Generalized quantum Onsager coefficients from a symmetrized Campbell-Hausdorff expansion

Generalized quantum Onsager coefficients from a symmetrized Campbell–Hausdorff expansion

K Lendi[1] **and A J van Wonderen**[2]

[1] Institute of Physical Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
[2] Instituut voor Theoretische Fysica, Universiteit van Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

E-mail: carlen@pci.unizh.ch and wonderen@phys.uva.nl

Abstract
The analogue of the classical Onsager theory of entropy production is systematically derived for weakly irreversible processes in open quantum systems with finite-dimensional Hilbert space. The dynamics is assumed to be given by a quantum dynamical semigroup with infinitesimal generator of Gorini–Kossakowski–Sudarshan type. The basic Spohn formula for entropy production is used to obtain an expansion in terms of powers of the deviation of the initial state relative to the final stationary state of irreversible dynamics. To this end, an appropriate Lie series is constructed from a particular symmetrization procedure applied to the ordinary Campbell–Hausdorff expansion. In this way, only Hermitian contributions by higher-order commutators are generated, which allow an identification with so-called generalized Onsager coefficients. The explicit derivations concentrate on second-, third- and fourth-order coefficients, whereas complete detailed expressions are worked out for second and third order. In a suitable coherence-vector representation of density matrices the results can be given in terms of the dynamical parameters fixing the infinitesimal semigroup generator and in terms of symmetric and antisymmetric structure constants of the Lie algebra of $SU(N)$. As an illustration, an application to generalized Bloch equations for two-level systems is studied, where the Onsager-like expansion can be compared with exact results for entropy production. We find that convergence is good even for rather large deviations between initial and final state if the calculation includes second- and third-order coefficients only. The formalism presented in this paper generalizes restrictions on admitted final states adopted in much simpler earlier treatments to the most general case of arbitrary unique final states of irreversible processes.

PACS number: 0570L

1. Introduction

Ever since the appearance of two seminal papers by Onsager [1] the concept of entropy production relative to a stationary state has played an important role in classical nonequilibrium thermodynamics [2, 3]. In the so-called weakly irreversible regime involving only modest deviations from the stationary state entropy production is given by a quadratic form in generalized forces and certain coefficients later named 'Onsager coefficients'. Within this phenomenological theory, under physically reasonable assumptions, the coefficient matrix is shown to be positive ('positive' will also be used in place of 'non-negative' throughout this paper). However, in concrete dynamical models the proof of positivity is far from being trivial [4]. Furthermore, in contrast to general belief the reciprocity relations due to symmetry of the coefficient matrix are not universally valid [1, 5]. In particular, even the necessity of assuming microreversibility, a symmetry attributed to stationary two-point correlation functions, has been questioned [6,7]. More than that, a theorem stating that entropy production is minimal for processes close to a steady state has been disproved to be generally valid by some concrete examples [7, 8].

After all, what certainly survives in general is the useful concept of positive entropy production P in its original form given by

$$P = \sum_i J_i \, X_i \tag{1}$$

where $\{J_i\}$ are the so-called generalized fluxes and $\{X_i\}$ the corresponding generalized forces inducing the fluxes. In the simplest approximation the dependence of fluxes upon forces has been assumed to be linear,

$$J_i = \sum_k L_{ik} \, X_k \tag{2}$$

with $\{L_{ik}\}$ being the phenomenological Onsager coefficients. This may be extended for processes further away from a stationary state by allowing for higher-order terms,

$$J_i = \sum_k L_{ik} \, X_k + \sum_{k,l} L_{ikl} \, X_k \, X_l + \sum_{k,l,m} L_{iklm} \, X_k \, X_l \, X_m + \cdots \tag{3}$$

and, correspondingly, entropy production will be given according to

$$P \cong \sum_{i,k} L_{ik} \, X_i \, X_k + \sum_{i,k,l} L_{ikl} \, X_i \, X_k \, X_l + \sum_{i,k,l,m} L_{iklm} \, X_i \, X_k \, X_l \, X_m \tag{4}$$

with additional higher-order coefficients $\{L_{ikl}, L_{iklm}\}$. So much for the classical case.

It may come as a surprise that an analogous quantum theoretic treatment is possible on a more fundamental non-phenomenological level by using mathematically rigorous results for quantum Markovian master equations. By 'non-phenomenological' we mean that, for example, a local equilibrium hypothesis as used in the classical theory [2, 5] is not required but may or may not even have a well defined meaning in the quantum context. This is evident since the present theory is also able to deal with smaller systems such as one or a few atoms or molecules interacting with radiation fields [20], where locality in the classical sense is inappropriate. Since the relevant quantum equations provide a well defined approach to either thermodynamic equilibrium or else, and much more general, to any stationary final state, the neighbourhood of the latter can be investigated without resorting to any additional phenomenological assumptions. In terms of the fundamental concept of quantum relative entropy the corresponding positive functional allows the desired derivation of Onsager-like coefficients.

In the related framework of completely positive quantum dynamical semigroup dynamics for irreversible processes in open systems several papers witness the quantum analogy with the

classical case. Important treatments refer to detailed balance condition for non-Hamiltonian systems [9], entropy production for the Davies model of heat conduction [10], a quantum open system as a model of a heat engine [11], general analysis of entropy production for quantum dynamical semigroups [12] and a general account of irreversible thermodynamics for quantum systems weakly coupled to thermal reservoirs [13]. Later, it could be shown that a coherence-vector representation of Markovian master equations for N-level systems is particularly suited to establish the close analogy to the classical formulae. For two-level systems there is even an exact formula for entropy production in terms of length and scalar product of the relevant vectors. However, in N dimensions a simple representation of the second-order Onsager coefficient could only be obtained by assuming the central state to be the unique final destination state of irreversible dynamics [14, 15]. Still within the same assumptions it has recently been proven that second- and higher-order coefficients can be deduced from time derivatives of functionals which otherwise are dynamical invariants under Hamiltonian, unitary reversible dynamics [16].

What are still missing are explicit expressions for second- as well as higher-order coefficients for general dynamical processes starting at an arbitrary initial state and ending in a general final state different from the central one. Due to divergences of the involved relative entropy for states characterized by singular density matrices the dynamics is restricted to faithful states (invertible density matrices) only, and the initial state must be close enough to the final stationary state in an appropriate sense to be specified later. These conditions are sufficiently general to cover a wide range of applications, particularly also for final states of thermodynamic equilibrium at finite temperatures.

It is the aim of this paper to close the above-mentioned gap by working out the mathematical details in a systematic way. In the next section 2 a condensed summary of the necessary settings for the underlying semigroup quantum dynamics and related entropy production will be given. In section 3 the details of the symmetrization procedure of the Campbell–Hausdorff (CH) expansion are worked out for Onsager coefficients up to fourth order. The explicit calculation of the coefficients is then outlined in section 4 and detailed results up to third order are given. Section 5 contains an application to irreversible dynamics in the case of generalized Bloch equations for a two-level system where a comparison with an exact solution is possible. Finally, the concluding section 6 discusses aspects of convergence of the Onsager-type expansion with some outlook to remaining problems for more general dynamical situations. Some mathematical and numerical details are postponed to appendices A–D.

2. Irreversible quantum dynamics and related entropy production

For an open quantum system coupled to its environment the dynamics may be very complicated and is given, in general, by an integro-differential equation, a so-called Nakajima–Zwanzig master equation [15, 17, 18]. For this general situation it is not even clear how to define a universal notion of entropy production although some attempts and proposals have been made in the case of concrete, rigorously solvable models [19–21]. It is only in the limiting case of open systems relatively weakly coupled to very large reservoirs that a mathematically sound definition could be established [12]. For this situation the dynamics is dictated by quantum dynamical semigroups with completely positive dual or, equivalently in differential form, by quantum Markovian master equations. There is a lot of experience showing that they cover a very wide range of experimental relevance. Since there are numerous papers and reviews on the subject (see, e.g., [15] and references therein) it seems sufficient to summarize here only the necessary definitions and notions.

