QUANTUM DYNAMICAL SEMIGROUPS AND COMPLETE POSITIVITY. AN APPLICATION TO ISOTROPIC SPIN RELAXATION (*)

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1. Quantum Dynamical Semigroups.

Let S denote a quantum system with associated Hilbert space $\mathcal{H}$. As is well known, a state of S is described by a self-adjoint, non-negative, trace one, linear operator ρ on $\mathcal{H}$ called the statistical operator or, more commonly, the density matrix. The expectation value of an observable of S, represented by a linear self-adjoint operator A on $\mathcal{H}$, is given by $\langle A \rangle = \mathrm{tr}(\rho A)$ (whenever the expression at the r.h.s. exhists).

We consider a system S evolving irreversibly under the action of its surroundings R, which we think of as an unexhaustible energy reservoir for S. Whenever S and R are initially uncorrelated and the decay time of the reservoir's correlations is much smaller than the typical relaxation times of the system, the dynamical evolution of the state of S is described to a good approximation by a Markovian master equation of the form

$$\frac{d}{dt}\rho = L\rho, \tag{1.1}$$

where L is a linear transformation ("superoperator") acting on the space $T(\mathcal{H})$ of linear operators on $\mathcal{H}$ having finite trace. The integrated form of (1.1) writes

$$\rho = \rho(t) = e^{Lt}\rho(0) = T_t\,\rho(0), \; t \geq 0, \tag{1.2}$$

where T_t is expected to have the following properties:

(i) T_t is positive, namely $\rho \geq 0$ implies $T_t\,\rho \geq 0$;

(ii) T_t preserves the trace, namely $\mathrm{tr}(T_t\,\rho) = \mathrm{tr}(\rho)$ for all $\rho \in T(\mathcal{H})$;

(iii) $T_{t+s}\,\rho = T_t(T_s\,\rho)$, T_o = identity operator on $T(\mathcal{H})$;

(iv) $tr[(T_t \rho) A]$ is a continuous function of t for all $\rho \in T(\mathcal{H})$ and for all $A \in B(\mathcal{H})$, where $B(\mathcal{H})$ is the space of linear bounded operators on $\mathcal{H}$.

Properties (i) and (ii) are demanded by the conservation of probability; (iii) is the semigroup property which formalizes the Markovian approximation; (iv) is a physical continuity requirement for expectation values of observables.

Conversely, if T_t, $t \geq 0$, is a one-parameter family of linear operators on $T(\mathcal{H})$ satisfying conditions (i) – (iv), there exists a (generally unbounded) linear operator L on $T(\mathcal{H})$, with dense domain of definition D(L), such that eq. (1.1) holds for all $\rho \in D(L)$ [1].

The family T_t gives the dynamics in the Schrödinger picture. By duality, we can define a dynamics T_t^* in the Heisenberg picture, acting on $B(\mathcal{H})$, as

$$tr[\rho(T_t^* A)] = tr[(T_t \rho)A], \qquad \rho \in T(\mathcal{H}),\ A \in B(\mathcal{H}). \tag{1.3}$$

Then T_t^* satisfies

(i') T_t^* is positive ;

(ii') $T_t^* \mathbb{1} = \mathbb{1}$;

(iii') $T_{t+s}^* = T_t^* \, T_s^*$, T_0^* = identity operator on $B(\mathcal{H})$,

as well as the continuity property following from (iv).

Actually, it turns out that the reduced dynamics T_t of the open system S must satisfy on physical grounds a considerably more stringent constraint than the positivity property (i) (or (i')). This requirement is called complete positivity and can best be expressed in the Heisenberg picture as follows. Let n be an arbitrary positive integer and, for any given n, let $\{\varphi_1, \ldots, \varphi_n\}$, $\varphi_i \in \mathcal{H}$, $i = 1, \ldots, n$, and $\{A_1, \ldots, A_n\}$, $A_i \in B(\mathcal{H})$, $i=1, \ldots, n$, be n arbitrary Hilbert space vectors and n arbitrary bounded operators. Then T_t^* must satisfy

$$\text{(i'')} \qquad \sum_{i,j=1}^{n} (\varphi_i, T_t^*(A_i^* A_j) \varphi_j) \geq 0, \qquad t \geq 0.$$

A linear map Φ on $B(\mathcal{H})$ satisfying (i'') is said to be <u>completely positive.</u> Taking n = 1 in (i'') we see that a completely positive map is positive. The converse is in general false.

