here.

The collision process of the particles is assumed governed by the Liouville equation (3) over the course of collision. Since at remote past and distant future where particles do not interact with each other, the probability distribution function \( \rho \) also obeys the free particle Liouville equation

\[
\frac{\partial \rho}{\partial t} = L_0 \rho,
\]

(34)
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where $L_0$ is the free Liouville operator defined by

$$L_0 = -i \sum_k \frac{p_k}{m} \frac{\partial}{\partial r_k}.$$  

(35)

If the system is prepared at an eigenstate $\lambda$ at remote past and thus we set

$$\rho(x, t) = \exp(-i\lambda t) \Phi_\lambda(x),$$  

(36)

the corresponding eigenvalue problem is

$$L_0 \Phi_\lambda(x) = \lambda \Phi_\lambda(x).$$  

(37)

This eigenfunction is of the form as in Eq. (33). To describe the scattering process it is useful to introduce the interaction representation. Therefore, we define

$$\tilde{\rho}(t) = \exp(L_0 t) \rho(t).$$  

(38)

This puts the Liouville equation (3) in the form

$$\frac{\partial}{\partial t} \Phi_L = \tilde{L}(t) \tilde{\rho}(t),$$  

(39)

where

$$\tilde{L}(t) = \exp(iL_0 t) L_1 \exp(-iL_0 t),$$  

(40)

with $L_1$ denoting the interaction Liouville operator

$$L_1 = i \sum_k \frac{\partial H}{\partial r_k} \frac{\partial}{\partial r_k}.$$  

(41)

The formal solution for Eq. (39) can be written in the form

$$\tilde{\rho}(t) = \exp(iL_0 t) \exp(-iL_0 t) \tilde{\rho}(t_0).$$  

(42)

As $t_0 \to -\infty$, where the interaction between the particles vanishes, there holds the limit $L \to L_0$ and therefore

$$\tilde{\rho}(t) = \exp(iL_0 t) \exp(-iL_0 t) \Phi_L = \Phi_L,$$  

(43)

and similarly as $t \to \infty$. Consequently, in the limit of $t_0 \to -\infty$ the distribution function is given by

$$\rho(t) = \lim_{t_0 \to -\infty} \exp[-iL(t-t_0)] \exp(-iL_0 t_0) \tilde{\rho}(t_0)$$

$$= \lim_{t_0 \to -\infty} \exp[-iL(t-t_0)] \exp(-iL_0 t_0) \Phi_L.$$  

(44)

This is a strong limit which may be written in an equivalent form by using the Abeli-Tauber theorem

$$\rho(t) = \lim_{t_0 \to -\infty} \int_0^{t_0} ds \ exp[-iL(t-t)] \exp(-iL_0 t_0) \Phi_L.$$  

Physically, this form implies a time average of a wave train released from remote past until $t = 0$. We define a time-independent function $\psi^{(\epsilon)}_L(x)$ by the formula

$$\psi^{(\epsilon)}_L = \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} ds \ exp[-iL(s)] \exp(-i\lambda s) \Phi_L.$$  

(46)

to formulate time-independent scattering theory, since it contains all the necessary information on the scattering system. The nature of the scattered function $\psi^{(\epsilon)}_L$ can be better understood by recasting Eq. (46) on performing the integration: with the definition of a complex number

$$z = \lambda + i \epsilon$$

we find

$$\psi^{(\epsilon)}_L = -i \epsilon R(L - z)^{-1} \Phi_L = -i \epsilon R(z) \Phi_L,$$  

(47)

where $R(z)$ is the resolvent operator and the limit sign $\epsilon \to 0^+$ is omitted for notational brevity. The limit must be taken when the calculation of the right-hand side is completed. This limit will be understood henceforth. Multiplying $(L - z)$ to Eq. (47) from left and taking the limit $\epsilon \to 0^+$, we obtain

$$L \psi^{(\epsilon)}_L = \lambda \psi^{(\epsilon)}_L.$$  

(48)

