Derivation of a Master Equation for Intramolecular Relaxation Using Projection Operator Techniques in Liouville Space

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A generalized master equation is derived to describe intramolecular rearrangement processes. It is an inhomogeneous equation, including memory effects. The derivation is based on the Liouville space formalism. Because chemically relevant information is contained in the off-diagonal elements of the density matrix, a non-diagonal coarse-graining projector is used. All necessary assumptions are stated explicitly. By making further approximations, the master equation can be reduced to an inhomogeneous von Neumann equation with an effective Liouville operator the imaginary part of which is responsible for relaxation-like coarse-grained solutions. All neglected terms are given in closed form. The character of the solutions of the master equation is discussed in "coordinate-free" manner, i.e. without referring to the underlying Hilbert space.

1. Introduction

It is a question of fundamental importance for chemical reaction kinetics, whether or not an isolated system of molecular dimensions can undergo — though in a somewhat restricted sense — an irreversible process. The theory by Rice, Ramsperger, Kassel and Marcus (RRKM)[1–4] describes a unimolecular reaction as a consequence of two interfering mechanisms, an "outer" and an "inner" one. By a strong external collision energy is provided to the molecule. The redistribution of this energy between the inner degrees of freedom then leads to unimolecular reaction. This "inner" mechanism of energy randomization is specified by the assumption that the ensemble of reacting molecules is microcanonical with respect to the inner energy. At this very point an intramolecular relaxation process is implied with a relaxation time short compared with the time between two subsequent external collisions. The succes of the RRKM-theory confirms the picture of two mechanisms. Because these time scales are so different, one would expect that a model without an explicit external mechanism should still be of chemical importance. The best-known example for a chemical process determined by an inner mechanism is the high pressure rate of a unimolecular gas phase reaction.

Master equations on a heuristic basis have been used previously in describing intramolecular processes, but they were a phenomenological tool only[5,6]. Recently this procedure was very much refined through application of Markov chain techniques[7]. For the first time, Hofacker[8–10] gave a "derivation" of a relaxation equation starting with the von Neumann equation and connecting the various terms to microscopic quantities.

The standard technique for the derivation of a master equation is presently the projection operator method in Liouville space, introduced by Zwanzig[11,12]. Keizer[13] applied it to the problem of relaxation of inner degrees of freedom; but this theory is based essentially on an "outer" mechanism and is valid only for a projection operator on the diagonal elements of the density operator. Every chemical reaction however, even a simple one as an isomerization, is connected with changing positions of the nuclei involved. Therefore relevant information is contained in the non-diagonal matrix elements of the density operator (if the otherwise practical representation of stationary states is used[10]).

It is the aim of this paper to derive a generalized master equation for intramolecular relaxation processes, i.e. an equation including memory effects. By using the above mentioned techniques with a non-diagonal projection operator, chemical processes are included. The underlying assumptions are stated clearly, as well as the additional approximations necessary to reduce the generalized master equation to the form given by Hofacker. The neglected terms are given explicitly to improve this first approximation.

In Section 2 the Liouville space formalism is reviewed briefly insofar as necessary for the theory developed here. The connection between coarse-graining and irreversibility leads to the definition

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of a non-diagonal projection operator in Section 3. In Section 4 the generalized master equation and the relaxation equation are derived using resolvent techniques. Section 5 gives a short discussion of the solution of the relaxation equation.

2. Liouville Space Formalism

Quantum statistics describes the state of a system by a density matrix W which is an operator acting in the usual Hilbert space $\mathfrak{H}$ of quantum mechanics. In dynamical problems, one considers operations mapping the manifold of density matrices onto itself. Also the so-called coarse-graining can be viewed as an operation on density matrices. So one is led naturally to study operations on a certain set of operators of the Hilbert space $\mathfrak{H}$. Things would be much easier, if this set were a Hilbert space itself.

Therefore, one associates with $\mathfrak{H}$ the set $\mathfrak{L}$ of all operators (more exactly: with finite trace), mapping $\mathfrak{H}$ onto itself, and provides this set $\mathfrak{L}$ with a scalar product by

$$(A \,\|\, B) := \mathrm{Tr}(A^\dagger B) \quad \text{for all } A, B \in \mathfrak{L} . \tag{1}$$

Elements of $\mathfrak{L}$ will be characterized by capital letters. One shows easily that the above defined scalar product fulfils the usual axioms[14]. By this procedure, $\mathfrak{L}$ becomes a Hilbert space, the so-called Liouville space[12]. The expectation value of an operator A in an ensemble described by an density matrix W is simply given by

$$\langle A \rangle_W = \mathrm{Tr}(W A) = (W \,\|\, A) . \tag{2}$$

The scalar product implies a norm in $\mathfrak{L}$ as usual:

$$\| A \| := \sqrt{(A \,\|\, A)} . \tag{3}$$

The equation of motion for elements of the Liouville space is the von Neumann equation:

$$i \frac{\mathrm{d}}{\mathrm{d}t} W = \mathscr{L} W . \tag{4}$$

It is formally equivalent to the Schrödinger equation. The Liouville operator $\mathscr{L}$ is defined by

$$\mathscr{L} A := [H, A] \quad \text{for all } A \in \mathfrak{L} \tag{5}$$

where H is the Hamilton operator of the system. Operators acting on elements of the Liouville space will be characterized by script letters.

