

# Two-Liouville Space Reactive Scattering Theory

G. W. Wei\* and R. F. Snider

*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*  
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A two-Liouville space scattering theory is formulated in order to understand and by-pass the channel strong orthogonality assumption standardly used in most quantum kinetic theories of reactive gases. This two-Liouville space scattering theory can be regarded as an adaption of the two-Hilbert space theories of Kato and of Chandler and Gibson to density operators. The aspects of superspace scattering theory presented here are consistent with the existing (one-Liouville space, non-reactive) formalism of Jauch and coworkers. Møller superoperators and transition superoperators are given in forms which are convenient for the kinetic theory description of a reactive gas.

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## I. INTRODUCTION

The first attempt [1] at a formal theory of reactive gas kinetic theory required an identification of bound and unbound components of the reduced density operators for the  $N$ -particle system. A major difficulty in carrying out that analysis was the lack of orthogonality of different rearrangement channels [2,3]. In particular, the set of states for the three-particle channel in which all particles move independently span the total Hilbert space of the three particles. Consequently, that channel cannot be orthogonal to any other channel. The intuitive treatment for solving such problems in kinetic theory was to assume strong orthogonality [1]. In contrast, the present paper uses the existing multichannel scattering theory [4–7] to develop a two-Liouville space scattering theory. It is expected that this could be a basis for understanding and possibly by-passing the strong orthogonality approximation standardly used in reactive gas quantum kinetic theory. An initial attempt at such a kinetic theory development has been made [8] and it is planned to elaborate on this in a future publication.

A two-Liouville space scattering theory is formulated in this paper after reviewing two-Hilbert space scattering theory. Abstract two-Hilbert space theories have been formulated by Kato [4], Chandler and Gibson [5] and others [6,7]. There is a certain flexibility in selecting identification operators and channel spaces, and more so when applied to a particular problem. This theory has been successfully applied to equilibrium statistical mechanics by Osborn and coworkers [9], with care being exerted to obtain connected kernels in the time independent formalism as emphasized by Faddeev [10]. A somewhat different two-Hilbert space theory was formulated by Evans in his effort to describe reactive gases [11]. But for kinetic theory applications, it is appropriate to develop a two-Liouville space scattering theory because quantum kinetics involves probabilistic arguments and these can only be formulated in Liouville spaces. The present formulation requires care in the definition of appropriate operator spaces and superoperators. The selection of superoperators is not unique, and physical considerations are indispensable for making a useful choice. The trace class norm discussed by Jauch and co-workers [12], and by Snider and Sanctuary [13] for single channel scattering theory in operator space has been adopted and certain physical arguments about asymptotic channel diagonality are assumed in order to obtain a two-Liouville space theory that is consistent with the standard chemical picture of a reacting system. Transition superoperators are defined in a nonsymmetric manner convenient for application to kinetic theory.

This paper is divided into six sections. Section II is devoted to the kinematical description of the channels and their spaces. In addition to the usual  $n$ -particle Hilbert space  $\mathfrak{H}$ , the notion of asymptotic channels and their associated asymptotic channel spaces are introduced both from a mathematical and a physical point of view. These are combined to form the asymptotic Hilbert space  $\mathfrak{H}$ . Identification operators mapping the asymptotic channel spaces to the fully interacting Hilbert space are introduced to connect the two spaces. A time dependent two-Hilbert space scattering theory is described in Sec. III with the emphasis on Møller operators. Assuming the existence of all channel Møller operators and their adjoints, a brief discussion of asymptotic completeness is given in order to enhance its physical meaning. The structure and properties of a two-Liouville space suitable for scattering theory is introduced in Sec. IV. A restriction of the Liouville spaces to be of Hilbert-Schmidt class seems appropriate for the formulation of scattering

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\*Permanent address: Department of Computational Science, National University of Singapore, Singapore 119260

theory. A two-Liouville space scattering theory is formulated in Sec. V. This formalism is guided mainly by the chemical conceptualization of the problem rather than by mathematical arguments and proofs, but the existence and properties of the channel superoperators is based on adapting the single channel theory of Jauch et al. [12]. The notation is chosen to be appropriate for kinetic theory application. Various Møller superoperators as well as transition superoperators are of primary importance for kinetic theory and the definition of these quantities is the main objective of the development. The paper ends with a discussion, Sec. VI.

## II. KINEMATICS OF MULTICHANNEL SCATTERING

### A. The $n$ -particle Hilbert space $\mathfrak{H}$

The states of an  $n$  particle system are elements of a Hilbert space  $\mathfrak{H}$ , which can be regarded as the linear span of all square integrable functions  $\Psi$  of  $\mathbb{R}^{3n}$  or more generally as the direct product

$$\mathfrak{H} = \bigotimes_{j=1}^n \mathfrak{H}_j, \quad (1)$$

of the separable Hilbert spaces  $\mathfrak{H}_j$ , one for each particle  $j$ . For simplicity, the particles have been assumed to be structureless and satisfying Boltzmann statistics. The time dependence of a state is governed by a self-adjoint Hamiltonian  $H$  generating a one-parameter strongly continuous Abelian group of unitary evolution operators

$$U(t) = \exp(-iHt). \quad (2)$$

Here and throughout this paper  $\hbar$  is set equal to 1. The Hamiltonian  $H = K + V$  consists of a kinetic energy operator  $K$  and a potential operator  $V$ , which is usually assumed to be pairwise additive and of short range. There may be  $n$ -particle bound states for this Hamiltonian spanning the subspace  $\mathfrak{B}$ , but since the emphasis of this paper is on scattering, the discussion is restricted to states that are orthogonal to such bound states, determining the scattering subspace  $\mathfrak{H}_\infty = \mathfrak{B}^\perp$ .

### B. Asymptotic channel spaces $\mathbb{H}_G$

For an  $n$ -particle system interacting with short ranged potentials, it is possible that, at large times, either positive or negative, the particles separate into many sets which are spatially separated while the particles within each set remain interacting with each other. Such sets of particles are referred to here as fragments. Clearly a set of particles which remain interacting for all time must be in a bound state for this set of particles. The classification of what asymptotic fragments are possible is thus equivalent to the analysis of what bound states (of the subsystems) are possible for the given  $n$ -particle system. Since the fragments are spatially separated, the bound state of a fragment is determined by the Hamiltonian for the particular set of particles constituting the fragment. Thus the Hamiltonian for each possible set of particles needs to be examined to see if it supports one or more bound states.

