Mori-Zwanzig Equations With Time-Dependent Liouvillian

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We extend the Mori-Zwanzig equations to the case where the Liouvillian is time-dependent by way of a Dyson identity due to Holian and Evans. This extension makes it possible to treat, for example, more general cases of continuous-wave (cw) or pulsed irradiation in NMR and coherent optics. The formalism immediately allows for reference frame changes and approximations based on coherent averaging.

Keywords: nuclear induction, non-equilibrium statistical mechanics, coherent optics, coherent averaging, spin relaxation, atomic relaxation, mori-zwanzig theory, mori theory

I. INTRODUCTION

Liouville space theories such as the Mori-Zwanzig theory may be used to describe the evolution of a set of quantum mechanical observables under conditions of non-equilibria. To the author’s knowledge, the current formalism published in the nuclear magnetic resonance (NMR) literature does not include the possibility for time-dependent Hamiltonian dynamics. The usual quantum mechanical master equation obtained from a perturbation approach is the tool of choice for describing time-dependent dynamics. These methods normally rely on the assumption of a short correlation time.

The Mori equations provide a convenient framework for describing time-evolution in more general and not necessarily perturbative cases, either by analytical or numerical solution. Modern experiments increasingly consist of rapid stochastic or periodic irradiations for which the timescale of the applied pulses may approach that of molecular motions. It is therefore sensible to extend the current formalism so these modern experiments can be described adequately.

We begin by summarizing the usual derivation of the Mori equations for time-independent Liouvillian dynamics. We then derive the equations in the case of time-dependent Liouvillian.

II. TIME-INDEPENDENT HAMILTONIANS

A. Dyson Formula

The usual derivation of the Mori equations starts from the Dyson formula, the derivation of which is repeated here for convenience. Differentiation of the function

\[ A(s) = e^{-sL}e^{s(1-\pi)L}, \]  

with respect to \( s \) gives:

\[ \frac{dA(s)}{ds} = -e^{-sL}\pi Le^{s(1-\pi)L}, \]  

where \( L \) is independent of \( s \). Integration from 0 to \( t \) leads to:

\[ A(t) = A(0) - \int_0^t e^{-sL}\pi Le^{s(1-\pi)L}ds. \]  

Substitution of Eq.(1) and \( A(0) = 1 \), and multiplication on the left by \( e^{tL} \) yields the desired result:

\[ e^{t(1-\pi)L} = e^{tL} - \int_0^t e^{(t-s)L}\pi Le^{s(1-\pi)L}ds. \]  

B. Heisenberg Equation of Motion

The Heisenberg equation of motion for an observable \( A(t) \):

\[ \frac{d}{dt}A(t) = L A(t) \]  

has the following solution

\[ A(t) = e^{tL}A(0). \]  

where \( L \) is the time-independent Liouvillian, defined by the commutator \( L A = i[H, A] \).

C. Matrix Operator Notation

Consider set of \( n \) quantum operators \( \{I_1, I_2, \ldots, I_n\} \) and write them as a column vector

\[ \vec{g} = \begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_n \end{bmatrix}. \]
To this column vector corresponds a row vector:

\[ \overrightarrow{\mathcal{I}} = [I_1 \ I_2 \ \ldots \ I_n]. \quad (8) \]

Next, an inner product is chosen which is most appropriate to the problem under study. The notation \((A|B)\) denotes the inner product of \(A\) and \(B\). There are several popular inner products which may be used, depending on the application:

(a) The trace projection\(^{10,11}\), also called the Hilbert-Schmidt inner product:

\[ (A|B)_{t.p.} = \text{Tr} [A^\dagger B]. \quad (9) \]

(b) The thermal average\(^{1,9}\), which depends on the temperature \(\beta = 1/kT\) and Hamiltonian \(H\) of the system:

\[ (A|B)_{t.a.} = \text{Tr} \left[ A^\dagger B \frac{e^{-\beta H}}{Z} \right]; \quad Z = \text{Tr} \left[ e^{-\beta H} \right], \quad (10) \]

where \(\exp(-\beta H)/Z\) is the canonical statistical operator.

\[ (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}}) = ( \begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_n \end{bmatrix} | [I_1 \ I_2 \ \ldots \ I_n] ) = \begin{bmatrix} (I_1|I_1) & (I_1|I_2) & \cdots & (I_1|I_n) \\ (I_2|I_1) & (I_2|I_2) & \cdots & (I_2|I_n) \\ \vdots & \vdots & \ddots & \vdots \\ (I_n|I_1) & (I_n|I_2) & \cdots & (I_n|I_n) \end{bmatrix} \quad (14) \]

whose entries are the inner products \((I_i|I_j)\), whereas \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})\) is the inverse of that matrix. Thus, a superoperator commutes with \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1}\) and \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})\) because the entries of those matrices are \(c\)-numbers.

