Arrangement Channel Quantum Mechanics :A General Time Dependent Formalism for Multiparticle SystemsD.J. Kouri⁺)

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Abstract

A new time dependent quantum mechanical formulation of the multichannel scattering problem is set up which takes explicit account of each separate arrangement channel. Such a formulation avoids the usual difficulties connected with the non-orthogonality of state vectors in different arrangements. It further leads in a natural way to the definition and explicit realization of a super-scattering operator as well as similar super-transition and Møller operators. Moreover this super-scattering operator is found to be the strong limit of the evolution operator in a generalized interaction picture. After projecting onto the channel arrangement basis vectors, these super-operators lead to matrices of more familiar channel arrangement operators, e.g., channel T operators in the case of the super T operator.

As an example of the considerable formal simplification resulting in the present approach, the problem of constructing orthogonal projection operators is discussed briefly: The method is also shown to yield simple approximation schemes for the general n-body scattering problem.

I. Introduction

Recently, Baer and Kouri ¹ presented new coupled integral equations for rearrangement channel T operators and applied them to various model problems ². A more general form of these equations was also developed by means of introducing the channel coupling array W_{ij} , the elements of which determine which arrangements are explicitly coupled in the integral equations ³. In this work, the Baer-Kouri equations were also applied to the case of $e^- + H$ scattering at low energies. In spite of quite good agreement of the phases with results of more accurate calculations, it was observed that flux conservation was violated. Subsequently, Kouri and Levin ⁴ have derived a new set of coupled equations for the rearrangement channel T operators which likewise yield the same accurate phases but which also lead to accurate flux conservation in similar approximate applications ⁵ to $e^- + H$. The techniques for obtaining these new equations and their form are similar to those of the equations derived by Baer-Kouri but there are important differences. In particular, the equations derived by Kouri-Levin lead to a simple Heitler damping equation relating the channel T operators to new channel reactance (K) operators, the equations for which are obtained by simply replacing outgoing wave boundary condition channel Green operators by standing wave boundary condition Green operators in the coupled T equations ⁶. In addition, this new formulation leads in simple fashion to coupled equations for channel Møller wave operators and their

concomitant Lippman-Schwinger equations for channel scattering states, to new Schrödinger-type equations, to channel matrix generalizations of Schwinger and Kohn-type variational principles, and to simple expressions for arrangement channel optical potentials which explicitly display the complex, non-local and energy-dependent effects of open rearrangement channels on the nonreactive channel ⁶⁻⁷. The fact that the equations derived by Kouri-Levin lead to a simple damping equation has been used to explain why the approximate application of the equations due to B-K violate flux conservation while the equations due to K-L satisfy it ⁸.

It has been also demonstrated that for a system involving N arrangements, that it is possible to find at least $(N-1)!$ distinct choices of the channel coupling array W_{ij} such that the $(N-1)$ st iterated kernel of these coupled equations is completely connected ^{4,6,9} (this is true for both types of coupled T equations). Thus, the presence of the W_{ij} provides a great flexibility in the resulting structure of the coupled equations and in particular, provides an extremely simple means of assuring that standard mathematical approximations may be applied in solving the coupled equations. Computational studies of the effect on low energy $e^- + H$ scattering parameters suggest that the W_{ij} which lead to connected iterated kernels provide the most accurate bases for approximate calculations ¹⁰.

In this present paper, we shall consider this approach from a time dependent viewpoint. Our approach is basically the same as that employed in earlier studies of similar coupled equations by Eyges ¹¹, Hahn ¹², Diestler and Krüger ¹³ and by Hahn, Kouri and Levin ¹⁴. A form of coupled equations with connected kernels has also been developed by Krüger ¹⁵ and used as the basis for deriving time dependent coupled equations for statevector partitions. These equations, like those of Levin and Kouri ^{4,6}, also lead to the simple introduction of a damping relation. Furthermore, these equations, by construction, are free of Federbush disease ¹⁶. The primary result of this analysis was the development of a generalized interaction picture by which one is able to introduce a single operator for describing multichannel scattering. This leads to new expressions for the arrangement channel S matrix elements. In our present study, we shall be applying similar procedures to the coupled equations into which we also introduce the W_{ij} . Thus, a special choice of W_{ij} yields the results obtained earlier by Krüger. Of course, the present results contain also an infinity of other possible choices of the W_{ij} .

In Section II, we present the derivation of the fundamental time dependent coupled equations for the state vector partitions and the concomitant formal apparatus. In addition, we explicitly display the connection of the present general formulation to the more conventional formulation of time dependent scattering in the Schrödinger picture.

In Section III, we briefly discuss the generalized interaction picture and explicitly show that a single "super-scattering operator" can be obtained as the limit of the "super-evolution operator", just as in the single channel scattering theory.

In Section IV, we present a brief consideration of orthogonal projectors to further illustrate the simplifications afforded by the present method.

Finally in Section V, we discuss several possible approximation schemes for applying this new quantum mechanical formulation.

II. Generalized Time Dependent Equation

We shall restrict our consideration to nonrelativistic systems of n -particles which can interact via velocity independent potentials. These are assumed to behave in such a way as to permit the definition of asymptotic states ¹⁷. (No restriction to pairwise additive interactions is made.)