Corresponding to the total Hamiltonian and on the basis of the indistinguishability of the particles, the simplest bound states to consider are the dimers satisfying, for particles 1 and 2,

$$H_{\text{rel}12}^{(2)} \phi_{\nu 12}^{(2)} = \varepsilon_\nu \phi_{\nu 12}^{(2)}, \quad (3)$$

involving the Hamiltonian for relative motion of the pair with  $\varepsilon_\nu$  negative. It may of course be the nature of  $H_{\text{rel}}^{(2)}$  that no such bound states exist, in which case no 2-particle fragments can asymptotically arise in a collision. Or there may be a very large number of such bound states, in which case a 2-particle fragment could be in a superposition of such bound states. Such a linear combination would be time dependent, not only because of the center of mass motion, but also because of the different bound state energies. Experimentally, some energy selection process of the measuring apparatus would usually reduce the linear combination to a single bound state, or to the measurement of a set of probabilities for the different bound states. For later purposes it is convenient to define the projection operator

$$P_{b12}^{(2)} \equiv \sum_\nu |\phi_{\nu 12}^{(2)}\rangle \langle \phi_{\nu 12}^{(2)}| \quad (4)$$

onto the bound states for the pair of particles (it is assumed that the  $|\phi_{\nu 12}^{(2)}\rangle$  are orthonormal,  $\langle \phi_{\nu 12}^{(2)} | \phi_{\mu 12}^{(2)} \rangle = \delta_{\nu, \mu}$ ).

Each relative Hamiltonian  $H_{\text{rel}}^{(3)}, H_{\text{rel}}^{(4)}, \dots, H_{\text{rel}}^{(n)}$  can be examined in turn to determine all the possible kinds of bound states, equivalently all kinds of fragments, that can occur within the  $n$ -particle system.

In a scattering process, each of the  $n$  particles must begin and end up in some fragment, so the fragments that arise will also carry a set of labels describing which particles are in each fragment. Each particular way of partitioning the  $n$  particles into a set of fragments  $C_1, \dots, C_m, \dots$  constitutes a (rearrangement) channel  $C = \{C_m\}$ . Each fragment  $C_m$  consists of a set of  $|C_m|$  labelled particles with the requirement that  $\sum_m |C_m| = n$  is the total number of particles in the system. The set of states for channel  $C$  define the asymptotic channel Hilbert space  $\mathbb{H}_C$  which is equivalent to the product of the space of  $L^2$  functions on  $\mathbb{R}^{3\ell}$ , with  $\ell$  the number of fragments in the asymptotic channel  $C$ , and the Euclidean space formed by the products of bound states of the fragments. Thus  $\mathbb{H}_C$  has the form

$$\mathbb{H}_C = \bigotimes_{C_m \in C} \mathbb{H}_{C_m}, \quad (5)$$

where  $\mathbb{H}_{C_m}$  is the asymptotic fragment Hilbert space for the  $m$ th fragment. This is in turn spanned by the tensor products  $\Phi_{C_m} \otimes \chi_{C_m}$  of the bound states  $\Phi_{C_m}$  of the fragment and square integrable functions  $\chi_{C_m}$  of  $\mathbb{R}^3$  for the center of mass of the fragment.

If fragments of all sizes occur, equivalently each Hamiltonian  $H_{\text{rel}}^{(j)}$  with  $j = 1, 2, \dots, n$  supports bound states then, see Appendix A, the number of possible channels for an  $n$ -particle system is the corresponding Bell number [14], in particular for  $n = 1, 2, \dots, 6$ , the number of channels are 1, 2, 5, 15, 52 and 203, with rapidly increasing numbers for larger  $n$ . This count includes the possibility of total bound states, which are not scattering states. In contrast, if only dimers (and of course unbound particles) are allowed as fragments, the number of channels is 1, 2, 4, 10, 26 and 76 for  $n = 1, 2, \dots, 6$ , see Appendix A.

The time evolution of an asymptotic channel is determined by a self-adjoint asymptotic channel Hamiltonian  $\mathbf{H}_C$  which is dense in  $\mathbb{H}_C$ . This consists of the sum of the Hamiltonians  $\mathbf{H}_{C_m}^{(|C_m|)}$  of the fragments restricted to the bound states of that set of particles,

$$\mathbf{H}_C \equiv \sum_{C_m \in C} \mathbf{H}_{C_m}^{(|C_m|)} P_{b_{C_m}}^{(|C_m|)}. \quad (6)$$

Apart from the discrete eigenvalues of various subsystems, this Hamiltonian has an absolutely continuous spectrum. In this way, the motion of an asymptotic channel is characterized by a set of freely moving bound fragments, which is described by an one-parameter unitary group

$$\mathbf{U}_C(t) = \exp(-i\mathbf{H}_C t). \quad (7)$$

It is important to note that, except for the  $n$ -body total bound states, no other bound state is uniquely defined by the  $n$ -particle Hamiltonian  $H$ . A bound state of  $s < n$  particles is only uniquely defined in terms of an appropriate  $s$ -body Hamiltonian  $H^{(s)}$ . For example, a bound state for the pair (12) is only uniquely defined by the two particle Hamiltonian  $H_{12}^{(2)}$ . Consequently, except for the  $n$ -body total bound states, projections onto bound states in the  $n$ -particle Hilbert space  $\mathfrak{H}$  are in general not mutually orthogonal and the identity of a bound state of fewer than  $n$ -particles in the Hilbert space  $\mathfrak{H}$  is not unique. In contrast, a bound fragment is defined only asymptotically in an appropriate subspace  $\mathbb{H}_{C_m}$  where the associated asymptotic Hamiltonian  $\mathbf{H}_{C_m}^{(|C_m|)}$  is the total Hamiltonian.

