Chemical Physics 20 (1977) 135–143

SUPEROPERATOR FORMALISM IN THE PERTURBATION THEORY OF DENSITY OPERATORS OBEYING GENERALIZED LIOUVILLE EQUATIONS

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Received 30 August 1976

The superoperator formalism is a very convenient tool in the perturbation theory for density – or any operators obeying equations of the general (stochastic) Liouville type. The new concept of a superoperator norm is introduced for the discussion of convergence of perturbation series as well as for the error estimates of finite-order approximations. Explicit formulas for the diagonal elements of the density matrix up to second order are given. The results hold for the stationary state of a system or for its time behavior at small or large times. The present formalism may find useful applications in problems like, e.g., chemically induced polarization phenomena, triplet–triplet annihilation (delayed fluorescence) and laser theory.

1. Mathematical preliminaries: unitary operator space

Consider linear operators $A, B, \ldots$ on $\mathcal{H}$ to itself [1,2], where $\mathcal{H}$ is a finite-dimensional Hilbert space of dimension N, and linear operations of these operators defined by

$$(\alpha A + \beta B)\varphi = \alpha(A\varphi) + \beta(B\varphi)\,,$$

$$\alpha, \beta \in \mathbf{C}\,, \quad \varphi \in \mathcal{H}\,. \qquad (1.1)$$

C is the field of complex numbers.

The set $\mathcal{B}(\mathcal{H})$ of all linear operators in $\mathcal{H}$ is a linear vector space with $\dim \mathcal{B} = N^2$ [3]. Since the product of operators is also defined and the ring axioms are satisfied $\mathcal{B}(\mathcal{H})$ is an algebra.

$\mathcal{H}$ is a unitary space since there is defined the ordinary scalar product (φ, ψ) for any pair $\varphi, \psi \in \mathcal{H}$ and the distinguished unitary norm (L^2-norm) is chosen to be

$$\|\varphi\| = (\varphi, \varphi)^{1/2}\,. \qquad (1.2)$$

The concept of convergence of a sequence of vectors in $\mathcal{H}$ can be extended to that of a sequence of operators in $\mathcal{B}$ in terms of suitable operator norm,

$$\|A\| = \sup_{\|\varphi\| \leq 1} \|A\varphi\|\,, \quad A \in \mathcal{B}\,, \quad \varphi \in \mathcal{H}\,. \qquad (1.3)$$

(The norm symbol for operators will not be distinguished from that for vectors.) Thus, $\mathcal{B}$ is a normed vector space. It can even be chosen to be a unitary space by introducing the so-called sesquilinear trace metric for the scalar product,

$$(A, B) = \mathrm{Tr}\, A^\dagger B\,, \qquad (1.4)$$

which satisfies all required axioms [4]. Consequently, the distinguished unitary norm in analogy to (1.2) would be

$$\|A\|_2 = (\mathrm{Tr}\, A^\dagger A)^{1/2}\,, \qquad (1.5)$$

which is the Hilbert–Schmidt or Frobenius norm with the property [5]

$$\|A\| \leqslant \|A\|_2\,. \qquad (1.6)$$

Because of this inequality we will prefer the norm (1.3) for convergence- and error estimates.

2. Superoperators

2.1. Norm and convergence

Consider linear operators P, Q, ... in $\mathcal{B}(\mathcal{H})$, so-called superoperators [6–8], as well as the corresponding

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superalgebra $\mathcal{S}(\mathcal{B})$ with

$$\dim \mathcal{S} = N^4 . \tag{2.1}$$

As for ordinary operators, one writes $\mathsf{PP} = \mathsf{P}^2$, $\mathsf{PPP} = \mathsf{P}^3$, and so on, including the definition $\mathsf{P}^0 \equiv 1$ (1 is the unit superoperator). Then,

$$\mathsf{P}^m \mathsf{P}^n = \mathsf{P}^{m+n} , \quad (\mathsf{P}^m)^n = \mathsf{P}^{mn} ;$$

$$m, n = 0, 1, 2, \ldots , \tag{2.2}$$

and for any polynomial $p_n(z) = a_0 + a_1 z + \ldots + a_n z^n$ in the indeterminate z the associated superoperator is defined to be

$$p_n(\mathsf{P}) = a_0 + a_1 \mathsf{P} + \ldots + a_n \mathsf{P}^n . \tag{2.3}$$

Tentatively, we even may consider infinite series of the form

$$p_\infty(\mathsf{P}) = \lim_{n\to\infty} p_n(\mathsf{P}) , \tag{2.4}$$

which give rise to convergence questions.