We therefore may decompose the full Hamiltonian H in a number of ways, corresponding to arrangement channels, so that

$$H = H_i + V_c, \quad i = 1, 2, \dots, N. \quad (1)$$

The full state vector $|\psi_i(t)\rangle$ satisfies

$$i\hbar \frac{\partial}{\partial t} |\psi_i(t)\rangle = H |\psi_i(t)\rangle, \quad (2)$$

where the index i denotes the initial arrangement of the systems from which the full state develops.

Then following Eyges ¹¹, Hahn ¹², Diestler and Krüger ¹³ and Hahn, Kouri and Levin ¹⁴, we decompose the statevector into channel components via

$$|\psi_i(t)\rangle = \sum_{k=1}^N |\psi_{ki}(t)\rangle. \quad (3)$$

We require that the $|\psi_{ki}(t)\rangle$ satisfy the system

$$i\hbar \frac{\partial}{\partial t} |\psi_{ki}(t)\rangle = \sum_{l=1}^N H_{kl} |\psi_{li}(t)\rangle, \quad (4)$$

where

$$H_{kl} = \delta_{kl} H_c + W_{kl} V_c. \quad (5)$$

By taking the elements of H_{kl} in the form of Eq. (5) above, we are assured that the solutions to Eq. (4) are the channel components of the state $|\psi_i(t)\rangle$ satisfying the usual time dependent Schrödinger equation.

For this to be true, we also require the W_{kl} to satisfy the doubly constraint relation

$$\sum_{k=1}^N W_{kl} = \sum_{l=1}^N W_{kl} = 1. \quad (6)$$

It is obvious, by direct summation over k in Eq. (4) and use of Eq. (6), that Eq. (3) does indeed satisfy the time dependent Schrödinger equation.

It is important to note, by the form of Eqs. (4) and (5), that the elements of the W -array determine which arrangements are explicitly coupled in the equations^{3-4,6}. In fact, the use of the W -array permits one to formulate the equations in the most general way rather than in terms of a specific choice of coupling^{1-2,13-15}. In addition, the W -array can be used to ensure that the integral equation form of (4) will possess a kernel which, upon iteration, is completely connected^{4,6}. Thus, it can be used to assure that the equations can be

solved by standard numerical methods. Finally, it has been noted elsewhere that the W -array permits one to explicitly incorporate all necessary boundary conditions ^{4,9} into the solution of Eq. (4). In order to illustrate, we note for example a three arrangement channel permuting W -array, which has been employed in earlier discussions to obtain equations having connected iterated kernels ^{4,7,9} :

$$\underline{W} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} .$$

The explicit form of (4) then becomes

$$\left(i\hbar \frac{\partial}{\partial t} - H_1 \right) |\psi_{1i}(t)\rangle = V_2 |\psi_{2i}(t)\rangle ,$$

$$\left(i\hbar \frac{\partial}{\partial t} - H_2 \right) |\psi_{2i}(t)\rangle = V_3 |\psi_{3i}(t)\rangle ,$$

$$\left(i\hbar \frac{\partial}{\partial t} - H_3 \right) |\psi_{3i}(t)\rangle = V_1 |\psi_{1i}(t)\rangle .$$

The cyclic nature of the coupling due to the channel permuting arrays is evident from this example.

It is convenient to introduce matrix notation by writing Eq. (4) as

$$i\hbar \frac{\partial}{\partial t} |\underline{\psi}(t)\rangle = \underline{H} |\underline{\psi}(t)\rangle \quad (7)$$

where clearly,

$$(\underline{H})_{kl} = H_{kl} \quad (8)$$

and

$$\left(|\underline{\Psi}(t)\rangle \right)_{ki} = |\Psi_{ki}(t)\rangle. \quad (9)$$

Noting Eq. (1), it will also be convenient to introduce the diagonal unperturbed Hamiltonian matrix by

$$\left(\underline{H}_0 \right)_{kl} = \delta_{kl} H_l. \quad (10)$$

We now wish to discuss the time evolution of $|\underline{\Psi}(t)\rangle$, and we therefore introduce in analogy to standard quantum mechanics an evolution operator by the condition

$$|\underline{\Psi}(t)\rangle = \underline{U}(t, t_0) |\underline{\Psi}(t_0)\rangle, \quad (11)$$

and for Hamiltonians $\underline{H}$ not depending explicitly on time, $\underline{U}(t, t_0)$ is given by

$$\underline{U}(t, t_0) = \exp(-i \underline{H}(t-t_0)/\hbar). \quad (12)$$

In addition, the unperturbed Hamiltonian $\underline{H}_0$ possesses eigenstates of the form

$$\left(|\underline{\varphi}\rangle \right)_{ki} = \delta_{ki} |\varphi_i(r)\rangle, \quad (13)$$

where i denotes the arrangement index and r the (collective) internal state quantum numbers. For physical initial or final states, we have

$$\underline{H}_0 |\underline{\varphi}\rangle = E |\underline{\varphi}\rangle. \quad (14)$$

Here, E is the total energy and we note that all initial states have the same total energy regardless of which particular internal states of each arrangement are involved. The time evolution of these states is given by

$$|\underline{\varphi}(t)\rangle = \exp(-i \underline{H}_0 t/\hbar) |\underline{\varphi}\rangle \quad (15)$$

$$= \exp(-i E t/\hbar) |\underline{\varphi}\rangle. \quad (16)$$

Since by assumption, all interactions V_i in Eq. (1) vanish sufficiently rapidly, we may define a matrix Møller operator $\underline{\Omega}_\pm$ as the strong limit¹⁸

$$\underline{\Omega}_\pm = \lim_{t \rightarrow \pm\infty} \exp(i \underline{H} t/\hbar) \exp(-i \underline{H}_0 t/\hbar). \quad (17)$$