Complete positivity is not an intuitive property of the reduced dynamics. On the other hand, it has a sound physical foundation. Indeed, it is a consequence of the assumption that the total dynamics of the system plus its surroundings, regarded globally as an isolated system, is Hamiltonian [2, 3]. Alternatively, it can be proved by an independent probability argument, even without making reference to the foregoing assumption [4]. In particular, a

Hamiltonian dynamics is completely positive.

A (quantum) dynamical semigroup is a one parameter family T_t , $t \geqslant 0$, of linear bounded operators on $T(\mathcal{H})$ satisfying conditions (ii), (iii), (iv) and (i"). From the above discussion, we conclude that the reduced dynamics of a quantum system is described in the Markovian limit by a dynamical semigroup. The operator L appearing in eq. (1.1) is called the (infinitesimal) generator of the semigroup. The general form of L was given in [4] for L bounded and independently in [3] for a finite- dimensional Hilbert space [5] .

2. Application to isotropic spin relaxation.

In the second part of this talk, we describe an application of the theory of dynamical semigroups to isotropic relaxation of two coupled spins, which is relevant in optical pumping phenomena [6, 7] . We find that complete positivity implies stringent restrictions on the reduced dynamics of the spins, in the form of inequalities among measurable parameters (such as relaxation rates of the irreducible spherical components of the density matrix). Our inequalities are stronger than those previously found by other authors [8] . For comparison between the conditions of complete positivity and of simple positivity, we examine as an illustration the simplest non trivial case of isotropic relaxation of a spin 1 magnetic moment. In this example, we exhibit explicitly the restrictions on the dipole and quadrupole relaxation rates imposed by positivity, and find that they are considerably weaker than those required by complete positivity. For similar comparisons in the case of axially symmetric spin 1/2 relaxation and of dynamical maps of two-level systems see [3, 9] . For a detailed discussion of the subject see our forthcoming papers [10, 11] .

For the applications that we have in mind, we can restrict our considerations to N-level systems. In this case, we can make the identifications $\mathcal{H} = \mathbb{C}^N$ and $B(\mathcal{H}) = T(\mathcal{H}) = M(N)$, the algebra of N x N complex matrices. The result of [3] can be stated in a slightly more general form as follows.

Theorem 2.1. [3] . Let $\{G_\alpha \in M(N) ;\ \alpha = 1, 2, \ldots, N^2\}$ be a complete orthonormal set (c.o.n.s.) in M(N), i.e. $\operatorname{tr}(G_\alpha^* G_\beta) = \delta_{\alpha\beta}$. Then, a linear transformation $L : M(N) \longrightarrow M(N)$ is the generator of a dynamical semigroup iff it has the form

$$L:\ \rho \rightarrow L\rho = \frac{1}{2} \sum_{\alpha,\beta=1}^{N^2} d_{\alpha\beta} \left\{ [G_\alpha \rho, G_\beta^*] + [G_\alpha, \rho G_\beta^*] \right\} \tag{2.1}$$

for all $\rho \in M(N)$, where [12]

$$d_{\alpha\beta} = \overline{d_{\beta\alpha}} \tag{2.1a}$$

and

$$\sum_{\alpha,\beta=1}^{N^2} \overline{y_\alpha}\, d_{\alpha\beta}\, y_\beta \geqslant 0 \tag{2.1b}$$

for all vectors $\{y_\alpha\}_{\alpha=1,2,\ldots,N^2}$ such that

$$\sum_{\alpha=1}^{N^2} (\operatorname{tr} G_\alpha)\, y_\alpha = 0. \tag{2.1c}$$

Remark 2.1. Eq. (2.1) automatically incorporates the condition $\operatorname{tr}(L\rho) = 0$ and eq.(2.1a) ensures that $(L\rho)^* = L\rho^*$. The requirement of complete positivity is expressed by (2.1b) and (2.1c).