For the consideration of perturbation series in $\mathcal{S}$ it is convenient to make $\mathcal{S}$ a normed space (and at the same time a normed algebra) by introducing the new concept of a superoperator norm defined by

$$\|\mathsf{P}\| = \sup_{\|A\|\leq 1} \|\mathsf{P}A\| , \quad \mathsf{P} \in \mathcal{S} , \quad A \in \mathcal{B} . \tag{2.5}$$

By virtue of this definition all theorems on ordinary operator norms as found, e.g., in [1] can literally be taken over for superoperators and will not be repeated here. We only note briefly that $\|\mathsf{P}\|$ is a continuous function of P and

$$\|\mathsf{PQ}\| \leq \|\mathsf{P}\| \, \|\mathsf{Q}\| , \tag{2.6}$$

from which one deduces

$$\|\mathsf{P}^{m+n}\| \leq \|\mathsf{P}^m\| \, \|\mathsf{P}^n\| , \tag{2.7}$$

and

$$\|\mathsf{P}^n\| \leq \|\mathsf{P}\|^n . \tag{2.8}$$

Again, the notion of convergence in the norm, but now for a sequence of superoperators, is well-defined. In particular, absolute convergence for (2.4) means

$$\sum_{n=0}^{\infty} |a_n| \, \|\mathsf{P}^n\| = r < \infty , \tag{2.9}$$

such that $p_\infty(\mathsf{P})$ exists with the property

$$\|p_\infty(\mathsf{P})\| \leq r . \tag{2.10}$$

Furthermore, if p_∞ exists and for any $\mathsf{Q} \in \mathcal{S}$ the products $\mathsf{P}^n\mathsf{Q}$ $(\forall n)$ are defined, the continuity guarantees that

$$p_\infty(\mathsf{P})\mathsf{Q} = \Big[\lim_{n\to\infty} p_n(\mathsf{P})\Big]\mathsf{Q} = \lim_{n\to\infty} [p_n(\mathsf{P})\mathsf{Q}] , \tag{2.11}$$

which will be of importance for later applications. Finally, consider the special sum

$$\mathsf{S} = \sum_{n=0}^{\infty} \mathsf{P}^n , \tag{2.12}$$

with the property

$$\mathsf{PS} = \mathsf{S} - 1 , \quad \text{or} \quad \mathsf{S}(1 - \mathsf{P}) = 1 . \tag{2.13}$$

This is the Neumann series

$$(1 - \mathsf{P})^{-1} = \sum_{n=0}^{\infty} \mathsf{P}^n . \tag{2.14}$$

It is absolutely convergent for $\|\mathsf{P}\| < 1$ because

$$\|(1 - \mathsf{P})^{-1}\| \leq \frac{1}{1 - \|\mathsf{P}\|} . \tag{2.15}$$

2.2. Matrixelements

The natural extension of the concept of matrixelements of ordinary operators to those of superoperators proceeds as follows: Choose an orthonormal basis $\{\varphi_k; k = 1, 2, \ldots, N\}$ in $\mathcal{H}$ and define the matrixelements of any operator $A \in \mathcal{B}$ as usually by $A_{lm} = (\varphi_l, A\varphi_m)$. Since any superoperator $\mathsf{P} \in \mathcal{S}$ transforms A into another $A' \in \mathcal{B}$ one can write the (i, k)-element of A' as

$$(\mathsf{P}A)_{ik} = \sum_{l,m} \mathsf{P}_{ik}^{lm} A_{lm} . \tag{2.16}$$

The construction of P_{ik}^{lm} can be given in terms of a basis $\{\tau_{\alpha\beta}; \alpha, \beta = 1, 2, \ldots, N\}$ in $\mathcal{B}$ such that

$$A = \sum_{\alpha,\beta} c_{\alpha\beta} \tau_{\alpha\beta} . \tag{2.17}$$

In fact, $\{\tau_{\alpha\beta}\}$ can be chosen to be an orthonormal operator basis [9] in the sense that

$$(\tau_{\alpha\beta}, \tau_{\mu\nu}) = \delta_{\alpha\mu}\delta_{\beta\nu} , \tag{2.18}$$

the scalar product being defined by (1.4). The coefficients $c_{\mu\nu}$ in the expansion (2.17) are given by

$$c_{\mu\nu} = (A, \tau_{\mu\nu}) . \tag{2.19}$$

A simple, but non-hermitian choice for the matrix representation of $\tau_{\alpha\beta}$ would be

$$(\varphi_l, \tau_{\alpha\beta}\varphi_m) = \delta_{l\alpha}\delta_{m\beta} ,$$

$$\{(\tau_{\alpha\beta})_{lm}\} = \begin{pmatrix} 0 & \vdots & 0 \\ \cdots & 1 & \cdots \\ 0 & \vdots & 0 \end{pmatrix} \begin{matrix} \\ \alpha \\ \\ \end{matrix} \quad \beta . \tag{2.20}$$

