

# Reduced equations of motion and reduced $S$ matrix for scattering processes

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Reduced equations of motion (REM) are derived for the reduced density matrix of some of the degrees of freedom taking part in a scattering process. The derivation is made making use of the Zwanzig-Mori projection operator technique and utilizing a partial time ordering prescription (POP) which results in simple REM which contain no convolution in time. The present formulation is convenient for the direct calculation of reduced information on scattering events since it avoids the necessity of calculating the complete  $S$  matrix. The entire dynamical information relevant for the present description is expressed in terms of a hierarchy of correlation functions which in turn depend on the potential surface only in the region of interest. We further develop an exponential approximation for the reduced tetradic scattering  $S$  matrix in Liouville space, which forms a convenient framework for systematic approximations.

## I. INTRODUCTION

There is currently an increased interest in formulating scattering theory in a way convenient for averaging over irrelevant information and focusing attention on few quantities which are of physical interest.<sup>1-9</sup>

In spite of the enormous theoretical progress in scattering theory such as the development of classical and semiclassical methods,<sup>10-12</sup> it is still extremely difficult to perform reliable calculations for complex collisions with more than a few degrees of freedom. The amount of labor in obtaining the necessary potential surfaces and the actual solution of the scattering problem increases very rapidly with the size of the system, which makes the rigorous solution of large systems impractical. On the other hand the complete solution of the scattering amplitudes with all their phases is often too detailed compared to the experimentally available information which is always coarse grained and limited to few observables. It is thus clear that attempts to calculate the complete scattering information in complex systems are neither feasible nor desirable. This state of affairs raises the theoretical challenge of developing methods for calculating just the right amount of information (rather than the complete scattering  $S$  matrix).

The formal problem of reduced scattering theory has a long history in the field of atomic and molecular radiative phenomena. It was shown by Fano and Ben-Reuven<sup>1-3</sup> that it is possible to formulate scattering theory for the density matrix in Liouville space (rather than the wave function in Hilbert space) in a way convenient for averaging over irrelevant degrees of freedom. In this context, however, collisions are usually treated perturbatively in the projectile-target interaction. More recent developments along these lines were made by Adelman and Doll<sup>4</sup> who applied Langevin-type equations to the problem of scattering of atoms from solid surfaces. The description of collision phenomena in terms of simple rate equations or the diffusion equation (which is a specific way of reducing information) was also dis-

cussed in the context of molecular<sup>7</sup> as well as nuclear<sup>8</sup> scattering problems. The definition of a "reaction path" in reactive<sup>12</sup> collisions is also a step in the direction of focusing attention on the relevant aspects of the interactions. The reaction path transformation<sup>12</sup> was recently extended by Miller and the co-workers<sup>13</sup> for reactive scattering in polyatomic molecules in a way convenient for utilizing information on the immediate neighborhood of the reaction path.

The projection operator techniques of Zwanzig and Mori<sup>14-16</sup> are extensively used in nonequilibrium statistical mechanics for the derivation of reduced equations of motion (REM) for relevant quantities of interest and thus seem to be the natural framework for treating scattering problems as well. Ordinarily this approach yields REM which are a set of coupled integro-differential equations. We have recently studied a new version of this formulation<sup>15,17,18</sup> which is based on a partial time ordering prescription (POP). This version yields exact REM which are simple differential equations and contain no memory kernels and thus seem to be most adequate for treating scattering problems. Recent applications of this reduction scheme to molecular multiphoton processes and line shape problems have been proven very useful.<sup>17</sup> It is our purpose in this paper to apply the POP method to derive REM for molecular scattering processes and to obtain closed and useful formal expressions for the *reduced  $S$  matrix*. In Sec. II we derive the general REM for the reduced density matrix of a preselected set of degrees of freedom in a scattering problem. These REM may be used for numerical calculations of reduced scattering cross sections. In Sec. III we derive the reduced  $S$  matrix using our REM and obtain a systematic exponential approximation for the  $S$  matrix.