This equation suggests that $\psi^{(\epsilon)}_L$ is an eigenfunction of $L$ belonging to the same eigenvalue $\lambda$ as for $L_0$. If it is recalled that the free state of the scattering system prepared in the remote past also has the eigenvalue $\lambda$ with eigenfunction $\Phi_L$, we see that the full scattering eigenfunction $\psi^{(\epsilon)}_L$ and the free eigenfunction $\Phi_L$ belong to the same eigenvalue spectrum, that is, the scattering process occurs on the shell of a given eigenvalue $\lambda$ of the Liouville operators and the total eigenvalue of the system does not change even if there is scattering of particles by each other. This is an important point worth keeping in mind when we apply the classical scattering theory formalism to kinetic theory and, in particular, to calculation of collision bracket integrals given in terms of classical collision operators.

The classical resolvent operator in Eq. (47) can be recast into another alternative form

$$R(z) = (L - z)^{-1}$$

$$= \frac{R_0(z) - R_0(z) L_1 R_0(z)}{R_0(z) - R_0(z) L_1 R_0(z)},$$  

(49)

where the free resolvent operator $R_0(z)$ is defined by

$$R_0(z) = (L_0 - z)^{-1}.$$  

(50)

Upon use of Eq. (49), Eq. (47) can be written in a more familiar form

$$\psi^{(\epsilon)}_L = \Phi_L - R_0(z) L_1 \psi^{(\epsilon)}_L,$$  

(51)

which is called the classical Lippmann-Schwinger equation for the scattered eigenfunction $\psi^{(\epsilon)}_L$ in analogy to the quantum mechanical Lippmann-Schwinger equation for scattering. It is an integral equation for $\psi^{(\epsilon)}_L$. By defining the classical collision operator $T(z)$

$$T(z) = L_1 - L_1 R_0(z) T(z),$$  

(52)

we may put the classical Lippmann-Schwinger equation in an alternative form

$$\psi^{(\epsilon)}_L = \Phi_L - R_0(z) T(z) \Phi_L.$$  

(53)

The operator relations (49) and (52) can be rearranged to obtain the relations
\[ \mathcal{R}(z) \mathbf{L}_1 = \mathcal{R}_0(z) \mathbf{T}(z), \quad \mathbf{L}_1 \mathcal{R}(z) = \mathbf{T}(z) \mathcal{R}_0(z), \quad \mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}_0(z) \mathbf{T}(z) \mathcal{R}_0(z), \quad \mathbf{T}(z) = \mathbf{L}_1 - \mathbf{L}_1 \mathcal{R}(z) \mathbf{L}_1. \] (54) (55) (56) (57)

These relations will be found useful in various calculations involving collision operators since the classical collision operators appear in the theory of transport processes. They have been in fact used in some of formal kinetic theories in the literature in 1960s and 1970s.

The equations presented remain structurally the same as for both two-particle and many-particle collisions. Since they can be easily transcribed into many-particle versions, we will simply consider the equations presented here applicable to a many-particle situation.

Since the many-particle collision operators are often computed in terms of collision operators of a smaller number of particles by using some sort of expansion-usually two-particle operators-owing to the inherent difficulty with many-particle dynamical problems, there are some precautions that must be taken when many-particle collision and resolvent operators are calculated in terms of operators involving smaller numbers of particles, for example, two-particle, three-particle operators, and so on. For example, the often used binary collision expansion of connected operators of particles for many-particle collision operators is accompanied by a divergence difficulty, which can and should be avoided by using a suitable cluster expansion.

Since many-particle operators are often decomposed into such lower-order operators of smaller numbers of particles disconnected from each other in statistical mechanics, the precautions mentioned become important when kinetic theory results are computed for experimental comparison. Detailed discussions on these points are given in Chapter 9 of Ref. (3) to which the interested reader is referred.