For this case one has directly from (2.17)

$$A_{lm} = c_{lm} . \tag{2.21}$$

For some purposes it may be more convenient to chose a set of hermitian τ's as, e.g., in spin-$\frac{1}{2}$ problems where any (2×2) matrix is usually written as a superposition of the three Pauli-matrices plus the unit matrix.

Now, the natural definition of matrixelements of P is

$$\mathsf{P}_{ik}^{lm} = (\tau_{ik}, \mathsf{P}\tau_{lm}) = \mathrm{Tr}\, \tau_{ik}^{\dagger} \mathsf{P} \tau_{lm} . \tag{2.22}$$

For illustration, we consider the superoperator P defined by a commutator,

$$\mathsf{P}A = [P, A] , \quad P, A \in \mathcal{B} , \tag{2.23}$$

and calculate, according to (2.22),

$$\begin{aligned} \mathsf{P}_{ik}^{lm} &= \mathrm{Tr}\{[\tau_{lm}, \tau_{ik}^{\dagger}] P\} \\ &= \sum_{s,t,p} \{(\tau_{lm})_{st} (\tau_{ki})_{tp} - (\tau_{ki})_{st}(\tau_{lm})_{tp}\} P_{ps} \\ &= P_{il}\delta_{mk} - P_{mk}\delta_{il} , \end{aligned} \tag{2.24}$$

where the special representation (2.20) has been used.

Finally, the (ik, lm)-element of a product PQ is calculated according to the prescription

$$(\mathsf{PQ})_{ik}^{lm} = \sum_{s,t} \mathsf{P}_{ik}^{st} \mathsf{Q}_{st}^{lm} . \tag{2.25}$$

This completes the few important rules needed for simple calculations.

3. Special stationary perturbation theory for superoperators

3.1. General

The foregoing superoperator formalism may find useful applications in problems of quantum statistical mechanics and stochastic processes in particular. We are going to consider a certain class of equations for density operators as they are important in theories of chemically induced dynamical nuclear- or electron polarization (CIDNP, CIDEP) [10,11], nuclear magnetic resonance (NMR) and electron spin resonance (ESR) [12], and delayed fluorescence [13,14]. This type of equation is sometimes called a generalized (also stochastic) Liouville equation and may be written as

$$\dot{X} = -\frac{i}{\hbar} [H, X] + \mathsf{L}X + B , \tag{3.1}$$

$$\mathsf{L} \in \mathcal{L}(\mathcal{B}) , \quad H, B \in \mathcal{B} , \quad X \in \mathcal{B}_{\rho} \subset \mathcal{B} ,$$

where $\mathcal{B}_{\rho}$ is a subset of $\mathcal{B}$ consisting of all positive operators ρ,

$$\rho \geqslant 0 . \tag{3.2}$$

For the later discussion of (3.1) for the steady state and short or large time behavior one may use the usual normalization,

$$\mathrm{Tr}\, \rho = 1 , \tag{3.3}$$

but in general, the trace depends upon time. $\dot{X}$ is the formal time-derivative and H a hamiltonian. Thus, the first term on the right of eq. (3.1) represents the ordinary quantum mechanical time evolution of X. The remaining terms arise because of a coupling of the physical system described internally by H to the environment. The second term, e.g., could arise due to the presence of stochastic potentials.

For stationary situations we set $\dot{X} = 0$ and assume in the following that $B \neq 0$. In addition, we introduce a splitting of operators,

$$H = H_0 + H_1 , \quad \mathsf{L} = \mathsf{L}_0 + \mathsf{L}_1 , \tag{3.4}$$

which may be arbitrary so far. Then, the general linear eq. (3.1) is rewritten in the form

$$(\mathsf{P}+\mathsf{Q})X = B\,, \tag{3.5}$$

with the abbreviations

$$\mathsf{P}X = \frac{i}{\hbar}\,[H_0, X] - \mathsf{L}_0 X\,, \tag{3.6}$$

$$\mathsf{Q}X = \frac{i}{\hbar}\,[H_1, X] - \mathsf{L}_1 X\,. \tag{3.7}$$

The perturbational approach for the solution of (3.5) is based on the assumption that the superoperator Q is "small compared with P" in a sense to be specified with mathematical rigor below, and that for P one already knows an appropriate set of basis vectors such that it is diagonal in the sense that

$$\mathsf{P}^{lm}_{ik} = \delta_{li}\delta_{mk}p_{ik}\,. \tag{3.8}$$

This implies according to (2.6) that the set of eigenfunctions of H_0 is known. Consequently, the splitting of L is no longer arbitrary because L_0 must be diagonal in the above basis.

