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Higher Order Quantum Onsager Coefficients from Dynamical Invariants

K. Lendi[1]

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Functionals representing dynamical invariants under unitary quantum dynamics of open systems are used to derive Onsager coefficients for entropy production in irreversible processes if the nonunitary time evolution is determined by quantum dynamical semigroups. The procedure allows a derivation from first principles of the quantum analogue to the classical case.

KEY WORDS: Quantum dynamical semigroups; irreversible processes; entropy production; quantum Onsager coefficients.

In the classical Onsager theory[1, 2] an expression for entropy production P is given by a quadratic form

$$P = \sum_{i,k} L_{ik} X_i X_k \tag{1}$$

where $\{X_i\}$ denote generalized forces and $\{L_{ik}\}$ the "phenomenological" Onsager coefficients with symmetry $L_{ik} = L_{ki}$. Formula (1) applies to the so-called linear or weakly irreversible regime since in the original version for P,

$$P = \sum_i J_i X_i \tag{2}$$

it has been assumed that the generalized fluxes J_i are related to the forces through

$$J_i = \sum_k L_{ik} X_k \tag{3}$$

[1] Institute of Physical Chemistry, University of Zürich, CH-8057 Zürich, Switzerland; e-mail: carlen@pci.unizh.ch.

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although, in general, $J_i = J_i(X_1, X_2, ...)$ may be nonlinear functions of the forces in the expanded form

$$J_i = \sum_k L_{ik} X_k + \sum_{k,l} L_{ikl} X_k X_l + \sum_{k,l,m} L_{iklm} X_k X_l X_m + \cdots \tag{4}$$

The question arises whether there is a suitable analogue of the above concepts in the framework of a quantum theory of irreversible processes. It is interesting to note that a direct analogy even to the generalized form (4) can be worked out and that ordinary and higher quantum Onsager coefficients can be obtained from first principles.

It is the aim of this report to show this derivation in simple cases where too complicated formulas can be avoided. In particular, we will consider irreversible processes as described by Markovian master equations and associated quantum dynamical semigroup time-evolution. Thus, the necessary settings will briefly be summarized.

Consider an open system[3] with associated Hilbert space $\mathscr{H}$ and $\dim(\mathscr{H}) = N < \infty$, as is sufficient for many practical applications. The time-dependent states ρ_t are given by density matrices as solutions of a master equation

$$\dot{\rho}_t = \mathscr{L}(\rho_t) \tag{5}$$

where the most general form of the infinitesimal generator $\mathscr{L}$ is given by[4]

$$\mathscr{L}(\rho_t) = -i[H, \rho_t] + \tfrac{1}{2} \sum_{i,k=1}^{M} a_{ik} \{ [F_i, \rho_t F_k] + [F_i \rho_t, F_k] \} \tag{6}$$

$$H = H^*, \qquad \mathrm{Tr}(H) = 0, \qquad F_i = F_i^*, \qquad \mathrm{Tr}(F_i) = 0$$

$$\mathrm{Tr}(F_i F_k) = \delta_{ik}, \qquad A = \{a_{ik}\}_i^M \geqslant 0, \qquad M = N^2 - 1 \tag{7}$$

The integrated form of (5) with initial state ρ reads

$$\rho_t = \Lambda_t(\rho), \qquad \Lambda_t = \exp(\mathscr{L} t), \qquad t \geqslant 0 \tag{8}$$

where Λ_t is called a (completely positive) quantum dynamical semigroup which preserves the von Neumann conditions $\{\rho_t = \rho_t^*, \rho_t \geqslant 0, \mathrm{Tr}(\rho_t) = 1, t \geqslant 0\}$ for any initial state ρ.

If Λ_t admits a unique invariant state σ with $\{\Lambda_t(\sigma) = \sigma$ or, else, $\lim_{t \to \infty} \Lambda_t(\rho) = \rho_\infty \equiv \sigma\}$ the transition $\rho \to \sigma$ is called a genuinely irreversible process with unique final destination state. Under these assumptions

Spohn has shown that the quantum version of entropy production[5, 6] is given by

$$P(\rho/\sigma) = -\left[\frac{d}{dt} S(\Lambda_t(\rho)/\sigma)\right]_{t=0} \tag{9}$$

where $S(\rho_t/\sigma)$ is the relative entropy

$$S(\rho_t/\sigma) = \mathrm{Tr}\{\rho_t(\ln \rho_t - \ln \sigma)\} \geqslant 0 \tag{10}$$

As is obvious from Spohn's derivation the above formula is valid in the vicinity of a thermodynamic equilibrium state σ but a closer examination shows that it applies also to larger deviations, at least as long as the dynamics involves only faithful states.[7] This extended range of validity is essentially due to the contractivity property[8] of S under completely positive mappings Λ_t,

$$S(\Lambda_t(\rho)/\Lambda_t(\rho')) \leqslant S(\rho/\rho') \tag{11}$$

for any two density operators $\{\rho, \rho'\}$. The consequence is a smooth monotonically decreasing behavior of S in (10) as a function of time. For fixed σ, therefore, S is a Lyapunov functional on state space.