### C. The asymptotic space $\mathbb{H}$

It is an immediate property of the strongly continuous group, Eq. (7), that the asymptotic channel evolution does not allow the interaction of asymptotic channels. If channel interaction does happen, the process can no longer be treated as being asymptotic. This lack of interaction among the different asymptotic channels implies a physical sense of uniqueness. To further emphasize this property of asymptotic channels, the following two physical arguments are offered: i) The experimental setup is usually such that a particular state of the  $n$  particle system is prepared in a particular channel and the physical observations are designed to select out (count) a particular asymptotic channel after scattering, thus the asymptotic state of the system can be uniquely identified as being in a particular channel [6], thus requiring the asymptotic channel spaces to be mutually distinct; ii) At asymptotic times, the particles belonging to different fragments are so far apart that their corresponding potential interaction dies out, thus the different asymptotic channels are unique. This picture of asymptotic physical uniqueness is mathematically implemented by the notion of asymptotic orthogonality. This involves contrasting the time evolution of the states belonging to different asymptotic channels through a time limiting process [see Eq. (19)].

In order to make multichannel scattering theory appear simple and conceptually concise, it is convenient to construct an asymptotic space, which is the direct sum of all asymptotic scattering channel spaces

$$\mathbb{H} \equiv \bigoplus_{C \in \mathcal{C}} \mathbb{H}_C, \quad (8)$$

where  $\mathcal{C}$  is the collection of all asymptotic scattering channels. It is this construction that leads to the two Hilbert spaces, namely  $\mathbb{H}$  and  $\mathfrak{H}$ , and the associated scattering theory which allows a clear distinction between different asymptotic states and also between asymptotic and fully interacting time evolutions. A function in  $\mathbb{H}$  is a direct sum of functions, one in each asymptotic channel

$$\Phi = \bigoplus_{C \in \mathcal{C}} \Phi_C, \quad \text{where } \Phi_C \in \mathbb{H}_C \quad (9)$$

with a norm defined as

$$\|\Phi\|^2 = \sum_C \|\Phi_C\|^2. \quad (10)$$

The asymptotic Hamiltonian  $\mathbf{H}$  is defined in terms of the asymptotic channel Hamiltonians and the structure of the asymptotic space namely, acting on  $\Phi \in \mathbb{H}$ ,

$$\mathbf{H}\Phi = \bigoplus_{C \in \mathcal{C}} \mathbf{H}_C \Phi_C. \quad (11)$$

#### D. Identification operators

Each channel Hilbert space  $\mathbb{H}_C$  can be identified with a subspace  $\mathfrak{H}_C$  of the  $n$ -particle Hilbert space  $\mathfrak{H}$ , so there is an identification operator  $J_C$  which carries out this mapping

$$J_C : \mathbb{H}_C \rightarrow \mathfrak{H}_C \subset \mathfrak{H}, \quad (12)$$

according to

$$J_C \Phi_C = \Psi_C, \quad \forall \Phi_C \in \mathbb{H}_C, \quad \text{with } \Psi_C \in \mathfrak{H}_C \subset \mathfrak{H}. \quad (13)$$

An arbitrary element  $\Phi$  of  $\mathbb{H}$  is a direct sum of subspace elements, see Eq. (9), so there is a linear identification operator  $J$  mapping the whole asymptotic space  $\mathbb{H}$  into  $\mathfrak{H}$ , namely

$$J : \mathbb{H} \rightarrow \mathfrak{H}, \quad (14)$$

as a composite of the  $J_C$

$$J\Phi = \sum_{C \in \mathcal{C}} J_C \Phi_C = \sum_{C \in \mathcal{C}} \Psi_C. \quad (15)$$

Operators adjoint to these identification operators are bounded and satisfy the mapping relations

$$J_C^\dagger : \mathfrak{H} \rightarrow \mathbb{H}_C \quad (16)$$

and

$$J^\dagger : \mathfrak{H} \rightarrow \mathbb{H}. \quad (17)$$

Note that, in general

$$J^\dagger J \Phi \neq \Phi, \quad J J^\dagger \Psi \neq \Psi. \quad (18)$$

This completes the kinematical description of the asymptotic channels and spaces of a system of  $n$  indistinguishable particles. Two-Hilbert space scattering theory is based on this structure.

### III. TWO-HILBERT SPACE SCATTERING THEORY

Hilbert space scattering involves the association of a scattering state  $\Psi$  with an asymptotic state  $\Phi$  at an asymptotic time  $t \rightarrow \pm\infty$ . The details of such an association depends on which asymptotic channel evolution operator  $\mathbf{U}_C(t)$  is to be used when comparing the full and asymptotic time dependence. Specifically only certain scattering states are related to asymptotic channel  $C$  and these are determined by the projection operators  $Q_C^\pm$ . Mathematically these projectors are determined by

$$Q_C^\pm \Psi = \begin{cases} \Psi & \text{if } \exists \Phi_C \in \mathbb{H}_C, \lim_{t \rightarrow \mp\infty} \|U(t)\Psi - J_C \mathbf{U}_C(t)\Phi_C\| \rightarrow 0 \\ 0 & \text{otherwise.} \end{cases} \quad (19)$$

Physically  $Q_C^-$  is an observable (projection operator) which verifies whether a scattering state  $\Psi$  will asymptotically develop into a state in the asymptotic channel  $C$  in the infinite future whereas  $Q_C^+$  is the analogous operator which verifies that a scattering state  $\Psi$  has asymptotically evolved from a state in asymptotic channel  $C$  in the infinite past.

These projection operators satisfy the orthogonality conditions

$$Q_C^+ Q_B^+ = Q_C^+ \delta_{C,B}, \quad \text{and} \quad Q_C^- Q_B^- = Q_C^- \delta_{C,B} \quad (20)$$

and strong completeness conditions (asymptotic conditions)

$$\sum_{C \in \mathcal{C}} Q_C^+ = I_\infty = \sum_{C \in \mathcal{C}} Q_C^-, \quad (21)$$

where  $I_\infty$  is the identity operator for  $\mathfrak{H}_\infty$ . The validity of these statements certainly depends on the form of the potentials but an elaboration of these conditions is not attempted here. That any initial asymptotic state will end up in (a combination of) final asymptotic states, and vice versa, is the essence of Eq. (21). As well, it also says that any  $n$ -particle state that is not totally bound is a scattering state, having well defined incoming and outgoing free motion (asymptotic) states.