Assume the existence of solution of the unperturbed problem,

$$\mathsf{P}X_0 = B\,, \quad \text{or} \quad X_0 = \mathsf{P}^{-1}B\,, \tag{3.9}$$

in terms of which the general eq. (3.5) is transformed into

$$(1 + \mathsf{P}^{-1}\mathsf{Q})\,X = X_0\,, \tag{3.10}$$

whose formal solution is

$$X = (1 + \mathsf{P}^{-1}\mathsf{Q})^{-1}\,X_0\,. \tag{3.11}$$

The alternating version of the Neumann series (2.14) for the inverse superoperator reads

$$(1 + \mathsf{P}^{-1}\mathsf{Q})^{-1} = \sum_{n=0}^{\infty}(-1)^n(\mathsf{P}^{-1}\mathsf{Q})^n\,, \tag{3.12}$$

whose absolute convergence is guaranteed if

$$\|\mathsf{P}^{-1}\mathsf{Q}\| < 1\,. \tag{3.13}$$

Thus, in the formulation (3.11) the perturbation appears as deviation from the unit superoperator 1, and the "smallness of Q with respect to P" has been established in the sense of (3.13). As a consequence, we have

$$\|\mathsf{P}^{-1}\mathsf{Q}\| \leqslant \|\mathsf{P}^{-1}\|\,\|\mathsf{Q}\|\,, \tag{3.14}$$

where $\|\mathsf{P}^{-1}\|$ is estimated as for ordinary operators [15] by

$$\|\mathsf{P}^{-1}\| \leqslant \frac{\|\mathsf{P}\|^{N^2-1}}{|\det \mathsf{P}|}\,, \tag{3.15}$$

which leads to the final result that

$$\|\mathsf{Q}\| < \frac{|\det \mathsf{P}|}{\|\mathsf{P}\|^{N^2-1}} \tag{3.16}$$

must hold in order to allow for a perturbational treatment of eq. (3.5). Furthermore, (3.12) may be applied termwise to X_0,

$$X = \sum_{n=0}^{\infty}[(-1)^n(\mathsf{P}^{-1}\mathsf{Q})^n X_0]\,. \tag{3.17}$$

It is interesting to establish a formal connection of the present superoperator perturbation theory with the well-known methods of quantum mechanical perturbation theory for ordinary operators. This can be done for non-singular B (which may not be true in general) by rewriting (3.10) in the form

$$X = X_0 + X_0(-B^{-1}\mathsf{Q})X\,. \tag{3.18}$$

Note that this structure is analogous to the resolvent method in formal scattering theory [16] and, in particular, to the Dyson equation for the Green functions in many body theory [17] with the operator $(-B^{-1}\mathsf{Q})$ playing formally the role of the "irreducible self-energy part". Successive iteration of (3.18) yields the power series

$$X = \sum_{n=0}^{\infty} X_0(-B^{-1}\mathsf{Q}X_0)^n\,, \tag{3.19}$$

and for (3.18) as well as (3.19) we can give a graphical representation in terms of "supergraphs" where ◍ symbolises the perturbed and ○ the unperturbed density operator and ▨ the "superinteraction" $(-B^{-1}\mathsf{Q})$, as shown in fig. 1.

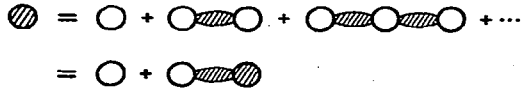

Fig. 1. Graphical representation of the generalized Liouville equation.