The von Neumann equation is solved by

$$W(t) = \mathscr{U}(t)\, W(0) \tag{6}$$

with the unitary operator

$$\mathscr{U}(t) = \exp(-i \mathscr{L} t) . \tag{7}$$

As is well known, its action on any element A of $\mathfrak{L}$ is connected with the Hamiltonian by

$$\mathscr{U}(t)\, A = e^{-iHt} A \, e^{iHt} . \tag{8}$$

The connection between H and $\mathscr{L}$ leads to

Theorem 1:

If H is hermitian in $\mathfrak{H}$, then $\mathscr{L}$ is hermitian in $\mathfrak{L}$.

Proof: $(A \,\|\, \mathscr{L} B) = \mathrm{Tr}(A^\dagger H B - A^\dagger B H)$
$= \mathrm{Tr}([H, A]^\dagger B) = (\mathscr{L} A \,\|\, B)$,

whence follows: $\mathscr{L}^{\#} = \mathscr{L}$. All eigenvalues of $\mathscr{L}$ are therefore real. The hermitian adjoint operator to an operator $\mathscr{O}$ will be denoted by $\mathscr{O}^{\#}$.

In the following, the adjointing operator $\mathscr{T}$ definded by

$$\mathscr{T} A := A^\dagger \quad \text{for all } A \in \mathfrak{L} \tag{9}$$

will be useful. $\mathscr{T}$ is an antilinear operator[14] and has the properties

$$\mathscr{T}^{\#} = \mathscr{T} , \tag{10}$$

$$\mathscr{T}^2 = \mathscr{E} . \tag{11}$$

$\mathscr{E}$ denotes the identity operator on $\mathfrak{L}$. Equation (11) is the minimal polynomial of the operator $\mathscr{T}$, therefore its eigenvalues are $\varepsilon_1 = 1$ and $\varepsilon_2 = -1$. The corresponding eigenmatrices are hermitian and antihermitian respectively. This can be used in proving the following theorem.

Theorem 2:

To every eigenvalue $\lambda \neq 0$ of $\mathscr{L}$ with corresponding eigenmatrix W there corresponds an eigenvalue $-\lambda$ with eigenmatrix $W^\dagger$. Hermitian and antihermitian eigenmatrices correspond to the eigenvalue $\lambda = 0$.

Proof: For all $A \in \mathfrak{L}$ one has

$$\mathscr{T} \mathscr{L} A = \mathscr{T}[H, A] = \\ = A^\dagger H - H A^\dagger = -[H, A^\dagger] = -\mathscr{L} \mathscr{T} A$$

or stated generally:

$$\mathscr{L} \mathscr{T} + \mathscr{T} \mathscr{L} = 0 . \tag{12}$$

Together with $\mathscr{L} W = \lambda W$, one obtains

$$\mathscr{L} W^\dagger = \mathscr{L} \mathscr{T} W = -\mathscr{T} \mathscr{L} W = -\lambda W^\dagger \tag{13}$$

which is the first proposition. Using $\mathscr{T} W = \varepsilon W$ with $\varepsilon = \pm 1$ the second part of the theorem follows from

$$\varepsilon \lambda W = \lambda \mathscr{T} W = \mathscr{T} \mathscr{L} W = - \mathscr{L} \mathscr{T} W = - \lambda \varepsilon W. \tag{14}$$

3. Coarse-graining and Irreversibility

Irreversible equations lika a master equation are obtained from the reversible von Neumann equation by constraining to that information which can be controlled by macroscopic observations [15,16]. In analogy to classical statistical mechanics one considers only those quantities which are averaged over energetically adjacent states. The Hamilton operator H is divided into an unperturbed part H_0 and a perturbation V[9]:

$$H = H_0 + V. \tag{15}$$

This implies a corresponding separation of the Liouville operator

$$\mathscr{L} = \mathscr{L}_0 + \mathscr{L}_1 \tag{16}$$

with

$$\mathscr{L}_1 A = [V, A]. \tag{17}$$

The eigenstates $|\alpha\rangle$ of the unperturbed Hamilton operator H_0:

$$H_0 \, |\alpha\rangle = E_\alpha \, |\alpha\rangle \tag{18}$$

are collected in mutually orthogonal subspaces according to their energy. To this end the energy axis is divided into intervals $\Delta E_1, \Delta E_2, \ldots, \Delta E_a, \ldots, \Delta E_b, \ldots$. For every cell of the phase space a projector is defined:

$$R_a = \sum_{\alpha \in a} |\alpha\rangle \langle\alpha| . \tag{19}$$

Here, $\alpha \in a$ is an abreviation for $E_\alpha \in \Delta E_a$. The macroscopic state belonging to the density matrix W is described by

$$\bar{W} = \sum_a c_a W_a \tag{20}$$

with the following definitions

$$c_a = \mathrm{Tr}(W R_a), \tag{21}$$

$$W_a = R_a / g_a , \tag{22}$$

and

$$g_a = \mathrm{Tr}(R_a). \tag{23}$$

In the same way, a correspondence is established between an observable A and the macroscopic observable $\bar{A}$ by:

$$\bar{A} = \sum_a A_a R_a \tag{24}$$

where

$$A_a = \mathrm{Tr}(W_a A) = \sum_{\alpha \in a} \langle\alpha| \, A \, |\alpha\rangle / g_a . \tag{25}$$

A_a is the expectation value averaged over the states $\alpha \in a$. For the expectation value of $\bar{A}$ in an ensemble $\bar{W}$ one gets:

$$\langle \bar{A} \rangle_{\bar{W}} = \mathrm{Tr}(\bar{W} \bar{A}) = \sum_a c_a A_a . \tag{26}$$

The derivation of a master equation could be simplified a lot by regarding the coarse-graining as operation in Liouville space [11,16]:

$$\bar{W} = \mathscr{D} W = \sum_a \mathrm{Tr}(W R_a) \, R_a / g_a . \tag{27}$$

$\mathscr{D}$ is a projector onto that subspace of $\mathfrak{L}$ which contains the macroscopically relevant information.