The existence of the  $Q_C^\pm$  projectors are equivalent to the existence of channel Møller operators

$$\Omega_C^\pm \equiv s - \lim_{t \rightarrow \mp\infty} e^{iHt} J_C e^{-i\mathbf{H}_C t}, \quad (22)$$

defined in terms of the strong operator limit. In particular, the channel Møller operator  $\Omega_C^+$  maps a channel state  $\Phi_C$  into a scattering state  $\Psi_C^{(+)}$ . For multichannel scattering, the adjoints  $\Omega_C^{\pm\dagger}$  are the weak operator limits [5]

$$\Omega_C^{\pm\dagger} \equiv w - \lim_{t \rightarrow \mp\infty} e^{i\mathbf{H}_C t} J_C^\dagger e^{-iHt}. \quad (23)$$

The ranges  $R(\Omega_C^\pm)$  of the different Møller operators are mutually orthogonal subspaces of  $\mathfrak{H}_\infty$ ,

$$\Omega_C^\pm \Omega_D^{\pm\dagger} = Q_D^\pm \delta_{C,D}. \quad (24)$$

From the properties of  $Q_C^\pm$ , Eqs. (20) and (21), it follows that the sum of the ranges of the Møller operators spans all of  $\mathfrak{H}_\infty$ . The sum of the Møller operators

$$\Omega_\pm \equiv \sum_C \Omega_C^\pm \quad (25)$$

is a mapping from  $\mathbb{H}$  to  $\mathfrak{H}$  satisfying the completeness relation

$$\Omega_\pm \Omega_\pm^\dagger = I_\infty. \quad (26)$$

By the construction of the asymptotic space, the asymptotic channels are orthogonal to each other, so the Møller operators satisfy

$$\Omega_C^{\pm\dagger} \Omega_D^\pm = \mathbf{P}_C^\pm \delta_{C,D}, \quad (27)$$

where  $\mathbf{P}_C^\pm$  are asymptotic channel projection operators selecting out the channel space  $\mathbb{H}_C$  from its direct sum  $\mathbb{H}$ . Necessarily the  $\mathbf{P}_C^\pm$  are mutually orthogonal to each other,

$$\mathbf{P}_C^\pm \mathbf{P}_D^\pm = \mathbf{P}_C^\pm \delta_{C,D}, \quad (28)$$

since their ranges act on different parts of the direct sum Hilbert space  $\mathbb{H}$ . Their sum is also the identity

$$\bigoplus_{C \in \mathcal{C}} \mathbf{P}_C^\pm = \Omega_\pm^\dagger \Omega_\pm = \mathbf{I} \quad (29)$$

of  $\mathbb{H}$ , where the interpretation of this sum in terms of the Møller operators is also indicated. The combination of Eqs. (26) and (29) implies that the  $\Omega_\pm$  are partial isometries.

An alternate method of identifying the Møller operators  $\Omega_\pm$  mapping  $\mathbb{H}$  to  $\mathfrak{H}$  is via the asymptotic time limit

$$\Omega_\pm \equiv s - \lim_{t \rightarrow \mp\infty} e^{iHt} J e^{-i\mathbf{H}t}. \quad (30)$$

From the point of view of the two-Hilbert spaces, the Møller operator  $\Omega_+$  ( $\Omega_-$ ) maps an asymptotic state  $\Phi \in \mathbb{H}$  into a scattering state  $\Psi_+$  ( $\Psi_-$ )  $\in \mathfrak{H}$ .

#### IV. KINEMATICS OF TWO-LIOUVILLE SPACE

In analogy with having separate Hilbert spaces for channel and fully interacting systems, separate Liouville spaces for channel and fully interacting density operators are introduced. Identification mappings between the channel and fully interacting spaces are defined. Various time evolution superoperators are introduced and their generators are identified as Liouville superoperators. Certain adjoint properties of these generators are discussed. The results of this formalism is used in the following section to develop a two-Liouville space scattering theory.

A state of a system is described by a density operator  $\rho$ . Necessarily,  $\rho$  is a positive, self-adjoint, trace class operator

$$\text{Tr}\rho < \infty \quad (31)$$

on the Hilbert space  $\mathfrak{H}$ . In this work the Banach space of Hilbert-Schmidt class operators [15] on  $\mathfrak{H}$  is referred to as the Liouville space  $\mathfrak{L}$ . This is a subspace of the tensor product space  $\mathfrak{H} \otimes \mathfrak{H}$ . An asymptotic Liouville space is introduced later. It should be stated that the terminology ‘‘Liouville space’’ has appeared in many places in the literature, being understood to be, to authors’ knowledge, the space of all operators on  $\mathfrak{H}$ . The present restriction seems more appropriate for this work. Any linear mapping from a Liouville space to the same or another Liouville space is referred to as a superoperator. The trace class operators, of which  $\rho$  is an element, is a subset of the Hilbert-Schmidt operators. The reason for explicitly selecting the Hilbert-Schmidt class, is that this allows the use of all the power of Hilbert space theory, in particular the notion of self-adjointness.

Since the expectation value for an observable  $A$  has the form

$$\langle A \rangle = \text{Tr}A\rho, \quad (32)$$

it is natural to write this expectation value as the Hilbert-Schmidt inner product  $\langle\langle A^\dagger | \rho \rangle\rangle$ . But this requires that the observable  $A$  corresponds to a Hilbert-Schmidt operator. But this does not fit all cases, for example, the normalization, Eq. (31), does not fit into this scheme since the identity is not a Hilbert-Schmidt operator. Thus only observables that are represented by Hilbert-Schmidt operators can be thought of in this way. But since real measurements are always limited in the range of values that they can observe, this latter restriction may be a reasonable compromise.

An alternate argument for the use of Hilbert-Schmidt theory in kinetic theory is when one considers only linear deviations from thermal equilibrium  $\rho_e = \exp(-H/k_B T) / \text{Tr} \exp(-H/k_B T)$ . One way of expanding the full density operator about equilibrium in terms of a perturbation  $\phi$  is to write

$$\rho = \rho_e + \rho_e^{1/2} \phi \rho_e^{1/2}. \quad (33)$$

This leaves the density operator to be self-adjoint even if  $\phi$  and  $\rho_e$  do not commute. An expectation value for observable  $A$  could then be written as

$$\langle A \rangle = \text{Tr}A\rho_e + \text{Tr}\rho_e^{1/4} A \rho_e^{1/4} \rho_e^{1/4} \phi \rho_e^{1/4}. \quad (34)$$

In the manner that it is written above each of  $\rho_e^{1/4} A \rho_e^{1/4}$  and  $\rho_e^{1/4} \phi \rho_e^{1/4}$  can be considered as a Hilbert-Schmidt operator even if  $A$  and/or  $\phi$  are only bounded, as long as the equilibrium density operator can provide sufficient convergence properties. Some other ways of linearization of the density operator are discussed in Ref. [16].