3.2. Second order perturbation

Using the definitions

$$\mathsf{T} = (1 + \mathsf{P}^{-1}\mathsf{Q})^{-1}\ ,\quad \mathsf{T}_n = \sum_{k=0}^{n} (-1)^k (\mathsf{P}^{-1}\mathsf{Q})^k\ , \tag{3.20}$$

the error introduced by cutting the infinite series (3.12) at the nth order is estimated by

$$\|\mathsf{T} - \mathsf{T}_n\| = \left\| \sum_{k=n+1}^{\infty} (-1)^k (\mathsf{P}^{-1}\mathsf{Q})^k \right\| \leqslant \frac{\|\mathsf{P}^{-1}\mathsf{Q}\|^{n+1}}{1 - \|\mathsf{P}^{-1}\mathsf{Q}\|}\ . \tag{3.21}$$

In many practical applications it may be sufficient to include $k = 0, 1, 2$ ($n = 2$) to approximate T in (3.20). Up to second order we write

$$X^{(2)} = X_0 + X_1 + X_2\ , \tag{3.22}$$

and note that

$$\|X - X^{(2)}\| \leqslant \|\mathsf{T} - \mathsf{T}_2\|\ . \tag{3.23}$$

This together with (3.21) for $n = 2$ gives the relative error

$$\frac{\|X - X^{(2)}\|}{\|X\|} \leqslant \frac{\|\mathsf{P}^{-1}\mathsf{Q}\|^3}{\|X\|(1 - \|\mathsf{P}^{-1}\mathsf{Q}\|)}\ . \tag{3.24}$$

To put this inequality into a more convenient form and to express it entirely in terms of known quantities one makes use of a theorem [18] valid for any normal operator $A \in \mathcal{B}$ with eigenvalues $\{\lambda_j; j = 1, 2, \ldots, N\}$:

$$\|A\| = \max_j |\lambda_j|\ . \tag{3.25}$$

The generalization for normal superoperators gives for the norm of P (see (3.8))

$$\|\mathsf{P}\| = \max_{i,k} |p_{ik}|\ . \tag{3.26}$$

Since $X \in \mathcal{B}_\rho$, it follows from the definitions (3.2) and (3.3) and from (3.25) that its spectrum is bounded by

$$\frac{1}{N} \leqslant \|X\| \leqslant 1\ . \tag{3.27}$$

With (3.14), (3.25), (3.27), the abbreviation

$$\alpha_0 = \min_{i,k} |p_{ik}|\ , \tag{3.28}$$

and the assumption that rank $\mathsf{P} = N^2$, the final estimate of (3.24) is

$$\frac{\|X - X^{(2)}\|}{\|X\|} \leqslant \frac{N\|\mathsf{Q}\|^3}{\alpha_0^2(\alpha_0 - \|\mathsf{Q}\|)}\ . \tag{3.29}$$

Thus, with the upper bound of $\|\mathsf{Q}\|$ expressed in terms of a small quantity $\epsilon > 0$,,

$$\|\mathsf{Q}\| = \alpha_0 \left(\frac{\epsilon}{2N}\right)^{1/3} \left\{ \left[1 + \left(1 + \frac{4\epsilon}{27}\right)^{1/2}\right]^{1/3} + \left[1 - \left(1 + \frac{4\epsilon}{27}\right)^{1/2}\right]^{1/3} \right\}, \tag{3.30}$$

the relative error in $X^{(2)}$ is bounded by

$$\frac{\|X - X^{(2)}\|}{\|X\|} \leqslant \epsilon\ . \tag{3.31}$$

This establishes an upper bound for the relative error, e.g., in any of the diagonal elements of the density matrix $\{X^{(2)}_{\mu\nu}\}$ which are of direct interest in physical applications.

Finally, let us give these diagonal elements explicitly. According to (3.17) and (3.22), the single contributions to $X^{(2)}$ are

$$X_0 = \mathsf{P}^{-1}B\ , \tag{3.32}$$

$$X_1 = -\mathsf{P}^{-1}\mathsf{Q}\mathsf{P}^{-1}B\ , \tag{3.33}$$

$$X_2 = \mathsf{P}^{-1}\mathsf{Q}\mathsf{P}^{-1}\mathsf{Q}\mathsf{P}^{-1}B\ , \tag{3.34}$$

whose matrixelements are calculated using the rules (2.16) and (2.25), respectively:

$$(X_0)_{\nu\nu} = \frac{B_{\nu\nu}}{p_{\nu\nu}}\ , \tag{3.35}$$

$$(X_1)_{\nu\nu} = -\sum_{\substack{i,k\\ s,t\\ l,m}} (\mathsf{P}^{-1})^{ik}_{\nu\nu}\, \mathsf{Q}^{st}_{ik} (\mathsf{P}^{-1})^{lm}_{st}\, B_{lm} = \frac{-1}{p_{\nu\nu}} \sum_{l,m} \mathsf{Q}^{lm}_{\nu\nu} \frac{B_{lm}}{p_{lm}}\ , \tag{3.36}$$

$$(X_2)_{\nu\nu} = \frac{1}{p_{\nu\nu}} \sum_{\substack{l,m\\ s,t}} \mathsf{Q}^{lm}_{\nu\nu} \frac{\mathsf{Q}^{st}_{lm}}{p_{lm}} \frac{B_{st}}{p_{st}}\ . \tag{3.37}$$