In the underlying setting time evolution carries an arbitrary initial state ρ of an open system

into a unique final state σ. During the irreversible process the time-dependent state ρ_t evolves according to a quantum dynamical semigroup Λ_t,

$$\rho_t = \Lambda_t(\rho) \qquad \Lambda_t = \exp(\mathcal{L}t) \qquad \Lambda_t \Lambda_s = \Lambda_{t+s} \qquad t, s \geqslant 0 \tag{5}$$

$$\lim_{t\to\infty} \Lambda_t(\rho) = \sigma \qquad \Lambda_t(\sigma) = \sigma \qquad \mathcal{L}(\sigma) = 0. \tag{6}$$

The associated master equation is given by

$$\dot{\rho}_t = \mathcal{L}(\rho_t) \qquad \mathcal{L} = \mathcal{L}_\text{H} + \mathcal{L}_\text{D} \tag{7}$$

where the dot denotes a time derivative, $\mathcal{L}_\text{H}$ is the Hamiltonian and $\mathcal{L}_\text{D}$ the relaxation-dissipation contribution to $\mathcal{L}$. For most applications it will be sufficient to consider a finite-dimensional Hilbert space $\mathcal{H}$ with $\dim(\mathcal{H}) = N < \infty$ on which the density matrices $\{\rho_t\}$ act. The semigroup mappings Λ_t leave the basic quantum mechanical properties of density matrices invariant or, in other words, the von Neumann conditions of hermiticity, trace normalization and positivity remain preserved at all times,

$$\rho_t = \rho_t^* \qquad \text{Tr}(\rho_t) = 1 \qquad \rho_t \geqslant 0 \quad t \geqslant 0. \tag{8}$$

One cannot stress enough the importance of these conditions for any reliable physical interpretation of results.

For the following derivations the most convenient and transparent explicit representation of the infinitesimal generator $\mathcal{L}$ is given by the Kossakowski normal form [22]

$$\mathcal{L}(\rho_t) = -\text{i}[H, \rho_t] + \tfrac{1}{2} \sum_{i,k=1}^{M} a_{ik}\{[F_i, \rho_t F_k] + [F_i \rho_t, F_k]\} \tag{9}$$

$$\begin{aligned} F_i &= F_i^* & \text{Tr}(F_i) &= 0 & \text{Tr}(F_i F_k) &= \delta_{ik} \\ H &= H^* & \text{Tr}(H) &= 0 & A &= \{a_{ik}\}_1^M \geqslant 0 & M &= N^2 - 1. \end{aligned} \tag{10}$$

The details of relaxation are fully determined by the matrix elements of A, which also fix the final state σ due to (6). Two points of view can be taken. On the one hand, the elements may be chosen according to some phenomenological reasoning but positivity sets restrictions through semi-inequalities. Just to quote a simple example for two-level systems, the well known Bloch equations of magnetic resonance are obtained by setting $a_{11} = a_{22} = 1/2T_1$, $a_{33} = 1/T_2 - 1/2T_1$, $a_{12} = -\text{i}\,\tilde{M}/\sqrt{2}T_1$ and $a_{13} = a_{23} = 0$, where T_1 and T_2 are the longitudinal and transverse relaxation times restricted by $T_1 \leqslant T_2/2$, and $\tilde{M}$ is the equilibrium magnetization [15]. On the other hand, a determination from first principles is possible if the explicit form of the total Hamiltonian for the closed system composed of the open one and the reservoir including their mutual interaction is given. Then, by tracing back structure (9), (10) to the fundamental Davies theory of the weak-coupling limit [23], the elements $\{a_{ik}\}$ can be expressed in terms of Fourier transforms of reservoir correlation functions [15].

For a formulation of entropy production a few remarkable properties of quantum entropy must be mentioned [24–26]. Particularly the associated relative entropy

$$S(\rho/\rho') = \text{Tr}\{\rho(\ln \rho - \ln \rho')\} \geqslant 0 \qquad \forall \rho, \rho' \in \Gamma \tag{11}$$

provides a desired measure to assess entropy of a state ρ relative to another state ρ' where Γ is the state space of all normalized trace-class operators in $\mathcal{H}$. In addition, S is jointly convex on Γ [26]. This provides the basis for the second most important property of contractivity under completely positive semigroup mappings Λ_t, as proven by Lindblad [27],

$$S(\Lambda_{t+s}(\rho)/\Lambda_{t+s}(\rho')) \leqslant S(\Lambda_s(\rho)/\Lambda_s(\rho')) \qquad t \geqslant s. \tag{12}$$

As a consequence, by choosing ρ' as invariant state σ and using (5) and (6), $S(\rho_t/\sigma)$ is a Lyapunov functional on Γ or, in other words, a monotonically decreasing function of time for

any given initial state ρ with dynamics Λ_t. Taking into account these outstanding relations Spohn, in a seminal paper, has succeeded in deriving the fundamental formula for entropy production P in the form

$$P(\rho/\sigma) = - \left[\frac{\mathrm{d}}{\mathrm{d}t} S(\Lambda_t(\rho)/\sigma) \right]_{t=0}. \tag{13}$$

Thus, P is entirely determined by the initial state ρ and the infinitesimal generator $\mathcal{L}$ since (13) can be rewritten as

$$P = \mathrm{Tr}\{\mathcal{L}(\rho)(\ln \sigma - \ln \rho)\}. \tag{14}$$

Obviously, the validity requires the dynamics to involve only faithful states, that is states with existing inverse. In addition, if a series expansion analogous to (4) is supposed to yield satisfactory values already through the lowest-order terms, ρ must be restricted to the vicinity of σ in the sense that, for example, the trace norm $\|\rho - \sigma\|$ does not exceed a prescribed tolerance, as will be quantified subsequently. Therefore, we set $\rho - \sigma = \omega$ to obtain

$$\rho = \sigma + \omega \qquad \mathcal{L}(\rho) = \mathcal{L}(\omega) \qquad \mathrm{Tr}(\omega) = 0 \tag{15}$$

and the final form of (14) reads

$$P = \mathrm{Tr}\{\mathcal{L}(\omega)(\ln \sigma - \ln(\sigma + \omega)\}. \tag{16}$$

It has been shown elsewhere [9, 14, 15] that the desired series expansion is obtained in a natural way by going over to coherence-vector representation for density operators defined by

$$\omega = \sum_{i=1}^{M} x_i F_i \qquad \sigma = \frac{1}{N} \mathbb{I} + \sum_{i=1}^{M} y_i F_i \qquad M = N^2 - 1 \tag{17}$$

where a special representation of the set of $\{F_i\}$-matrices as a straightforward generalization of the Pauli matrices to higher dimension will be used. The Lie algebra of these infinitesimal generators of $SU(N)$ is characterized by

$$[F_i, F_k] = \mathrm{i} \sum_{l=1}^{M} f_{ikl} F_l \qquad \{F_i, F_k\} = \frac{2}{N} \mathbb{I} \delta_{ik} + \sum_{l=1}^{M} d_{ikl} F_l. \tag{18}$$

$\{\cdot, \cdot\}$ denotes an anticommutator, d_{ikl} are completely symmetric and f_{ikl} completely antisymmetric real structure constants. Up to $N = 4$ matrices and constants are explicitly listed in [15].

Since $\mathcal{L}(\omega)$ is linear in ω the second- and higher-order Onsager coefficients must be obtained from an expansion of the logarithm in (16). The main problem arises from non-commutativity of σ with ρ but also from the slow convergence of the log series. It turns out that the best expansion by far is a modified CH series as will be outlined in the following section.