## II. REDUCED EQUATIONS OF MOTION (REM) FOR SCATTERING PROCESSES

The scattering problem is defined by the Hamiltonian

$$H = H_0 + \lambda H', \quad (1)$$

where

$$H_0 = H_s(Q_s) + H_B(Q_B) \quad (1a)$$

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and

$$H' = H'(Q_S, Q_B) . \quad (1b)$$

Here we have separated our degrees of freedom into two groups: the relevant "system" coordinates  $Q_S$  and the irrelevant "bath" coordinates  $Q_B$ .  $Q_B$  contains the relative translation of the projectile and the target ( $Q_T$ ) as well as some of their internal degrees of freedom which are not explicitly resolved under the experimental conditions to be considered.  $Q_S$  contains all other degrees of freedom. As is common in scattering theory<sup>10</sup> we define  $H'$  such that it vanishes when  $Q_T \rightarrow \infty$ . The parameter  $\lambda$  is introduced for bookkeeping purposes in the forthcoming expansions and may be taken to be  $\lambda = 1$  at the end. The Liouville space operators (commutators) corresponding to  $H$ ,  $H_0$ ,  $H'$ ,  $H_S$ , and  $H_B$  will be denoted by  $L$ ,  $L_0$ ,  $L'$ ,  $L_S$ , and  $L_B$ , respectively, i.e.,

$$L \equiv [H, \ ] . \quad (2)$$

We start the scattering process at the time  $t_1$  where we form a wave packet of translational states so that the projectile and target are far apart.<sup>10</sup> We further assume that the total density matrix is

$$\rho(t_1) = \rho_B(t_1)\sigma(t_1) , \quad (3)$$

where

$$\sigma(\tau) \equiv \text{Tr}_{\text{bath}} \rho(\tau) \quad (4)$$

is the reduced system density matrix whose time evolution is of interest to us, whereas  $\rho_B$  is the bath initial density matrix. The reduced equations of motion for  $\sigma$  are derived in Appendix A and are given by<sup>17</sup>

$$\frac{d\sigma(t)}{dt} = -iL_S\sigma(t) - iK(t, t_1)\sigma(t) , \quad (5)$$

where

$$K(t, t_1) = WV^{-1} , \quad (6)$$

$$\begin{aligned} W &= \langle PL' \exp[-iL(t-t_1)]P \rangle \\ &\equiv \text{Tr}_{\text{bath}} \{ PL' \exp[-iL(t-t_1)]P \} , \end{aligned} \quad (7)$$

and

$$V = \langle P \exp[-iL(t-t_1)]P \rangle \equiv \text{Tr}_{\text{bath}} \{ P \exp[-iL(t-t_1)]P \} . \quad (8)$$

Here  $P$  is the Zwanzig projection operator<sup>14</sup>

$$P = \rho_B(t_1) \text{Tr}_{\text{bath}} , \quad (9)$$

so that

$$P\rho(t_1) = \rho(t_1) = \rho_B(t_1)\sigma(t_1) , \quad (9a)$$

and the angular brackets  $\langle \rangle$  in Eqs. (7) and (8) denote trace over the bath, i.e.,

$$\langle \dots \rangle \equiv \text{Tr}_{\text{bath}} . \quad (10)$$

We now switch to the interaction representation

$$\sigma_I(t) \equiv \exp(iL_S t)\sigma(t) . \quad (11)$$

Equation (11), when substituted in Eq. (5), results in

$$\frac{d\sigma_I(t)}{dt} = -iK_I(t, t_1)\sigma_I(t) , \quad (12)$$

where

$$K_I(t, t_1) = \exp(iL_S t)K(t, t_1)\exp(-iL_S t) . \quad (13)$$

$K_I(t, t_1)$  may be expanded in a power series in  $\lambda$  using the relation<sup>19</sup>