The above arguments suggest that a derivation of higher order Onsager coefficients, as indicated in (4), should be possible and meaningful.[6, 9, 10] In order to keep the procedure transparent we consider the special case where the final state is given by the central state $\sigma = (1/N)\,\mathbb{1}$ and decompose ρ_t according to

$$\rho_t = \sigma + \omega_t, \qquad \mathrm{Tr}(\omega_t) = 0, \qquad [\sigma, \omega_t] = 0, \qquad \lim_{t\to\infty} \omega_t = 0 \tag{12}$$

Since σ and ω_t commute one gets for $S_t \equiv S(\rho_t/\sigma)$

$$S_t = \frac{1}{N}\,\mathrm{Tr}\{(\mathbb{1} + N\omega_t)\ln(\mathbb{1} + N\omega_t)\} \tag{13}$$

and, by expansion of the logarithm,

$$S_t = \frac{N}{2}\,\mathrm{Tr}(\omega_t^2) - \frac{N^2}{6}\,\mathrm{Tr}(\omega_t^3) + \frac{N^3}{12}\,\mathrm{Tr}(\omega_t^4) + O(\omega_t^5) \tag{14}$$

where the higher order terms will not be calculated since ω_t is considered to be a sufficiently small deviation from σ such that $\|\omega_t\| \ll 1$ holds in trace norm. Under unitary time-evolution functionals of the form

$$\Omega_l(t) = \mathrm{Tr}(\omega_t^l) \tag{15}$$

are dynamical invariants[11] satisfying $\dot{\Omega}_l(t) = 0$, the dot denoting derivative with respect to time. This is the case if the relaxation matrix A vanishes such that Λ_t is no longer a semigroup but the group of unitary transformations $U_t = \exp(-iHt)$ in $\mathscr{H}$ with $\rho \to \rho_t = U_t \rho U_{-t}$. On the other hand, for $A \neq 0$ one will find $\dot{\Omega}_l(t) \neq 0$ and entropy production can be calculated directly from derivatives of homogeneous polynomials in corresponding coherence-vector invariants. To show this in detail one transforms (5) into coherence-vector representation,

$$\omega_t = \sum_{i=1}^{M} v_i(t)\, F_i, \qquad v_i(t) = \mathrm{Tr}(\rho_t F_i) \tag{16}$$

where the components of vector $\mathbf{v}_t = \{v_i(t)\}_1^M$ are real-valued functions of time and $\{F_i\}$ is an orthonormal matrix basis as in (7). A convenient choice is given by the Lie-algebra of infinitesimal generators of $SU(N)$[3] with

$$[F_i, F_k] = i \sum_{l=1}^{M} f_{ikl} F_l, \qquad \{F_i, F_k\} = \frac{2}{N} \mathbb{1} \delta_{ik} + \sum_{l=1}^{M} d_{ikl} F_l \tag{17}$$

where, under arbitrary permutations π applied to the triple $[ikl]$, the following symmetries hold,

$$\begin{aligned} f_{\pi[ikl]} &= \begin{cases} +f_{ikl}, & \pi \text{ even} \\ -f_{ikl}, & \pi \text{ odd} \end{cases} \\ d_{\pi[ikl]} &= d_{ikl} \end{aligned} \tag{18}$$

For later use a derived practical contraction formula reads

$$F_i F_k = \frac{1}{N} \mathbb{1} \delta_{ik} + \frac{1}{2} \sum_{l=1}^{M} z_{ikl} F_l, \qquad z_{ikl} = d_{ikl} + i f_{ikl} \tag{19}$$

In this representation the first few elementary unitary invariants are given by[11]

$$T_2 = \sum_{i=1}^{M} v_i^2, \qquad T_3 = \tfrac{1}{2} \sum_{i,k,l=1}^{M} d_{ikl} v_i v_k v_l \tag{20}$$

$$T_4 = \tfrac{1}{4} \sum_{i,k,l,m,n=1}^{M} d_{ikn} d_{lmn} v_i v_k v_l v_m \tag{21}$$

Evaluation of the traces in (14) upon use of (19) yields

$$\mathrm{Tr}(\omega_t^2) = T_2, \qquad \mathrm{Tr}(\omega_t^3) = T_3, \qquad \mathrm{Tr}(\omega_t^4) = \frac{1}{N}\, T_2^2 + T_4 \tag{22}$$

For $A \neq 0$ and, consequently, nonunitary dynamics Λ_t the invariants $T_i \to T_i(t)$ become time-dependent functionals the derivatives of which enter formula (9) for entropy production according to

$$P(\rho/\sigma) = -\frac{N}{2}\, \dot{T}_2(0) + \frac{N^2}{6}\, \dot{T}_3(0) - \frac{N^3}{12} \left\{ \frac{2}{N}\, T_2(0)\, \dot{T}_2(0) + \dot{T}_4(0) \right\} \tag{23}$$