It has already been mentioned that the usual derivations of a master equation [15,16] are not applicable to chemical problems. There are three essential differences in the case of an intramolecular rearrangement process [9]:

(I) The system under consideration has a finite number of degrees of freedom;
(II) Non-diagonal elements of the density matrix contain relevant information;
(III) The density matrix at time $t = 0$ does not commute with the unperturbed Hamiltonian H_0.

Because of (I), the master equation to be derived is only valid on a certain time scale (cf. the detailed argumentation in [9]). (III) gives rise to a somewhat more complicated derivation than usual [12,16]. (II) can be handled by the introduction of a new coarse-graining projector $\mathscr{P}$. Consider the following set of elements of $\mathfrak{L}$:

$$P_{ab} = (g_a g_b)^{-1/2} \sum_{\alpha \in a} \sum_{\beta \in b} |\alpha\rangle \langle\beta| . \tag{28}$$

The following equations turn out to be very useful:

$$P_{ab} = P_{ba}{}^\dagger , \tag{29}$$

$$P_{ab} P_{a'b'} = \delta_{a'b} P_{ab'} , \tag{30}$$

$$\mathrm{Tr}\, P_{ab} = \delta_{ab} , \tag{31}$$

$$(P_{ab} \| \, P_{a'b'}) = \delta_{aa'} \delta_{bb'} . \tag{32}$$

Equations (29) – (32) can easily be proved.

The set $\{P_{ab}\}$ consists of orthonormal elements [17]. The new coarse-graining operator $\mathscr{P}$ is given by

$$\begin{aligned} \mathscr{P} A &:= \sum_{a,b} \mathrm{Tr}(P_{ab}{}^\dagger A) \, P_{ab} \\ &= \sum_{a,b} \| P_{ab}) (P_{ab} \| \, A) \quad \text{for all } A \in \mathfrak{L} . \end{aligned} \tag{33}$$

By an obvious extension of Dirac's formalism, Eq. (33) reads:

$$\mathscr{P} = \sum_{a,b} \| P_{ab})\,(P_{ab} \| \,. \tag{34}$$

Theorem 3:

The operator $\mathscr{P}$, defined by Eq. (34) is a projector[14], i.e.

$$\text{a)} \qquad \mathscr{P}^2 = \mathscr{P}\,, \tag{35}$$

$$\text{b)} \qquad \mathscr{P}^{\#} = \mathscr{P}\,. \tag{36}$$

Proof: a)

$$\begin{aligned} \mathscr{P}^2 &= \mathscr{P} \sum_{a,b} \| P_{ab})\,(P_{ab} \| \\ &= \sum_{a,b} \sum_{c,d} \| P_{cd})\,(P_{cd} \| P_{ab})\,(P_{ab} \| \\ &= \sum_{a,b} \sum_{c,d} \| P_{cd})\,\delta_{ac}\,\delta_{bd}\,(P_{ab} \| = \mathscr{P}\,. \end{aligned}$$

b)

$$\begin{aligned} (A \| \mathscr{P} B) &= \sum_{a,b} (A \| P_{ab})\,(P_{ab} \| B) \\ &= \sum_{a,b} (P_{ab} \| A)^*\,(P_{ab} \| B) \\ &= (\sum_{a,b} P_{ab}(P_{ab} \| A) \| B) \\ &= (\mathscr{P} A \| B)\,. \end{aligned}$$

The coarse-graining introduced above is completely equivalent to that used by HOFACKER[9]. There, the coarse-graining of the perturbation V e.g. is carried out by

$$V \to \bar{V} = \sum_{a,b} \sum_{\substack{\alpha \in a \\ \beta \in b}} |\alpha\rangle\, V_{ab} \langle \beta | \tag{37}$$

with

$$V_{ab} = V(E_a, E_b) = (g_a\, g_b)^{-1} \sum_{\substack{\alpha \in a \\ \beta \in b}} \langle \alpha |\, V \,| \beta \rangle\,. \tag{38}$$

Taking into account that

$$(P_{ab} \| V) = (g_a\, g_b)^{-1/2}\, V_{ab} \tag{39}$$

one recognizes immediately

$$\bar{V} = \mathscr{P} V\,. \tag{40}$$

Definition (30) unifies the treatment of observables and density operators [cf. Eqs. (20), (24)]. The original coarse-graining projector $\mathscr{D}$ can be retained through restriction of $\mathscr{P}$ to diagonal elements which is allowed for macroscopic observables A:

$$(P_{ab} \| A) = \mathrm{Tr}(P_{ab}{}^{\dagger} A) = 0 \quad \text{for} \quad a \neq b \tag{41}$$

and

$$\mathscr{D} A = \sum_a \| P_{aa})\,(P_{aa} \| A)\,. \tag{42}$$

For operators A which are diagonal in the $\{|\alpha\rangle\}$-representation one has

$$\begin{aligned} (P_{ab} \| A) &= (g_a\, g_b)^{-1/2} \sum_{\substack{\alpha \in a \\ \beta \in b}} \langle \alpha |\, A \,| \alpha \rangle\, \delta_{\alpha\beta} \\ &= g_a{}^{-1}\, \delta_{ab} \sum_{\alpha \in a} \langle \alpha |\, A \,| \alpha \rangle\,. \end{aligned} \tag{43}$$