We note that $\underline{\Omega}_+$ maps the statevector $|\underline{\varphi}\rangle$ into $|\underline{\psi}(0)\rangle$:

$$|\underline{\psi}(0)\rangle = \underline{\Omega}_+ |\underline{\varphi}\rangle, \quad (18)$$

so that $|\underline{\psi}(t)\rangle$ is expressed as

$$|\underline{\psi}(t)\rangle = \exp(-i \underline{H} t/\hbar) \underline{\Omega}_+ |\underline{\varphi}\rangle. \quad (19)$$

Also, $\underline{\Omega}_+$ satisfies a general intertwining relation

$$\underline{H} \underline{\Omega}_+ = \underline{\Omega}_+ \underline{H}_0. \quad (20)$$

Combining Eqs. (19) and (20), we see that

$$|\underline{\Psi}(t)\rangle = \exp(-iEt/\hbar) \underline{\Omega}_+ |\underline{\varphi}\rangle. \quad (21)$$

At this stage, we are now prepared to show how one obtains the S-matrix elements in this formalism. The standard approach leads to the expression ^{17,19}

$$\bar{S}_{fi} = \lim_{t \rightarrow +\infty} \langle \varphi_f(y') | \exp(iH_f t/\hbar) | \psi_i(t) \rangle. \quad (22)$$

We now show that this is given by the f, i matrix element of

$$\underline{S} = \lim_{t \rightarrow +\infty} \langle \underline{\varphi}' | \exp(i\underline{H}_0 t/\hbar) | \underline{\Psi}(t) \rangle, \quad (23)$$

where the state $|\underline{\varphi}'\rangle$ is the diagonal matrix

$$(|\underline{\varphi}'\rangle)_{f\ell} = \delta_{f\ell} |\varphi_f(y')\rangle \quad (24)$$

satisfying the energy eigenvalue equation

$$\underline{H}_0 |\underline{\varphi}'\rangle = E' |\underline{\varphi}'\rangle. \quad (25)$$

Note, the energy E' may, at this point, differ from the energy E of the states $|\underline{\Psi}(t)\rangle$ and $|\underline{\varphi}\rangle$.

Thus, we consider the matrix element of Eq. (23), making use of the diagonal character of $\langle \underline{\varphi}' |$ and $\exp(i H_0 t / \hbar)$

$$S_{fi} = \lim_{t \rightarrow +\infty} \langle \varphi_f(y') | \exp(i H_f t / \hbar) | \psi_{fi}(t) \rangle. \quad (26)$$

We now recall the partitioning of $|\psi_i(t)\rangle$, Eq. (3), so that the standard $\bar{S}_{fi}$ expression, Eq. (22), is written as

$$\bar{S}_{fi} = \lim_{t \rightarrow \infty} \langle \varphi_f(y') | \exp(i H_f t / \hbar) \sum_{k=1}^N |\psi_{ki}(t)\rangle, \quad (27)$$

and we must show the asymptotic projection property

$$\lim_{t \rightarrow \infty} \langle \varphi_f(y') | \exp(i H_f t / \hbar) | \psi_{ki}(t) \rangle = 0, \quad k \neq f. \quad (28)$$

We may trivially rewrite Eq. (28) by inserting the identity in the form $\exp(-i H_k t / \hbar) \exp(i H_k t / \hbar)$ and the complete set of channel eigenstates of H_k , so that

$$\begin{aligned} \lim_{t \rightarrow \infty} \sum_j \langle \varphi_f(y') | \exp(i H_f t / \hbar) \exp(-i H_k t / \hbar) | \varphi_k(y) \rangle \langle \varphi_k(y) | \exp(i H_k t / \hbar) | \psi_{ki}(t) \rangle &= \\ &= \lim_{t \rightarrow \infty} \sum_j \langle \varphi_f(y') | \exp(i H_f t / \hbar) \exp(-i H_k t / \hbar) | \varphi_k(y) \rangle b_k^j(t) \end{aligned} \quad (29)$$

Now the overlap $\langle \varphi_f(y') | \exp(i H_f t / \hbar) \exp(-i H_k t / \hbar) | \varphi_k(y) \rangle$ for $k \neq f$ vanishes in the limit¹⁹ and furthermore $b_k^j(t)$ remains bounded. This latter may be seen from an interaction picture description of the $|\psi_{ki}(t)\rangle$ as developed, e.g., in Eqs. (63) and (75) of this paper. It then follows that Eq. (28) above does hold, which then implies that Eq. (22) for the standard

scattering matrix element $\bar{S}_{fi}$ and S_{fi} of Eq. (26) are equal. It is of interest to contrast the extreme simplicity with which we obtain the result Eq. (26), involving only the f channel component $|\psi_{fi}(t)\rangle$, by our new generalized formalism with the conventional approach to rearrangements. This is the first of a number of points at which the present formalism provides a much more convenient description of multi-channel scattering than is afforded by formalisms in which the arrangement channel aspect is implicit. Furthermore, although we have employed standard expressions for $\bar{S}_{fi}$ in order to demonstrate that Eq. (23) is the proper generalized $\underline{S}$ matrix, we could have avoided using Eq. (22) and shown directly that all measurable quantities are obtained from the generalized $\underline{S}$ matrix, by dealing instead with wavepackets and their time evolution²⁰.