We check that this is indeed a valid projection operator:

\[ \pi^2 |\overrightarrow{\mathcal{F}}\rangle = (|\overrightarrow{\mathcal{F}}\rangle \cdot (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} |\overrightarrow{\mathcal{I}}\rangle \cdot (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} |\overrightarrow{\mathcal{I}}\rangle = (\overrightarrow{\mathcal{F}} | \overrightarrow{\mathcal{F}}) \cdot (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} |\overrightarrow{\mathcal{I}}\rangle = (\overrightarrow{\mathcal{F}} | \overrightarrow{\mathcal{F}}) \cdot (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} = \pi |\overrightarrow{\mathcal{F}}\rangle. \]

(c) The Mori product, which also depends on \(\beta\) and \(H\):

\[ (A|B)_{m.p.} = \frac{1}{\beta} \int_0^\beta \text{Tr} \left[ \frac{e^{-\beta H}}{Z} A^\dagger e^{-u\beta H} Be^{u\beta H} \right] du. \quad (11) \]

Next, we define the following projection superoperator,

\[ \pi |\overrightarrow{\mathcal{F}}\rangle = (\overrightarrow{\mathcal{F}} | \overrightarrow{\mathcal{I}}) \cdot (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} |\overrightarrow{\mathcal{I}}\rangle. \quad (12) \]

In component form, this is:

\[ \pi |\mathcal{F}_i\rangle = \sum_{j,k} (\mathcal{F}_i | \mathcal{F}_j) \left( (\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1} \right)_{jk} |\mathcal{I}_k\rangle. \quad (13) \]

The symbol \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})\) denotes the \(n\)-by-\(n\) matrix formed by outer product of the column vector \((\overrightarrow{\mathcal{I}})\) and the row vector \((\overrightarrow{\mathcal{I}})\).

The form of the projector is particularly simple if the set of operators is orthogonal. For example, with \(\{I_+, I_-, I_z\}\) the matrix \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})\) is diagonal:

\[ \begin{bmatrix} I_+ \\ I_- \\ I_z \end{bmatrix} | [I_+ \ I_- \ I_z] \rangle = \begin{bmatrix} (I_+|I_+) & 0 & 0 \\ 0 & (I_-|I_-) & 0 \\ 0 & 0 & (I_z|I_z) \end{bmatrix} \quad (15) \]

and the inverse matrix \((\overrightarrow{\mathcal{I}} | \overrightarrow{\mathcal{I}})^{-1}\) takes the diagonal form:

\[ \begin{bmatrix} 1/((I_+|I_+)) & 0 & 0 \\ 0 & 1/((I_-|I_-)) & 0 \\ 0 & 0 & 1/((I_z|I_z)) \end{bmatrix}. \quad (16) \]

We note also that the entries of matrices \((15)\) and \((16)\) are \(c\)-numbers and therefore commute with any linear superoperator.
D. Derivation of Mori’s Equation

The projector method separates the Liouville space into two subsets:

(a) Deterministic and slow variables,
(b) Rapid random fluctuations.

These two orthogonal subspaces of the Liouville space are decomposed using projectors as follows: \( \pi \) is the projector onto the deterministic variables while \( 1 - \pi \) is the projector onto the random part.

The usual treatment begins from the Dyson formula (Eq. 1)

\[
e^{\mathbf{L}t} = e^{(1-\pi)\mathbf{L}} + \int_0^t e^{(t-s)\mathbf{L}} \pi \mathbf{L} e^{(1-\pi)\mathbf{L}} ds. \tag{17}
\]

We operate with this expression on the column vector \((1-\pi)\mathbf{L} |\mathcal{F}\rangle\). For the left hand side of Eq. (17), \(e^{\mathbf{L}t} (1-\pi)\mathbf{L} |\mathcal{F}\rangle\), we get

\[
\left( \frac{\partial}{\partial t} e^{\mathbf{L}t} \right) |\mathcal{F}\rangle - e^{\mathbf{L}t} (\mathbf{L} |\mathcal{F}\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1} |\mathcal{F}\rangle) = \frac{\partial}{\partial t} |\mathcal{F}(t)\rangle - (\mathbf{L} |\mathcal{F}\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1} |\mathcal{F}\rangle) , \tag{18}
\]

where \( |\mathcal{F}(t)\rangle \) is shorthand for \(e^{\mathbf{L}t} |\mathcal{F}\rangle\). For the right hand side of Eq. (17)

\[
e^{(1-\pi)\mathbf{L}} + \int_0^t e^{(t-s)\mathbf{L}} \pi \mathbf{L} e^{(1-\pi)\mathbf{L}} ds\tag{17}
\]

we have:

\[
e^{(1-\pi)\mathbf{L}} (1-\pi)\mathbf{L} |\mathcal{F}\rangle + \int_0^t e^{(t-s)\mathbf{L}} \pi \mathbf{L} e^{(1-\pi)\mathbf{L}} (1-\pi)\mathbf{L} |\mathcal{F}\rangle ds
\]