For $A = H_0$, this yields:

$$\mathscr{P} H_0 = \sum_a E_a\, P_{aa} \tag{44}$$

with

$$E_a = \sum_{\alpha \in a} E_\alpha / g_a\,. \tag{45}$$

Two assumptions will be stated now which underlie the derivation of the master equation given in the next section:

$$\mathscr{P} \mathscr{L}_0 \mathscr{P} = \mathscr{P} \mathscr{L}_0\,. \tag{A1}$$

This equation holds only approximately; both of its sides are calculated separately to estimate the error. Here use is made of the identity

$$\mathscr{P}[A, \mathscr{P} B] = [\mathscr{P} A, \mathscr{P} B] \tag{46}$$

which can be proved using Eqs. (29)—(32):

$$\begin{aligned} \mathscr{P}[A, \mathscr{P} B] &= \sum_{a,b} \sum_{a',b'} P_{ab}(P_{ab} \| [A, P_{a'b'})\,(P_{a'b'} \| B) \\ &= \sum_{a,b,c} P_{ab}\{(P_{ac} \| A)\,(P_{cb} \| B) - (P_{ac} \| B)\,(P_{cb} \| A)\} \\ &= \sum_{a,b} \sum_{a',b'} (\delta_{a'b}\, P_{ab'} - \delta_{ab'}\, P_{a'b})\,(P_{ab} \| A)\,(P_{a'b'} \| B) \\ &= [\mathscr{P} A, \mathscr{P} B]\,. \end{aligned} \tag{47}$$

Taking into account Eqs. (38)—(40) and (43)—(45) and putting $A = H_0$, one obtaines:

$$\mathscr{P} \mathscr{L}_0 \mathscr{P} B = \sum_{a,b} P_{ab}(P_{ab} \| B)\,(E_a - E_b)\,. \tag{48}$$

On the other side of relation (A1), one has

$$\mathscr{P} \mathscr{L}_0 B = \sum_{a,b} P_{ab}(P_{ab} \| [H_0, B])\,. \tag{49}$$

To arrive at Eq. (A1), the following equation must hold for every $B \in \mathfrak{L}$:

$$(P_{ab} \| B)\,(E_a - E_b) \simeq (P_{ab} \| [H_0, B])\,. \tag{50}$$

This is equivalent to:

$$(E_a - E_b) \sum_{\substack{\alpha \in a \\ \beta \in b}} \langle \alpha |\, A \,| \beta \rangle \simeq \sum_{\substack{\alpha \in a \\ \beta \in b}} (E_\alpha - E_\beta)\, \langle \alpha |\, A \,| \beta \rangle\,. \tag{51}$$

If the respective coarse-graining intervals ΔE_a and ΔE_b are small enough and the number of states within them, i.e. g_a and g_b, are large enough, and if there are no correlations between $E_\alpha - E_\beta$ and

$\langle \alpha | A | \beta \rangle$ — which seems reasonable for all non-pathological $A \in \mathfrak{L}$ —, then Eq. (51) may be a good approximation and relation (A1) should hold.

The second essential assumption concerns the initial state $W(t=0)$:

$$\mathscr{P} W(0) = W(0) . \tag{A2}$$

To justify this assumption, consider the following relation among the relevant time scales[10]:

$$E_{at}^{-1} \ll \tau_{\mathrm{m}} \ll \tau_{\mathrm{r}} \ll \tau_{\mathrm{tr}} . \tag{52}$$

The symbols have the following meaning: E_{at}^{-1} atomic time, τ_{m} measuring time available for the preparation of $W(0)$, τ_{r} chemical relaxation time, τ_{tr} translational time.

The width of the coarse-graining intervals ΔE_a has been chosen as to meet the constraint[9]

$$\Delta E_a \ll \Delta E_{cg} \ll \tau_{\mathrm{r}}^{-1} . \tag{53}$$

According to Eq. (52) one has a fortiori:

$$\Delta E_{cg} \ll \tau_{\mathrm{m}}^{-1} . \tag{54}$$

Therefore, the coarse-graining intervals ΔE_a can never be resolved by an initial measurement with an uncertainty τ_{m}^{-1}, i.e. no measurement can distinguish $\mathscr{P} W(0)$ from $W(0)$. Relation (A2) corresponds to the random phases approximation of statistical mechanics[15], more exactly to the assumption of a macroscopic initial state[16]. If one defines

$$\mathscr{Q} := \mathscr{E} - \mathscr{P} , \tag{55}$$

$\mathscr{Q}$ is also a projector and relation (A2) may be written as

$$\mathscr{Q} W(0) = 0 . \tag{56}$$

The projector $\mathscr{Q}$ measures the fluctuations around the average of the different cells of phase space. As an example, take the expectation value of an observable A in the state $\mathscr{Q} W$:

$$\begin{aligned}(\mathscr{Q} W \| A) &= (W \| A) - (\mathscr{P} W \| \mathscr{P} A) \\ &= \langle A \rangle_W - \langle \bar{A} \rangle_{\bar{W}} .\end{aligned} \tag{57}$$

The abreviations $\bar{A} = \mathscr{P} A$ and $\bar{\mathscr{L}} = \mathscr{P} \mathscr{L} \mathscr{P}$ will be used subsequently [cf. Eq. (20) and (24)].