$$\exp[-iL(t-t_1)] = \exp\left[-i\lambda \int_{t_1}^t d\tau L'(\tau)\right] \exp[-iL_0(t-t_1)] , \quad (14)$$

where

$$L'(\tau) = \exp(-iL_0\tau)L'\exp(iL_0\tau) , \quad (15)$$

and  $\exp_-$  is the negative time ordering exponential, i.e.,

$$\begin{aligned} \exp_- \left[ -i\lambda \int_{t_1}^t d\tau L'(\tau) \right] &= 1 - i\lambda \int_{t_1}^t d\tau L'(\tau) \\ &+ (-i\lambda)^2 \int_{t_1}^t d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 L'(\tau_2)L'(\tau_1) + \dots . \end{aligned} \quad (16)$$

Equation (16) may be substituted into the definitions of  $W$  and  $V$  [Eqs. (7) and (8)] and we may then collect terms according to the powers of  $\lambda$ . We thus get

$$K_I(t, t_1) = \lambda K_I^{(1)} + \lambda^2 K_I^{(2)} + \dots , \quad (17)$$

where

$$K_I^{(1)} = \exp(iL_S t) \langle L'(0)\rho_B(t) \rangle \exp(-iL_S t) , \quad (17a)$$

$$\begin{aligned} K_I^{(2)} &= -i \exp(iL_S t) \int_{t_1}^t d\tau [ \langle L'(0)L'(\tau)\rho_B(t) \rangle \\ &- \langle L'(0)\rho_B(t) \rangle \langle L'(\tau)\rho_B(t) \rangle ] \exp(-iL_S t) , \end{aligned} \quad (17b)$$

and

$$\begin{aligned} K_I^{(3)} &= (-i)^2 \exp(iL_S t) \int_{t_1}^t d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 [ \langle L'(0)L'(\tau_2)L'(\tau_1)\rho_B(t) \rangle \\ &- \langle L'(0)\rho_B(t) \rangle \langle L'(\tau_2)L'(\tau_1)\rho_B(t) \rangle \\ &- \langle L'(0)L'(\tau_2)\rho_B(t) \rangle \langle L'(\tau_1)\rho_B(t) \rangle \\ &- \langle L'(0)L'(\tau_1)\rho_B(t) \rangle \langle L'(\tau_2)\rho_B(t) \rangle ] \exp(-iL_S t) . \end{aligned} \quad (17c)$$

Here we have defined

$$\rho_B(t) \equiv \exp[-iL_0(t-t_1)]\rho_B(t_1) . \quad (18)$$

For the sake of the subsequent expansions we further introduce a hierarchy of moments

$$M_1(\tau_2, \tau_1) = \exp(iL_S \tau_1) \langle L'(\tau_2)\rho_B(\tau_1) \rangle \exp(-iL_S \tau_1) , \quad (19a)$$

$$M_2(\tau_3, \tau_2, \tau_1) = \exp(iL_S \tau_1) \langle L'(\tau_3)L'(\tau_2)\rho_B(\tau_1) \rangle \exp(-iL_S \tau_1) , \quad (19b)$$

$$\begin{aligned} M_3(\tau_4, \tau_3, \tau_2, \tau_1) &= \exp(iL_S \tau_1) \\ &\times \langle L'(\tau_4)L'(\tau_3)L'(\tau_2)\rho_B(\tau_1) \rangle \exp(-iL_S \tau_1) , \\ &\vdots \end{aligned} \quad (19c)$$

These moments form the complete set of molecular information relevant for our reduced description of the scattering process. The various terms in expansion (17) may be expressed in terms of the moments (19) as follows:

$$K_I^{(1)} = M_1(0, t) , \quad (20a)$$

$$K_I^{(2)} = -i \int_{t_1}^t d\tau [ M_2(0, \tau, t) - M_1(0, t)M_1(\tau, t) ] , \quad (20b)$$

and

$$K_I^{(3)} = (-i)^2 \int_{t_1}^t d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 [M_3(0, \tau_2, \tau_1, t) - M_2(0, \tau_2, t)M_1(\tau_1, t) - M_2(0, \tau_1, t)M_1(\tau_2, t) - M_1(0, t)M_2(\tau_2, \tau_1, t)] \quad (20c)$$