\[
= |\mathcal{F}(t)\rangle + \int_0^t e^{(t-s)\mathbf{L}} \pi \mathbf{L} |\mathcal{F}(s)\rangle ds
\]

\[
= |\mathcal{F}(t)\rangle + \int_0^t (\mathbf{L} |\mathcal{F}(s)\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1} |\mathcal{F}\rangle) ds
\]

\[
= |\mathcal{F}(t)\rangle + \int_0^t (\mathbf{L} |\mathcal{F}(s)\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1} |\mathcal{F}(t-s)\rangle) ds, \tag{19}
\]

where we have made the following abbreviation:

\[
|\mathcal{F}(t)\rangle = e^{(1-\pi)\mathbf{L}} (1-\pi)\mathbf{L} |\mathcal{F}\rangle. \tag{20}
\]

The last equality follows from the commutativity of the operator \(e^{(t-s)\mathbf{L}}\) with the matrices \((\mathbf{L} |\mathcal{F}(s)\rangle \langle \mathcal{F}|)\) and \((|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1}\) whose entries are \(e\)-numbers.

Combining the left and right hand sides together and making the following definitions

\[
\mathcal{F}(s) = (\mathbf{L} |\mathcal{F}(s)\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1}, \tag{21}
\]

\[
i \mathbf{\Omega} = (\mathbf{L} |\mathcal{F}\rangle \cdot (|\mathcal{F}\rangle \langle \mathcal{F}|)^{-1}, \tag{22}
\]

we get the following set of coupled integro-differential equations:

\[
\frac{\partial}{\partial t} |\mathcal{F}(t)\rangle = i \mathbf{\Omega} |\mathcal{F}(t)\rangle + |\mathcal{F}(t)\rangle
\]

\[
+ \int_0^t \mathcal{F}(s) |\mathcal{F}(t-s)\rangle ds \tag{23}
\]

which read, in component form:

\[
\frac{\partial}{\partial t} |\mathcal{F}_j(t)\rangle = \sum_k i \Omega_{jk} |\mathcal{F}_k(t)\rangle + |\mathcal{F}_j(t)\rangle
\]

\[
+ \int_0^t ds \sum_k \mathcal{F}_{jk}(s) |\mathcal{F}_k(t-s)\rangle . \tag{24}
\]

These are the famous Mori-Zwanzig equations describing the time-evolution of quantum operators in the presence of lattice degrees of freedom.

- The first term on the right hand side is an instantaneous oscillation term. It is a Markovian term, in the sense that it is evaluated at the same time \(t\) as the left hand side of the equation, regardless of the past.
- The second term, \(|\mathcal{F}_j(t)\rangle\), is a random driving force because it is constructed using projectors \((1-\pi)\) onto the “noise subspace” of random variables, according to Eq. (20). This random force describes the effects of the bath dynamics on the behavior of the spin system.
- The last term describes relaxation and is not necessarily exponential; rather, it is a time-lagged memory term giving the effects of past behavior on the present. Note that the quantity \((\mathbf{L} |\mathcal{F}(s)\rangle \langle \mathcal{F}|)\) can be viewed as the covariance of \((\mathbf{L} |\mathcal{F}(s)\rangle)\) and the initial value \(|\mathcal{F}\rangle\), assuming stationary (in the wide sense) random processes.

E. Weak Coupling Approximation

Using definition of adjoint operator \((\mathbf{L}^\dagger|\mathcal{P}, \mathcal{Q}) = (\mathcal{P}, \mathcal{Q})\) and assuming an inner product is chosen such that the Liouvillian is self-adjoint i.e. \(\mathbf{L}^\dagger = \mathbf{L}\), we can write the memory function (Eq. 21) as:
\[ \overline{\mathcal{K}}(s) = (e^{s(1-\pi)}L(1-\pi)L|\mathcal{G}| - 1 \cdot (\mathcal{G}|\mathcal{G})^{-1} \] (25)

where

\[ C(s) = (e^{s(1-\pi)}L(1-\pi)L|\mathcal{G}| - 1. \]

is a time-correlation function.

Following Chorin\textsuperscript{15}, we consider two asymptotic regimes with respect to the correlation time of the dynamics. This correlation function contains the superoperator,

\[ \pi L e^{s(1-\pi)}L(1-\pi)L|\mathcal{G}| \] (26)

which remains unchanged if we insert the projector \((1-\pi)\):

\[ \pi L(1-\pi)e^{s(1-\pi)}L(1-\pi)L|\mathcal{G}|. \] (27)

This expression is also equal to

\[ \pi L(1-\pi)e^{sL}(1-\pi)L|\mathcal{G}| + \pi L(1-\pi)\left[e^{s(1-\pi)} - e^{sL}\right]L(1-\pi)L|\mathcal{G}|. \] (28)

Expanding the second term in a Taylor series:

\[ e^{s(1-\pi)} - e^{sL} = 1 + s(1-\pi)L + \cdots - 1 - sL - \cdots \]
\[ = -sL + O(s^2) \] (29)

and since \((1-\pi)L = 0\), expression \((28)\) becomes:

\[ \pi L(1-\pi)e^{sL}(1-\pi)L|\mathcal{G}| + O(s^2). \] (30)