Next we derive the time independent form of the generalized S operator. By Eq. (19), we can write Eq. (23) in the form

$$\underline{S} = \lim_{t \rightarrow \infty} \langle \underline{\varphi}' | \exp(i \underline{H}_0 t / \hbar) \exp(-i \underline{H} t / \hbar) \underline{\Omega}_+ | \underline{\varphi} \rangle, \quad (30)$$

which, by the standard manipulation of expressing the time limit in integral form, becomes

$$\begin{aligned} \underline{S} = \lim_{t \rightarrow \infty} \langle \underline{\varphi}' | \exp(i \underline{H}_0 t / \hbar) \exp(-i \underline{H} t / \hbar) | \underline{\varphi} \rangle - \\ - \frac{i}{\hbar} \int_{-\infty}^{+\infty} dt \langle \underline{\varphi}' | \exp(i \underline{H}_0 t / \hbar) (\underline{H} - \underline{H}_0) \exp(i \underline{H} t / \hbar) \underline{\Omega}_+ | \underline{\varphi} \rangle. \end{aligned} \quad (31)$$

However, by Eqs. (5), (8), (10), (21) and (25) this may be transformed into

$$\underline{\underline{S}} = \langle \underline{\varphi}' | \underline{\varphi} \rangle - \frac{i}{\hbar} \int_{-\infty}^{+\infty} dt \langle \underline{\varphi}' | \exp(i[\underline{H}_0 - E]t/\hbar) \underline{W} \underline{V} \underline{\Omega}_+ | \underline{\varphi} \rangle. \quad (32)$$

Introducing the matrix of transition operators $\underline{\underline{T}}$ by

$$\underline{\underline{T}} = \underline{W} \underline{V} \underline{\Omega}_+, \quad (33)$$

we find the result (on factoring out the energy conserving delta function) for the $\underline{\underline{S}}$ matrix

$$\underline{\underline{S}} = \underline{\underline{I}} - 2\pi i \underline{\underline{T}}, \quad (34)$$

where the matrix of numbers $\underline{\underline{T}}$ is defined in terms of the matrix of operators $\underline{\underline{T}}$ by

$$\underline{\underline{T}} = \langle \underline{\varphi}' | \underline{\underline{T}} | \underline{\varphi} \rangle. \quad (35)$$

Further, corresponding to Eqs. (34) and (35), we may now introduce a matrix of channel scattering operators $\underline{\underline{S}}$ such that

$$\underline{\underline{S}} = \underline{\underline{I}} - 2\pi i \delta(E_{\underline{\underline{S}}} - \underline{H}_0) \underline{\underline{T}} \quad (36)$$

where we note that $\underline{\underline{I}}$ is the identity operator in channel space and the operators $\underline{H}$ and $\underline{H}_0$ are also matrix representations in channel space of super Hamiltonian operators. It is

extremely important to emphasize that $\underline{T}$, $\underline{S}$, $\underline{I}$, $\underline{H}$ and $\underline{H}_0$ are all matrices of operators and in fact, are the matrix representations in channel arrangement space of super operators $\mathcal{T}$, $\mathcal{S}$, $\mathcal{I}$, $\mathcal{H}$ and $\mathcal{H}_0$, and the various arrangement channel operators (rather than numbers) are precisely the elements of the representation matrices. We therefore define them to be the channel matrix representation of the abstract super operators.

In the standard representation theory of quantum mechanics, given the basis of the representation, one may obtain the actual elements of the representation in terms of the matrix elements of the operators with respect to the basis. For example, the transition operator from arrangement i to arrangement j may be represented as a matrix of ordinary numbers by computing the matrix elements

$$T_{ji}(\mu'|\mu) = \langle \varphi_j(\mu') | T_{ji} | \varphi_i(\mu) \rangle$$

Now, the channel matrix, representation of the super $\mathcal{T}$ operator is also given in terms of a matrix element of $\mathcal{T}$ between members of the channel representation basis defined by the relation

$$T_{ji} = (j | \mathcal{T} | i).$$

We contrast the above two equations by noting that the j, i element of $\mathcal{T}$ is not a number but an operator, namely the channel $\mathcal{T}$ operator for transitions between arrangement i and j . It is clear that the vectors $|i\rangle$ are fundamentally different from the $|\varphi_i(\mu)\rangle$. In fact, for a given N arrangement system, they are simply the vector basis spanning an N dimen-

sional (orthogonal) space so that any vector in this space may be expressed in terms of them. Equally important is the fact that any $N \times N$ array of channel operators (such as $\underline{J}$, $\underline{S}$, $\underline{H}$, $\underline{H}_0$, etc.) can be expressed in terms of the N^2 dyads of the form

$$\underline{u}_{ij} = |i\rangle\langle j|.$$

To illustrate this point (and provide an explicit realization of the $|i\rangle$ for a specific case), let us consider $N=2$. Then the $|i\rangle$ are such that any 2×2 array in arrangement channel space can be expressed in terms of the $\underline{u}_{ij}$. This means an arbitrary matrix

$$\underline{O} = \begin{pmatrix} O_{11} & O_{12} \\ O_{21} & O_{22} \end{pmatrix}$$

is given by

$$\underline{O} = \sum_{i,j=1}^2 O_{ij} \underline{u}_{ij}.$$

It is trivially seen that

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$

$$|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

and

$$\underline{u}_{11} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (1 \ 0) = |1\rangle\langle 1|,$$

$$\underline{u}_{21} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} (1 \ 0) = |2\rangle\langle 1|,$$

$$\underline{u}_{11} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} (0 \ 1) = |1\rangle\langle 2|,$$

$$\underline{u}_{22} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} (0 \ 1) = |2\rangle\langle 2|.$$