The time evolution of a density operator is given by a combination of Hilbert space evolution operators, Eq. (2), according to

$$\rho(t) = U(t)\rho U^\dagger(t) \equiv U(t)\rho. \quad (35)$$

Algebraically it is easily shown that the evolution superoperator can be written in exponential form

$$U(t) = e^{-i\mathbf{L}t} \quad (36)$$

in terms of its generator, the Liouville superoperator  $\mathbf{L}$ , which is the commutator of the Hamiltonian  $H$  with the operator on which it acts, in particular, acting on  $\rho$ ,

$$\mathbf{L}\rho \equiv H\rho - \rho H. \quad (37)$$

Technically, if equations involving  $\mathbf{L}\rho$  are to be used in kinetic theory,  $\rho$  must be in the domain of definition of  $\mathbf{L}$ . On the basis of our formulation in Hilbert-Schmidt space,  $\mathbf{L}$  can be defined as the self-adjoint extension of the commutator. As a self-adjoint superoperator  $\mathbf{L}$  has a domain of definition that is dense in  $\mathfrak{L}$ , so the requirements on the operator on which it can act is in principle well defined. Of course the evolution superoperator  $U(t)$  is bounded so is defined on all of  $\mathfrak{L}$ .

It is natural to further define an asymptotic density operator  $\wp$ , which is required to be a positive, self-adjoint and trace class operator on the Hilbert space  $\mathbb{H}$  and thus an element of  $\mathbb{H} \otimes \mathbb{H}$ . Mathematically the matrix elements of a density operator  $\wp$  have two channel indices and both diagonal and off-diagonal elements in channel label can occur. Physically, in a scattering experiment, the fragments are expected to be prepared in a particular channel long before a collision and a scattered state to be well resolved into one asymptotic channel at a time long after a collision. This is also assumed by Evans *et al.* [17]. As a consequence, in the remainder of this paper, the channel off-diagonal elements of  $\wp$  are taken to be identically zero and  $\wp$  reduces to the simple direct sum

$$\wp = \bigoplus_C \wp_C. \quad (38)$$

In this way the asymptotic Liouville space  $\mathbb{L}$  is considered in this work to be the restriction of  $\mathbb{H} \otimes \mathbb{H}$  to the direct sum of channel Liouville spaces  $\mathbb{L}_C$ . These are, in turn, the Hilbert-Schmidt subspaces of the respective tensor products  $\mathbb{H}_C \otimes \mathbb{H}_C$ . Thus,  $\mathbb{L} = \bigoplus_C \mathbb{L}_C$ , with each  $\mathbb{L}_C$  a proper subspace of  $\mathbb{L}$ ,  $\mathbb{L}_C \subset \mathbb{L}$ . For each channel  $C$  there is an asymptotic self-adjoint Liouville operator  $\mathbf{L}_C$  [here acting on  $\wp_C$ ] which is defined in terms of the asymptotic channel Hamiltonian  $\mathbf{H}_C$

$$\mathbf{L}_C \wp_C \equiv \mathbf{H}_C \wp_C - \wp_C \mathbf{H}_C, \quad \text{for } \wp_C \in \mathbb{L}_C. \quad (39)$$

In an analogous manner, an asymptotic Liouville operator  $\mathbf{L}$  is defined in terms of the asymptotic channel Hamiltonian  $\mathbf{H}$ . In particular, acting on the asymptotic density operator  $\wp$ , it is

$$\mathbf{L}\wp = \mathbf{H}\wp - \wp\mathbf{H}, \quad \text{for } \wp \in \mathbb{L}. \quad (40)$$

As a consequence of the restricted channel diagonality of  $\wp$ , it follows that the asymptotic Liouville operator  $\mathbf{L}$  is diagonal in channel label according to

$$\mathbf{L}\wp = \bigoplus_C \mathbf{L}_C \wp_C. \quad (41)$$

This argument of asymptotic diagonality leads to a two-Liouville space scattering formalism which parallels the existing Liouville space multichannel scattering theory both of Lowry and Snider [1] and of Evans *et al.* [17].

While the full evolution of the  $n$ -body system is governed by the superoperator  $U(t)$ , Eq. (36), the asymptotic evolution is determined by the asymptotic evolution superoperator

$$\mathbf{U}(t) = e^{-i\mathbf{L}t}. \quad (42)$$

The connection between the Liouville space  $\mathfrak{L}$  and the asymptotic Liouville space  $\mathbb{L}$  is via the identification mapping  $\mathcal{J}$ . This is the composite of channel identification superoperators according to

$$\mathcal{J}\wp \equiv \bigoplus_C \mathcal{J}_C \wp_C \equiv \bigoplus_C \mathcal{J}_C \wp_C \mathcal{J}_C^\dagger = \bigoplus_C \rho_C = \rho, \quad \forall \wp \in \mathbb{L}. \quad (43)$$

It is the channel diagonality of  $\wp$  that simplifies this identification to a direct sum. The adjoint  $\mathcal{J}^\dagger$  of the identification mapping maps  $\mathbb{L}$  to  $\mathfrak{L}$ , but in a nonunique manner, compare the analogous properties of the adjoint Hilbert space identification operator, Eq. (18).

## V. TWO-LIOUVILLE SPACE SCATTERING THEORY

A two-Liouville space scattering formalism suitable for kinetic theory is now developed. Jauch *et al.*'s [12] method of defining what is referred to here as a Møller superoperator is adapted for each channel. These are then combined to give a Møller superoperator appropriate for the complete asymptotic state space  $\mathbb{L}$ . A non-symmetrical transition superoperator and its channel components are defined from the asymptotic Liouville space back to itself. Such non-symmetrical transition superoperators are found to be convenient for formulating kinetic theory in the asymptotic channel Liouville spaces [1,8].