3. Symmetrized Campbell–Hausdorff expansion

According to the general formula (16) a power series expansion of $\ln(\sigma + \omega)$ yields real values for P in a finite-order approximation only if single contributions in any order are Hermitian. To achieve this in a CH expansion the following symmetrization procedure will be neccessary. In a first step one transforms the sum into a product,

$$\ln(\sigma + \omega) = \ln(\sigma \eta) \qquad \eta = \mathbb{I} + \varepsilon \quad \varepsilon = \sigma^{-1} \omega. \tag{19}$$

Next, we set

$$\sigma = \mathrm{e}^u \qquad \eta = \mathrm{e}^v \tag{20}$$

to obtain the leading terms in the CH series [28, 29] as

$$z(u, v) = \ln(e^u\, e^v) = u + v + \tfrac{1}{2}[u, v] + \tfrac{1}{12}\{[[u, v], v] + [[v, u], u]\}$$
$$- \tfrac{1}{24}[[[u, v], v], u] + \cdots. \tag{21}$$

However, since an expansion in powers of ω implies expansion of

$$v = \ln(\mathbb{I} + \varepsilon) \stackrel{\sim}{=} \varepsilon - \tfrac{1}{2}\varepsilon^2 + \tfrac{1}{3}\varepsilon^3 - \cdots \tag{22}$$

the single terms are not Hermitian since $\varepsilon \neq \varepsilon^*$ for noncommuting σ^{-1} and ω. Therefore, consider in place of (19) the adjoint representation

$$\ln(\sigma + \omega) = \ln(\eta^* \sigma) \qquad \eta^* = \mathbb{I} + \varepsilon^* \quad \varepsilon^* = \omega \sigma^{-1} \tag{23}$$

and set

$$\eta^* = e^{v^*} \qquad \sigma = e^u \tag{24}$$

to obtain the counterpart of (21) in the form

$$z(v^*, u) = \ln(e^{v^*} e^u) = v^* + u + \tfrac{1}{2}[v^*, u] + \tfrac{1}{12}\{[[v^*, u], u] + [[u, v^*], v^*]\}$$
$$- \tfrac{1}{24}[[[v^*, u], u], v^*] + \cdots. \tag{25}$$

Now, in symmetrized form formula (16) is rewritten as

$$P = \text{Tr}\{\mathcal{L}(\omega)\, D(\sigma + \omega)\} \tag{26}$$
$$D(\sigma + \omega) = \ln \sigma - \tfrac{1}{2}\{\ln(\sigma\, \eta) + \ln(\eta^* \sigma)\} \tag{27}$$

or, equivalently,

$$D(u, v) = u - \tfrac{1}{2}\{z(u, v) + z(v^*, u)\}. \tag{28}$$

The different contributions by successively iterated commutators will be denoted by $D^{(\nu)}(u, v)$, and we have

$$D(u, v) = \sum_{\nu=1}^{4} D^{(\nu)}(u, v) \tag{29}$$

$$D^{(1)}(u, v) = -\tfrac{1}{2}(v + v^*) \tag{30}$$

$$D^{(2)}(u, v) = \tfrac{1}{4}[(v - v^*), u] \tag{31}$$

$$D^{(3)}(u, v) = \tfrac{1}{24}\{[v, [u, v]] + [v^*, [u, v^*]] + [u, [(v + v^*), u]]\} \tag{32}$$

$$D^{(4)}(u, v) = \tfrac{1}{48}\{[[[u, v], v], u] + [[[v^*, u], u], v^*]\}. \tag{33}$$

Since $\mathcal{L}(\omega)$ is linear in ω an expansion of v up to nth order in $\varepsilon(\omega) = \sigma^{-1}\omega$ provides Onsager coefficients up to order $(n + 1)$. Inserting (22) into (30)–(33) and labelling powers in ε by subindex μ in $D_\mu^{(\nu)}(u, \varepsilon)$ yields the expressions below.

$$D_1^{(1)}(u, \varepsilon) = -\tfrac{1}{2}(\varepsilon + \varepsilon^*)$$
$$D_2^{(1)}(u, \varepsilon) = \tfrac{1}{4}(\varepsilon^2 + \varepsilon^{*2}) \tag{34}$$
$$D_3^{(1)}(u, \varepsilon) = -\tfrac{1}{6}(\varepsilon^3 + \varepsilon^{*3})$$

$$D_1^{(2)}(u, \varepsilon) = -\tfrac{1}{4}[u, (\varepsilon - \varepsilon^*)]$$
$$D_2^{(2)}(u, \varepsilon) = \tfrac{1}{8}[u, (\varepsilon^2 - \varepsilon^{*2})] \tag{35}$$
$$D_3^{(2)}(u, \varepsilon) = -\tfrac{1}{12}[u, (\varepsilon^3 - \varepsilon^{*3})]$$

$$D_1^{(3)}(u, \varepsilon) = \tfrac{1}{24}[u, [(\varepsilon + \varepsilon^*), u]]$$
$$D_2^{(3)}(u, \varepsilon) = \tfrac{1}{24}\{[\varepsilon, [u, \varepsilon]] + [\varepsilon^*, [u, \varepsilon^*]]\} - \tfrac{1}{48}[u, [(\varepsilon^2 + \varepsilon^{*2}), u]] \tag{36}$$
$$D_3^{(3)}(u, \varepsilon) = \tfrac{1}{24}\{[[u, \varepsilon], \varepsilon^2] + [[u, \varepsilon^*], \varepsilon^{*2}]\} + \tfrac{1}{72}[u, [(\varepsilon^3 + \varepsilon^{*3}), u]]$$

$$D_1^{(4)}(u, \varepsilon) = 0$$
$$D_2^{(4)}(u, \varepsilon) = \tfrac{1}{48}\{[[[u, \varepsilon], \varepsilon], u] + [[\varepsilon^*, u], u], \varepsilon^*]\} \tag{37}$$
$$D_3^{(4)}(u, \varepsilon) = \tfrac{1}{48}[u, [[u, \varepsilon], \varepsilon^2]] + \tfrac{1}{96}\{[\varepsilon^{*2}, [[\varepsilon^*, u], u]] + [\varepsilon^*, [[\varepsilon^{*2}, u], u]]\}.$$

With the above definitions P becomes

$$P = \sum_{\mu=1}^{3} \sum_{\nu=1}^{4} \mathrm{Tr}\{\mathcal{L}(\omega) D_\mu^{(\nu)}(u, \varepsilon)\} \tag{38}$$

and provides the desired representation for computing Onsager coefficients.

4. Onsager coefficients

Going over to coherence-vector representation we write, from now on, $\omega = \omega(\boldsymbol{x})$ and $\varepsilon = \varepsilon(\boldsymbol{x})$ and note that both are linear in $\boldsymbol{x}$. Therefore, $\mathcal{L}(\omega(\boldsymbol{x}))$ is also linear in $\boldsymbol{x}$ and $D_\mu^{(\nu)}(u, \varepsilon(\boldsymbol{x}))$ are homogeneous polynomials of degree μ in the vector components for all ν. The norm $\|\boldsymbol{x}\|^2 = \mathrm{Tr}(\omega^*(\boldsymbol{x})\omega(\boldsymbol{x}))$ is a measure for the deviation of initial from final state whereas in analogy to the classical case the components $\{x_i\}_1^M$ take over the role of generalized forces which drive the system back to its stationary state. Now, the second-, third- and fourth-order contributions to quantum entropy production P are given by

$$P = p^{(2)}(\boldsymbol{x}) + p^{(3)}(\boldsymbol{x}) + p^{(4)}(\boldsymbol{x}) \tag{39}$$

whereas comparison with the common notation (4) and with (38) identifies the coefficients through

$$p^{(2)}(\boldsymbol{x}) = \sum_{\nu=1}^{4} \mathrm{Tr}\{\mathcal{L}(\omega(\boldsymbol{x})) D_1^{(\nu)}(u, \varepsilon(\boldsymbol{x}))\} = \sum_{i,k} L_{ik}\, x_i\, x_k \tag{40}$$

$$p^{(3)}(\boldsymbol{x}) = \sum_{\nu=1}^{4} \mathrm{Tr}\{\mathcal{L}(\omega(\boldsymbol{x})) D_2^{(\nu)}(u, \varepsilon(\boldsymbol{x}))\} = \sum_{i,k,l} L_{ikl}\, x_i\, x_k\, x_l \tag{41}$$

$$p^{(4)}(\boldsymbol{x}) = \sum_{\nu=1}^{4} \mathrm{Tr}\{\mathcal{L}(\omega(\boldsymbol{x})) D_3^{(\nu)}(u, \varepsilon(\boldsymbol{x}))\} = \sum_{i,k,l,m} L_{iklm}\, x_i\, x_k\, x_l\, x_m. \tag{42}$$

Here and in all the following formulae the summations are understood to go from 1 to M.