Integration from 0 to \(t\) yields

\[ \int_0^t \pi L(1-\pi)e^{sL}(1-\pi)L|\mathcal{G}| \, ds + O(t^3). \] (31)

The term \(O(t^3)\) can be neglected if the correlation time

\[ \tau_c = ((1-\pi)L|\mathcal{G}| L|\mathcal{G}|)^{-1} \times \int_0^\infty (e^{s(1-\pi)L}(1-\pi)L|\mathcal{G}| L|\mathcal{G}|) \, ds \] (32)

corresponding to \(C(t)\) is short. In this case, we may approximate \(e^{s(1-\pi)L}\) by \(e^{sL}\) in the expression for the memory function.

At the other extreme where \(C(t)\) decays very slowly, the exponential \(e^{s(1-\pi)L}\) does not vary appreciably and the approximation

\[ e^{s(1-\pi)L} = e^{sL} \] (33)

holds (expand the memory function in powers of \(s\) and retain the zeroth order term).

In both cases, this approximation reflects the fact that the random fluctuations have negligible effect on the time-evolution. This is called the weak-coupling approximation\textsuperscript{15}.

In this approximation, the memory function is given by:

\[ \overline{\mathcal{K}}(s) = ((1-\pi)e^{sL}(1-\pi)L|\mathcal{G}| L|\mathcal{G}|) \cdot (\mathcal{G}|\mathcal{G})^{-1}. \] (34)

F. Short Correlation Times

The integral term,

\[ \int_0^t ds \sum_k \mathcal{K}_{jk}(s) |\mathcal{G}_k(t-s)\] (35)

can be approximated by

\[ |\mathcal{G}_k(t)| \int_0^\infty ds \sum_k \mathcal{K}_{jk}(s) \] (36)

if the correlation time \(\tau_c\) is much shorter than the observation time \(t\). Such approximations are accurate, for example, when the random fluctuations in the lattice are very rapid \((\tau_c \sim 10^{-12}s)\) compared to the observation time \(t \sim 10^{-3}s\).

G. Strong Zeeman Fields

In this section, we work out the strong field approximation needed to derive the famous example of the NMR Bloch equations. To keep the presentation simple, we make use of the inner product of Eq.\textsuperscript{19}. While this approach foregoes the concept of spin temperature and equilibrium as is normally done in the standard treatments of NMR relaxation\textsuperscript{2}, it does simplify the presentation and provides some relaxation rates. We write\textsuperscript{19,19}

\[ F = \sum_i I_i \] (37)

for the total nuclear spin angular momentum operator. For a Hamiltonian \(H\) which consists of a
lattice part $H_L$, and a spin part subdivided into Zeeman $H_0 = \omega_0 F_z$ and small perturbation $H_1 (\|H_1\| \ll \|H_0\|)$:

$$H = H_L + H_0 + H_1,$$  \tag{38}

the oscillation term for the transverse component $F_\pm = F_x \pm iF_y$ of $\mathcal{G}$ is

$$\frac{1}{i} \left( \frac{\langle F_\pm | \mathbf{L} | F_\pm \rangle}{\langle F_\pm | F_\pm \rangle} \right) = \left( \frac{\langle F_\pm | [H_0, F_\pm] \rangle}{\langle F_\pm | F_\pm \rangle} \right) + \left( \frac{\langle F_\pm | [H_1, F_\pm] \rangle}{\langle F_\pm | F_\pm \rangle} \right).$$  \tag{39}

Using the commutator $[F_z, F_\pm] = \pm F_\pm$ and neglecting the second term since $H_1$ is assumed small compared to $H_0$ we are left with

$$\Omega_\pm = \left( \frac{\langle F_\pm | [\omega_0 F_z, F_\pm] \rangle}{\langle F_\pm | F_\pm \rangle} \right) = \pm \omega_0. \tag{40}$$

For the longitudinal component we have:

$$\Omega_{zz} = \frac{1}{i} \frac{\langle F_z | [H_0, F_z] \rangle}{\langle F_z | F_z \rangle} = 0. \tag{41}$$

Thus, the $\Omega$ matrix for the set of operators $\{F_+, F_-, F_z\}$ is

$$\Omega = \begin{pmatrix} \Omega_{++} & \Omega_{+-} & \Omega_{+z} \\ \Omega_{-+} & \Omega_{--} & \Omega_{-z} \\ \Omega_{z+} & \Omega_{z-} & \Omega_{zz} \end{pmatrix} = \begin{pmatrix} +\omega_0 & 0 & 0 \\ 0 & -\omega_0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{42}$$