4. Derivation of a Master Equation

As a starting point for the derivation of a master equation for an intramolecular rearrangement reaction the damping form of the von Neumann equation will be used[8–10]. The operator equivalent of Eq. (4) is

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{U}(t) = -i \mathscr{L} \mathscr{U}(t) \tag{58}$$

with the initial condition

$$\mathscr{U}(0) = \mathscr{E} . \tag{59}$$

The Laplace transform of Eq. (58) is

$$z \mathscr{R}(z) - \mathscr{E} = -i \mathscr{L} \mathscr{R}(z) . \tag{60}$$

Here,

$$\mathscr{R}(z) = 1/(z + i \mathscr{L}) \tag{61}$$

is the resolvent of $\mathscr{U}(t) = \exp(-i \mathscr{L} t)$. This resolvent is connected with the resolvent

$$\mathscr{R}_0(z) = 1/(z + i \mathscr{L}_0) \tag{62}$$

of the unperturbed evolution operator

$$\mathscr{U}_0(t) = \exp(-i \mathscr{L}_0 t)$$

by the operator identity [cf. Eq. (16)]:

$$\mathscr{R}(z) = \mathscr{R}_0(z) - \mathscr{R}_0(z)\, i \mathscr{L}_1 \mathscr{R}(z) . \tag{63}$$

The application of this identity to the right hand side of Eq. (60) yields:

$$z \mathscr{R}(z) - \mathscr{E} = -i \mathscr{L}_0 \mathscr{R} - i \mathscr{L}_1 \mathscr{R}_0 - \mathscr{L}_1 \mathscr{R}_0 \mathscr{L}_1 \mathscr{R} . \tag{64}$$

If one performs the inverse Laplace transform, one obtains:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{U}(t) &= -i \mathscr{L}_0 \mathscr{U}(t) - i \mathscr{L}_1 \mathscr{U}_0(t) \\ &\quad - \int_0^t \mathrm{d}\tau\, \mathscr{L}_1 \mathscr{U}_0(\tau) \mathscr{L}_1 \mathscr{U}(t-\tau) .\end{aligned} \tag{65}$$

Out of this equation the damping form of the von Neumann equation results if one applies it to $W(0)$ [cf. Eq. (6)]:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t} W &= -i \mathscr{L}_0 W - i \mathscr{L}_1 e^{-i \mathscr{L}_0 t} W(0) \\ &\quad - \int_0^t \mathrm{d}\tau\, \mathscr{L}_1 e^{-i \mathscr{L}_0 \tau} \mathscr{L}_1 W(t-\tau) .\end{aligned} \tag{66}$$

It seems evident after the discussions of the last section that one must concentrate only on that part of the density matrix accessible by measurement. The aim of this section is therefore to derive an equation that governs the time development of $\mathscr{P} W$. If one applies the projector $\mathscr{P}$ to Eq. (64) and considers the relations (A1) and (55), one gets:

$$\begin{aligned}\mathscr{P}(z \mathscr{R} - \mathscr{E}) &= -i \mathscr{P} \mathscr{L}_0 \mathscr{P} \mathscr{R} - i \mathscr{P} \mathscr{L}_1 \mathscr{P} \mathscr{R}_0 \\ &\quad - i \mathscr{P} \mathscr{L}_1 \mathscr{Q} \mathscr{R}_0 \\ &\quad - \mathscr{P} \mathscr{L}_1 \mathscr{R}_0 \mathscr{L}_1 (\mathscr{P} + \mathscr{Q}) \mathscr{R} .\end{aligned} \tag{67}$$

Multiplying Eq. (60) by $\mathcal{Q}$ from the left yields[12]:

$$\mathcal{Q}(z\mathcal{R} - \mathcal{E}) = -i\,\mathcal{Q}\mathcal{L}\mathcal{R}$$

or

$$z\,\mathcal{Q}\mathcal{R} = \mathcal{Q} - i\,\mathcal{Q}\mathcal{L}\mathcal{R}\,. \tag{68}$$

If one adds $i\,\mathcal{Q}\mathcal{L}\mathcal{Q}\mathcal{R}$ on both sides, one obtains

$$[z + i\,\mathcal{Q}\mathcal{L}\mathcal{Q}]\,\mathcal{Q}\mathcal{R} = \mathcal{Q} - i\,\mathcal{Q}\mathcal{L}\mathcal{P}\mathcal{R}\,. \tag{69}$$

so that

$$\mathcal{Q}\mathcal{R}(z) = \mathcal{Q}\mathcal{S}(z)\,[\mathcal{Q} - i\mathcal{Q}\mathcal{L}_1\mathcal{P}\mathcal{R}(z)] \tag{70}$$

where $\mathcal{S}(z)$ is the resolvent of

$$\mathcal{V}(t) = \exp(-i\,\mathcal{Q}\mathcal{L}\mathcal{Q}t)\,. \tag{71}$$

Now, $\mathcal{Q}\mathcal{R}$ in the last term of Eq. (67) can be replaced:

$$\begin{aligned}\mathcal{P}(z\mathcal{R} - \mathcal{E}) = &-i\mathcal{P}\mathcal{L}_0\mathcal{P}\mathcal{R} - i\mathcal{P}\mathcal{L}_1\mathcal{P}\mathcal{R}_0\\ &-i\mathcal{P}\mathcal{L}_1\mathcal{Q}\mathcal{R}_0\mathcal{Q}\\ &-\mathcal{P}\mathcal{L}_1\mathcal{P}\mathcal{R}_0\mathcal{P}\mathcal{L}_1\mathcal{R}\\ &-\mathcal{P}\mathcal{L}_1\mathcal{Q}\mathcal{R}_0\mathcal{Q}\mathcal{L}_1\mathcal{P}\mathcal{R}\\ &-\mathcal{P}\mathcal{L}_1\mathcal{R}_0\mathcal{L}_1\mathcal{Q}\mathcal{S}\mathcal{Q}\\ &+i\mathcal{P}\mathcal{L}_1\mathcal{R}_0\mathcal{L}_1\mathcal{Q}\mathcal{S}\mathcal{Q}\mathcal{L}_1\mathcal{P}\mathcal{R}\,.\end{aligned} \tag{72}$$