It is equally evident that these do indeed span the space and further are orthonormal. It is also trivially seen that the $|i\rangle$ and $\underline{u}_{ij}$ may be explicitly constructed even in the general case of N arrangements; and that in general one has orthonormality of the $|i\rangle$:

$$\langle j | i \rangle = \delta_{ij}.$$

Now the arrangement channel representation of the super identity operator $\mathcal{I}$ is evidently given by

$$\mathcal{I} = \sum_{i=1}^N |i\rangle\langle i|, \quad (37)$$

and therefore we easily deduce that

$$\underline{\mathcal{I}} = \sum_{i,j=1}^N |i\rangle\langle i| \mathcal{I} |j\rangle\langle j|, \quad (38)$$

$$\underline{\mathcal{S}} = \sum_{i,j=1}^N |i\rangle\langle i| \mathcal{S} |j\rangle\langle j| \quad (39)$$

$$\underline{H} = \sum_{i,j=1}^N |i\rangle\langle i| H |j\rangle\langle j| \quad (40)$$

and

$$\underline{H}_0 = \sum_{i,j=1}^N |i\rangle \langle i| H_0 |j\rangle \langle j|. \quad (41)$$

Furthermore, in the cases of $\underline{H}$ and $\underline{H}_0$, by Eqs. (5) and (10), we note that

$$\langle i|H|j\rangle = \delta_{ij} H_j + W_{ij} V_j \quad (42)$$

and

$$\langle i|H_0|j\rangle = \delta_{ij} H_j. \quad (43)$$

It is important to emphasize that by introducing the arrangement channel aspect explicitly everywhere in our equations, we have thus been lead naturally to consider arrangement channel matrices for all the usual quantum mechanical operators. Out of the introduction of these (finite - dimensional) matrices naturally come the orthonormal basis vectors $|i\rangle$ which are simply the basis for representing the more abstract super operators. We shall find later that the introduction of the vectors will lead to an extremely simple solution to the problem of constructing orthogonal projection operators for multi-channel scattering. For the present, we now continue our discussion of the arrangement channel generalizations of various operators of interest in scattering theory.

By standard manipulations, it is also readily shown that

Eqs. (17) and (18) lead to the following time independent form of the Møller operator matrix:

$$\underline{\underline{\Omega}}_+ = \underline{\underline{I}} + \underline{\underline{G}}^+ \underline{\underline{W}} \underline{\underline{V}} \quad (44)$$

where the full Green's operator matrix $\underline{\underline{G}}^+$ is defined by

$$\underline{\underline{G}}^+ = \left[(\underline{\underline{E}} + i\underline{\underline{\epsilon}}) \underline{\underline{I}} - \underline{\underline{H}}_0 - \underline{\underline{W}} \underline{\underline{V}} \right]^{-1} \quad (45)$$

By this result, we immediately recover a Lippmann-Schwinger equation for $|\underline{\underline{\Psi}}(0)\rangle$ in Eq. (18) of the form

$$|\underline{\underline{\Psi}}(0)\rangle \equiv |\underline{\underline{\Psi}}^+\rangle = |\underline{\underline{\varphi}}\rangle + \underline{\underline{G}}^+ \underline{\underline{W}} \underline{\underline{V}} |\underline{\underline{\varphi}}\rangle. \quad (46)$$

Further, it is easily proved that

$$\underline{\underline{G}}^+ = \underline{\underline{g}}^+ + \underline{\underline{g}}^+ \underline{\underline{W}} \underline{\underline{V}} \underline{\underline{G}}^+ = \quad (47)$$

$$= \underline{\underline{g}}^+ + \underline{\underline{G}}^+ \underline{\underline{W}} \underline{\underline{V}} \underline{\underline{g}}^+, \quad (48)$$

where $\underline{\underline{g}}^+$ is the non interacting resolvent matrix

$$\underline{\underline{g}}^+ = \left[(\underline{\underline{E}} + i\underline{\underline{\epsilon}}) \underline{\underline{I}} - \underline{\underline{H}}_0 \right]^{-1}. \quad (49)$$

By these relations, Eq. (46) is easily shown to yield

$$|\underline{\underline{\Psi}}^+\rangle = |\underline{\underline{\varphi}}\rangle + \underline{\underline{g}}^+ \underline{\underline{W}} \underline{\underline{V}} |\underline{\underline{\Psi}}^+\rangle. \quad (50)$$