### Alternative Forms for the Collision Bracket Integral

In kinetic theory, either the kinetic equation is derived approximately from the Liouville equation in a form breaking the time-reversal invariance, or an irreversible equation is postulated on the basis of the viewpoint that the kinetic equation is a fundamental and irreversible equation for mesoscopic description of a many-particle system, built on (reversible) classical or quantum mechanics: it is not something that can be derived from time-reversal-invariant Hamiltonian equations of motion. The difference between these approaches is just philosophical in practice. Either way, we are treating macroscopic systems from the molecular viewpoint by using an irreversible equation, which is qualitatively different from the Newtonian equation of motion or the Schrödinger equation in the sense that the former is time-reversal symmetry breaking whereas the latter is time-reversal invariant.

The time reversal symmetry is broken by the kinetic equation (e.g., Boltzmann equation) because of the time-reversal symmetry-breaking collision term (e.g., the Boltzmann collision term) in which energy dissipation accompanying irreversible processes is vested. The collision term is given in terms of the collision cross section or collision operator which is relatively simple to calculate in the case of two-particle elastic scattering, but becomes hard to calculate as the complexity of the system increases if the number of particles involved increases beyond two. All material functions such as transport coefficients are given as collision-weighted averages of dynamical quantities, and the theoretical formulas for material functions derived by any kinetic theory cannot transcend the formalistic level to make connection with experimental data unless a practicable method of computing collision-weighted averages is developed. By method we do not mean some sort of analytical theoretic method, but an algorithm by which the aforementioned averages can be efficiently computed on a computer, for example, in a manner similar to the molecular dynamics or Monte Carlo simulations for equilibrium fluids.

Therefore, the aim is to transform the formal expressions for material functions in kinetic theory to relatively simple quadratures or forms readily computable electronically by a simulation method. It is the main objective in this section and, in fact, of this paper. To the end stated, it is sufficient to consider the following collision bracket integral appearing in the dense fluid kinetic theory formulated elsewhere (Ref. 3):

\[ I_c = \langle h(x) \mathcal{T}(z) h(x) F_{c_{eq}}(x) \rangle = \langle I_c \rangle, \] (58)

where \( h(x) \) is a function of phase \( x = (p, r) = (p^{(N)}, r^{(N)}) \) for an \( N \)-particle system and the angular brackets denote integration over the phase space; for example, in the case of dilute gases \( h(x) \) is given by

\[ h^{0\alpha}(x) = \sum_j m_j C_j C_j h^{0\beta}(x) = \frac{1}{2} \sum_j m_j C_j^2 C_j (C_j = v - u) \] (59)

with \( v \) and \( u \) denoting respectively the particle velocity and the mean fluid velocity; \( F_{c_{eq}}(x) \) is the equilibrium distribution function; \( \mathcal{T}(z) \) is the \( N \)-particle collision operator obeying the \( N \)-particle version of the classical Lippmann-Schwinger equation (52); and \( i = \sqrt{-1} \). The first member on the right hand side of Eq. (59) is for the shear stress and the second member is for the heat flux in the case of a dilute monatomic gas. In the case of dense gases and liquids, \( h(x) \) consists of virial tentors, energy flux vectors, \( h^{0\alpha}_v \) and \( h^{0\alpha}_h \), respectively: for pressure (stress) tensor \( h^{0\alpha}_v \)

\[ \sum_{j=1}^{N} h^{0\alpha}_v = \sum_{j=1}^{N} m_j C_j \delta(r_j - r) + \frac{1}{2} \sum_{j=1}^{N} \sum_{k \neq j=1}^{N} W_{jk} \cdot \delta(r_j - r) \] (60)

and for heat flux vector \( h^{0\alpha}_h \)

\[ \sum_{j=1}^{N} h^{0\alpha}_h = \sum_{j=1}^{N} \left[ \frac{1}{2} m_j C_j^2 + \frac{1}{2} \sum_{k \neq j=1}^{N} V_{jk} (r_j) \right] C_j \delta(r_j - r) \]

\[ + \frac{1}{2} \sum_{j=1}^{N} \sum_{k \neq j=1}^{N} W_{jk} \cdot C_j \delta(r_j - r) \] (61)

where \( W_{jk} \) is the virial tensor defined by
By using the definition of the resolvent operator the integral \( J_c \) can be written in the form of integral
\[
J_c = \frac{i}{\epsilon} \int_0^\infty dt \ e^{-\epsilon t} \langle \chi(t) \rangle \langle \gamma(t) \rangle - \int_0^\infty dt \ e^{-\epsilon t} \langle \chi(t) \rangle \langle \gamma(t) \rangle .
\] 

