Entropy production in coherence-vector formulation for N-level systems

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(Received 25 February 1986)

If the time evolution of an irreversible process is described by a completely positive quantum-dynamical semigroup a systematic formulation in terms of coherence vectors is of particular advantage since the time change of their length and relative scalar product determines, to a large extent, the relative entropy with respect to a unique final state and, ultimately, the total entropy production. As examples, general exact formulas for two-level systems are given and, in arbitrary dimensions, for a weakly irreversible process close to the central state, a first-principles derivation of the phenomenological Onsager coefficients is outlined.

A quantum theory of irreversible processes is expected to provide more theoretical insight as well as a reliable basis for computations from first principles of details of important and useful quantities of the phenomenological theory as, e.g., entropy production.[1,2] In particular, the theory of quantum Markovian master equations[3,4] allows for a concise quantitative treatment not only in the linear Onsager regime of so-called weakly irreversible processes close to equilibrium but also for more general processes starting far from equilibrium but ending in a unique asymptotically stationary state.[5]

For many applications concerning N-level systems, particularly for problems of optical or magnetic resonance spectroscopy, a convenient formulation of master equations is provided in terms of a coherence vector and an associated evolution matrix[6–9] and it is worthwhile to discuss entropy production under this aspect. The coherence vector $\mathbf{v}_t=[v_1(t),v_2(t),\ldots,v_M(t)]^T$ with $M=N^2-1$ real-valued functions of time as components is then given through the decomposition of a time-dependent $(N\times N)$-density matrix ρ_t in terms of the M Hermitian infinitesimal generators of SU(N), denoted by $\mathbf{F}=(F_1,F_2,\ldots,F_M)^T$,

$$\rho_t=\frac{1}{N}\mathbb{1}_N+\sum_{k=1}^{M}v_k(t)F_k=\frac{1}{N}\mathbb{1}_N+(\mathbf{v}_t\cdot\mathbf{F}) . \tag{1}$$

Due to trace normalization and the positiveness of ρ_t its Frobenius norm $||\rho_t||=[\mathrm{Tr}(\rho_t^2)]^{1/2}$ is bounded by $0<||\rho_t||\le 1$ and this, in turn, implies for the length of the coherence vector the bounds

$$0\le||\mathbf{v}_t||\le(1-1/N)^{1/2},\quad t\ge 0 \tag{2}$$

as directly obtained from $\mathrm{Tr}(F_i)=0$ and $\mathrm{Tr}(F_iF_k)=\delta_{ik}$ $(1\le i,k\le M)$. Since the minimum in (2) is attained for the central state $\zeta=(1/N)\mathbb{1}_N$ of maximum von Neumann entropy $s_t=-\mathrm{Tr}(\rho_t\ln\rho_t)=\ln N$ and the maximum for pure states with $s_t=0$, one is tempted to conjecture that entropy production can be related directly to the time change of the length of the coherence vector but, unfortunately, the details are more complicated, in general. In any case, $\mathbf{v}_t$ must be obtained from the original master equation $\dot\rho_t=\mathscr{L}\rho_t$, where $\mathscr{L}$ is the time-independent infinitesimal generator of a completely positive quantum-dynamical semigroup.[10] By the decomposition (1) one finds the correspondent dynamical equation

$$\dot\rho_t=\mathscr{L}\rho_t\to\dot{\mathbf{v}}_t=G\mathbf{v}_t+\mathbf{k} , \tag{3}$$

all details of derivation being available in Refs. 6–9. If $\mathscr{L}$ is taken in Kossakowski-normal form[8–10] it contains, apart from a Hamiltonian H, an $(M\times M)$ relaxation matrix A with

$$A=A^*\ge 0 . \tag{4}$$

Thus, the $(M\times M)$ evolution matrix G also depends upon the matrix-elements of H and of A but, somewhat unusually, it acquires a general structure with nontrivial Jordan canonical form, i.e., it may not be completely diagonalizable.[9,10] The constant vector $\mathbf{k}$ depends only on the imaginary part of A. Time evolution $\rho_t=\Lambda_t\rho_0$ with $\Lambda_t=\exp(\mathscr{L}t)$ is then translated into the vector picture by

$$\mathbf{v}_t=\Gamma_t(\mathbf{x}-\mathbf{y})+\mathbf{y},\quad \Gamma_t=\exp(Gt) , \tag{5}$$

with initial condition $\mathbf{v}_0\equiv\mathbf{x}$ and final state

$$\mathbf{y}=\lim_{t\to\infty}\mathbf{v}_t=-G^{-1}\mathbf{k} . \tag{6}$$

This is true for so-called uniquely relaxing semigroups since $\mathbf{y}$ is uniquely determined by the pair $\{G,\mathbf{k}\}$, or else by $\mathscr{L}$ irrespective of initial conditions, as obviously guaranteed if and only if $\det(G)\neq 0$. We will only consider this type of semigroup which is certainly of most physical interest since it comprises also the situation where the final destination state of the open system describes thermodynamic equilibrium with the reservoir as obtained in the weak coupling limit by use of the Kubo-Martin-Schwinger (KMS) condition for the reservoir correlation functions.[4] Let us rewrite (5) as $\mathbf{v}_t=\mathbf{v}_t^{(0)}+\mathbf{y}$ and introduce the equivalent decomposition

$$\rho_t=\Omega+\omega_t,\quad \Omega=\zeta+(\mathbf{y}\cdot\mathbf{F}),\quad \omega_t=(\mathbf{v}_t^{(0)}\cdot\mathbf{F}) , \tag{7}$$

where $\zeta=(1/N)\mathbb{1}_N$ and, again, $\lim_{t\to\infty}\rho_t=\Omega$. For a meaningful definition of entropy production the von Neumann entropy is not well suited but the relative entropy