These results are of the same sort as those discussed in detail in the works of Kouri and Levin ⁶. Finally, in complete analogy with the earlier definitions of super quantities, we can now introduce a super-Møller operator $\underline{\Omega}_+$ and ^asuper-Lippmann-Schwinger equation for the most general abstract vector state:

$$\underline{\Omega}_+ = \sum_{i,j=1}^N |i\rangle\langle i| \underline{\Omega}_+ |j\rangle\langle j| \quad (51)$$

$$|\underline{\Psi}^+\rangle = \sum_{i,j=1}^N |i\rangle\langle i| \underline{\Psi}^+ |j\rangle\langle j| \quad (52)$$

where

$$\langle i|\underline{\Psi}^+|j\rangle = |\psi_{ij}\rangle. \quad (53)$$

The state $\underline{\Psi}^+$ satisfies the super-Lippmann-Schwinger equation

$$\underline{\Psi}^+ = \phi + g^+ W V \underline{\Psi}^+ \quad (54)$$

where

$$\underline{W} = \sum_{i,j=1}^N |i\rangle\langle i| W |j\rangle\langle j|, \quad (55)$$

$$\underline{V} = \sum_{i,j=1}^N |i\rangle \langle i| V |j\rangle \langle j|, \quad (56)$$

$$|\underline{\psi}\rangle = \sum_{i,j=1}^N |i\rangle \langle i| \Phi |j\rangle \langle j| \equiv \quad (57)$$

$$\equiv \sum_{i=1}^N |i\rangle |\varphi_i(t)\rangle \langle i|. \quad (58)$$

Further, our original coupled time dependent Schrödinger equations, Eq. (4), are now seen to be the matrix representation in channel arrangement space, of the super Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \mathbb{H} \Psi(t). \quad (59)$$

Comparing Eqs. (2) and (59), one is struck by their formal similarity. However, we must emphasize that the arrangement channel aspect of the problem is quite implicit in Eq. (2) whereas in Eq. (59) it has been made explicit. This is evident when one notes Eq. (42) giving the channel arrangement space representation of the super operator $\mathbb{H}$.

III. Generalized Interaction Picture

To introduce our generalized interaction picture, we take as the starting point Eq. (59), where we note that the full H can be expressed as

$$H = H_0 + W V \quad (60)$$

and therefore

$$\left(i\hbar \frac{\partial}{\partial t} - H_0 \right) \Psi = W V \Psi \quad (61)$$

We then separate from Ψ the time dependence associated with H_0 so that

$$\Psi(t) = \exp(-i H_0 t / \hbar) \chi(t), \quad (62)$$

and χ satisfies

$$i\hbar \frac{\partial}{\partial t} \chi(t) = \exp(i H_0 t / \hbar) W V \exp(-i H_0 t / \hbar) \chi(t). \quad (63)$$

Clearly, we now identify the potential in the interaction picture as

$$V(t) = \exp(i H_0 t / \hbar) W V \exp(-i H_0 t / \hbar). \quad (64)$$

The evolution operator in this picture is readily seen to be given by

$$U(t, t_0) = \exp(iH_0 t/\hbar) \exp(-iH(t-t_0)/\hbar) \exp(-iH_0 t_0/\hbar). \quad (65)$$

Furthermore, because U gives the time evolution of the $\chi(t)$ it must also satisfy Eq. (63) so that

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = V(t) U(t, t_0), \quad (66)$$

Together with the initial condition

$$U(t, t) = \mathbb{I}. \quad (67)$$

With the help of Eq. (17) defining $\underline{\Omega}_+$, we find from Eq. (23), that

$$\underline{\mathcal{S}} = \lim_{\substack{t \rightarrow +\infty \\ t_0 \rightarrow -\infty}} \exp(iH_0 t/\hbar) \exp(-iH(t-t_0)/\hbar) \exp(-iH_0 t_0/\hbar) \quad (68)$$

and this result is clearly just the channel matrix representation of Eq. (65) in the form

$$\mathcal{S} = \lim_{\substack{t \rightarrow +\infty \\ t_0 \rightarrow -\infty}} \exp(iH_0 t/\hbar) \exp(-iH(t-t_0)/\hbar) \exp(-iH_0 t_0/\hbar). \quad (69)$$

Eq. (69) is an extremely interesting result and, in contrast to the pioneering work of Eckstein¹⁷, is seen to yield the definition of a single scattering super operator for describing rearrangement collisions. Moreover, just as in the ordinary single channel scattering theory, this super scattering

operator is the double time limit of the sequence of unitary time evolution super operators in the interaction picture. We note that the existence of such a super scattering operator is indicated in the reference work by Taylor¹⁹. However it is emphasized that the present treatment leads not only to the formal introduction of such an operator, but also this operator will play a central role in potential applications of our new theory. Thus, we may develop computational schemes based directly on the explicit representation of $\mathcal{S}$ in Eq. (68). Further, the present expressions represent a more consistent development of the super $\mathcal{S}$ operator, since now, one has super operators appearing throughout the expression. The simplification arising from this is illustrated by the analysis in Eqs. (22) - (29) for the S matrix elements, in that one is never faced with having to evaluate quantities such as

$$\langle \varphi_f(x') | \exp(i H_f t/\hbar) \exp(-i H_k t/\hbar) | \varphi_k(x) \rangle.$$