Before evaluating the traces in (40)–(42) in detail all quantities must be transformed into vector representation. For the dynamical part one obtains [15]

$$\mathcal{L}(\omega(\boldsymbol{x})) = \sum_{i,k} g_{ik}\, x_k\, F_i \qquad g_{ik} = q_{ik} + r_{ik} \tag{43}$$

where g_{ik} are matrix elements of the general evolution matrix [15,30] comprising a Hamiltonian contribution q_{ik} from $\mathcal{L}_\mathcal{H}$ and a relaxation part r_{ik} from $\mathcal{L}_\mathcal{D}$. The explicit relations in terms of the original quantities defining generator $\mathcal{L}$ in (9) are given by

$$q_{ik} = -\sum_l f_{ikl}\, h_l \qquad h_l = \mathrm{Tr}(H F_l) \tag{44}$$

$$r_{ik} = -\tfrac{1}{4} \sum_{\substack{l,m,n \\ (l \leqslant m)}} (2 - \delta_{lm})(f_{iln} f_{kmn} + f_{imn} f_{kln})\, \mathrm{Re}\,(a_{lm})$$

$$+ \tfrac{1}{2} \sum_{\substack{l,m,n \\ (l < m)}} (f_{imn} d_{kln} - f_{iln} d_{kmn})\, \mathrm{Im}\,(a_{lm}). \tag{45}$$

Furthermore, one needs

$$\sigma^{-1} = a_0 \, \mathbb{1} + \sum_l a_l \, F_l \tag{46}$$

$$u = \ln \sigma = b_0 \, \mathbb{1} + \sum_l b_l \, F_l. \tag{47}$$

Note again that for any matrix $W = W^*$ with representation $W = w_0 \, \mathbb{1} + \sum_l w_l \, F_l$ the coefficients are obtained using (10) from $w_0 = \frac{1}{N} \operatorname{Tr}(W)$ and $w_l = \operatorname{Tr}(W \, F_l)$. Finally, for

$$\varepsilon(\boldsymbol{x}) = c_0 \, \mathbb{1} + \sum_l c_l \, F_l \tag{48}$$

equations (46) and (47) yield

$$c_0 = \frac{1}{N}(\boldsymbol{a}, \boldsymbol{x}) \qquad c_l = a_0 \, x_l + \frac{1}{2} \sum_{i,k} a_i \, x_k \, z_{ikl} \qquad (1 \leqslant l \leqslant M) \tag{49}$$

where $(\cdot, \cdot)$ denotes the scalar product and z_{ikl} are complex structure constants derived from (18), namely

$$F_i \, F_k = \frac{1}{N} \, \mathbb{1}\delta_{ik} + \frac{1}{2} \sum_l z_{ikl} \, F_l \qquad z_{ikl} = d_{ikl} + \mathrm{i} f_{ikl}. \tag{50}$$

With all the above relations formulae (40)–(42) can be evaluated. The calculations are straightforward but quite lengthy, such that only the final results for the second- and third-order Onsager coefficient will explicitly be given below whereas an illustrative example is worked out in appendix A:

$$
\begin{aligned}
L_{ik} = -a_0 \, r_{ik} - \frac{1}{2} \sum_{l,m} \Bigg\{ & d_{ilm} \, a_m + \frac{1}{2} \, b_m \sum_{n,p} \Bigg(f_{lnm} \, f_{inp} \, a_p - \frac{a_0}{3} \, f_{lnp} \, f_{imn} \, b_p \\
& - \frac{1}{6} f_{lnp} \, b_p \sum_{q,r} f_{mnr} \, d_{irq} \, a_q \Bigg) \Bigg\} g_{lk}.
\end{aligned}
\tag{51}
$$

Note that in the classical case the Onsager symmetry relations among the coefficients are attributed to properties of equilibrium [1, 5] and nonequilibrium fluctuations [31]. Here, the situation turns out to be more complicated. Analogous fluctuations do exist in the quantum case and, according to the Davies theory [13, 15, 23], the elements $\{a_{lm}\}$ of the relaxation matrix are given in terms of Fourier transforms of stationary reservoir correlation functions, but due to (45)–(47) the relationship with L_{ik} is nonlinear and nonsymmetric, in general. However, since the total contribution is a positive quadratic form the trivial transformation $L_{ik} \to (L_{ik} + L_{ki})/2$ leaves it invariant and restores the symmetry [5, 13].

For a better overview the lengthy third-order coefficient is given in decomposed form, where, in analogy to the ν-decomposition in (29), we define

$$L_{ikl} = \sum_{\nu=1}^4 L_{ikl}^{(\nu)}. \tag{52}$$

The single contributions are as follows:

$$
\begin{aligned}
L_{ikl}^{(1)} = \frac{a_0}{N} \, a_i \, r_{kl} + \frac{a_0^2}{4} \sum_m d_{ikm} \, g_{ml} + \frac{1}{2N} \, a_i \sum_{m,n} d_{kmn} \, a_n \, g_{ml} \\
- \frac{1}{8} \sum_{m,n,p} \{ f_{imp} \, f_{knp} + f_{inp} \, f_{kmp} - d_{imp} \, d_{knp} - d_{inp} \, d_{kmp} \} a_n \, g_{ml}
\end{aligned}
$$

$$+\frac{1}{16}\sum_{\substack{m,n,p\\q,r}}\{(d_{irn}\,d_{kpq}-f_{irn}\,f_{kpq})\,d_{nqm}$$

$$+(d_{irp}\,f_{kpq}+d_{kpq}\,f_{irn})\,f_{nqm}\}a_r\,a_p\,g_{ml} \tag{53}$$

$$L^{(2)}_{ikl}=-\frac{1}{4N}\,a_i\sum_{m,n,p,q}f_{kqn}\,f_{npm}\,a_q\,b_p\,g_{ml}+\frac{a_0^2}{8}\sum_{m,n,p}f_{ikn}\,f_{mnp}\,b_p\,g_{ml}$$

$$+\frac{a_0}{16}\sum_{\substack{m,n,p\\q,r}}(d_{ipq}\,f_{knp}+d_{kpq}\,f_{ipn}+d_{ipn}\,f_{kpq}+d_{knp}\,f_{ipq})\,f_{mnr}\,a_q\,b_r\,g_{ml}$$

$$-\frac{1}{32}\sum_{\substack{m,n,p,q\\r,s,t}}\{d_{irs}\,(d_{kpt}\,f_{qrt}-d_{qrt}\,f_{kpt})$$

$$+f_{irs}\,(f_{kpt}\,f_{qrt}-d_{kpt}\,d_{qrt})\}f_{mnq}\,a_s\,a_p\,b_n\,g_{ml} \tag{54}$$