The last term of this equation is of third order in the perturbation V and can be regarded as a small renormalization of the unperturbed Hamiltonian H_0. It shall be neglected henceforth, because it does not contribute to the relaxation. The inverse Laplace transform of the equation above is:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{P}\mathcal{U}(t) = &-i\mathcal{P}\mathcal{L}_0\mathcal{P}\mathcal{U}(t) - i\mathcal{P}\mathcal{L}_1\mathcal{P}\mathcal{U}_0(t)\\ &-i\mathcal{P}\mathcal{L}_1\mathcal{Q}\mathcal{U}_0(t)\,\mathcal{Q}\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{P}\mathcal{U}_0(\tau)\,\mathcal{P}\mathcal{L}_1\mathcal{P}\mathcal{U}(t-\tau)\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{Q}\mathcal{U}_0(\tau)\,\mathcal{Q}\mathcal{L}_1\mathcal{P}\mathcal{U}(t-\tau)\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{U}_0(\tau)\,\mathcal{L}_1\mathcal{Q}\mathcal{V}(t-\tau)\,\mathcal{Q}.\end{aligned} \tag{73}$$

Operating with this equation on $W(0)$ and taking into account relation (A2) one obtains:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{P}W(t) = &-i\mathcal{P}\mathcal{L}_0\mathcal{P}W - i\mathcal{P}\mathcal{L}_1\mathcal{P}e^{-i\mathcal{L}_0 t}W(0)\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{P}e^{-i\mathcal{L}_0\tau}\mathcal{P}\mathcal{L}_1\mathcal{P}W(t-\tau)\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{P}e^{-i\mathcal{L}_0\tau}\mathcal{Q}\mathcal{L}_1\mathcal{Q}W(t-\tau)\,.\end{aligned} \tag{74}$$

This is the generalized master equation for the density matrix $\mathcal{P}W$ which was sought; it is a closed equation in $\mathcal{P}W$ and contains memory effects because of the integral terms.

This equation can be simplified[8–10] if one observes the underlying time scales (52). Under the first integral $\mathcal{L}_0$ is of the order of E_{at} so that the integration can be continued to infinity as one recognizes by changing the integration variable to τE_{at}. Moreover, it can be shown[9], that $\mathcal{P}W(t-\tau)$ can be replaced by $\mathcal{P}W(t)$. The series expansion of the exponential function together with relation (A1) gives:

$$\mathcal{P}\exp(-i\mathcal{L}_0 t) = \mathcal{P}\exp(-i\mathcal{P}\mathcal{L}_0\mathcal{P}t)\,\mathcal{P}\,. \tag{75}$$

Taking all this into account, the first integral can be carried out formally to yield:

$$\begin{aligned}\int_0^\infty \mathrm{d}\tau\,\mathcal{P}e^{-i\mathcal{L}_0\tau}\mathcal{P} &= \lim_{\varepsilon\to 0}\mathcal{P}\,\frac{1}{\varepsilon + i\mathcal{P}\mathcal{L}_0\mathcal{P}}\,\mathcal{P}\\ &= \pi\,\mathcal{P}\,\delta(\mathcal{P}\mathcal{L}_0\mathcal{P})\,\mathcal{P} - i\,\mathcal{P}\,\mathrm{Pv}\left(\frac{1}{\mathcal{P}\mathcal{L}_0\mathcal{P}}\right)\mathcal{P}\,.\end{aligned} \tag{76}$$

Pv stands for Cauchy's principal value. The imaginary part of the integral will be neglected furtheron[9]; the real part allows for a simplification because of Eq. (48):

$$\begin{aligned}&\mathcal{P}\,\delta(\mathcal{P}\mathcal{L}_0\mathcal{P})\,\mathcal{P}B\\ &\quad= \sum_{a,b} P_{ab}(P_{ab}\,\|\,B)\,\delta(E_a - E_b) = \mathcal{D}B\,.\end{aligned} \tag{77}$$

The master equation (74) now reads

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{P}W = &-i\mathcal{P}\mathcal{L}_0\mathcal{P}W - i\mathcal{P}\mathcal{L}_1\mathcal{P}e^{-i\mathcal{L}_0 t}W(0)\\ &-\pi\mathcal{P}\mathcal{L}_1\mathcal{D}\mathcal{L}_1\mathcal{P}W\\ &-\int_0^t \mathrm{d}\tau\,\mathcal{P}\mathcal{L}_1\mathcal{Q}e^{-i\mathcal{L}_0\tau}\mathcal{Q}\mathcal{L}_1\mathcal{P}W(t-\tau)\,.\end{aligned} \tag{78}$$

This is the relaxation equation which has been derived previously by other methods[8,9] — if one neglects the integral term. For larger molecules with a nearly continous distribution of states on the energy scale terms of the form $\mathcal{Q}\mathcal{L}_0\mathcal{Q}$ and $\mathcal{P}\mathcal{L}_1\mathcal{Q}$ should cause no drastic effects.