For single channel scattering, Jauch and co-workers [12] argued that the trace norm is appropriate for the formulation of the asymptotic scattering condition. Adapting their criteria to the single channel  $C$ , with the insertion of the identification mapping  $\mathcal{J}_C$  and using the superoperator notation introduced above, their asymptotic condition is the question of the existence of  $\Omega_C \wp_C$  as determined by the existence of the limit

$$\text{Tr}|U(-t)\mathcal{J}_C\mathbf{U}_C(t)\wp_C - \Omega_C\wp_C| \rightarrow 0 \quad (44)$$

as  $t \rightarrow -\infty$ . [see Refs. [12,15] for the definition of the positive operator  $|A|$  associated with operator  $A$ .] Jauch *et al.* [12] further prove (for the single channel case, so here applied to an individual channel  $C$ ) that there is a partial isometry  $\Omega_C$  of the Hilbert space in terms of which the Møller superoperator may be expressed, namely

$$\Omega_C\wp_C = \Omega_C\wp_C\Omega_C^\dagger. \quad (45)$$

This  $\Omega_C$  is a generalization [12] of the Møller operator in that there is, in general, a time dependent phase factor  $\xi_C(t)$  that enters into the Hilbert space convergence criteria, Eq. (19), namely

$$\lim_{t \rightarrow -\infty} \|U(t)\Psi - \xi_C(t)\mathcal{J}_C\mathbf{U}_C(t)\Phi_C\| \rightarrow 0, \quad (46)$$

where again the appropriate identification mapping  $\mathcal{J}_C$  has been introduced. If the Møller operator for channel  $C$  exists, Eq. (19), then clearly  $\xi_C(t) = 1$  and the isometry  $\Omega_C$  is the corresponding Møller operator.

Since  $\mathbb{L}$  is just the direct sum of the channel Liouville spaces, the two-Liouville space Møller superoperator  $\Omega$  acting on  $\mathbb{L}$  is just the sum

$$\Omega = \sum_C \Omega_C \quad (47)$$

of the individual channel Møller superoperators acting on their respective asymptotic channel spaces. An equivalent formulation is in terms of the trace operator limit of the two Liouville space evolution superoperators

$$\begin{aligned} \Omega &\equiv \lim_{t \rightarrow -\infty} U(-t)\mathcal{J}\mathbf{U}(t) \\ &= \lim_{t \rightarrow -\infty} e^{i\mathbf{L}t}\mathcal{J}e^{-i\mathbf{L}t}. \end{aligned} \quad (48)$$

On the basis that  $\mathcal{J}_C$  vanishes on all  $\mathbb{H}_{C'}$  for  $C' \neq C$ , the sum

$$\Omega = \sum_C \Omega_C \quad (49)$$

of channel isometric operators can be used to express the action of the total Møller superoperator as

$$\Omega\wp = \Omega\wp\Omega^\dagger. \quad (50)$$

Note that this reduces to the sum of actions on the individual channel Liouville spaces. The properties of the partial isometries  $\Omega_C$  have not been explored, specifically whether their ranges are orthogonal. A non-orthogonality could arise because of the presence of the  $\xi_C(t)$  factors. But if the analogous Møller operators exist, then the  $\Omega_C$  coincide with their respective Møller operators with their well known properties, and  $\Omega$  becomes a partial isometry, but now from the full asymptotic Hilbert space  $\mathbb{H}$  to  $\mathcal{H}_\infty$ .

Since the Liouville spaces are defined as being of Hilbert-Schmidt class, the adjoints for the channel Møller superoperators are well defined. As in Hilbert space scattering, the evolution superoperators for different channels are different, with the consequence that the channel Møller superoperators satisfy an asymptotic channel orthogonality condition,

$$\Omega_C^\dagger \Omega_B = \delta_{C,B} \mathbf{P}_C, \quad (51)$$

a completeness condition,

$$\sum_C \Omega_C \Omega_C^\dagger = \sum_C \mathbf{Q}_C = \mathbf{Q}, \quad (52)$$

and intertwining relations

$$\mathbf{L} \Omega_C = \Omega_C \mathbf{L}_C. \quad (53)$$

Here the  $\mathbf{P}_C$  ( $\mathbf{P}_C \mathbf{A} \equiv \mathbf{P}_C \mathbf{A} \mathbf{P}_C$ ) are the asymptotic channel projection superoperators on  $\mathbb{L}$ , the asymptotic Liouville space [note that  $\mathbf{L}$  has been assumed to be diagonal in channel label].  $\mathbf{Q}_C$  is an orthogonal projection of the full  $n$ -particle Liouville space  $\mathcal{L}$  onto the range  $\mathcal{R}(\Omega_C)$  of the Møller superoperator.  $\mathbf{Q}$  projects onto all scattering states that are standardly considered as chemically relevant, with the  $n$ -particle bound states as the remainder. But what is left out of this, is the projection onto the parts of  $\mathcal{L}$  which are naturally associated with channel off-diagonal parts of the asymptotic space (the Hilbert-Schmidt part of)  $\mathbb{H} \otimes \mathbb{H}$ . Such subspaces as  $\mathbb{H}_C \otimes \mathbb{H}_D$  with  $C \neq D$ , and consequently their scattering analogs  $\Omega_{\mathbb{H}_C} \otimes \mathbb{H}_D \Omega^\dagger$ , are standardly not considered in the chemical literature, contrast Ref. [18]. In this work  $\mathbf{L}$  was defined to exclude such possible contributions to an asymptotic state, but formally they exist and must be included in a complete analysis of the decomposition of  $\mathcal{L}$  into subspaces associated with scattering processes. Finally, the intertwining relations, Eq. (53), imply frequency conservation and are useful in kinetic theory calculations.

A transition superoperator  $\mathbf{T} : \mathbb{L} \rightarrow \mathbb{L}$  is defined as

$$\mathbf{T} \equiv \mathcal{V}^\dagger \Omega, \quad (54)$$

where the potential superoperator  $\mathcal{V} : \mathbb{L} \rightarrow \mathcal{L}$  is defined as

$$\mathcal{V} \equiv \mathbf{L} \mathcal{J} - \mathcal{J} \mathbf{L}, \quad (55)$$

compare the definition of the potential in two-Hilbert space theory, see e.g. Ref. [5], and

$$\mathcal{V}^\dagger \equiv \mathcal{J}^\dagger \mathbf{L} - \mathbf{L} \mathcal{J}^\dagger. \quad (56)$$

Here the adjoint is defined via the properties of the space of Hilbert-Schmidt operators.  $\mathbf{L}$  and  $\mathbf{L}_C$  are self-adjoint in their appropriate Liouville spaces. As defined here, the transition superoperator appears as it does in kinetic theory [1,13,19], and is, as shown in Appendix B, also consistent with the standard work of Chandler and Gibson [5].