Omitting the random driving force and using these approximations for $\Omega$, the Mori master equations for $F_\pm$ and $F_z$ read

$$\frac{\partial}{\partial t} |F_\pm(t)\rangle = \pm i\omega_0 |F_\pm(t)\rangle + \int_0^\infty ds \sum_{j=+,-,z} K_{\pm,j}(s) |F_j(t-s)\rangle$$

$$\frac{\partial}{\partial t} |F_z(t)\rangle = \int_0^\infty ds \sum_{j=+,-,z} K_{zz,j}(s) |F_j(t-s)\rangle$$

where $K_{ij}(s)$ is the $3 \times 3$ matrix whose elements are

$$K_{ij}(s) = \frac{\langle F_i | e^{i\omega_0 s} (1 - \pi) | F_j \rangle}{\langle F_j | F_j \rangle}. \tag{43}$$

These equations involve integral operators with past information. Instead of scalar relaxation rates $1/T_1$ and $1/T_2$ they contain convolution integrals over the memory functions $K_{ij}(s)$. Consequently, spin relaxation is not necessarily exponential.

**H. Bloch Equations**

To recover the classical Bloch equations, we make the following assumptions:

(a) The memory function is a diagonal matrix. We will return to this point shortly.

(b) The correlation time is short (see Section II F)

(c) The set of operators is still $\{F_+, F_-, F_z\}$, however, in the equations of motion, we substitute the deviations from thermal equilibrium

$$\mathbf{F}(t) \rightarrow \mathbf{F}(t) - \langle \mathbf{F} \rangle_{eq}$$

We then obtain the classical Bloch equations

$$\frac{\partial}{\partial t} |F_\pm(t)\rangle = \pm i\omega_0 |F_\pm(t)\rangle - \frac{|F_\pm(t)\rangle}{T_2},$$

$$\frac{\partial}{\partial t} |F_z(t)\rangle = -\frac{|F_z(t)\rangle - \langle F_z \rangle_{eq}}{T_1}, \tag{44}$$

where the relaxation rates are

$$\frac{1}{T_2} = -\int_0^\infty \langle LF_{\pm} | e^{i\omega_0 t} (1 - \pi) LF_{\pm} \rangle (F_{\pm} | F_{\pm}) ds,$$

$$\frac{1}{T_1} = -\int_0^\infty \langle LF_z | e^{i\omega_0 t} (1 - \pi) LF_z \rangle (F_z | F_z) ds. \tag{45}$$

The memory function is diagonal if there are no couplings. The projection superoperator

$$\pi |\mathbf{L} F\rangle = (\mathbf{L} \mathbf{F} | \mathbf{F} \rangle \cdot (\mathbf{F} | \mathbf{F} \rangle)^{-1} | \mathbf{F} \rangle, \tag{46}$$

takes the following form

$$\begin{pmatrix} \langle LF_+ | LF_+ \rangle & \langle LF_+ | LF_- \rangle & \langle LF_+ | LF_z \rangle \\ \langle LF_- | LF_+ \rangle & \langle LF_- | LF_- \rangle & \langle LF_- | LF_z \rangle \\ \langle LF_z | LF_+ \rangle & \langle LF_z | LF_- \rangle & \langle LF_z | LF_z \rangle \end{pmatrix} |F_+ \rangle |F_\mp \rangle |F_z \rangle. \tag{47}$$

In the case of no couplings, $H = H_L + H_Z$, and off-diagonal elements such as

$$\langle LF_+ | LF_- \rangle = - (F_+ | F_-)$$

vanish due to the orthogonality of the $F_i$’s. The matrix then simplifies to

$$\begin{pmatrix} \langle LF_+ | LF_+ \rangle & 0 & 0 \\ 0 & \langle LF_- | LF_- \rangle & 0 \\ 0 & 0 & \langle LF_z | LF_z \rangle \end{pmatrix} |F_+ \rangle |F_- \rangle |F_z \rangle. \tag{48}$$

When couplings are weak ($\|H_D\| \ll \|H_Z\|$), these simplified equations of motion $[\text{uncoupled Bloch equations, Eq.} \ (44)]$ yield a reasonable approximation.
III. TIME-DEPENDENT HAMILTONIANS

We now show how the previous treatment can be extended to accommodate time-dependent Hamiltonians.

A. Time-Evolution Operator

The starting point is the Heisenberg equation of motion for an observable $A(t)$:

$$\frac{d}{dt} A(t) = L(t) A(t)$$  \hspace{1cm} (49)

where $L(t)$ is a time-dependent Liouvillian defined by

$$L(t) A(t) = i[H(t), A(t)].$$  \hspace{1cm} (50)

If we write the solution in the form

$$A(t) = U(0, t) A(0)$$  \hspace{1cm} (51)

then Eq. (49) implies:

$$\frac{d}{dt} A(t) = \frac{dU}{dt} A(0) = L(t) U(0, t) A(0)$$  \hspace{1cm} (52)

and since this relation holds for arbitrary initial conditions $A(0)$, we have the general formula which defines the time-evolution operator:

$$\frac{dU(0, t)}{dt} = L(t) U(0, t).$$  \hspace{1cm} (53)