To show the claimed identity of master equations explicitly remember Eq. (46) and the statement made after Eq. (57), and note the identity

$$\mathcal{D} = \mathcal{D}\mathcal{P} = \mathcal{P}\mathcal{D} = \mathcal{P}\mathcal{D}\mathcal{P}\,. \tag{79}$$

Then Eq. (78) can be rewritten as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\bar{W} = &-i\,\bar{\mathcal{L}}_0\bar{W} - i\,\bar{\mathcal{L}}_1 e^{-i\bar{\mathcal{L}}_0 t}\,\bar{W}(0)\\ &-\pi\,\bar{\mathcal{L}}_1\mathcal{D}\bar{\mathcal{L}}_1\bar{W}\end{aligned} \tag{80}$$

or more explicitly:

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\bar{W} = -\,i[\bar{H}_0, \bar{W}] - i[\bar{V}, e^{-i\bar{H}_0 t}\,\bar{W}(0)\,e^{i\bar{H}_0 t}] - \pi[\bar{V}, \mathscr{D}[\bar{V}, \bar{W}]]\,. \tag{81}$$

This equation is identical to Eq. (18) of Ref.[9].

5. Character of the Solutions

The master Eq. (80) has the form of a von Neumann equation with an inhomogeneous term:

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\bar{W} = -\,i\,\mathscr{L}_{\mathrm{eff}}\,\bar{W} - i\,\bar{\mathscr{L}}_1\,e^{-i\bar{\mathscr{L}}_0 t}\,\bar{W}(0)\,. \tag{82}$$

The effective Liouville operator $\mathscr{L}_{\mathrm{eff}}$ is given by:

$$\mathscr{L}_{\mathrm{eff}} = \bar{\mathscr{L}}_0 - i\,\pi\,\bar{\mathscr{L}}_1\mathscr{D}\,\bar{\mathscr{L}}_1\,. \tag{83}$$

As one recognizes, $\mathscr{L}_{\mathrm{eff}}$ is no longer a hermitian operator on $\mathfrak{L}$. To assure the completeness of the set of eigenmatrices of $\mathscr{L}_{\mathrm{eff}}$ in $\mathfrak{L}$, it is assumed subsequently that $\mathscr{L}_{\mathrm{eff}}$ is at least similar to a normal operator on $\mathfrak{L}$.

Because of the discussion following relation (A2), one may expect $\bar{W}(0)$ to be sufficiently smooth, so that the inhomogeneous term in Eq. (82) vanishes according to the Riemann-Lebesgue Lemma[9]. The general case can be treated analogously to Ref.[9].

The eigenvalue problem

$$\mathscr{L}_{\mathrm{eff}}\,W_q = \lambda_q\,W_q\,, \quad \|W_q\| = 1 \tag{84}$$

has been treated previously[9,10]. The results of that discussion are summarized for completeness. The proofs of the following theorems are given here in a "coordinate-free" manner using the techniques of Liouville space. The assumption made in Ref.[9,10], that the perturbation V is represented by a real matrix can be avoided here.

The operator relation [cf. Eq. (46)]

$$\mathscr{P}\,\mathscr{L}_{\mathrm{eff}}\,\mathscr{P} = \mathscr{L}_{\mathrm{eff}} \tag{85}$$

shows that the eigenvalue problem (84) can be restricted to the subspace of $\mathfrak{L}$ onto which $\mathscr{P}$ projects. All elements of the orthogonal complement of that subspace are trivial eigenmatrices of $\mathscr{L}_{\mathrm{eff}}$ corresponding to the eigenvalue $\lambda_q = 0$; they are of no interest in the subsequent discussion.

Theorem 4:

Diagonal matrices $W_q = \mathscr{D}\,W_q$ are the only eigenmatrices of $\mathscr{L}_{\mathrm{eff}}$ which belong to the eigenvalue $\lambda_q = 0$.

Proof:

The identity

$$\mathscr{D}[A, \mathscr{D}\,B] = 0 \quad \text{for all} \quad A, B \in \mathfrak{L} \tag{86}$$

yields for $A = \bar{H}_0$ and arbitrary B

$$\mathscr{D}\,\bar{\mathscr{L}}_0\mathscr{D} = \mathscr{D}\,\bar{\mathscr{L}}_0 = \bar{\mathscr{L}}_0\mathscr{D} = 0 \tag{87}$$

and for $A = \bar{V}$ and $B = \bar{\mathscr{L}}_1\,W$

$$\mathscr{D}\,\bar{\mathscr{L}}_1\mathscr{D}\,\bar{\mathscr{L}}_1\,W = 0\,. \tag{88}$$

These equations can be combined to

$$\mathscr{D}\,\mathscr{L}_{\mathrm{eff}} = 0\,. \tag{89}$$

Together with Eq. (84) one has

$$0 = \mathscr{D}\,\mathscr{L}_{\mathrm{eff}}\,W_q = \lambda_q\mathscr{D}\,W_q = \lambda_q\,W_q\,. \tag{90}$$

Therefore, diagonal matrices belong to the eigenvalue $\lambda_q = 0$. To prove that they are the only ones, one starts with

$$\mathscr{L}_{\mathrm{eff}}\,W_q = 0\,. \tag{91}$$

This leads to

$$\begin{aligned} 0 &= (W_q \,\|\, \bar{\mathscr{L}}_0\,W_q) - i\,\pi\,(W_q \,\|\, \bar{\mathscr{L}}_1\mathscr{D}\,\bar{\mathscr{L}}_1\,W_q) \\ &= (W_q \,\|\, \bar{\mathscr{L}}_0\,W_q) - i\,\pi\,\|\mathscr{D}\,\bar{\mathscr{L}}_1\,W_q\|^2\,. \end{aligned} \tag{92}$$

Hence, one obtains

$$\mathscr{D}\,\bar{\mathscr{L}}_1\,W_q = 0 \tag{93}$$

and combined with Eq. (91):

$$\bar{\mathscr{L}}_0\,W_q = 0\,. \tag{94}$$

Therefore $\bar{H}_0$ and W_q commute and can be diagonalized together.