For a final state σ the coupled differential equations equivalent to (5) are found to be

$$\dot{\mathbf{v}}_t = G\mathbf{v}_t, \qquad G = Q + R \tag{24}$$

where the real matrix $G = \{g_{ik}\}_1^M$ is decomposed into an antisymmetric contribution $Q = \{q_{ik}\}_1^M$ with $Q^T = -Q$ arising from the Hamiltonian part of (6) and a symmetric contribution $R = \{r_{ik}\}_1^M$ with $R^T = R$ arising from the relaxation part. For details, the reader is referred to refs. 3, 12. Using the abbreviation

$$\mathbf{x} \equiv \mathbf{v}_0, \qquad x_i = \mathrm{Tr}(\rho F_i), \qquad 1 \leqslant i \leqslant M \tag{25}$$

all derivatives in (23) can be expressed in terms of $\{g_{ik}\}$ and the components of $\mathbf{x}$ after repeated use of (18) and (19). The result can be written in the form

$$P(\rho/\sigma) \cong \sum_{i,\,k} L_{ik} x_i x_k + \sum_{i,\,k,\,l} L_{ikl} x_i x_k x_l + \sum_{i,\,k,\,l,\,m} L_{iklm} x_i x_k x_l x_m \tag{26}$$

in analogy to the classical, generalized form. The second, third and fourth order quantum Onsager coefficients appear in this representation as

$$L_{ik} = -N r_{ik}, \qquad L_{ikl} = \frac{N^2}{4} \sum_{n=1}^{M} d_{nkl}\, g_{ni} \tag{27}$$

$$L_{iklm} = -\frac{N^3}{12} \left(\frac{4}{N}\, r_{ik} \delta_{lm} + \sum_{n,\,p=1}^{M} d_{pkn} d_{lmn}\, g_{pi} \right) \tag{28}$$

For completeness, the list of matrixelements $\{g_{ik} = q_{ik} + r_{ik}\}$ is given by[3]

$$q_{ik} = -\sum_{l=1}^{M} f_{ikl} h_l, \qquad h_l = \mathrm{Tr}(HF_l)$$
$$r_{ik} = -\tfrac{1}{4} \sum_{\substack{l,m,n=1 \\ (l \leqslant m)}}^{M} (2 - \delta_{lm})(f_{iln} f_{kmn} + f_{imn} f_{kln})\, a_{lm} \tag{29}$$

where the relaxation matrix A has been assumed to be real-symmetric in order to guarantee that the dynamics ends in the invariant state σ and this, in turn, implies $R = R^T$ as mentioned earlier.

As a consequence, the second order coefficients are given by a symmetric matrix. In the classical case this symmetry property is derived under rather general assumptions[1, 2, 14] if a detailed balance condition with respect to a thermodynamic equilibrium state holds. Similarly, in the quantum case the assumptions needed to establish symmetry under quantum dynamical semigroup dynamics have been discussed in refs. 6, 9 where exceptions are also mentioned[6]. It must be noted that for a general Kossakowski generator (6) and more general assumptions than those adopted in this paper, symmetry may be violated. However, this does not affect the result for entropy production since the second order contribution will always be given by a positive-definite quadratic form.

Finally, the choice of the final central state σ may appear as being too special. Nevertheless, this situation occurs frequently in a wide range of applications. It is well-known, for instance, that in nuclear magnetic resonance at moderate fields and low temperatures different levels are equally populated. In general, for N-level systems with very small level spacings the central state is an acceptable equilibrium state already at low temperatures whereas for large spacings the obtained results may be considered as high-temperature expansion for T such that the Boltzman factors approach unity to satisfactory approximation. The above treatment becomes considerably more complicated for arbitrary final state σ due to the nonvanishing commutator $[\sigma, \omega_t]$ in (12). In this most general case Lie-algebraic techniques and rather lengthy calculations still lead to the desired Onsager coefficients as will be shown in a forthcoming extended paper.

In conclusion, it is obvious that for a given Hamiltonian H and relaxation-dissipation matrix A the dynamics is entirely determined by the infinitesimal semigroup generator $\mathscr{L}$. Then, the coherence-vector coordinates $\mathbf{x}$ of the initial nonstationary state ρ take the role of generalized forces which drive the system back to its stationary ("equilibrium") state σ,

whereas the strength of the irreversible transition $\rho \to \sigma$ and corresponding entropy production is determined by the derived Onsager coefficients. It should be emphasized that in the fundamental Davies theory of the weak-coupling limit [13] the relevant matrixelements $\{a_{lm}\}$ are obtained by Fourier transforms of stationary two-point correlation functions of those reservoir operators[6] which appear in the Hamiltonian for the interaction between open system and environment. It is for this reason that one can say that the above procedure provides a derivation of quantum Onsager coefficients from first principles.

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