Thus, the diagonal elements of $X^{(2)}$ are given in terms

of the matrixelements of the superoperators P and Q and the ordinary operator B by the formula

$$X^{(2)}_{\nu\nu} = \frac{B_{\nu\nu}}{p_{\nu\nu}} + \frac{1}{p_{\nu\nu}} \sum_{l,m} \frac{Q^{lm}_{\nu\nu}}{p_{lm}} \left\{ \sum_{s,t} Q^{st}_{lm} \frac{B_{st}}{p_{st}} - B_{lm} \right\} . \quad (3.38)$$

4. Dependence on time

For some purposes it may be desirable to know the time-dependent solutions of eq. (3.1),

$$\dot{X}(t) = -(\mathsf{P} + \mathsf{Q}) X(t) + B . \quad (4.1)$$

By formal Laplace transform [19] we set

$$X(t) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} ds\, \tilde{X}(s)\, e^{st} , \quad s = \sigma + i\tau , \quad (4.2)$$

and assume for the following considerations that P, Q and B do not depend explicitly on time. The transformed eq. (4.1) is then

$$(\mathsf{P} + \mathsf{Q} + s\mathsf{1})\, \tilde{X}(s) = \frac{1}{s} B + X(0) . \quad (4.3)$$

With the definitions

$$\mathsf{P}(s) = \mathsf{P} + s\mathsf{1} , \quad B(s) = \frac{1}{s} B + X(0) , \quad (4.4)$$

eq. (4.3) becomes

$$(\mathsf{P}(s) + \mathsf{Q})\, \tilde{X}(s) = B(s) , \quad (4.5)$$

in analogy to the stationary formulation (3.5). The only additional difficulties to be considered now carefully are the convergence estimates for the Neumann series corresponding to (4.5),

$$\mathsf{T}(s) = (\mathsf{1} + \mathsf{P}^{-1}(s)\mathsf{Q})^{-1} = \sum_{n=0}^{\infty} (-1)^n\, (\mathsf{P}^{-1}(s)\mathsf{Q})^n , \quad (4.6)$$

from which the solution $\tilde{X}(s)$ is obtained in terms of $\tilde{X}_0(s) = \mathsf{P}^{-1}(s) B(s)$ by

$$\tilde{X}(s) = \mathsf{T}(s)\, \tilde{X}_0(s) . \quad (4.7)$$

At the same time there arise existence questions of the Laplace transform

$$\tilde{X}(s) = \int_0^{\infty} dt\, X(t)\, e^{-st} . \quad (4.8)$$

In analogy to (3.28) one defines

$$\alpha_0(s) = \min_{i,k} |p_{ik} + s| \quad (4.9)$$

for the discussion of convergence. First of all, since $\mathsf{P}(s)$ as well as P have to be non-singular, s must take on those values only for which

$$s \notin \mathrm{Sp}(-\mathsf{P}) , \quad \text{or} \quad \alpha_0(s) > 0 , \quad (4.10)$$

where Sp(P) denotes the spectrum of P. Furthermore, the Neumann series for $\mathsf{T}(s)$ exists for a given s if

$$\|\mathsf{Q}\| < \alpha_0(s) . \quad (4.11)$$

Thus, the complex halfplane of convergence of the Laplace transform $\tilde{X}(s)$ $\|\mathsf{Q}\| < \alpha_0$ is found from the following considerations:

Define

$$r_0 = \inf\{\mathrm{Re}[\mathrm{Sp}(\mathsf{P})]\} , \quad (4.12)$$

and choose s such that

$$\mathrm{Re}[s] = \sigma \geqslant r_0 + \alpha_0 . \quad (4.13)$$

It follows that for all s fulfilling (4.13),

$$\alpha_0(s) \geqslant \alpha_0 , \quad (4.14)$$

and therefore, if (3.12) exists, (4.7) exists a fortiori in the open halfplane defined through (4.13).

Unfortunately, no general criteria for an approximation of $X(t)$ by, e.g., second order perturbation theory applied to $\tilde{X}(s)$ can be deduced over the entire time interval since small terms in the series (4.7) do not necessarily mean small contributions to the backtransform $X(t)$, in general. However, there are two limiting cases which can be handled by a second order approach, if second order is already appropriate in the stationary case, i.e., the behavior of $X(t)$ for small and for large times, the latter being in most cases of direct physical interest since it allows for studying the approach to the stationary equilibrium state and, therefore, for an approximate determination of relaxation times.