The asymptotic channel transition superoperators  $\mathbf{T}_{C,B} : \mathbb{L}_B \rightarrow \mathbb{L}_C$  can also be defined as

$$\mathbf{T}_{C,B} \equiv \mathcal{V}_{C,B}^\dagger \Omega_B \quad (57)$$

with

$$\mathcal{V}_C \equiv \mathbf{L} \mathcal{J}_C - \mathcal{J}_C \mathbf{L}_C, \quad (58)$$

and

$$\mathcal{V}_C^\dagger \equiv \mathcal{J}_C^\dagger \mathbf{L} - \mathbf{L}_C \mathcal{J}_C^\dagger. \quad (59)$$

These are restricted forms of Eqs. (55) and (56). The channel transition superoperators  $\mathbf{T}_{C,B}$  describe rearrangement scattering from the asymptotic channel  $B$  to the asymptotic channel  $C$ . There are also channel transition superoperators emphasizing the final operator state interactions

$$\mathbf{T}_C \equiv \mathcal{V}_C^\dagger \Omega = \sum_B \mathbf{T}_{C,B}. \quad (60)$$

The transition superoperator  $\mathbf{T}$  can be expressed in terms of the channel transition superoperators  $\mathbf{T}_C$  according to

$$\mathbf{T} = \bigoplus_C \mathcal{V}_C^\dagger \Omega = \bigoplus_C \mathbf{T}_C = \bigoplus_C \sum_B \mathbf{T}_{C,B}. \quad (61)$$

This makes multichannel scattering theory appear like single channel scattering theory, thus simplifying the formal structure of multichannel scattering theory.

## VI. DISCUSSION

A major problem in setting up a fundamentally based kinetic theory for the description of a chemically reacting system is the inherent inability to uniquely specify which particles are bound together, or even if any particles are bound together. For example, is particle 1 bound to particle 8?, to particle 888?, to both?, or to neither? This is due to the lack of orthogonality of different bound states in the  $N$ -particle system. Essentially, whether a set of particles are bound together is determined by the Hamiltonian for that set of particles, and not by the total Hamiltonian of the  $N$ -particle system. The introduction of an asymptotic space provides a way of uniquely deciding such questions.

As a part of statistical mechanics, kinetic theory necessarily involves probabilities and must therefore be formulated in terms of distribution functions, or their quantum analogs, density operators. Thus a Liouville space description of all aspects of the time evolution of the system is required, in particular the description of scattering processes and chemically reacting collisions. In order to also express the various asymptotic states, this paper has introduced a two-Liouville space scattering theory. The structure of this formulation is based on the standard two-Hilbert space scattering theory of Kato [4], Chandler and Gibson [5] and others [6,7]. This is in contrast to the arrangement channel quantum mechanics formulation of Evans *et al.* [17] of multichannel scattering theory that they introduced for application to kinetic theory. It is the authors opinion that the present formulation is more direct than that of Evans *et al.*, for example, there are no non-physical (spurious) parts of the mathematics that must be avoided. While the emphasis of the presentation is on trying to properly describe the physical picture, it is necessary that various operator spaces have to be properly identified. Thus it is recognized that density operators are elements of the Banach space of trace class operators. This has the disadvantage that the thermodynamic limit cannot be rigorously taken, an aspect that is of great utility in kinetic theory, but has the advantage that it allows the convergence properties of superspace scattering theory [12,13] to be used as a justification for the existence of various Møller superoperators. Moreover, for mathematical convenience, Liouville space has been restricted here to be a Hilbert-Schmidt space, of which the trace class operators are a particular subset.

In any multichannel scattering theory, superpositions among different rearrangement channels naturally arise, necessarily so, for rearrangement reactions to occur. Asymptotically, the method of preparation and/or measurement of the scattering system usually selects out the specific rearrangement channel, so that at that stage there is no physical meaning for any channel superposition. Essentially, a decoherence among the different channel states at asymptotic times is indispensable in the detection process. The same argument has been applied here to exclude off-diagonalities in asymptotic channels in an asymptotic density operator  $\varphi$ , Eq. (38). In contrast, an off-diagonality in channel labels is naturally present in the (full) interacting density operator  $\rho$ , being responsible for the rearrangement processes. The resulting two-Liouville space theory with asymptotic channel diagonality is consistent both with the physical picture of a chemically reacting system and with the existing one-Liouville space multichannel scattering treatment [1], which is based on an assumption of strong orthogonality. The resulting two-Liouville space formalism provides a suitable basis for the description of chemical reactions in gas kinetic theory, clarifying various concepts and simplifying the structure of the kinetic equations [8]. In contrast, the statistical presence of certain off-diagonal elements at equilibrium have been discussed by Krishnan and Snider [18].

A number of different transition operators have been discussed in Chandler and Gibson's work [5]. As explicitly demonstrated in Appendix B, the transition superoperators defined here are parallel to the nonsymmetric transition operators ( $\mathbf{T}^{(+)}$ ) defined in their work. The form of the transition superoperators in this work, Eqs. (54) and (57), is similar in form to the superspace scattering theory discussed by Evans *et al.* [17], and that used in kinetic theories [1,13,19]. The validity of the latter has been questioned [20–22]. Similar non-symmetric multichannel transition operators have been used by Lovelace [23], see also the monographs by Schmid and Ziegelmann [24] and by Glöckle [25]. Some recent progress on the existence of the Møller operator and strong completeness can be found in the books by Cycon, Froese, Kirsch and Simon [26] and Yafaev [27].

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## APPENDIX A: COUNTING NUMBERS OF CHANNELS

The number of channels depends on which sets of particles have a Hamiltonian which supports bound states. One extreme is that in which there are no bound states, and consequently only one channel, in which all particles are free. The opposite extreme is when the Hamiltonian for every set of particles supports bound states. In this case, the number of possible channels  $N(n)$  for an  $n$ -particle system can be calculated in the following way.