Therefore, the collision integral \( I_c \) may be written as
\[
I_c = \epsilon \int_0^\infty dt \ e^{-\epsilon t} \langle \chi(t) \rangle \langle \gamma(t) \rangle .
\]

Since
\[
g(t) = e^{\epsilon t} g = F_{eq}^{1/2} e^{\epsilon t} h,
\]
owing to the fact that the equilibrium distribution function consists of invariants of \( \mathbf{L} \), we finally obtain
\[
I_c = \epsilon \int_0^\infty dt \ e^{-\epsilon t} \langle \chi(t) \rangle \langle \gamma(t) \rangle .
\]

This form and, particularly, the second term on the right in the first line, is rather reminiscent of the time autocorrelation functions appearing in the linear response theory. Here \( \epsilon \) may be taken with the inverse of a sufficiently large value of \( \tau_c \), so that
\[
I_c = -\tau_c^{-2} \int_0^\tau dt \ e^{-\epsilon t} \langle \chi(t) \rangle \langle \gamma(t) \rangle = -\tau_c^{-1} \int_0^\tau ds \ e^{-\epsilon t} \langle \Delta g(s, \tau_c) \rangle (s = t/\tau_c),
\]

where
\[
\Delta g(s, \tau_c) = g - g(s, \tau_c).
\]

This is an alternative form for the collision bracket integral in Eq. (58). It is given in terms of a time correlation function which is certainly more readily amenable to molecular dynamic simulation methods than the one involving the classical \( N \)-particle collision operator \( \mathbf{T}(z) \).

If there exists a plateau value region in the integrand, \( \Delta g(s, \tau_c) = g - g(s, \tau_c) \) may be approximated by \( \Delta g(\tau_c) \), the integral may be approximated by
\[
I_c = \frac{1}{\tau_c} \langle \Delta g(\tau_c) \rangle \langle \gamma(\tau_c) \rangle .
\]

By reversing the collision process in the phase space and using the time reversal invariance of the phase volume, it is possible to put this integral in a symmetric form
\[
I_c = \frac{1}{2} \langle \Delta g(\tau_c) \rangle \langle \gamma(\tau_c) \rangle
\]
\[
= \frac{1}{2} \tau_c^{-1} \int d\mathbf{x}^{(N)} \Delta g(\tau_c) \Delta g(\tau_c) F_{eq}^{(N)}(x^{(N)}),
\]

which is reminiscent of the collision bracket integrals in the Chapman-Enskog theory of dilute gases, but the present form is applicable to dense gases and liquids as well as solids. It is the alternative form for the collision bracket integral we set out to show in this paper. The form not only obviates the direct computation of the collision operator.
\( T(\tau) \) in the collision bracket integral for the transport coefficients in Eq. (58), but also makes the computation of collision bracket integrals comparable to the time correlation formulas in the linear response theory of transport coefficients, rendering the former directly amenable to computer simulation methods including Monte Carlo simulation methods. In this way, the kinetic theory of liquids developed in the generalized Boltzmann equation approach\(^{1,15,16} \) can be made computationally feasible to implement.

This integral indeed can be shown to be the Chapman-Enskog collision bracket integral for \( \Delta g(\tau) \) if we consider the case of two particles for \( I_c \), which is the leading order term in the low density limit if the collision bracket integral is expanded in density series.\(^3 \) For this purpose, let us write \( I_c \) explicitly for two particles:

\[
I_c = \frac{1}{2} \frac{1}{\tau_c} \int d\tau_c^2 \Delta g(\tau_c) \Delta g(\tau) F_{eq}(x(\tau)) . \tag{78}
\]