Remark 2.2. Define

$$\hat{G}_\alpha = G_\alpha - [(\operatorname{tr} G_\alpha)/N]\mathbb{1} \tag{2.2}$$

and

$$H = H^* = \frac{i}{2N} \sum_{\alpha,\beta=1}^{N^2} \left\{ (\operatorname{tr} G_\alpha^*)\overline{d_{\alpha\beta}}\,\hat{G}_\beta - (\operatorname{tr} G_\alpha) d_{\alpha\beta}\,\hat{G}_\beta^* \right\}. \tag{2.3}$$

Then (2.1) can be rewritten as

$$L : \rho \to L\rho = -i[H,\rho] + \frac{1}{2}\sum_{\alpha,\beta=1}^{N^2} d_{\alpha\beta}\left\{ [\hat{G}_\alpha \rho, \hat{G}_\beta^*] + [\hat{G}_\alpha, \rho \hat{G}_\beta^*] \right\}. \tag{2.4}$$

The decomposition (2.4) of L into the sum of a Hamiltonian part $L_H = -i\,[H,\,.]$ plus a dissipative part $L_D = L - L_H$ is unique, namely it does not depend on the choice of the c.o.n.s. $\{G_\alpha\}$. In particular, choosing $G_\alpha = F_\alpha$, where $F_{N^2} = (1/\sqrt{N})\mathbb{1}$ (so that $\operatorname{tr} F_i = 0$, $i = 1, 2, \ldots, N^2-1$) we recover the form (2.3) of [3], namely

$$L\rho = -i[H,\rho] + \frac{1}{2}\sum_{i,j=1}^{N^2-1} c_{ij}\left\{ [F_i\rho, F_j^*] + [F_i, \rho F_j^*] \right\}, \tag{2.5}$$

where $\{c_{ij}\}$ is a self-adjoint non-negative matrix.

We consider the Markovian relaxation of two coupled spins $\vec{I}$ and $\vec{J}$. The situation that we have in mind is the relaxation, in an external magnetic field. among the Zeeman sublevels of an optically pumped atomic vapor with hyperfine structure [6, 7]. Here $\vec{J}$ stands for the electronic angular momentum and $\vec{I}$ for the nuclear spin. In typical experiments, mean free times between collisions are much smaller than spin relaxation times, so that the Markovian approximation is justified. Then the density matrix of $\vec{I} + \vec{J}$ satisfies a master equation of the form (1.1) and $N = (2I + 1)(2J + 1)$. We shall confine our considerations to the case when the external magnetic fields is sufficiently weak that the relaxation is to a good approximation isotropic. This situation has been frequently studied experimentally [6, 7]. The isotropy condition reads

$$L(\Delta(R)\rho\Delta(R)^*) = \Delta(R)(L\rho)\Delta(R)^*, \tag{2.6}$$

for all $\rho \in M(N)$ and for all $R \in SO(3)$, where Δ is the tensor product of the two irreducible representations $D^{(I)}$ and $D^{(J)}$ of SO(3) corresponding to spin I and J respectively. It is convenient to write (2.1) with the choice $G_\alpha \equiv T_{KQ}(FG)$ ($F, G = |I-J|, \ldots, (I+J)$; $K = |F-G|, \ldots, (F+G)$; $Q = -K, \ldots, K$), the standard basis of irreducible spherical tensors [13] :

$$\Delta(R)\, T_{KQ}(FG)\, \Delta(R)^* = \sum_M D_{MQ}^{(K|FG)}(R)\, T_{KM}(FG). \tag{2.7}$$