In concluding this section we note the following:

(i) The reduced equations of motion (12) provide us with a general and useful method for the direct calculation of quantities of interest in scattering problems. The entire relevant molecular information needed for this purpose is given by the set of moments  $M_k$ ,  $k=1, 2, \dots$  [Eq. (19)], which are required for the evaluation of  $K_I(t, t_1)$  [Eq. (20)].

(ii) The solution of the scattering problem within the present formulation is done in two stages. We first have to evaluate the moments  $M_k$  and the second step is the solution of the REM (12) starting at  $t_1 = -\infty$  and proceeding to  $t = \infty$ . It is clear that in practice the moments  $M_k$  do not depend on the entire potential surface  $L'(Q)$ . The presence of  $\rho_B(t)$  in all the moments  $M_k$  (19) causes them to depend on the potential surface only in the immediate neighborhood of the "reaction path" defined by the zero-order distribution function  $\rho_B(t)$ .

(iii) The first moment  $M_1 = \langle L'(0)\rho_B(t) \rangle$  is a driving term and determines the motion of the relevant system degrees of freedom in the mean force caused by the motion of the bath. The higher moments  $M_2$ , etc., may contain damping (imaginary) terms which describe the relaxations and dephasing of the relevant system degrees of freedom due to their interactions with the bath.

(iv) Within a semiclassical treatment<sup>11</sup> it is common to treat the relative translation of the projectile and the target ( $Q_T$ ) classically, and the other degrees of freedom quantum mechanically. In order to see how this is obtained from the present formulation we have to put

$$\rho_B(t) - \delta(Q_T - Q_T(t))\delta(P_T - P_T(t)), \quad (21)$$

where  $Q_T(t)$ ,  $P_T(t)$  are the solutions of the classical equations of motion for  $Q_T$ ,  $P_T$  being the conjugate momentum of  $Q_T$ . We further have

$$\text{Tr}_{\text{bath}} \rightarrow \int dQ_T dP_T \quad (22)$$

Substitution of Eqs. (21) and (22) in Eqs. (7) and (8) results in

$$\frac{d\sigma_I}{dt} = -i \exp(-iL_S t) L'(Q_T(t), P_T(t), Q_S) \exp(iL_S t) \sigma_I, \quad (23)$$

which are the usual semiclassical equations<sup>11</sup> (no higher order terms in  $L'$  appear in this case).

### III. EVALUATION OF THE TETRADIC REDUCED S MATRIX

The formal solution of Eq. (12) is

$$\sigma_I(t) = U_I(t, t_1) \sigma_I(t_1), \quad (24)$$

where  $U_I(t, t_1)$  is the reduced time evolution operator

$$U_I(t, t_1) \equiv \exp_* \left[ -i \int_{t_1}^t d\tau K_I(\tau, t_1) \right] \quad (25)$$

and  $\exp_*$  is the positive time ordered exponential,<sup>19</sup> i.e.,

$$\exp_* \left[ -i \int_{t_1}^t d\tau K_I(\tau, t_1) \right] = 1 - i \int_{t_1}^t d\tau K_I(\tau, t_1) + (-i)^2 \int_{t_1}^t d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 K_I(\tau_1, t_1) K_I(\tau_2, t_1) + \dots \quad (26)$$