The solution of this equation is given by:

$$U(0, t) = \sum_{n=0}^{\infty} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n L(\tau_1)L(\tau_2)\cdots L(\tau_n)$$  \hspace{1cm} (54)

where the Liouvillians are left time ordered. Consequently, Eq. (49) is a causal relation. That Eq. (54) is the solution of Eq. (53) can be seen by differentiating Eq. (54) with respect to $t$:

$$\frac{dU(0, t)}{dt} = L(t) \sum_{n=0}^{\infty} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n L(\tau_1)L(\tau_2)\cdots L(\tau_n).$$  \hspace{1cm} (55)

A shorthand notation for $U(0, t)$ uses the left Dyson time-ordering operator $\overleftarrow{T}$:

$$U(0, t) = \overleftarrow{T} \exp \left( \int_0^t L(\tau) d\tau \right)$$  \hspace{1cm} (56)

For general time evolution, we have:

$$U(s, t) = \sum_{n=0}^{\infty} \int_s^t d\tau_1 \int_s^{\tau_1} d\tau_2 \cdots \int_s^{\tau_{n-1}} d\tau_n L(\tau_1)L(\tau_2)\cdots L(\tau_n)$$  \hspace{1cm} (57)

which corresponds to

$$U(s, t) = \overleftarrow{T} \exp \left( \int_s^t L(\tau) d\tau \right).$$  \hspace{1cm} (58)
B. Dyson Formula for Time-Dependent Liouvillian

Now we prove the following identity, which holds, for time-dependent Liouvillian,

\[
\overrightarrow{T} \exp \left( \int_0^t d\tau L(\tau) \right) = \overrightarrow{T} \exp \left( \int_0^t d\tau (1 - \pi)L(\tau) \right) + \int_0^t \overrightarrow{T} \exp \left( \int_0^s d\tau L(\tau) \right) \pi L(s) \overrightarrow{T} \exp \left( \int_s^t d\tau (1 - \pi)L(\tau) \right) ds,
\]

(59)

where the right time ordering operator is defined by the time arguments increasing as we go from the left to the right

\[
\overrightarrow{T} \exp \left( \int_s^t d\tau L(\tau) \right) = \sum_{n=0}^{\infty} \int_s^t d\tau_1 \int_s^{\tau_1} d\tau_2 \ldots \int_s^{\tau_{n-1}} d\tau_n L(\tau_n) L(\tau_{n-1}) \ldots L(\tau_1).
\]

(60)

We first rewrite Eq. (59) as

\[
-\overrightarrow{T} \exp \left( \int_0^t d\tau (1 - \pi)L(\tau) \right) = -\overrightarrow{T} \exp \left( \int_0^t d\tau L(\tau) \right) + \int_0^t \overrightarrow{T} \exp \left( \int_0^s d\tau L(\tau) \right) \pi L(s) \overrightarrow{T} \exp \left( \int_s^t d\tau (1 - \pi)L(\tau) \right) ds
\]

(61)

and show that each side of the equality obeys the same differential equation for the same initial conditions. For the left hand side, we have:

\[
\frac{d}{dt} LHS = LHS \cdot (1 - \pi)L(t).
\]

(62)

While for the right hand side:

\[
\frac{d}{dt} RHS = -\overrightarrow{T} \exp \left( \int_0^t d\tau L(\tau) \right) L(t) + \overrightarrow{T} \exp \left( \int_0^t d\tau L(\tau) \right) \pi L(t)
\]

\[
+ \int_0^t \overrightarrow{T} \exp \left( \int_0^s d\tau L(\tau) \right) \pi L(s) \overrightarrow{T} \exp \left( \int_s^t d\tau (1 - \pi)L(\tau) \right) ds(1 - \pi)L(t)
\]

\[
=RHS \cdot (1 - \pi)L(t)
\]

(63)

These identical differential equations, combined with the initial condition at \( t = 0 \), complete the proof of the Dyson formula for time-dependent Li-
C. Derivation of the Mori Formulae Using Time-Dependent Dyson Formula

Using Eq. (69) we may derive the Mori equations in a manner analogous to the time-independent case. The analogue of Eq. (18) is the following: let the left hand side of Eq. (59) act on \((1 - \pi)\mathbf{L}(t) \left| \mathcal{G} \right. \rangle\),

\[
\frac{\partial}{\partial t} \mathcal{G}^\dagger(t) = (\mathbf{L}(t) \mathcal{G}^\dagger \cdot \mathcal{G}^\dagger)^{-1} \mathcal{G}^\dagger(t) \tag{64}
\]

where

\[
\mathcal{G}^\dagger(t) \equiv \mathcal{T} \exp \left( \int_0^t d\tau \mathbf{L}(\tau) \right) \mathcal{G} \tag{65}
\]

is the anti-causal propagation of \(\mathcal{G}\). Next, we let the right hand side of Eq. (69) act on \((1 - \pi)\mathbf{L}(t) \left| \mathcal{G} \right. \rangle\), and obtain an expression analogous to Eq. (19):