Then, using (2.6), we get

$$\begin{aligned}
\frac{d}{dt}\rho &= L\rho \\
&= \frac{1}{2}\sum_K \sum_{F,G,F',G'} \lambda_K(FG,F'G') \sum_Q \Big\{ \big[T_{KQ}(FG)\rho,\ T_{KQ}(F'G')^*\big] \\
&\qquad + \big[T_{KQ}(FG),\ \rho\, T_{KQ}(F'G')^*\big] \Big\} \qquad (2.8) \\
&= -i[H,\rho] + \frac{1}{2}\sum_K \sum_{F,G,F',G'} \lambda_K(FG,F'G') \\
&\qquad + \sum_Q \Big\{ \big[\hat{T}_{KQ}(FG)\rho,\ \hat{T}_{KQ}(F'G')^*\big] + \big[\hat{T}_{KQ}(FG),\ \rho\, \hat{T}_{KQ}(F'G')^*\big] \Big\},
\end{aligned}$$

where

$$H = \sum_F h_F \mathbb{1}_F, \tag{2.9}$$

the h_F being arbitrary real constants (note that H is defined up to an additive multiple of the unit matrix $\mathbb{1}$). Define the matrices Λ_K $(K = 1, \ldots 2(I+J))$ by

$$(\Lambda_K)_{FG,F'G'} = \lambda_K(FG, F'G'). \tag{2.10}$$

Then, the complete positivity conditions (2.1b), (2.1c) are equivalent to

$$\Lambda_K \geqslant 0, \qquad K = 1, \ldots, 2(I+J) \tag{2.11}$$

and

$$\sum_F \bar{y}_F \, \lambda_0(FF, GG) \, y_G \geqslant 0 \tag{2.12}$$

for all $\{y_F\}$ such that $\sum_F \sqrt{2F+1}\; y_F = 0$. Using the identity

$$\begin{aligned}\sum_Q T_{KQ}(FG)\, T_{LM}(F'G')\, T_{KQ}(F''G'')^* \\ = (-)^{K+L+F''+G} \sqrt{2K+1}\; \delta_{F'G}\, \delta_{G'G''} \begin{Bmatrix} F'' & F & L \\ G & G'' & K \end{Bmatrix} T_{LM}(FF'')\end{aligned} \tag{2.13}$$

and the relation $T^*_{LM}(FG) = (-)^{F-G+M}\, T_{L,-M}(G,F)$, eq. (2.8) gives

$$\mathrm{L}\, T_{LM}(GG')^* = -\sum_{FF'} \gamma_L(FF'; GG')\, T_{LM}(FF')^* \tag{2.14}$$

where

$$\gamma_L(FF'; GG') = \sum_K (-)^{K+L+F'+G+1} \sqrt{2K+1} \begin{Bmatrix} F' & F & L \\ G & G' & K \end{Bmatrix} \lambda_K(F'G', FG). \tag{2.15}$$

The inverse of relation (2.15) is

$$\lambda_K(FG, F'G') = \sum_L (-)^{K+L+1-F-G'} \sqrt{2L+1} \begin{Bmatrix} G' & G & L \\ F & F' & K \end{Bmatrix} \gamma_L(F'F, G'G). \tag{2.16}$$

The master equation (2.8) can be written in terms of the expectation values of the $T_{KQ}(FF')$

(the standard irreducible components of the density matrix), $\langle T_{KQ}(FF')\rangle = \mathrm{tr}\left[\rho T_{KQ}(FF')\right]$ as [14]

$$\frac{d}{dt} \langle T_{KQ}(FF')\rangle = -\sum_{GG'} \gamma_K(FF', GG') \langle T_{KQ}(GG')\rangle. \tag{2.17}$$

The coefficients $\gamma_K(FF, FF)$, $\gamma_K(FF, GG)$ $(F \neq G)$ and $\gamma_K(FF', FF')$ $(F \neq F')$ represent respectively the decay rates within the hyperfine multiplet **F**, the transfer rates between the multiplets F and G and the decay rates of " hyperfine coherences". The remaining γ' s are usually expected to be small by the secular approximation if the hyperfine splittings are much greater than the natural widths. Inserting (2.16) into (2.11) and (2.12) we get the set of inequalities among the rates $\gamma_K(FF', GG')$ which follow from complete positivity and which therefore must be satisfied regardless of the interactions which are responsible for the relaxation. These inequalities are stronger than those previously reported by Omont [7] . Indeed, Omont's inequalities only amount to the condition of nonnegativity of the diagonal matrix elements $\lambda_K(FG, FG)$.