Theorem 5:

Eigenvalues different from zero have a negative imaginary part; the diagonal part of the corresponding eigenmatrices vanishes.

Proof: According to Eq. (84), one has

$$\lambda_q = (W_q \,\|\, \bar{\mathscr{L}}_0\,W_q) - i\,\pi\,(W_q \,\|\, \bar{\mathscr{L}}_1\mathscr{D}\,\bar{\mathscr{L}}_1\,W_q)\,. \tag{95}$$

$\bar{\mathscr{L}}_0$ and $\bar{\mathscr{L}}_1\mathscr{D}\,\bar{\mathscr{L}}_1$ are hermitian; this implies:

$$\operatorname{Im}\lambda_q = -\,\pi\,\|\mathscr{D}\,\bar{\mathscr{L}}_1\,W_q\|^2 < 0\,. \tag{96}$$

Because of Eq. (89), the application of the operator $\mathscr{D}$ to Eq. (84) yields:

$$0 = \lambda_q\mathscr{D}\,W_q\,, \tag{97}$$

whence $\mathscr{D}\,W_q = 0$ for $\lambda_q \neq 0$.

Theorem 6:

If λ_q is an eigenvalue with corresponding eigenmatrix W_q, then so is $-\lambda_q^*$ with eigenmatrix $W_q^\dagger$.

The proof runs as that of Theorem 2 if one takes into account the antilinearity of $\mathcal{T}$ and the relation

$$\mathcal{T}\mathcal{L}_{\text{eff}} = \mathcal{T}(\bar{\mathcal{L}}_0 - i\pi\bar{\mathcal{L}}_1\mathcal{D}\bar{\mathcal{L}}_1) = -\mathcal{L}_{\text{eff}}\mathcal{T}. \quad (98)$$

With these theorems in mind the discussion of the time evolution for the general solution of the master Eq. (82) is performed easily. Because of Eq. (89), one has

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{D}\bar{W}(t) = -i\mathcal{D}\mathcal{L}_{\text{eff}}\bar{W} = 0 \quad (99)$$

whence:

$$\mathcal{D}\bar{W}(t) = \mathcal{D}\bar{W}(0). \quad (100)$$

The non-diagonal part of $\bar{W}(0)$ may be expanded by the eigenmatrices of $\mathcal{L}_{\text{eff}}$:

$$(\mathcal{E} - \mathcal{D})\bar{W}(0) = \sum_{\lambda_q \neq 0} d_q W_q. \quad (101)$$

From this follows:

$$(\mathcal{E} - \mathcal{D})\bar{W}(t) = \sum_{\lambda_q \neq 0} d_q e^{-i\lambda_q t} W_q. \quad (102)$$

Because of Theorem 5, the non-diagonal part of the density matrix decays exponentially, and $\bar{W}(t)$ relaxes to $\bar{W}(\infty) = \mathcal{D}W(0)$. The density matrix $\bar{W}(t)$ stays hermitian through all times as $\bar{W}$ and $\bar{W}_\dagger$ obey the same differential equation.

6. Conclusion

Using projection operator techniques in Liouville space a generalized master Eq. (74) for intramolecular relaxation could be derived. Relations (A1) and (A2) are necessary assumptions for that derivation and should hold for large enough molecules (containing more than 4 atoms). The change of the density matrix depends on its past form through the integral terms which therefore include memory effects. However, these memory effects are small as is shown by the reduction of the generalized master Eq. (74) to a von Neumann Eq. (82) with an effective Liouville operator $\mathcal{L}_{\text{eff}}$ (83). The main effect of the integral terms is the imaginary part of $\mathcal{L}_{\text{eff}}$ which is responsible for the relaxation-like behaviour of the solutions (cf. Theorem 5). Equation (82) can also be applied to intramolecular rearrangement processes because a non-diagonal coarse-graining projector has been used. The chemically relevant information contained in the off-diagonal elements of the density matrix is not lost by this procedure. To obtain the rate R of an isomerization reaction, for example, one has to calculate the change of the expectation value of the species operator[10] P for the reaction products (cf. Eq. (102)):

$$R = \frac{\mathrm{d}}{\mathrm{d}t}\operatorname{Tr}(\bar{W}(t)P) = -i\sum_{\lambda_q \neq 0} d_q\lambda_q e^{-i\lambda_q t}\operatorname{Tr}(W_q P). \quad (103)$$

This shows that the rate constant is connected with that eigenvalue of $\mathcal{L}_{\text{eff}}$ which has the smallest imaginary part. It should be emphasized, however, that the relaxation Eq. (82) is valid only for times shorter than that between two "outer" collisions.

Because of the formalism, all neglected terms could be given explicitly. The formalism also allows for better higher approximations through inclusion of neglected terms.

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