Consider the first particle, particle 1. This particle can be in a given channel either as an unbound particle, as a particle bound to one other particle, as a particle bound to two other particles, etc. If unbound, then there are  $N(n-1)$  ways in which the remaining  $n-1$  particles can be distributed among bound states. On the other hand, if particle 1 is pairwise bound, there are  $n-1$  possible particles with which it could be bound. As well, there are  $N(n-2)$  ways in which the remaining  $n-2$  particles can be distributed among bound states. Continuing in this way, the number of ways that particle 1 can form a  $j+1$ -bound state is a combinatorial factor, and the remaining particles have  $N(n-j-1)$  ways of forming bound states. Summing these possibilities together gives

$$N(n) = \sum_{j=0}^{n-1} \binom{n-1}{j} N(n-1-j) \tag{A1}$$

as an equation that can be solved iteratively, starting with  $N(0) = 1$ , for the maximum number of channels. The values for  $n=1$  to 6 are given in Sec. II.B. These numbers can be recognized as the Bell numbers [14].

An intermediate, but important case, is the situation where only dimer bound states are allowed, besides the possibility that the particles are not bound. This can be calculated by summing over all possible numbers of dimers, the count given in Ref. [1] for a fixed number of dimers. Alternatively the count can be obtained by keeping only the first two terms in Eq. (A1), namely

$$N_2(n) = N_2(n-1) + [n-1]N_2(n-2), \tag{A2}$$

and solving iteratively, starting with  $N_2(0) = 1$ . The values for  $n=1$  to 6 are also given in Sec. II.B.

## APPENDIX B: DIFFERENT FORMS FOR THE TRANSITION SUPEROPERATOR

The transition superoperator in this work as defined by Eq. (54), ( $\mathbf{T} = \mathcal{V}^\dagger \Omega$ ), is consistent with existing work on superspace scattering [1,13,17,19] and convenient for kinetic theory applications. The transition operator in Chandler and Gibson's [5] two-Hilbert space theory has a different formal structure, namely

$$\mathbf{T}(z) \equiv (z - \mathbf{H}) \{ \mathcal{J}^\dagger (z - H)^{-1} J - (z - \mathbf{H})^{-1} \mathcal{J}^\dagger J \} (z - \mathbf{H}). \quad (\text{B1})$$

Besides the obvious difference between one formula being for an operator and the other for a superoperator, Chandler and Gibson's formula contains an energy parameter  $z$  with positive imaginary part. It is the purpose of this appendix to introduce the analog of Eq. (B1) for a transition superoperator, and to clarify the relation between this and the  $\mathbf{T}$  of Eq. (54).

The abstract Møller superoperator  $\Omega$  of Eq. (48) is defined only when acting on trace class operators. In order to introduce a convergence parameter, it is necessary to extend this definition to include the spectral measure for the Liouville operator. This is conveniently done through the integral form for the Møller superoperator

$$\Omega = \mathcal{J} - i \int_{-\infty}^0 e^{i\mathbf{L}t} \mathcal{V} e^{-i\mathbf{L}t} dt. \quad (\text{B2})$$

Note that the usual identity in this type of equation must be replaced by the identification mapping  $\mathcal{J}$ . With the introduction of a convergence factor  $e^{\epsilon t}$ , the integral form

$$\begin{aligned} \Omega &= \mathcal{J} - i \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^0 dt e^{\epsilon t} e^{i\mathbf{L}t} \mathcal{V} e^{-i\mathbf{L}t} \\ &= \mathcal{J} - i \lim_{\epsilon \rightarrow 0^+} \int \int_{-\infty}^0 dt e^{(-i\omega + \epsilon)t} e^{i\mathbf{L}t} \mathcal{V} d\mathcal{P}_\omega \end{aligned} \quad (\text{B3})$$

can be extended so that it is defined on more general operators. This procedure is similar to that presented for the Hilbert space Møller operator by Chandler and Gibson's [5]. Here  $\mathcal{V}$  is given by Eq. (55) and the spectral representation of the asymptotic evolution superoperator is given by

$$e^{-i\mathbf{L}t} = \int e^{-i\omega t} d\mathcal{P}_\omega \quad (\text{B4})$$

in terms of the spectral measure  $\mathcal{P}_\omega$  of the self-adjoint superoperator  $\mathbf{L}$  in the Hilbert-Schmidt space  $\mathbb{L}$ . By carrying out the time integral in Eq. (B3), the Møller superoperator can be written as

$$\begin{aligned} \Omega &= \lim_{\epsilon \rightarrow 0^+} \int [\mathcal{J} + (\omega - \mathbf{L} + i\epsilon)^{-1} \mathcal{V}] d\mathcal{P}_\omega \\ &\equiv \lim_{\epsilon \rightarrow 0^+} \int \Omega(\omega + i\epsilon) d\mathcal{P}_\omega. \end{aligned} \quad (\text{B5})$$

The transition superoperator can also be written (for  $z$  an arbitrary complex number with positive imaginary part) in terms of the spectral representation of the asymptotic Liouville operator

$$\mathbf{T} = \lim_{\epsilon \rightarrow 0^+} \int \mathbf{T}(\omega + i\epsilon) d\mathcal{P}_\omega \quad (\text{B6})$$

with spectral component

$$\begin{aligned} \mathbf{T}(z) &\equiv \mathcal{V}^\dagger \Omega(z) = \mathcal{V}^\dagger [\mathcal{J} + (z - \mathbf{L})^{-1} \mathcal{V}] \\ &= (\mathcal{J}^\dagger \mathbf{L} - \mathbf{L} \mathcal{J}^\dagger) [\mathcal{J} + (z - \mathbf{L})^{-1} (\mathbf{L} \mathcal{J} - \mathcal{J} \mathbf{L})] \\ &= [(z - \mathbf{L}) \mathcal{J}^\dagger - \mathcal{J}^\dagger (z - \mathbf{L})] (z - \mathbf{L})^{-1} \mathcal{J} (z - \mathbf{L}) \\ &= (z - \mathbf{L}) \left[ \mathcal{J}^\dagger (z - \mathbf{L})^{-1} \mathcal{J} - (z - \mathbf{L})^{-1} \mathcal{J}^\dagger \mathcal{J} \right] (z - \mathbf{L}). \end{aligned} \quad (\text{B7})$$

Clearly this is the two-Liouville space analog of the two-Hilbert space transition operator (B1) of Chandler and Gibson [5].