If it is assumed that \( \Delta g(\tau) \) depends only on the momenta and \( F_{eq}(x(\tau)) = f_{eq}(p_1) f_{eq}(p_2) \) as is the case of the Chapman-Enskog collision bracket integrals, then it is possible to show\(^3\) that

\[
\int d\tau_c^2 = \tau_c V \int d\nu_1 \int d\nu_2 \int_0^{2\pi} d\phi \int_0^\infty db g_{12} \ldots \tag{79}
\]

in the standard notation. Here \( V \) is the volume of the container, \( b \) is the impact parameter, \( \phi \) is the azimuthal scattering angle, \( g_{12} \) is the relative speed of two particles, and \( f_{eq}(p_i) \) is a singlet equilibrium momentum distribution function. By using this result, we finally get

\[
I_c^{(2)} = \frac{1}{2} V \int d\nu_1 \int d\nu_2 \int_0^{2\pi} d\phi \int_0^\infty db g_{12} \Delta g(\tau) f_{eq}(p_1) f_{eq}(p_2) , \tag{80}
\]

which, apart from the constant factor, is clearly the Chapman-Enskog collision bracket integral\(^{23,24} \) for \( \Delta g(\tau) = g - g(\tau) \) where \( g(\tau) \) is the post-collision value of \( g \) if \( \tau_c \) is taken for the collision time for the particles.

In the case of \( I_c \) involving three particles, we employ, for example, mass-normalized coordinates\(^25 \) which are subsequently expressed in hyperspherical coordinates.\(^26 \) In the aforementioned mass-normalized hyperspherical coordinates the three-particle phase integral can be written as\(^2,27 \)

\[
\int d\tau_c^3 = \nu_c V \int dP_c \int d\nu_1 \int d\nu_2 \int d\Omega_3 \int_0^\infty d\lambda \lambda^3 b^4 (P | \mu) , \tag{81}
\]

where \( P_c \) is the center of mass momentum, \( \nu_1 \) and \( \nu_2 \) are two components of mass-normalized relative momenta of the three particles, \( P = |\nu_1 + \nu_2| \), \( \mu^2 = m_1 m_2 m_3 (m_1 + m_2 + m_3) = m^2/3 \),

\[
d\Omega_3 = \sin^2 \theta_2 \sin^2 \theta_3 \sin^3 \theta_1 d\theta_2 d\theta_3 d\theta_2 d\theta_3 d\theta_1 \tag{82}
\]

with \( \theta_2, \theta_3, \theta_1 \) denoting the hyperpolar angles (0 \( \leq \theta \leq \pi \): \( i = 2, 3, 4 \)), \( \theta_i \) is the hyperazimuthal angle (0 \( \leq \theta_i \leq 2\pi \)), and \( b \) is the generalized impact parameter. For details of the coordinate transformation and the collision dynamics leading to Eqs. (81) and (82), see Sec. 13.6 of Ref. (3). By using this result, the three-particle collision bracket integral can be written as

\[
\nu_c^{(3)} = \frac{1}{2} V \int d\nu_1 \int d\nu_2 \int d\Omega_4 \int_0^\infty db b^4 (P | \mu) \Delta g(\tau_c) \Delta g(\tau) \times f_{eq}(\nu_1) f_{eq}(\nu_2) f_{eq}(P_c) , \tag{83}
\]

in the case where \( \Delta g(\tau) \) depends on the momenta of three particles only and

\[
\nu_c^{(3)} = f_{eq}(\nu_1) f_{eq}(\nu_2) f_{eq}(P_c) .
\]

It must be noted that parameter \( \tau_c \) is canceled out in \( \nu_c^{(3)} \) if \( \tau_c \) is taken as the collision time of the three particles.

Here we remark that in the case of \( N \)-particle collisions \( I_c \) in Eq. (78), that is, \( T(\tau) \), may be expanded into a cluster expansion\(^3 \) of collision operators of connected particles where \( I_c^{(2)} \) and \( I_c^{(3)} \) appear as the leading order contributions in a density series. Since such an expansion is not the aim of this work, we will not discuss it in this paper.