$S(\rho_t/\Omega)$ of a state ρ_t with respect to the unique final state Ω,

$$S(\rho_t/\Omega)=\mathrm{Tr}[\rho_t(\ln\rho_t-\ln\Omega)]\geq 0,\quad t\geq 0 \tag{8}$$

has the desired convexity properties [we will also write $S(\mathbf{v}_t/\mathbf{y})$]. It has been shown by Spohn[5] that the entropy production in an irreversible process starting from state ρ_0 and ending in state Ω is then given by

$$\sigma(\rho_0/\Omega)=-\frac{d}{dt}S(\rho_t/\Omega)\bigg|_{t=0}, \tag{9}$$

and, again, we will write $\sigma(\mathbf{x}/\mathbf{y})$.

To emphasize the usefulness of the coherence-vector concept for a calculation of σ we are going to work out two examples. Consider first the case of two-level systems where closed formulas can be obtained for the most general dynamics compatible with (5) and (6). We use the abbreviations $v_t=||\mathbf{v}_t||$ and $y=||\mathbf{y}||$ and find for the relative entropy

$$S(\mathbf{v}_t/\mathbf{y})=\tfrac{1}{2}\ln\left[\frac{1-4v_t^2}{1-4y^2}\right]+2v_t\,\mathrm{arctanh}(2v_t) - \frac{2}{y}(\mathbf{v}_t\cdot\mathbf{y})\,\mathrm{arctanh}(2y)\,. \tag{10}$$

This shows that not only the length but also the scalar product between the coherence vectors determines S. The evolution matrix G can always be decomposed into Hamiltonian (Q) and non-Hamiltonian (R) contributions,[8,9] $G=Q+R$, where $Q^T=-Q$ and (for $N=2$) $R^T=R$. In terms of these quantities and with $\rho_0=\frac{1}{2}\mathbb{1}_2^+(\mathbf{x}\cdot\mathbf{F})$, $x=||\mathbf{x}||$, where $\mathbf{F}$ are the normalized Pauli matrices, the entropy production is given by

$$\sigma(\mathbf{x}/\mathbf{y})=2[(\mathbf{x}\cdot R\mathbf{x})+(\mathbf{x}\cdot\mathbf{k})]\times\left[\frac{2}{1-2x}-\frac{1}{x}\,\mathrm{arctanh}(2x)\right] +\frac{2}{y}[(\mathbf{y}\cdot G\mathbf{x})+(\mathbf{y}\cdot\mathbf{k})]\,\mathrm{arctanh}(2y)\,. \tag{11}$$

Note that this formula does not involve any approximations and holds for any initial condition $\mathbf{x}$ arbitrarily far from the stationary state $\mathbf{y}$. Of course, by series expansions for $\mathbf{x}\rightarrow\mathbf{y}$ one can get a quadratic form in the components of $(\mathbf{x}-\mathbf{y})$ of Onsager type. This will be done in the second example for arbitrary N but we need some additional assumptions to avoid too complicated formulas. Consider then a weakly irreversible process in the vicinity of the central state characterized by

$$\Omega=\zeta=\frac{1}{N}\mathbb{1}_N,\quad ||\omega_t||\ll 1/N\,, \tag{12}$$

implying $\mathbf{y}=0$ and $\mathbf{k}=0$ [again $\det(G)\neq 0$]. Since $[\Omega,\omega_t]=0$, condition (12) allows one to approximate

$$\ln\rho_t-\ln\Omega\cong N\omega_t-\tfrac{1}{2}N^2\omega_t^2\,, \tag{13}$$

and, consequently, to second order in ω_t one has

$$\sigma(\mathbf{x}/0)\cong-\frac{N}{2}\frac{d}{dt}\mathrm{Tr}(\omega_t^2)\bigg|_{t=0}=-\frac{N}{2}\frac{d}{dt}v_t^2\bigg|_{t=0}\,. \tag{14}$$

Thus, in this simple example entropy production is entirely given by the time change of the length of the coherence vector as conjectured in the introductory remarks. Furthermore, $\mathbf{k}=0$ implies for the matrix A in the original Kossakowski generator[8,9] $A=A^T$ and as a consequence for the relaxation part R of G the symmetry $R=R^T$. This allows one to rewrite (14) in Onsager form,[2]

$$\sigma(\mathbf{x}/0)\cong\sum_{s,m=1}^{M}L_{sm}x_sx_m\,, \tag{15}$$

where the symmetric Onsager coefficients $L_{sm}=L_{ms}$ can be expressed in terms of the matrix elements a_{ik} of A and the completely antisymmetric structure constants[11] f_{ikl} of the Lie algebra of SU(N) through

$$L_{sm}=\frac{N}{4}\sum_{\substack{i,k,l=1\\(i\leq k)}}^{M}(2-\delta_{ik})a_{ik}(f_{ils}f_{klm}+f_{kls}f_{ilm})\,. \tag{16}$$

Thus, in (15) the vector coordinates of the initial state play the role of the generalized forces introduced in the phenomenological theory which drive the system back to its equilibrium state. It must be emphasized that (16) can be considered a quantum-theoretic calculation from first principles of the phenomenological Onsager coefficients since relating the Kossakowski generator $\mathscr{L}$ to the Davies theory of the weak-coupling limit for the open system plus reservoir[3,4] makes it possible to express the elements a_{ik} as one-sided Fourier transforms of reservoir cross-correlation functions if the reservoir is appropriately modeled as infinite quantum system. For further details concerning this point the reader is referred to the forthcoming lecture notes.[9]

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