$$L^{(3)}_{ikl}=-\frac{a_0^2}{12}\sum_{m,n,p}f_{inp}\,f_{knm}\,b_m\,g_{pl}-\frac{a_0}{24}\sum_{\substack{m,n,p\\q,r}}(f_{krn}\,f_{pqr}+f_{nqr}\,f_{krp})d_{lmq}\,a_m\,b_n\,g_{pi}$$

$$-\frac{1}{48}\sum_{\substack{m,n,p,q\\r,s,t}}f_{rst}\,f_{pqr}\,(d_{lmt}\,d_{knq}-f_{lmt}\,f_{knq})\,a_m\,a_n\,b_s\,g_{pi}$$

$$-\frac{a_0}{12N}\sum_{m,n,p,q}f_{kmn}\,f_{npq}\,a_i\,b_m\,b_p\,g_{ql}$$

$$-\frac{1}{24N}\sum_{\substack{m,n,p\\q,r,s}}d_{kmn}\,f_{npq}\,f_{qrs}\,a_i\,a_m\,b_p\,g_{sl}-\frac{a_0^2}{48}\sum_{\substack{m,n,p\\q,r}}d_{ikm}\,f_{mnp}\,f_{pqr}\,b_n\,b_q\,g_{rl}$$

$$-\frac{a_0}{96}\sum_{\substack{m,n,p,q\\r,s,t}}(d_{kmp}\,d_{inp}+d_{imp}\,d_{knp}+f_{kpm}\,f_{ipn}$$

$$+f_{ipm}\,f_{kpn})\,f_{nqr}\,f_{rst}\,a_m\,b_q\,b_s\,g_{tl}-\frac{1}{192}\sum_{\substack{m,n,p,q,r\\s,t,u,w}}\{(d_{imr}\,d_{kpu}+f_{irm}\,f_{kpu})d_{nru}$$

$$+(d_{imr}\,f_{kup}+d_{kpu}\,f_{irm})\,f_{nru}\}\,f_{nqw}\,f_{stw}\,a_m\,a_p\,b_q\,b_s\,g_{tl} \tag{55}$$

$$L^{(4)}_{ikl}=-\frac{1}{96}\sum_{\substack{m,n,p,q,r\\s,t,u,w}}f_{qrs}\,f_{stu}\,f_{nuw}\,(d_{imr}\,f_{kpt}+d_{kpt}\,f_{imr})a_m\,a_p\,b_q\,b_w\,g_{nl}. \tag{56}$$

All quantities in the above formulae are known as soon as the dynamical generator $\mathcal{L}$ is determined. The a- and b-coefficients in (46) and (47) can be calculated by taking into account (6) and solving (9) for σ. Furthermore, the structure constants are obtained from a systematic treatment outlined in [15]. The details will become more transparent from the example treated in the following section.

5. Convergence test of entropy production for generalized Bloch equations

In order to have a transparent example of great physical importance we analyse the derived coefficients in the framework of generalized Bloch equations. These are well known to provide an adequate description of damping phenomena in various fields such as magnetic resonance [32,33] and quantum optics [34–36]. For $N = 2$ we use an exact closed formula for entropy production in terms of coherence vectors and compare numerical results with those from an Onsager expansion. In particular, we will study the differences as a function of the

initial deviation length $\|x\|$ of $\omega(x)$. The time-dependent state will be denoted by

$$\rho_t = \tfrac{1}{2}\,\mathbb{I} + (v_t\,,\,F) \qquad v_t = (v_1(t),\,v_2(t),\,v_3(t)\,)^{\mathrm{T}} \tag{57}$$

with initial and final vectors renamed,

$$v_0 = x + y \qquad y = v_\infty. \tag{58}$$

The most general Bloch equations for two-level systems admitted by completely positive semigroup dynamics read [15]

$$\begin{aligned}
\dot{v}_1(t) &= -\gamma_3\,v_1(t) + (\alpha - \omega_0)v_2(t) + (\beta - \omega_2)v_3(t) - \sqrt{2}\,\lambda \\
\dot{v}_2(t) &= (\alpha + \omega_0)v_1(t) - \gamma_2\,v_2(t) + (\delta - \omega_1)\,v_3(t) + \sqrt{2}\,\mu \\
\dot{v}_3(t) &= (\beta + \omega_2)\,v_1(t) + (\delta + \omega_1)v_2(t) - \gamma_1\,v_3(t) - \sqrt{2}\,\nu
\end{aligned} \tag{59}$$

or, in compact form,

$$\dot{v}(t) = G\,v(t) + k \qquad G = Q + R \qquad k = -\sqrt{2}(\lambda,\,-\mu,\,\nu)^{\mathrm{T}} \tag{60}$$

$$Q = \begin{pmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{pmatrix} \qquad R = \begin{pmatrix} -\gamma_3 & \alpha & \beta \\ \alpha & -\gamma_2 & \delta \\ \beta & \delta & -\gamma_1 \end{pmatrix}. \tag{61}$$

A convenient parametrization has been introduced such that the original semigroup generator $\mathcal{L}$ is expressed in terms of a Hamiltonian H and a relaxation matrix A,

$$H = \tfrac{1}{2}\begin{pmatrix} \omega_0 & \omega_1 + \mathrm{i}\omega_2 \\ \omega_1 - \mathrm{i}\omega_2 & -\omega_0 \end{pmatrix}$$

$$A = \begin{pmatrix} \tfrac{1}{2}(\gamma_1 + \gamma_2 - \gamma_3) & \alpha + \mathrm{i}\nu & \beta + \mathrm{i}\mu \\ \alpha - \mathrm{i}\nu & \tfrac{1}{2}(\gamma_1 + \gamma_3 - \gamma_2) & \delta + \mathrm{i}\lambda \\ \beta - \mathrm{i}\mu & \delta - \mathrm{i}\lambda & \tfrac{1}{2}(\gamma_2 + \gamma_3 - \gamma_1) \end{pmatrix} \tag{62}$$

where positivity $A \geqslant 0$ sets mutual restrictions among the parameters by semi-inequalities. As orthonormal basis $\{F_i\}$ the normalized Pauli matrices have been used,

$$F_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad F_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad F_3 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{63}$$

Note now that the final state vector y is determined from the stationary solution $\dot{v}_t = 0$ for regular G,

$$y = v_\infty = -G^{-1}k \qquad \sigma(y) = \tfrac{1}{2}\,\mathbb{I} + (y,\,F). \tag{64}$$

For a given final state also vectors a and b in (46) and (47) can be given analytically. To find a one proves that

$$\sigma(y)\,\sigma(-y) = D(\sigma)\,\mathbb{I} \tag{65}$$

where the determinant $D(\sigma)$ is

$$D(\sigma) = \tfrac{1}{4}(1 - 2\,y^2) \qquad y = \|y\| = (y_1^2 + y_2^2 + y_3^2)^{1/2}. \tag{66}$$

Thus, the inverse $\sigma^{-1} = a_0\,\mathbb{I} + (a,\,F)$ is determined from

$$\sigma^{-1} = \frac{1}{D(\sigma)}\sigma(-y) \qquad a_0 = \frac{2}{1 - 2\,y^2} \qquad a = \left(\frac{4}{2\,y^2 - 1}\right)y. \tag{67}$$

The logarithm is derived in appendix B,

$$\ln \sigma = b_0\,\mathbb{I} + (b,\,F) \qquad b_0 = \tfrac{1}{2}\ln(\tfrac{1}{4} - \tfrac{1}{2}\,y^2) \quad b = \left(\frac{\sqrt{2}}{y}\tanh^{-1}(\sqrt{2}\,y)\right)y. \tag{68}$$
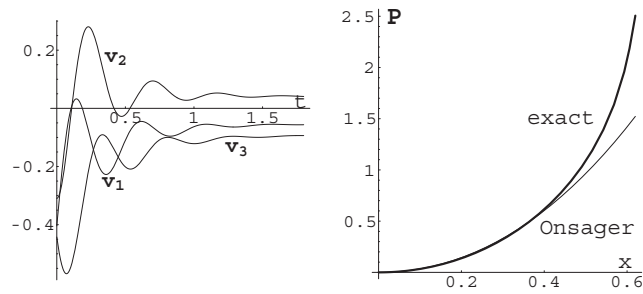
Figure 1. Solutions of generalized Bloch equations (left) and comparison between exact and approximate entropy production (right).