**Concluding Remarks**

In this paper, we have re-examined the eigenvalue problem of the Liouville operator in the context of kinetic theory. The eigenfunctions of the Liouville operator are shown possible to construct by making use of canonical transformation. The eigenfunctions obtained enable us to consider classical scattering theory in a mathematically precise manner, but a rather suggestive form. An important point realized in this investigation is that the classical scattering involves waves moving perpendicularly to the characteristic function \( W \) with phases given by Eq. (32) and occurs on the shell of a fixed eigenvalue which is shared by both the incident and scattered waves in the phase space. The fact that eigenfunctions can be expressed in a path integral form is very interesting and worth a further study in connection with chemical dynamics of complex molecular systems in the classical limit for some degrees of freedom. Note that this would be often the case for translational degrees of freedom.

By using the notion that the collision occurs on the shell of a fixed eigenvalue in the calculation of the collision bracket integrals appearing in kinetic theory of dense fluids, it is possible to recast them in terms of a time correlation function. This latter form can be put in an approximate form reminiscent of the collision bracket integral in the Chapman-Enskog theory of dilute gases, if the there exists a plateau value region in the dynamic quantities involved in the time correlation functions. Otherwise, the collision bracket integrals are expressed in the form of a time integral of time correlation functions of \( \Delta g(\tau) \) averaged over the equilibrium ensemble distribution functions.

The recast forms for the collision bracket integral are certainly more suitable for numerical computation on a computer than the form given in terms of the classical collision operator \( T(\tau) \). The two-particle example is shown to give rise to the traditional Chapman-Enskog theory result for dilute monatomic gases. We have also presented a three-
particle collision bracket integral in the case of dilute gases where there is no statistical correlation. The alternative forms of the collision bracket integral present a possibility of developing a new way (i.e., computer simulation methods) of computing many-particle collision bracket integrals on a computer. With this investigation we now have achieved a set of numerical algorithms to compute the transport coefficients appearing in the kinetic theory of dense fluids that is comparable to that of linear response theory. Numerical simulation methods might possibly include a Monte Carlo method.

Finally, we note here an example for the relation of the collision bracket integral to the transport coefficient. For example, the viscosity is related to the collision bracket integral in the following manner:

$$\eta = \frac{5m}{16\pi^2} \int R^{(1,1)} \frac{1}{R^{(1,1)}} \psi$$

(84)

where \(\sigma\) is the diameter of the molecule, \(m\) is the reduced mass, \(n\) is the number density, and

$$R^{(1,1)} = \int dx^{(N)} F^{eq}_{eq}(x^{(N)}) \sum_{i=1}^N \delta(r_i - r) \left[h^{(1)}_l \right]^2 \cdot T^{(N)}(z) [h^{(1)}_k]^2$$

(85)

with \(h^{(1)}_l\) standing for the virial tensor

$$\left[h^{(1)}_l \right]^2 = [mC_lC_l]^{(2)} \frac{1}{2} \sum_{j=1}^N [W_{jl}]^2$$

(86)

$$[A]^{(2)} = \frac{1}{2} (A + A^* - \frac{3}{2} \delta Tr A,$$ traceless symmetric part of tensor \(A\).

(87)

An approximate form of \([W_{jl}]^2\) is given by

$$[W_{jl}]^2 = \frac{V'}{r_{jl}} \left[r_{jl} \cdot r_{jl}\right]$$

(88)

where \(V' = \frac{\partial V(r)}{\partial r}\), \(r_{jl} = |r_j - r_l|\). According to the analysis made in Sec. IV, \(R^{(1,1)}\) can be put in the form of collision bracket integral considered in the previous section. The collision bracket integral on the right can be expressed in the alternative form

$$R^{(1,1)} = \tau \int_0^\infty ds (\Delta h(s \tau_j) / \Delta h(s \tau_k)),$$

(89)

$$\Delta h(s \tau_j) = \sum_j \left[h^{(1)}_l(s \tau_j) - h^{(1)}_l(0)\right]^2$$

(90)

presented in the previous section. Thus the viscosity of the dense fluid is inversely proportional to the collision bracket integral. Separating the center of mass part of \(dx^{(N)}\) so that \(dx^{(N)} = drdPdx^{(N)}\), \(\Delta h(s \tau_j) / \Delta h(s \tau_k)\) may be cast into the form

$$\langle \Delta h(s \tau_j) / \Delta h(s \tau_k) \rangle = \int dP \int dx^{(N)} F^{eq}_{eq}(x^{(N)}) \Delta h(s \tau_j) / \Delta h(s \tau_k)$$

(91)

where \(F^{eq}_{eq}\) is the equilibrium distribution function excluding the center of mass motion part of the \(N\) particles.