Let us first look at the case $t \to 0$ by using a theorem for Laplace transforms [20] for this particular case. If for

$$t \to 0 , \quad X(t) \simeq a t^{\lambda} , \quad \mathrm{Re}[\lambda] > -1 ,$$

$$\Leftrightarrow \tilde{X}(s) \simeq a \frac{\Gamma(\lambda + 1)}{s^{\lambda+1}} \quad \text{for} \quad s \to \infty , \quad (4.15)$$

where Γ is the Gamma function and s, of course, goes to infinity in the halfplane of existence of $\tilde{X}(s)$. As a consequence, the leading term for large s in an expansion of $\tilde{X}(s)$ in negative powers of s determines the behavior of $X(t)$ close to $t = 0$. We take advantage of this fact by evaluating (4.7) for this limiting case. Since the nth order term contributes two summands $\sim(s^{n+1} + s^{n+2})$ one may simply concentrate on the lowest order which gives, e.g., for the diagonal elements

$$(\tilde{X}_0(s))_{\nu\nu} \simeq \frac{1}{s} X_{\nu\nu}(0) + \frac{1}{s^2} B_{\nu\nu} . \tag{4.16}$$

Thus, the small-time behavior is like

$$X_{\nu\nu}(t) \simeq X_{\nu\nu}(0) + B_{\nu\nu} t , \quad t \to 0 . \tag{4.17}$$

For extremely well convergent series (4.7), i.e., for very small $\|Q\| \ll \alpha_0$, we even could take the leading term

$$(\tilde{X}_0(s))_{\nu\nu} \simeq \frac{X_{\nu\nu}(0)}{s + p_{\nu\nu}} + \frac{B_{\nu\nu}}{s(s + p_{\nu\nu})} , \tag{4.18}$$

with the solution

$$X_{\nu\nu}(t) \simeq X_{\nu\nu}(0)\, e^{-p_{\nu\nu} t} + \frac{B_{\nu\nu}}{p_{\nu\nu}} (1 - e^{-p_{\nu\nu} t}) , \quad t \to 0 . \tag{4.19}$$

The discussion of the physically more interesting behavior of $X(t)$ for $t \to \infty$ is based on the following theorem [21] for the stationary limit:

If

$$\lim_{t \to \infty} X(t) = X , \quad \Rightarrow \lim_{s \downarrow 0} s\, \tilde{X}(s) = X , \tag{4.20}$$

where $s \downarrow 0$ means $\sigma \downarrow 0$ and either $\tau \uparrow 0$ or $\tau \downarrow 0$. It must be emphasized that this theorem is only true from left to right, but not necessarily in the opposite direction, as is illustrated by the following example (for an ordinary function F):

$$\tilde{F}(s) = \frac{1}{s(s^2 + a^2)} , \tag{4.21}$$

$$\lim_{s \downarrow 0} s\, \tilde{F}(s) = \frac{1}{a^2} . \tag{4.22}$$

However, the original function $F(t)$ of the Laplace transform (4.21) is

$$F(t) = \frac{2}{a^2} \sin^2(\tfrac{1}{2} a t) , \tag{4.23}$$

which has no limit at all for $t \to \infty$. In our case, this point does not give rise to troubles since we have proved the existence of the stationary solution X (which is unique) under the requirements on P and Q quoted earlier. Another question concerns the existence of $\tilde{X}(s)$ as Laplace transform of $X(t)$ as well as convergent solution in the sense of eq. (4.7) for small s because the neighbourhood of the origin $s = 0$ lies outside the complex halfplane of existence deduced before. It is therefore necessary to introduce the following additional conditions,

$$\sigma_0 = \inf\{\mathrm{Re}[\mathrm{Sp}(P)]\} > 0 , \tag{4.24}$$

$$\|Q\| < \sigma_0 , \tag{4.25}$$

which guarantee the existence of $\tilde{X}(s)$ in the entire right halfplane. From the purely mathematical point of view this may seem rather restrictive, but it turned out in all concrete applications we have dealt with so far and on which will be reported elsewhere later, that (4.24) and (4.25) can be satisfied and are, therefore, quite realistic assumptions.