\[
\mathcal{F}^\dagger(0, t) + \int_0^t \left( \mathbf{L}(s) \mathcal{F}^\dagger(s,t) \left| \mathcal{G} \right. \rangle \cdot \left( \mathcal{G}^\dagger \mathcal{G}^\dagger \right)^{-1} \mathcal{G}^\dagger(s) \right) ds \tag{66}
\]

where

\[
\mathcal{F}^\dagger(s,t) \equiv \mathcal{T} \exp \left( \int_s^t d\tau (1 - \pi)\mathbf{L}(\tau) \right) (1 - \pi)\mathbf{L}(t) \left| \mathcal{G} \right. \rangle. \tag{67}
\]

Combining these expressions and making the following definitions

\[
\mathcal{X}^\dagger(s,t) \equiv (\mathbf{L}(s) \mathcal{F}^\dagger(s,t) \left| \mathcal{G} \right. \rangle \cdot \left( \mathcal{G}^\dagger \mathcal{G}^\dagger \right)^{-1}, \tag{68}
\]

\[
i \mathcal{\Omega}^\dagger(t) \equiv (\mathbf{L}(t) \mathcal{G}^\dagger \cdot \left( \mathcal{G}^\dagger \mathcal{G}^\dagger \right)^{-1}, \tag{69}
\]

we get the following set of coupled integro-differential equations

\[
\frac{\partial}{\partial t} \mathcal{G}^\dagger(t) = i \mathcal{\Omega}^\dagger(t) \left| \mathcal{G}^\dagger(t) \right. \rangle + \mathcal{F}^\dagger(0, t)
\]

\[
+ \int_0^t \mathcal{X}^\dagger(s,t) \left| \mathcal{G}^\dagger(s) \right. \rangle ds, \tag{70}
\]

which read in component form

\[
\frac{\partial}{\partial t} \mathcal{G}^\dagger_j(t) = \sum_k i\Omega^\dagger_{jk}(t) \mathcal{G}^\dagger_k(t) + \left| \mathcal{G}^\dagger_j(0, t) \right. \rangle
\]

\[
+ \int_0^t ds \sum_k \mathcal{X}^\dagger_{jk}(s,t) \left| \mathcal{G}^\dagger_k(s) \right. \rangle. \tag{71}
\]

These are the Mori equations for time-dependent Liouvillian. It is noteworthy that the memory kernel \(\mathcal{X}^\dagger_{jk}(s,t)\) no longer depends on the time difference \(t - s\), but also depends on the origin of time \(s\). This is a consequence of the non-commutativity of the Hamiltonian at different points in time.

Another point of interest is that the dynamics are given for the anti-causal operators. An adjoint equation of motion can also be derived which describes causal evolution, but requires adjoint definitions of the propagator and the expression upon which the Dyson equation is applied to. The weak coupling approximation of the previous sections remains applicable, if it is needed.

We also note that the Liouvillian which appears under the integral sign of Eq. (71) cannot be replaced by an average Liouvillian (see Eqs. 67 and 68). Such a substitution is not generally justified. However, it is possible to replace the exponential function of Eq. (74) by a Magnus expansion.

D. Change of Reference Frames

For convenience, we may change frames of reference at will. This is done using time-ordered transformations, as is normally done when solving the Liouville von Neumann equation. We summarize these well-known transformations in the notation of this article.

1. Interaction Representation

If the time-dependent Liouvillian decomposes into the form \(\mathbf{L}(t) = \mathbf{L}_0(t) + \mathbf{L}_V(t)\), the Heisenberg equation of motion is

\[
\frac{dA(t)}{dt} = [\mathbf{L}_0(t) + \mathbf{L}_V(t)] A(t). \tag{72}
\]

We define the transformed operators:

\[
\tilde{A} = \mathcal{T} \exp \left( - \int_0^t d\tau \mathbf{L}_0(\tau) \right) A, \tag{73}
\]

\[
\tilde{\mathbf{L}} = \mathcal{T} \exp \left( - \int_0^t d\tau \mathbf{L}_0(\tau) \right) \mathbf{L}, \tag{74}
\]

where \(\mathcal{T}\) indicates a time-ordering from left to right, with the most recent Liouvillian to the right. These transformations are anti-causal. Then,
\[
\frac{d\tilde{A}}{dt} = \frac{d}{dt} \overrightarrow{T} \exp \left( - \int_0^t d\tau L_0(\tau) \right) A
\]
\[
= - \overrightarrow{T} \exp \left( - \int_0^t d\tau L_0(\tau) \right) \dot{L}_0(t) A + \overrightarrow{T} \exp \left( - \int_0^t d\tau L_0(\tau) \right) [L_0(t)A + \dot{L}_V(t)A(t)]
\]
\[
= \tilde{L}_V(t) \tilde{A}.
\]

(75)

Thus, in a rotating frame of reference, a Liouville equation

\[
\frac{d\tilde{A}}{dt} = \tilde{L}_V \tilde{A}
\]

(76)

holds, where \( \tilde{L}_V \) is the perturbation part of the Liouvillian expressed in the rotating frame.