Finally, there is a simplification in formulae (53)–(56) since the symmetric structure constants vanish for $N = 2$. This completes all necessary details for computing P in second and third Onsager approximations, denoted from now on as

$$P_O(x) = p^{(2)}(x) + p^{(3)}(x).\tag{69}$$

On the other hand, there is the exact formula $P_E(x)$ for entropy production derived in appendix C,

$$P_E(x) = [f(v) - f(y)](x, (Q - R)y) - f(v)(x, R\,x)\tag{70}$$

$$v = \|x + y\| \qquad f(z) = \frac{\sqrt{2}}{z}\tanh^{-1}(\sqrt{2}\,z) \qquad 0 \leqslant z < \frac{1}{\sqrt{2}}.\tag{71}$$

The data of the following numerical example are listed in appendix D. Note that rescaling the parameters by appropriate negative powers of ten adjusts them to experimentally realistic values, for example, in the megahertz or gigahertz region of magnetic resonance.

The time-dependent solutions of (59) are displayed in the left-hand part of figure 1 whereas P_E and P_O are plotted in the right-hand part. To be precise, according to the derived formulae the values of P depend not only upon the norm $\|x\|$ but also on the direction of x relative to y. In order to make all Onsager coefficients effective vector x has been chosen along a $(-1, -1, -1)$-direction, also because y has three negative components.

It is remarkable that the Onsager approximation yields surprisingly good values even for relatively large initial-state deviations x from the final state. In particular, for $x = 0.5$, which amounts to about five-sevenths of the radius of the Bloch-sphere the error in P_O is less than 12%. Tentatively assuming Boltzmann distributions for initial and final states a detailed analysis of data yields a temperature increase by a factor of 4.6 during this irreversible process. This shows that the Onsager expansion yields satisfactory values even for large temperature differences and that, under the above conditions, initial and final states need not be close to each other.

However, it must be stressed that the above temperature factor will depend on the dimension N, and for $N > 2$ it could be considerably smaller. Of course, the relative order of magnitude between second- and third-order contributions depends on x. In our example, up to $x = 0.5$, $p^{(3)}$ amounts to less than 13% of $p^{(2)}$.

6. Discussion and conclusion

Although the procedure outlined in this paper provides a systematic derivation of Onsager coefficients, in principle to arbitrary higher order, it must be considered formal so far.
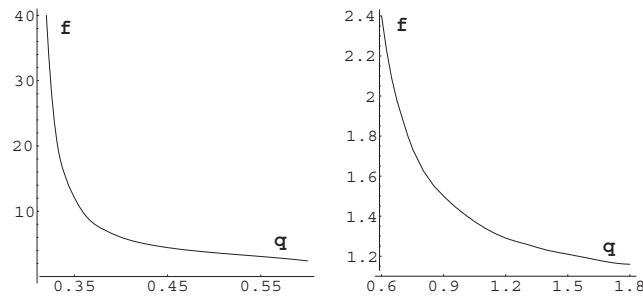
Figure 2. Temperature enhancement factor $f = T_2/T_1$ as function of $q = \Delta E/kT_1$ for an equidistant four-level system admitting an error of about 3% in the lowest Onsager coefficients.

Therefore, some considerations of convergence will be necessary. First of all, mathematically rigorous criteria for convergence of the CH expansion are difficult. Application of a known result [38, 39] to our case states that the symmetrized series $\frac{1}{2}(z(u, v) + z(v^*, u))$ in (28) is norm convergent for $(\|u\| + \frac{1}{2}\|v + v^*\|) < \frac{1}{2}\ln 2$. However, this is sufficient but for our special settings by far not always necessary. More subtle estimates would be extremely demanding and are outside the scope of this paper, but findings of numerical estimates in lower dimensions can be summarized as follows.

Cutting the series as in (21) and (25) is sufficient for practical applications if the spectral norm of the inverse of σ does not exceed a given tolerance, say $\|\sigma^{-1}\| \leqslant \delta$, where, typically, $\delta \cong 20$. Two properties contribute to this fact. First, commutators of increasing order show a tendency to yield matrices with decreasing elements and, second, the numerical coefficients in front will also rapidly decrease [40]. Of course, an additional error is introduced when replacing v and v^* by power expansion as in (22). Up to third order, the error in the norm is less than about 3% if $\|(\varepsilon + \varepsilon^*)\| \leqslant 1$. Under such conditions, P can be obtained with an error of less than 10%. At the same time, one may ask, for instance, about the magnitude of the first neglected contribution to the second-order coefficient $L^{(2)}$ which would be calculated from $\frac{1}{720}[[[[u, \frac{1}{2}(\varepsilon + \varepsilon^*)], u], u], u]$ in the extended CH series [28, 40]. Again, under the above-mentioned conditions the error in $L^{(2)}$ is less than 1%. In any case, choosing ρ sufficiently close to σ such that $\|\omega\| \ll 1$ will improve the convergence towards a desired tolerance.

Finally, we would like to give an illustrative example for a simple, but frequently occurring situation. Assume that initial and final states are Gibbs states with $\rho = Z_1^{-1}\exp(-H/kT_1)$ and $\sigma = Z_2^{-1}\exp(-H/kT_2)$, $T_2 > T_1$, and the irreversible process $\rho \to \sigma$ takes place due to appropriate change of external conditions imposed on the open system. Assume further for simplicity that H has an equidistant spectrum with spacing ΔE. In this case the CH series becomes trivial since $[u, v] = 0$, and the desired convergence can be set, for example, by requiring the bound $\|\varepsilon\| \leqslant \frac{1}{2}$. Then, depending on the ratio between initial thermal energy kT_1 and ΔE one can deduce the uppermost final temperature T_2 or, else, the admitted temperature enhancement factor T_2/T_1. Figure 2 shows a plot for $N = 4$ and demonstrates a considerable increase in T_2 with respect to T_1 if kT_1 increases with respect to the level spacing ΔE.

In conclusion, the presented formalism is valid for open system dynamics as determined by quantum Markovian master equations. The analogy to the classical case is basically due to the underlying assumptions that the open system $\mathcal{S}$ is weakly coupled to a very large reservoir $\mathcal{R}$, which is in a quasi-free state [13, 15, 23]. The ultimate consequence then is the existence of a contractivity property (12), which allows a meaningful definition of entropy production [12]. Note also that a factorization of the initial state of the entire system $\mathcal{Q} = \mathcal{S} \cup \mathcal{R}$ is crucial

to this type of dynamics and that both systems start in states with entropy different from zero. In contrast, for more general interactions and properties of $\mathcal{R}$ with resulting equations of Nakajima–Zwanzig type the situation and, consequently, appropriate treatments may change drastically. Then, even the common concepts of relative entropy, entropy flow and entropy production have to be revisited [19–21]. Future investigations along these lines will certainly be necessary.