A particular class of master equations for the system $\vec{I} + \vec{J}$ having the form (2.8) can be obtained from a model in which the effect of the reservoir on the system is simulated by the action of a stationary isotropic fluctuating Hamiltonian

$$\tilde{H}(t) = \sum_{F,G,K,Q} T_{KQ}(FG)\, V_{KQ}^{FG}(t) \tag{2.18}$$

with Gaussian correlations

$$\begin{aligned} &\langle V_{KQ}^{FG}(t), \overline{V_{K'Q'}^{F'G'}(s)}\rangle \\ &= \lambda_K(FG, F'G')\, \delta_{KK'}\, \delta_{QQ'}\, \frac{1}{\varepsilon\sqrt{\pi}} \exp\left[-(t-s)^2/\varepsilon^2\right]. \end{aligned} \tag{2.19}$$

The Markovian limit is obtained by letting $\varepsilon \downarrow 0$ (white noise) and one obtains a generator of the form (2.8), the $\lambda_K(FG, F'G')$ being those in (2.19) and H being the Hamiltonian of the isolated system $\vec{I} + \vec{J}$ (of course, the actual H is only approximatively of the form (2.9) since, besides the rotationally invariant coupling between $\vec{I}$ and $\vec{J}$, it also contains the small term due to the weak external magnetic field). The model based on (2.18) an (2.19) corresponds to a singular coupling to an "infinite temperature" bath. It is expected to give an accurate description of the spin dynamics in actual situations, since kT is in general much larger than the hyperfine splittings. In this model, the matrix $\{c_{ij}\}$ of (2.5) is real whenever we choose $F_i = F_i^*$ $(i = 1,\dots, N^2-1)$. This implies as expected that the central state $\rho_0 = \mathbb{1}/\mathcal{N}$ (the equilibrium state at infinite temperature) is stationary and that the dynamics satisfies detailed balance with respect to ρ_0 [15, 9]. In general, for a dynamics of the form (2.8), if the stationary state is unique, by rotational invariance it will be of the form $\rho_0 = \sum_F \rho_F \mathbb{1}_F$, and one can prove that any initial state will approach ρ_0 as $t \to \infty$.

Next, consider the particular case $\vec{I} = 0$ (zero nuclear spin). In this circumstance, we have λ_K (FG, F'G') = λ_K and γ_K(FG, F'G') = γ_K. Furthermore, conservation of probability implies $\gamma_0 = 0$. Complete positivity is equivalent to $\lambda_K \geqslant 0$ so that by (2.16) we have [16, 17]

$$\sum_{L=1}^{2J} (-)^{2J+1+L+K} (2L+1) \begin{Bmatrix} L & J & J \\ K & J & J \end{Bmatrix} \gamma_L \geqslant 0. \tag{2.20}$$

These are the inequalities which must be satisfied by the relaxation rates of the multipole components of the density matrix. As an example, we consider the case J = 1. There are two relaxation rates, the dipole rate γ_1 and the quadrupole rate γ_2, and (2.10) gives (see also [7])

$$\frac{3}{5}\gamma_1 \leq \gamma_2 \leq 3\gamma_1. \tag{2.21}$$

The simple requirement of positivity, namely condition (i) of Sec. 1., is expressed by [11]

$$0 \leq \gamma_2 \leq 3\gamma_1 \tag{2.22}$$

which is weaker than (2.21) [18]. To our knowledge, all experimental data are consistent with (2.21) [6, 7].

FOOTNOTES AND REFERENCES.

1. Here the derivative at the l.h.s of (1.1) is defined as $\lim_{t\downarrow 0} \left\| \frac{d}{dt}\rho - t^{-1}(T_t\rho - \rho) \right\|_1 = 0,$

where $\|\sigma\|_1 = tr[(\sigma^*\sigma)^{1/2}]$ is the trace norm on $T(\mathcal{H})$ (we denote by B^* the adjoint of an operator B). The domain D(L) is the set of all $\rho \in T(\mathcal{H})$ for which $d\rho/dt$ exists.

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18. The statement in [17] that for isotropic relaxation of a single spin positivity and complete positivity are equivalent is false. Actually, the argument given there allows only to prove that positivity implies $\lambda_{2J} \geq 0$.

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