2. Toggling Frame Transformation

In Equation (75), we may further decompose the interaction representation Liouvillian

\[
\tilde{L}_V = \tilde{L}_1 + \tilde{L}_2,
\]

(77)

where \( \tilde{L}_1 \) is the part corresponding to the RF field and \( \tilde{L}_2 \) is the remaining “internal” part of the Liouvillian (e.g. spin-spin interactions).

Consider a transformation to the so-called “toggling frame”,

\[
\tilde{A} = \overrightarrow{T} \exp \left( - \int_0^t \tilde{L}_1(t') dt' \right) \hat{A},
\]

(78)

where \( \overrightarrow{T} \) is the Dyson time-ordering operator, which places the most recent events to the right. Then,

\[
\frac{d\hat{A}(t)}{dt} = \tilde{L}_2 \hat{A}(t).
\]

(79)

The solution to this equation is,

\[
\hat{A}(t) = \overrightarrow{T} \exp \left( \int_0^t \tilde{L}_2(t') dt' \right) \hat{A}(0),
\]

(80)

where

\[
\tilde{L}_2 = \overrightarrow{T} \exp \left( - \int_0^t d\tau L_0(\tau) \right) L_2.
\]

(82)

IV. CONCLUSION

We have extended the Mori theory to the case of time-dependent Hamiltonians. To the author’s knowledge, the previously published treatments of Mori relaxation theory in the NMR literature did not include the case of time-dependent Liouvillian. This makes it possible to treat general cases of cw or pulsed irradiations in NMR and/or coherent optics, for arbitrary timescales of the molecular motions relative to the period of irradiation. Also, we have outlined a way of introducing coherent averaging effects into the Mori equations.

* URL: http://waugh.cchem.berkeley.edu

1 E. Fick and G. Sauermann. The Quantum Statistics of Dynamic Processes. Springer-Verlag, 1990.
2 M. Mehring. Principles of high resolution NMR in solids. Springer-Verlag, Berlin, 1983.
3 A. Abragam and M. Goldman. Nuclear magnetism: order and disorder. Clarendon Press, Oxford, 1982.
4 A. Abragam. Principles of Nuclear Magnetism. Oxford, New York, 1983.
5 M.H. Levitt and L. Di Bari. Steady state in magnetic resonance pulse experiments. Phys. Rev. Lett., 69:3124–3127, 1992.
6 W.-K. Rhim, D.P. Burum, and D.D. Ellerman. Calculation of spin-lattice relaxation during pulsed spin locking in solids. J. Chem. Phys., 68:692–695, 1978.
7 S. Baskin and A.H. Zewail. Freezing atoms in motion:
Principles of femtochemistry and demonstration by laser stroboscopy. *J. Chem. Educ.*, 78:737, 2001.

8. R. Zwanzig. *Nonequilibrium Statistical Mechanics*. Oxford University Press, New York, 2001.

9. D. Kivelson and K. Ogan. Spin relaxation theory in terms of Mori’s formalism. In J.S. Waugh, editor, *Advances in Magnetic Resonance*, volume 7, pages 71–155. Academic Press, New York, 1974.

10. R.R. Ernst, G. Bodenhausen, and A. Wokaun. *Principles of nuclear magnetic resonance in one and two dimensions*. Oxford: Clarendon Press, New York, 1987.

11. J. Jeener. Superoperators in quantum mechanics. *Advances in magnetic resonance*, 1:1–1, 1899.

12. R. Kubo, M. Toda, and N. Hatshitsume. *Statistical Physics II: Nonequilibrium Statistical Mechanics*. Springer, Berlin, 2nd edition, 1991.

13. H. Mori and H. Fujisaka. On nonlinear dynamics of fluctuations. *Prog. Theor. Phys.*, 49(3):764–775, 1973.

14. R. Zwanzig. Ensemble method in the theory of irreversibility. *J. Chem. Phys.*, 33(5):1338–1341, 1960.

15. A.J. Chorin and O.H. Hald, editors. *Stochastic tools in mathematics and science*, volume 1 of *Surveys and tutorials in the applied mathematical sciences*. Springer, Berlin, Heidelberg, 2006.

16. D. Budker, D.F. Kimball, and D.P. DeMille, editors. *Atomic Physics: An Exploration through Problems and Solutions*. Oxford University Press, New York, 2004.

17. B.L. Holian and D.J. Evans. Classical response theory in the Heisenberg picture. *J. Chem. Phys.*, 83:3560–3566, 1985.

18. D.J. Evans and G.P. Morriss. Time-dependent response theory. *Mol. Phys.*, 64:521–534, 1988.

19. A mere replacement of the time-independent Liouvil- lian by a time-dependent Liouvillian is not possible unless further justification is provided.