The reduced S matrix is defined as<sup>1-3, 10</sup>

$$S = U_I(\infty, -\infty). \quad (27)$$

Making use of the Magnus expansion,<sup>19, 20</sup> we may rewrite  $S$  in the form

$$S = \exp(-iA), \quad (28)$$

where

$$A = A_1 + A_2 + A_3 + \dots \quad (29)$$

$A_k$  may be obtained by comparing Eqs. (24)–(28) term by term, resulting in

$$A_1 = \int_{-\infty}^{\infty} d\tau K_I(\tau, -\infty), \quad (30a)$$

$$A_2 = -\frac{i}{2} \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 [K_I(\tau_1, -\infty) K_I(\tau_2, -\infty)], \quad (30b)$$

and

$$A_3 = -\frac{1}{6} \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \{ [K_I(\tau_1), [K_I(\tau_2), K_I(\tau_3)]] + [K_I(\tau_3), [K_I(\tau_2), K_I(\tau_1)]] \}. \quad (30c)$$

We shall now rearrange  $A$  [Eq. (29)] according to power series in  $\lambda$ , i.e.,

$$A \equiv \lambda A^{(1)} + \lambda^2 A^{(2)} + \dots; \quad (31)$$

each  $A^{(k)}$  may be evaluated using  $A_i$ ,  $i=1, 2, \dots, k$ . We thus get, using Eqs. (20) and (29)–(31),

$$A^{(1)} = \int_{-\infty}^{\infty} d\tau M_1(0, \tau), \quad (32a)$$

$$A^{(2)} = -i \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 [M_2(0, \tau_2, \tau_1) - M_1(0, \tau_1)M_1(\tau_2, \tau_1) - \frac{1}{2}M_1(0, \tau_1)M_1(0, \tau_2) + \frac{1}{2}M_1(0, \tau_2)M_1(0, \tau_1)], \quad (32b)$$

$$A^{(3)} = - \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \{ M_3(0, \tau_3, \tau_2, \tau_1) - M_1(0, \tau_1)M_2(\tau_3, \tau_2, \tau_1) - M_2(0, \tau_3, \tau_1)M_1(\tau_2, \tau_1) - M_2(0, \tau_2, \tau_1)M_1(\tau_3, \tau_1) + \frac{1}{2}[M_2(0, \tau_3, \tau_1) - M_1(0, \tau_1)M_1(\tau_3, \tau_1), M_1(0, \tau_2)] + \frac{1}{2}[M_1(0, \tau_1), M_2(0, \tau_3, \tau_2) - M_1(0, \tau_2)M_1(\tau_3, \tau_2)] + \frac{1}{6}[M_1(0, \tau_1), [M_1(0, \tau_2), M_1(0, \tau_3)]] + \frac{1}{6}[M_1(0, \tau_3), [M_1(0, \tau_2), M_1(0, \tau_1)]] \}, \quad (32c)$$

The higher order terms may be obtained in a similar manner. The following remarks should be made at this stage:

(i) Equation (28) together with (31) and (32) provide us with a closed expression for the reduced tetradic S matrix in Liouville space which enables us to average over irrelevant degrees of freedom. An exponential representation of the form (28) was proved useful in ordinary scattering theory in Hilbert space for the complete scattering S matrix.<sup>10,20</sup> We thus expect the present form to be a convenient starting point for the reduced calculations of scattering processes.

(ii) The  $k$ th term in expansion (31)  $A^{(k)}$  depends on all the lower moments  $M_j$ ,  $j=1, 2, \dots, k$ .  $A^{(1)}$  thus represents a mean field approximation for the S matrix whereas the higher terms contain also damping dissipative contributions which represent the effect of the bath degrees of freedom during the collision.