To get some insight into the long-time behavior of $X(t)$ we assume the second order contribution to $\tilde{X}(s)$ to be sufficient. Again, the upper bound for $\|Q\|$ obeys then (3.30) but with α_0 replaced by σ_0, the error in $\tilde{X}(s)$ being given by (3.31) in virtue of

$$\|P(s)\| \geqslant \sigma_0 , \tag{4.26}$$

under all foregoing conditions. The time can always be chosen so large that this gives also a sufficiently accurate answer to $X(t)$. In analogy to (3.35), (3.36) and (3.37) one has then

$$(\tilde{X}_0(s))_{\nu\nu} = \frac{X_{\nu\nu}(0) + (1/s) B_{\nu\nu}}{s + p_{\nu\nu}} , \tag{4.27}$$

$$(\tilde{X}_1(s))_{\nu\nu} = \frac{-1}{s + p_{\nu\nu}} \sum_{l,m} Q_{\nu\nu}^{lm} \left\{ \frac{X_{lm}(0) + (1/s) B_{lm}}{s + p_{lm}} \right\} , \tag{4.28}$$

$$(\tilde{X}_2(s))_{\nu\nu} =$$

$$\frac{1}{s + p_{\nu\nu}} \sum_{l,m} Q_{\nu\nu}^{lm} Q_{lm}^{st} \left\{ \frac{X_{lm}(0) + (1/s) B_{st}}{(s + p_{lm})(s + p_{st})} \right\} . \tag{4.29}$$

From these equations one finds the time-dependent solutions [22],

$$(X_0(t))_{vv} = X_{vv}(0)\,e^{-p_{vv}t} + \frac{B_{vv}}{p_{vv}}\,(1 - e^{-p_{vv}t}), \quad (4.30)$$

$$(X_1(t))_{vv} = \sum_{l,m} Q_{vv}^{lm} \left\{ \frac{-B_{lm}}{p_{vv}p_{lm}} + (p_{vv} - p_{lm})^{-1} [(X_{lm}(0) - B_{lm}/p_{vv})\,e^{-p_{vv}t} - (X_{lm}(0) - B_{lm}/p_{lm})\,e^{-p_{lm}t}] \right\}, \quad (4.31)$$

$$(X_2(t))_{vv} = \sum_{\substack{l,m \\ s,t}} Q_{vv}^{lm} Q_{lm}^{st} \left\{ \frac{B_{st}}{p_{vv}p_{lm}p_{st}} + \left(\frac{X_{st}(0) - B_{st}/p_{vv}}{(p_{vv} - p_{lm})(p_{vv} - p_{st})} \right) e^{-p_{vv}t} + \left(\frac{X_{st}(0) - B_{st}/p_{lm}}{(p_{lm} - p_{vv})(p_{lm} - p_{st})} \right) e^{-p_{lm}t} + \left(\frac{X_{st}(0) - B_{st}/p_{st}}{(p_{st} - p_{vv})(p_{st} - p_{lm})} \right) e^{-p_{st}t} \right\}. \quad (4.32)$$

Of course, the correct stationary limit, which does not depend on the initial condition $X(0)$, is approached for $t \to \infty$.

The above formulas might suggest that this treatment is only valid if the spectrum of P does not exhibit any degeneracies. This is not the case. It can be shown that the limit for any two (or more) eigenvalues approaching each other exists and gives no enhanced contributions, making the inclusion of higher order terms necessary at the same fixed time. This should also be clear due to the validity of theorem (4.21).

Note in conclusion that in any concrete application the above approach for $X(t)$ gives a reliable answer for times which are large compared with σ_0^{-1} where σ_0 (see (4.24)) is determined essentially by typical interaction energies (divided by Planck's constant $\hbar$) and any kind of rate constants entering the matrix-elements of P.

Acknowledgement

I would like to thank Professor H. Labhart and the Swiss National Science Foundation for making these investigations possible.

Note added in proof

In several papers by Freed and co-workers [J. Chem. Phys. 55 (1971) 5270; J. Chem. Phys. 58 (1973) 3185; J. Chem. Phys. 62 (1975) 1706; see also G.T. Evans, Mol. Phys. 31 (1976) 1337] perturbation methods for density operators have been used in connection with specific applications and, therefore, with very special types of Liouville equations, mainly in the framework of perturbation theory for time evolution as described generally, e.g., by R.W. Zwanzig [in: Quantum Statistical Mechanics, ed. by P.H.E. Meijer (Gordon & Breach, New York, 1966)] where the connection to resolvent methods is also discussed.

Our present method puts emphasis on stationary perturbation theory for more general Liouville equations and formulates the problem from a general, unified mathematical point of view in order to establish existence proofs and error estimates with rigor.

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