Acknowledgment

Appendix A

As an example calculate the $(\mu = 1, \nu = 3)$-contribution $p_{13}^{(2)}$ to the second-order term $p^{(2)}(x)$ defined by

$$p_{13}^{(2)} = \text{Tr}\{\mathcal{L}(\omega(x)D_1^{(3)}(u, \varepsilon(x))\}. \tag{A.1}$$

From (43) we have

$$\mathcal{L}(\omega(x)) = \sum_{s,t} g_{st} \, x_t \, F_s \tag{A.2}$$

and from (36)

$$D_1^{(3)} = \tfrac{1}{24}[u, X] \qquad X = [(\varepsilon + \varepsilon^*), u]. \tag{A.3}$$

From (48) and (49) one finds

$$\varepsilon + \varepsilon^* = w_0 \, \mathbb{1} + \sum_l w_l \, F_l \qquad w_0 = \frac{2}{N} \sum_i a_i \, x_i \quad w_l = 2 \, a_0 \, x_l + \sum_{i,k} a_i \, x_k \, d_{ikl}. \tag{A.4}$$

Using the commutator relations in (18) for F-matrices and (47) for u one obtains

$$X = \sum_{l,m} w_l \, b_m [F_l, F_m] = \mathrm{i} \sum_{l,m,n} w_l \, b_m \, f_{lmn} \, F_n \tag{A.5}$$

and, similarly,

$$D_1^{(3)} = \frac{\mathrm{i}}{24} \sum_{l,m,n,p} w_l \, b_m \, b_p \, f_{lmn}[F_p, F_n] = -\frac{1}{24} \sum_{\substack{l,m,n \\ p,q}} w_l \, b_m \, b_p \, f_{lmn} \, f_{pnq} \, F_q. \tag{A.6}$$

Using $\text{Tr}(F_i \, F_k) = \delta_{ik}$ an intermediate result is

$$p_{13}^{(2)} = -\tfrac{1}{24} \sum_{\substack{l,m,n \\ p,q,t}} w_l \, b_m \, b_p \, f_{lmn} \, f_{pnq} \, g_{qt} \, x_t \tag{A.7}$$

from which the final result, after inserting w_l and renaming summation indices, is found to be

$$p_{13}^{(2)} = \frac{a_0}{12} \sum_{\substack{i,k,l \\ m,n,p}} (b_m \, b_p \, f_{imn} \, f_{lnp} \, g_{lk}) \, x_i \, x_k + \frac{1}{24} \sum_{\substack{i,k,l,m \\ n,p,q,r}} (a_q \, b_m \, b_p \, f_{lnp} \, f_{mnr} \, d_{iqr} \, g_{lk}) \, x_i \, x_k. \tag{A.8}$$

All other terms are calculated by repeatedly applying the same technique of reducing multiple products of F-matrices to linear forms.

Appendix B

For regular σ the logarithm is given by

$$u = \ln \sigma = \ln(\mathbb{I} + 2\,(\boldsymbol{y}, \boldsymbol{F})) - (\ln 2)\,\mathbb{I} \tag{B.1}$$

with series expansion

$$\ln(\mathbb{I} + M) = M - \tfrac{1}{2}M^2 + \tfrac{1}{3}M^3 - \tfrac{1}{4}M^4 + \cdots \tag{B.2}$$

for any regular matrix M with $\|M\| \leqslant 1$. Later, we will use the vector representation

$$u = \ln \sigma = b_0\,\mathbb{I} + (\boldsymbol{b}, \boldsymbol{F}) \tag{B.3}$$

and the coefficients must be expressed in terms of $\boldsymbol{y}$. To this end, set

$$M = 2\,(\boldsymbol{y}, \boldsymbol{F}) \qquad z = \sqrt{2}\,y \qquad y = (\boldsymbol{y}, \boldsymbol{y})^{1/2}. \tag{B.4}$$

Note that the F-matrices, as defined in (63), satisfy

$$\{F_i, F_k\} = 0 \qquad i \neq k \qquad F_i^2 = \tfrac{1}{2}\,\mathbb{I} \qquad \forall(i, k). \tag{B.5}$$

Therefore, the powers of M reduce to

$$M^2 = z^2\,\mathbb{I} \qquad M^3 = z^2\,M, \ldots \tag{B.6}$$

giving rise to the series

$$\ln(\mathbb{I} + M) = \left(1 + \frac{1}{3}z^2 + \frac{1}{5}z^4 + \cdots + \frac{1}{n}z^{n-1} + \cdots \right) M \tag{B.7}$$

$$- \left(\frac{1}{2}z^2 + \frac{1}{4}z^4 + \frac{1}{6}z^6 + \cdots + \frac{1}{2n}z^{2n} + \cdots \right) \mathbb{I}. \tag{B.8}$$

In terms of known series [37],

$$\frac{1}{2}\ln\left(\frac{1 + z}{1 - z} \right) = \tanh^{-1}(z) = z + \frac{1}{3}z^3 + \cdots + \frac{1}{n}z^n + \cdots \tag{B.9}$$

$$\ln(1 - z^2) = -\left(z^2 + \frac{1}{2}z^4 + \cdots + \frac{1}{n}z^{2n} + \cdots \right) \tag{B.10}$$

one finds

$$\ln \sigma = \left[\frac{1}{2}\ln\left(\frac{1}{4} - \frac{1}{2}y^2 \right) \right] \mathbb{I} + \left[\frac{\sqrt{2}}{y}\tanh^{-1}(\sqrt{2}\,y) \right] (\boldsymbol{y}, \boldsymbol{F}). \tag{B.11}$$

Therefore, the desired coefficients are

$$b_0 = \tfrac{1}{2}\ln(\tfrac{1}{4} - \tfrac{1}{2}y^2) \qquad \boldsymbol{b} = \left[\frac{\sqrt{2}}{y}\tanh^{-1}(\sqrt{2}\,y) \right] \boldsymbol{y}. \tag{B.12}$$

Appendix C

The translation of (16),

$$P = \mathrm{Tr}\{\mathcal{L}(\omega(\boldsymbol{x}))(\ln \sigma - \ln \rho)\} \tag{C.1}$$

into coherence vectors proceeds as follows. Recall the earlier definitions for initial and final states,

$$\rho = \omega(\boldsymbol{x}) + \sigma \qquad \omega = (\boldsymbol{x}, \boldsymbol{F}) \qquad \sigma = \tfrac{1}{2}\mathbb{I} + (\boldsymbol{y}, \boldsymbol{F}) \tag{C.2}$$

$$\rho = \tfrac{1}{2}\mathbb{I} + (\boldsymbol{v}, \boldsymbol{F}) \qquad \boldsymbol{v} = \boldsymbol{x} + \boldsymbol{y} \tag{C.3}$$

and introduce the logarithms

$$\ln \rho = w_0 \, \mathbb{I} + (\boldsymbol{w}, \boldsymbol{F}) \qquad \ln \sigma = b_0 \, \mathbb{I} + (\boldsymbol{b}, \boldsymbol{F}). \tag{C.4}$$

According to (B.12) we have

$$\boldsymbol{w} = f(v)\,\boldsymbol{v} \qquad \boldsymbol{b} = f(y)\,\boldsymbol{y} \qquad f(z) = \frac{\sqrt{2}}{z}\,\tanh^{-1}(\sqrt{2}\,z). \tag{C.5}$$

Furthermore, $\mathcal{L}(\omega)$ of (43) can be written as

$$\mathcal{L}(\omega(\boldsymbol{x})) = \sum_i (G\,\boldsymbol{x})_i \, F_i. \tag{C.6}$$

Inserting the above relations into (C.1) and using $\mathrm{Tr}(F_i\,F_k) = \delta_{ik}$ leads to

$$P = \sum_i (G\,\boldsymbol{x})_i \, \mathrm{Tr}\{F_i((\boldsymbol{b}-\boldsymbol{w}), \boldsymbol{F})\} = ((\boldsymbol{b}-\boldsymbol{w}), G\,\boldsymbol{x}). \tag{C.7}$$

Since $G = Q + R$, $Q^T = -Q$, one has $(\boldsymbol{x}, G\,\boldsymbol{x}) = (\boldsymbol{x}, R\,\boldsymbol{x})$, and the final formula is obtained as

$$P = (f(y) - f(v))\,(\boldsymbol{y}, G\,\boldsymbol{x}) - f(v)(\boldsymbol{x}, R\,\boldsymbol{x}). \tag{C.8}$$