(iii) As a consistency check let us verify how the complete S matrix (no reduction) is obtained from our present equations. To that end we include all the degrees of freedom in the system so that  $H_B=0$  and  $\rho_B(t)=1$ . We may then perform one of the integrations in each of the terms (32) resulting in

$$A^{(1)} = 2\pi\delta(\omega_{ij} - L_0)L', \quad (33)$$

etc., which will generate finally the series<sup>1-3</sup>

$$S = 1 - 2\pi i\delta(\omega_{ij} - L_0)\mathcal{T}(\omega_{ij}), \quad (34)$$

where

$$\begin{aligned} \mathcal{T}(\omega) &= L' + L'(\omega - L)^{-1}L' \\ &= L' + L'(\omega - L_0)^{-1}L' + L'(\omega - L_0)^{-1}L'(\omega - L_0)^{-1}L' + \dots, \end{aligned} \quad (35)$$

and where  $\omega_{ij}$  is the eigenfrequency of the initial density matrix, i.e.,

$$L_0\sigma_{ij}(-\infty) = \omega_{ij}\sigma_{ij}(-\infty). \quad (36)$$

The  $\delta$  function in (34) represents the fact that the complete S matrix conserves the initial frequency. This is no longer the case for the reduced S matrix where we cannot perform in a trivial way any of the integrations. (No conservation of frequency for the system only!)

(iv) The first order approximation  $A \cong A^{(1)}$  is the reduced analog of the sudden approximation<sup>10</sup> which is particularly useful for fast collisions (compared to the strength of the interactions).

(v) The conventional way of deriving reduced equations of motion in statistical mechanics is based on a chronological time-ordering prescription (COP) and results in REM which are nonlocal in time and have the form of coupled integro-differential equations<sup>14,16</sup>

$$\frac{d\sigma}{dt} = i\langle L \rangle \sigma - \int_0^t d\tau \langle R(t, \tau) \rangle \sigma(\tau), \quad (37)$$

where  $\langle R(t, \tau) \rangle$  may be defined in terms of the complete Hamiltonian. Lax<sup>21</sup> and Willis and Picard<sup>22</sup> have utilized the COP formalism to derive a self-consistent set of equations for the "system" and "bath" degrees of freedom, in a way which seems most suitable for scattering

problems. Fano<sup>1</sup> had derived closed expressions for the reduced tetradic  $\mathcal{T}$  matrix making use of the COP formulation. His result is

$$P\mathcal{T}(\omega)P = PR(\omega)P + PR(\omega)P\{1/[\omega - L_0 - PR(\omega)P]\}PR(\omega)P, \quad (38)$$

where

$$R(\omega) = L' + L'Q[1/(\omega - QLQ)]QL' \quad (39)$$

and

$$Q = 1 - P. \quad (40)$$

The REM (37) and the corresponding expression for the reduced  $\mathcal{T}$  matrix (38) which are based on the COP formalism are in principle equivalent to the present POP expressions [(12) with (17) for the REM and (28) with (31) and (32) for the reduced S matrix]. The reason is that both formulations are formally exact. However, they are very different once approximations are made for the relevant operators [ $R(t, \tau)$  or  $K_I(t, t_1)$ , respectively]. A general comparison of the COP and the POP reduction schemes was made recently for line shape problems and multiphoton processes<sup>17</sup> and it was shown that they are based on different statistical properties for the bath. In several cases the POP formalism gave much simpler and better results (e.g., line shapes in the binary collision approximation, Gaussian processes<sup>17</sup>). The present REM (12) have also the advantage of being much easier to solve numerically compared to the integral equations (37). In addition, our exponential expression for the S matrix (28) is the reduced analogue of the sudden approximation which is well known for the complete S matrix.<sup>10</sup> We thus anticipate that the present formulation will provide a useful means for achieving a systematic reduction scheme for collision phenomena.

(vi) The choice of the projection operator  $P$  [Eq. (9)] is not unique and the present formulation holds for any choice of  $P$ .<sup>15,17</sup> This provides us with further flexibility which may be used to, e.g., focus attention directly on few operators which are of physical interest [rather than the entire density matrix for the system  $\sigma$  (Ref. 17)], if that is desirable.