IV. Projection Operators in Multichannel Scattering

One of the best examples of the simplifications afforded by the present formulation is that of multichannel projection operators. In previous discussions of multichannel scattering the problem of non orthogonality of states in different arrangements has either forced one to work with abstractly defined projectors for which constructive methods were not given for their practical realization or it has lead to quite complicated schemes for obtaining the relevant projection operator. For example, the Chen-Mittleman²¹ approach leads to integral equations which must be solved in order to construct the desired projection operators. In the discussion of reactive scattering given in the reference text of Levine²², the question of the explicit realization of the channel projectors is not addressed. For certain simple problems such as $e^- + H$, it is possible to relatively easily construct projectors but these methods are cumbersome for more complicated systems. An interesting discussion from a purely practical standpoint has been given by Hahn¹². In particular, Hahn has considered his reduction method equations from the standpoint of projection operators and has shown that one may, in fact, employ non-orthogonal projection operators in a coupled equations approach to reactions which is similar to the present one. However, in that work, it was stated that one cannot (in a simple way) construct the relevant projectors as a sum of the individual projectors for each individual channel. In particular,

the projectors that would enter such a sum are quite complicated (except, as we note in the simple $e^- + H$ system). Our purpose in this section is to show how the introduction of the orthonormal channel index vectors $|i\rangle$ enables one to obtain orthogonal projectors as simple sums of projectors constructed from the ordinary arrangement channel projectors.

The problem is as follows. We wish to construct an operator $\hat{P}$ which will project out all the open channels of the wavefunction. Its complement $\hat{Q}$ can be obtained by subtracting $\hat{P}$ from the proper identity operator. We consider first a given arrangement j and construct the operator $\hat{P}_j$ that projects only non-breakup states in j . This is easily seen to be

$$\hat{P}_j = \sum_{\mu}' |\varphi_j(\mu)\rangle \langle \varphi_j(\mu)|, \quad (70)$$

where we note that

$$\langle \varphi_j(\mu) | \varphi_j(\mu') \rangle = \delta_{\mu\mu'}, \quad (71)$$

and the prime limits the summation to non-breakup states only. Now the essential problem in previous treatments has been that $\langle \varphi_j(\mu) | \varphi_k(\mu') \rangle$ does not vanish for $j \neq k$. However, we notice that the vectors $|j\rangle$ do give an orthonormal basis in the channel index space. We thus conclude that the proper "states" to use in constructing projectors which are orthogonal in the channel index are those of a product space:

$$|\Phi_j(x)\rangle = |\varphi_j(x)\rangle \otimes |j\rangle. \quad (72)$$

Then by the fact that $(i|j) = \delta_{ij}$ and Eq. (71), we readily see that for $j \neq k$,

$$\langle \Phi_j(x) | \Phi_k(\mu) \rangle = \delta_{jk} \delta_{x\mu}. \quad (73)$$

We therefore conclude that

$$\mathcal{P} = \sum_j \sum_{\mu} |\Phi_j(\mu)\rangle \langle \Phi_j(\mu)| \quad (74)$$

is our proper orthogonalized open channel projector. However, we see that $\mathcal{P}$ must be applied only to states $|\underline{\Psi}^+\rangle$ given by Eq. (52). In this way one sees that the $|\varphi_j(x)\rangle \langle \varphi_j(x)|$ portion of the projectors always acts only the j^{th} component of $|\Psi_i\rangle$, the scattering state describing the system initially in arrangement i .

We note that the projector $\sum_{\mu} |\Phi_j(\mu)\rangle \langle \Phi_j(\mu)|$ is an explicit realization of the C_i discussed by Levine²². However, in that work the necessity of introducing the vectors $|j\rangle$ was not examined.

V. Approximation Procedures

The solution to Eqs. (66) - (67) is, as usual, a Volterra-type integral equation

$$U(t, t_0) = \mathcal{I} - \frac{i}{\hbar} \int_{t_0}^t dt' V(t') U(t', t_0), \quad (75)$$

which, upon iteration yields the generalized Dyson series

$$U(t, t_0) = \mathcal{I} - \frac{i}{\hbar} \int_{t_0}^t dt' V(t') - \frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' V(t') V(t'') + \dots \quad (76)$$

The $\mathcal{S}$ operator obtained from the above expression, by use of Eq. (69), is

$$\mathcal{S} = \sum_{n=0}^{\infty} \mathcal{S}^{(n)} \quad (77)$$

where

$$\begin{aligned} \mathcal{S}^{(0)} &= \mathcal{I}, \\ \mathcal{S}^{(1)} &= -\frac{i}{\hbar} \int_{-\infty}^{+\infty} dt V(t), \\ \mathcal{S}^{(2)} &= -\frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^t dt' V(t) V(t'), \\ &\vdots \end{aligned} \quad (78)$$

Alternatively, we may solve Eq. (75) by the Magnus method²³ so that the solution is

$$\mathcal{S} = \exp(-i \Delta) \quad (79)$$

where, to lowest order,

$$\Delta = -\frac{1}{\hbar} \int_{-\infty}^{+\infty} dt \mathcal{V}(t), \quad (80)$$

and higher order approximations may also be obtained by standard methods²³. A detailed discussion of Eq. (79) will be presented later in a separate paper²⁴.

Another type^{of} approximation may be obtained by considering the equation for $\underline{\mathcal{I}}$ which is readily shown to be

$$\underline{\mathcal{I}} = \underline{\mathcal{V}} + \underline{\mathcal{V}} \underline{\mathcal{G}}^+ \underline{\mathcal{V}} \quad (81)$$

where $\underline{\mathcal{V}}$ stands for $\underline{W} \underline{V}$.