Other transport coefficients may be similarly expressed in terms of the collision bracket integrals considered earlier in this work. It should be noted that the manner in which the time correlation function Eq. (77) appears in the transport coefficient and also the meaning of the time correlation function are different from those in the linear response theory. This difference stems from the fact that the present kinetic theory and the linear response theory differ in their basic approach to transport processes, the notable point of the difference being the presence of an irreversible kinetic equation in the present theory.

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**Appendix A. Some Mathematical Properties of Eigenfunctions and Eigenvalues**

The Liouville operator \(L\) may have eigenfunctions and eigenvalues, but also has some important mathematical properties, which are useful and necessary for developing physical theory with it. We list them in the following.

**Property 1.** The Liouville operator is Hermitian. Consider

$$L^* \psi = \int dx \psi^* L \psi$$

Then

$$L^* \psi = \int dx \psi^* L \psi = \int dx \psi^* [iH, \psi]_{pq} = \int dx \psi^* (-i) [H, \psi]_{pq} = \int dx \psi^* L \psi \psi = I \psi$$

Therefore \(L\) is Hermitian and hence

$$L^* = L$$

(A1)

**Property 2.** Since \(L\) is Hermitian, its eigenvalues are real. Let

$$L \psi = \lambda \psi$$

Then

$$L^* \psi^* = \lambda^* \psi^*$$

Hence it follows that

$$\int dx (\psi \psi^* L \psi - \psi L \psi^*) = (\lambda - \lambda^*) \int dx \psi \psi^* L \psi = \lambda - \lambda^*$$

But by virtue of hermiticity

$$\int dx (\psi \psi^* L \psi - \psi L \psi^*) = 0$$

Therefore

$$\lambda = \lambda^*$$

(A2)

which implies \(\lambda\) is real.
Property 3. The eigenfunctions belonging to different eigenvalues are orthogonal. Proof for this follows from Property 2.

Property 4. Any function in the phase space can be expanded into the eigenfunctions of \( L \).

\[
\rho(p,q,t) = \sum_k a_k \psi_k(p,q),
\]

where

\[
a_k = \int \mathcal{D}f(p,q) \psi_k^* (p,q).
\]

This property follows from the fact that \( L \) is a linear operator. In the case of time-dependent functions

\[
\rho(p,q,t) = \sum_k a_k(t) \psi_k(p,q) .
\]

Inserting it into the Liouville equation yields

\[
i \frac{d}{dt} = \sum_k a_k(t) L \psi_k(p,q) = \sum_k a_k(t) \lambda_k \psi_k(p,q) = i \sum_k \frac{da_k}{dt} \psi_k(p,q),
\]

which gives rise to the ordinary differential equation

\[
\frac{da_k}{dt} = \lambda_k a_k(t) .
\]

Integrating this we obtain

\[
a_k(t) = c_i \exp(\lambda_k t).
\]

Finally,

\[
\rho(p,q,t) = \sum_k c_i e^{-i \lambda_k t} \psi_k(p,q) .
\]

Of course, the eigenvalues and eigenfunctions appearing here are not known in terms of the system properties. Nevertheless, it is possible to deduce some general properties of the expansion, eigenvalues, and eigenfunctions, and they may help assess eigenvalues and eigenfunctions we will obtain later.