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## APPENDIX: EXPANSION OF THE REM

We start with the complete Liouville equation for the density matrix of the system + bath

$$\frac{d\rho}{dt} = -i[H, \rho] \equiv -iL\rho. \quad (A1)$$

We further define the reduced density matrix for the system

$$\sigma \equiv \text{Tr}_{\text{bath}} \rho. \quad (A2)$$

At time  $t_1$ , which is the starting point for the scattering process we assume

$$\rho(t_1) = \rho_B(t_1)\sigma(t_1), \quad (A3)$$

i.e., the system and bath are not correlated initially. We next define a projection operator  $P$ ,<sup>14-16</sup>

$$P = \rho_B(t_1) \text{Tr}_{\text{bath}} \quad (\text{A4})$$

Using Eqs. (A3) and (A4), we have

$$P\rho(t_1) = \rho(t_1). \quad (\text{A5})$$

The formal solution of (A1) is

$$\rho(t) = \exp[-iL(t-t_1)]\rho(t_1), \quad (\text{A6})$$

upon differentiating (A6) with respect to  $t$ ,

$$\frac{d\rho(t)}{dt} = -iL \exp[-iL(t-t_1)]\rho(t_1), \quad (\text{A7})$$

multiplying (A7) by  $P$  from the left, and since  $\rho(t_1) = P\rho(t_1)$ , we get

$$\frac{d\sigma(t)}{dt} = -i\langle PL \exp[-iL(t-t_1)]P \rangle \sigma(t_1). \quad (\text{A8})$$

Similarly, repeating the same operation on (A6), we have

$$\sigma(t) = \langle P \exp[-iL(t-t_1)]P \rangle \sigma(t_1), \quad (\text{A9})$$

inverting (A9), and substitution in (A8), we finally get

$$\frac{d\sigma}{dt} = -i\langle PL \exp[iL(t-t_1)]P \rangle \langle P \exp[-iL(t-t_1)]P \rangle^{-1} \sigma. \quad (\text{A10})$$

This is the general REM using the POP (partial time ordering prescription). Up to now the REM are very general and the only restriction is the assumption

$$P\rho(t_1) = \rho(t_1). \quad (\text{A11})$$

In the present scattering problem we have

$$L = L_0 + L', \quad (\text{A12})$$

where

$$L_0 = L_S + L_B. \quad (\text{A13})$$

It is clear that  $P$  commutes with  $L_S$  (since  $P$  operates on the  $Q_B$  subspace, whereas  $L_S$  is defined in the  $Q_S$  subspace), so that

$$PL_S = L_S P \quad (\text{A14})$$

regarding  $L_B$ ,  $PL_B$  is simply a number corresponding to the translational energy of the bath. We can always include this number in  $L'$  so that without loss of generality we have

$$PL_B = 0. \quad (\text{A15})$$

We thus get, using Eqs. (A13)–(A15),

$$PL_0 = L_S P \quad (\text{A16})$$

and

$$PL_0 P = L_S, \quad (\text{A17})$$

so that

$$PL \exp[-iL(t-t_1)]P = L_S \{P \exp[-iL(t-t_1)]P + PL' \exp[-iL(t-t_1)]P\}. \quad (\text{A18})$$

Substitution of Eq. (A18) in Eq. (A10) results in our final form

$$\frac{d\sigma}{dt} = -iL_S \sigma - iK(t, t_1) \sigma, \quad (\text{A19})$$

where

$$K(t, t_1) = W V^{-1}, \quad (\text{A20})$$

and where

$$W \equiv \langle PL' \exp[-iL(t-t_1)]P \rangle \quad (\text{A21a})$$

and

$$V \equiv \langle P \exp[-iL(t-t_1)]P \rangle, \quad (\text{A21b})$$

Equation (A19) is the REM used in Sec. II.

<sup>1</sup>U. Fano, Phys. Rev. 131, 259 (1963).

<sup>2</sup>A. Ben-Reuven, Adv. Chem. Phys. 33, 235 (1975).

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