Following Levine²⁵ study the variation in $\underline{\mathcal{I}}$ due to variations in $\underline{\mathcal{V}}$:

$$\delta \underline{\mathcal{I}} = \delta \underline{\mathcal{V}} + (\delta \underline{\mathcal{V}}) \underline{\mathcal{G}}^+ \underline{\mathcal{V}} + \underline{\mathcal{V}} (\delta \underline{\mathcal{G}}^+) \underline{\mathcal{V}} + \underline{\mathcal{V}} \underline{\mathcal{G}}^+ (\delta \underline{\mathcal{V}}). \quad (82)$$

To obtain $\delta \underline{\mathcal{G}}^+$, we note that

$$\begin{aligned} \delta [\underline{\mathcal{G}}^+ (\underline{\mathcal{G}}^+)^{-1}] &= \delta (\underline{\mathcal{I}}) \\ &= \underline{0}, \end{aligned} \quad (83)$$

so that we conclude

$$\delta \underline{\underline{Q}}^+ = \underline{\underline{Q}}^+ [\delta (\underline{\underline{Q}}^+)^{-1}] \underline{\underline{Q}}^+ \quad (84)$$

Now by Eq. (45), we immediately find

$$\delta \underline{\underline{Q}}^+ = \underline{\underline{Q}}^+ (\delta \underline{\underline{U}}) \underline{\underline{Q}}^+, \quad (85)$$

and we use this to write Eq. (82) as

$$\delta \underline{\underline{T}} = \delta \underline{\underline{U}} + (\delta \underline{\underline{U}}) \underline{\underline{Q}}^+ \underline{\underline{U}} + \underline{\underline{U}} \underline{\underline{Q}}^+ (\delta \underline{\underline{U}}) \underline{\underline{Q}}^+ \underline{\underline{U}} + \underline{\underline{U}} \underline{\underline{Q}}^+ (\delta \underline{\underline{U}}). \quad (86)$$

Rearranging the above yields

$$\delta \underline{\underline{T}} = (\underline{\underline{J}} + \underline{\underline{U}} \underline{\underline{Q}}^+) \delta \underline{\underline{U}} (\underline{\underline{J}} + \underline{\underline{Q}}^+ \underline{\underline{U}}) \quad (87)$$

and we recall Eq. (44) for $\underline{\underline{\Omega}}_+$, so that

$$\delta \underline{\underline{T}} = (\underline{\underline{\Omega}}_+)^T (\delta \underline{\underline{U}}) \underline{\underline{\Omega}}_+. \quad (88)$$

This equation is recognized as a generalization of the Hellmann-Feynmann theorem for collisions as discussed by Levine²⁵.

It is seen from Eqs. (17) and (30) that

$$\underline{\underline{J}} = (\underline{\underline{\Omega}}_-)^T \underline{\underline{\Omega}}_+ \quad (89)$$

and further,

$$(\underline{\underline{\Omega}}_-)^T = (\underline{\underline{\Omega}}_+)^T. \quad (90)$$

Armed with these results, we now write

$$\begin{aligned}\delta \underline{\underline{T}} &= (\underline{\underline{\Omega}}_-)^\dagger (\delta \underline{\underline{V}}) (\underline{\underline{\Omega}}_-)^\dagger (\underline{\underline{\Omega}}_- \underline{\underline{\Omega}}_+)^{-1} \\ &= \underline{\underline{\Omega}}_-^\dagger (\delta \underline{\underline{V}}) (\underline{\underline{\Omega}}_-)^\dagger \underline{\underline{S}}.\end{aligned}\quad (91)$$

Finally, we use Eq. (36) to write the above as

$$\delta \underline{\underline{S}} = -2\pi i \delta \underline{\underline{T}} \quad (92)$$

or

$$\delta \underline{\underline{S}} = -2\pi i \underline{\underline{\Omega}}_-^\dagger (\delta \underline{\underline{V}}) (\underline{\underline{\Omega}}_-)^\dagger \underline{\underline{S}} \quad (93)$$

which is our desired result. As our lowest order approximation, we assume that $\underline{\underline{\Omega}}_-^\dagger$ and $\delta \underline{\underline{V}}$ commute, so that an approximate form of Eq. (93) is

$$\delta \underline{\underline{S}} \cong -2\pi i \delta \underline{\underline{V}} \underline{\underline{S}}. \quad (94)$$

We next consider the variation $\delta \underline{\underline{V}}$ by noting that

$$\delta \underline{\underline{V}} = (\delta \underline{\underline{W}}) \underline{\underline{V}} + \underline{\underline{W}} \delta \underline{\underline{V}}. \quad (95)$$

However, $\underline{\underline{V}}$ is the diagonal matrix of channel potentials and we require

$$\delta \underline{\underline{V}} = \underline{\underline{0}}, \quad (96)$$

so that only $(\delta \underline{W}) \underline{V}$ survives. Next, we take $\underline{W}$ to be of the form

$$\underline{W} = \lambda \underline{W}_0, \quad (97)$$

where the physical collision problem corresponds to the particular value $\lambda = 1$. Obviously, we then have

$$\delta \underline{W} = \underline{W}_0 \delta \lambda, \quad (98)$$

and further, $\frac{d\underline{W}}{d\lambda}$ commutes with $\underline{W}$. Therefore, we integrate Eq. (94) from $\lambda = 0$ to $\lambda = 1$, noting that $\underline{S}(\lambda = 0) = \underline{I}$, to obtain the exact solution (of the approximate Eq.(94) as

$$\underline{S} = \exp(-2\pi i \underline{U}). \quad (99)$$

This expression should be relatively simple to use in applications.

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