Property 5. Since the distribution function is normalized,

\[
\int dx \rho(p,q,t) = 1,
\]

it follows

\[
\sum_k c_k e^{-i \lambda_k t} \int dx \psi_k(p,q) = 1.
\]

Since

\[
\int dx L \psi_k(p,q) = \lambda_k \int dx \psi_k(p,q)
\]

but

\[
\int dx L \psi_k(p,q) = -i \sum_j \left[ \int dx \left( \frac{\partial H}{\partial q_j} \psi_k - \frac{\partial H}{\partial p_j} \psi_k \right) \right] = -i \sum_j \left[ \int dx \left( \frac{\partial H}{\partial q_j} \psi_k - \frac{\partial H}{\partial p_j} \psi_k \right) \right] = -i \sum_j \left[ \int dx \left( \frac{\partial H}{\partial q_j} \psi_k - \frac{\partial H}{\partial p_j} \psi_k \right) \right] = 0
\]

and the eigenvalues are real we have

\[
L \psi_k = \lambda_k \psi_k
\]

and hence

\[
L \psi_k = -\lambda_k \psi_k
\]

This means that \( \psi_k \) is the eigenfunction belonging to \(-\lambda_k\). Furthermore, since

\[
\theta L = -L
\]

and the normalization of \( \rho(p,q,t) \) is fulfilled.

In this manner, the distribution function in the nuclear space—the phase space—is expandable in the eigenfunctions and its expansion is reconciled with the notion of eigenfunctions being \( L^2 \) functions in the Hilbert space.

Property 6. It is well known that the Liouville operator is invariant to time reversal times complex conjugation. That is, if we denote by \( \theta \) the time reversal operator then

\[
\theta L = -L
\]

and the normalization of \( \rho(p,q,t) \) is fulfilled.

Therefore if we denote the compound operator of time reversal and complex conjugation by \( \theta \)

\[
\theta = \theta^* = (\theta^*)\theta
\]

then

\[
\theta L = L
\]

and the time reversed distribution function \( \rho(-p,q,-t) \) obeys the same Liouville equation as \( \rho(p,q,t) \). We note that this is in the root cause of the difficulty in kinetic theory of matter when we develop it by means of the Liouville equation, which is time reversal invariant. In connection with this operator \( \theta \), we note the following: Since

\[
L^* = -L
\]

and the eigenvalues are real we have

\[
L^* \psi_k = \lambda_k \psi_k
\]

and hence

\[
L \psi_k^* = -\lambda_k \psi_k^*
\]

This means that \( \psi_k^* \) is the eigenfunction belonging to \(-\lambda_k\). Furthermore, since

\[
\theta L^* = -\theta L = \theta L = L
\]

Now operating \( \theta \) on Eq. (A11) we obtain

\[
\theta L^* \psi_k = \lambda_k \theta \psi_k^*
\]

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but
\[ \theta L^* \psi_{\lambda_i} = L \theta \psi_{\lambda_i}^* \]
and hence
\[ L \theta \psi_{\lambda_i}^* = \lambda_i \theta \psi_{\lambda_i}^* , \]
which implies that
\[ \theta \psi_{\lambda_i}^* = \text{an eigenfunction of } L \text{ belonging to } \lambda_i = \psi_{\lambda_i} . \]
That is,
\[ \psi_{\lambda_i}^* = \theta \psi_{\lambda_i} . \tag{A12} \]
This property is important for proving the orthogonality of eigenfunctions.

**Property 7.** The eigenfunctions \( \psi_{\lambda} \) are generally complex and hence they can be written in terms of amplitude and phase:
\[ \psi_{\lambda}(p, q) = A_{\lambda}(p, q) \exp[i \Gamma_{\lambda}(p, q)] \tag{A13} \]
where
\[ L A_{\lambda}(p, q) = 0, \tag{A14} \]
\[ L \Gamma_{\lambda}(p, q) = -i \lambda . \tag{A15} \]
This easily follows from the eigenvalue problem of \( L \) on substituting Eq. (A13). Eq. (A14) implies \( A_{\lambda}(p, q) \) is made up of invariants of motion and \( \Gamma_{\lambda}(p, q) \) is the phase of a wave in the \( \Gamma \) space that corresponds to the eigenvalue \( \lambda \). The eigenvalue problem of \( L \) is now reduced to finding the amplitude and the phase of waves. It is done in the main text.

**References**