Appendix D

The following dimensionless values of dynamical parameters have been used for the example in section 5.

$$\omega_0 = 10 \qquad \omega_1 = 8 \qquad \omega_2 = 4 \qquad \gamma_1 = 3.8 \qquad \gamma_2 = 3 \qquad \gamma_3 = 2.5$$
$$\alpha = 0.4 \qquad \beta = 1.1 \qquad \delta = 0.6 \qquad \lambda = 0.009 \qquad \mu = 0 \qquad v = 0.3. \tag{D.1}$$

The matrix $L^{(2)}$ of rounded second-order coefficients L_{ik} is obtained as

$$L^{(2)} = \begin{pmatrix} 5.06 & -1.22 & -2.33 \\ -0.46 & 6.10 & -1.52 \\ -2.05 & -1.02 & 7.72 \end{pmatrix}. \tag{D.2}$$

As was to be expected in general, $L^{(2)}$ turns out to be non-symmetric positive with eigenvalues $\{9.09, 6.58, 3.2\}$. Due to the associated quadratic form one can define the symmetrized representation $\tilde{L}^{(2)} = \frac{1}{2}(L^{(2)} + L^{(2)\mathrm{T}})$ having eigenvalues $\{9.13, 6.57, 3.17\}$.

It is interesting to note that the third-order coefficients L_{ikl} listed below are found to be of comparable magnitude:

(ikl)	L_{ikl}						
(111)	−0.67	(211)	1.82	(311)	−0.88	(112)	−4.65
(212)	2.12	(312)	−4.62				
(113)	−0.50	(213)	−0.10	(313)	−2.12	(121)	1.93
(221)	−3.19	(321)	5.63				
(122)	1.21	(222)	−0.65	(322)	−2.49	(123)	−0.57
(223)	3.40	(323)	−3.99				
(131)	−0.25	(231)	0.71	(331)	4.33	(132)	−2.48
(232)	−2.79	(332)	5.01				
(133)	−1.69	(233)	−0.46	(333)	2.08.		

$$\tag{D.3}$$

For completeness, the data of initial and final state are also given. The dynamics starts at $x = 0.61$ or, else, $v = \|\boldsymbol{x}+\boldsymbol{y}\| = 0.67$ with vector $\boldsymbol{v} = (-0.4, -0.31, -0.44)^{\mathrm{T}}$ corresponding to a density matrix

$$\rho = \begin{pmatrix} 0.19 & -0.29 - \mathrm{i}\,0.22 \\ -0.29 + \mathrm{i}\,0.22 & 0.81 \end{pmatrix} \qquad S(\rho) = 0.11 \tag{D.4}$$

where $S(\rho) = -\mathrm{Tr}(\rho \ln \rho)$ is the von Neumann entropy with bounds $0 \leqslant S \leqslant \ln 2 = 0.69$. The final destination state is reached at $x = 0$ or, else, $y = 0.11$ with vector $\boldsymbol{y} = (-0.05, -0.04, -0.09)^{\mathrm{T}}$ equivalent to

$$\sigma = \begin{pmatrix} 0.43 & -0.04 - \mathrm{i}\,0.03 \\ -0.04 + \mathrm{i}\,0.03 & 0.57 \end{pmatrix} \qquad S(\sigma) = 0.68. \tag{D.5}$$

These data show that the dynamics starts not far from a pure state close to the surface of the Bloch sphere (radius $= 0.71$) and ends almost in the centre, which belongs to maximum entropy $S = 0.69$.

References

[1] Onsager L 1931 *Phys. Rev.* **37** 405
    Onsager L 1931 *Phys. Rev.* **38** 2265
[2] de Groot S R and Mazur P 1962 *Non-Equilibrium Thermodynamics* (Amsterdam: North-Holland)
[3] Callen H B 1960 *Thermodynamics* (New York: Wiley)
[4] Ruelle D 1996 *J. Stat. Phys.* **85** 1
[5] de Groot S R 1960 *Thermodynamik Irreversibler Prozesse* (Mannheim: Bibliographisches Institut)
[6] Gabrielli D, Jona-Lasinio G and Landim C 1996 *Phys. Rev. Lett.* **77** 1202
[7] Landauer R 1975 *Phys. Rev.* A **12** 636
[8] Streater R F 1993 *J. Phys. A: Math. Gen.* **26** 1553
[9] Alicki R 1976 *Rep. Math. Phys.* **10** 249
[10] Alicki R 1979 *J. Stat. Phys.* **20** 671
[11] Alicki R 1979 *J. Phys. A: Math. Gen.* **12** L103
[12] Spohn H 1978 *J. Math. Phys.* **19** 1227
[13] Spohn H and Lebowitz J L 1978 *Advances in Chemical Physics* vol 38, ed S A Rice (New York: Wiley)
[14] Lendi K 1986 *Phys. Rev.* A **34** 662
[15] Alicki R and Lendi K 1987 *Quantum Dynamical Semigroups and Applications (Lecture Notes in Physics vol 286)* (Berlin: Springer)
[16] Lendi K 2000 *J. Stat. Phys.* **99** 1037
[17] Haake F 1973 *Springer Tracts in Modern Physics* vol 66, ed G Höhler (Berlin: Springer)
[18] van Wonderen A J and Lendi K 1995 *J. Stat. Phys.* **80** 273
[19] Lendi K, Farhadmotamed F and van Wonderen A J 1998 *J. Stat. Phys.* **92** 1115
[20] Farhadmotamed F, van Wonderen A J and Lendi K 1998 *J. Phys. A: Math. Gen.* **31** 3395
[21] Farhadmotamed F 1998 *Thesis* University of Zürich
[22] Gorini V, Kossakowski A and Sudarshan E C G 1976 *J. Math. Phys.* **17** 821
[23] Davies E B 1974 *Commun. Math. Phys.* **39** 91
    Davies E B 1976 *Math. Ann.* **219** 147
    Davies E B 1975 *Ann. Inst. Henri Poincaré* **11** 265
[24] Ohya M and Petz D 1993 *Quantum Entropy and its Use* (Berlin: Springer)
[25] Wehrl A 1978 *Rev. Mod. Phys.* **50** 221
[26] Thirring W 1980 *Lehrbuch der Theoretischen Physik* vol 4 (Vienna: Springer)
[27] Lindblad G 1975 *Commun. Math. Phys.* **40** 147
[28] Magnus W 1954 *Commun. Pure Appl. Math.* **7** 649
[29] Weiss G H and Maradudin A A 1962 *J. Math. Phys.* **3** 771
[30] Lendi K 1987 *J. Phys. A: Math. Gen.* **20** 15
[31] Dufty J W and Rubi J M 1987 *Phys. Rev.* A **36** 222
[32] Abragam A 1986 *Principles of Nuclear Magnetism* (Oxford: Oxford University Press)
[33] Slichter C P 1973 *Priciples of Magnetic Resonance* (Berlin: Springer)
[34] Allen L and Eberly J H 1975 *Optical Resonance and Two-Level Atoms* (New York: Wiley)
[35] Louisell W H 1973 *Quantum Statistical Properties of Radiation* (New York: Wiley)
[36] Loudon R 1978 *The Quantum Theory of Light* (Oxford: Oxford University Press)
[37] Dwight H B 1961 *Tables of Integrals and other Mathematical Data* (New York: Macmillan)
[38] Hilgert J, Hofmann K H and Lawson J D 1989 *Lie Groups, Convex Cones, and Semigroups* (Oxford: Clarendon)
[39] Bourbaki N 1989 *Lie Groups and Lie Algebras* (Berlin: Springer)
[40] Oteo J A 1991 *J. Math. Phys.* **32** 419