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CONCEPTS IN NUCLEAR SPIN DYNAMICS OF LIQUIDS. 4

(*Presented by E. Lippmaa*)

In this paper a discussion of general properties of the master equation is given. For preceding papers of this series see [1].

4. Master Equation. General Properties

4.1. Interaction superoperator. Time-evolution of the density operator $P(t) \in \mathbf{O}$ is governed by the master equation

$$\frac{dP}{dt} = (\mathcal{H}(t) + \mathcal{R}(t))P \tag{4.1}$$

in which the Superhamiltonian $\mathcal{H}(t)$ specifies the coherent interactions of a spin system, whereas the superoperator of relaxation refers to the stochastic ones.

In case $P(t)$ is represented as the sum

$$P(t) = P_s(t) + \Delta(t) \tag{4.2}$$

of a suitable reference trajectory $P_s(t) \in \mathbf{O}$ and of the deviation operator $\Delta(t) \in \mathbf{O}^0$, the master equation for the latter

$$\frac{d\Delta}{dt} = (\mathcal{H}^0(t) + \mathcal{R}^0(t))\Delta \tag{4.3}$$

is governed by superoperators $\mathcal{H}^0(t)$, $\mathcal{R}^0(t)$ induced in the subspace $\mathbf{O}^0$ by $\mathcal{H}(t)$ and $\mathcal{R}(t)$, respectively.

Terms like coherent and stochastic are not well defined from the phenomenological point of view. In order to be precise, one must list the general algebraic and analytical properties of $\mathcal{H}(t)$ and $\mathcal{R}(t)$. In case of the Superhamiltonian one simply defines: $\mathcal{H}(t)$ is the adjoint representation Eq. (1.11) of the Hamiltonian $H(t) \in \mathbf{su}(d)$. In order to narrow down the manifold of linear superoperators, which can be chosen for the superoperator of relaxation, a list of general properties of $\mathcal{R}(t)$ is given below. This list describes the demands of the dynamical axioms.

Let us first make the dynamical axiom V more exact. For this we define the thermodynamic quasistatic process $P_0(t) \in \mathbf{O}$ as follows

$$P_0(t) = I_0 + M_0(t) = (1/Z)\exp(-\hbar H(t)/kT), \tag{4.4}$$

$$Z = \mathrm{tr}\exp(-\hbar H(t)/kT). \tag{4.5}$$

It is to be emphasized that $P_0(t)$ is not a particular solution of Eq. (4.1). If one starts from the equilibrium state of Eq. (3.8), then $P_0(t)$ is the asymptotic limit for the corresponding solution of Eq. (4.1) in case the rate of change of $H(t)$ becomes infinitely slow. Thus, $P_0(t)$ describes a reversible thermodynamic process, In case the solutions of Eq. (4.1) are presented in the form

$$P(t)=I_0+M(t), \tag{4.6}$$

one gets for $M(t) \in \mathbf{O}^0$ the inhomogeneous master equation

$$\frac{dM}{dt}=\mathcal{H}^0(t)M+\mathfrak{R}^0(t)(M-M_0(t)), \tag{4.7}$$

where $M_0(t)$ refers to the quasistatic process Eq. (4.4).

Note that Eq. (4.7) is a generalization of Bloch's phenomenological equation [2] for many-spin systems, but it is made more accurate by the introduction of the quasistatic state. In case of a single spin $^1/_2$, system $M(t)$ corresponds to the vector of nuclear magnetization. Microscopic theories [3–5] lead to Eq. (4.7), provided the correlation times of stochastic molecular motions are sufficiently short.

Due to time-irreversibility of the master equation (4.1) the deviation operator vanishes as time proceeds. If the time-dependence of $H(t)$ is periodic or quasi-periodic, Eq. (4.1) will possess a particular solution $P_s(t)$ (we take this trajectory for reference) the time-dependence of which is also periodic or quasi-periodic. In this case Eq. (4.2) describes relaxation toward the steady state $P_s(t)$. The inhomogeneous master equation (4.7) is often useful to calculate the steady state, whereas Eq. (4.3) is adapted to treat transient phenomena.

Time-dependence of $H(t)$ can be due to the time-dependence of its eigenvalues as well as of its eigenvectors $|a_m(t)\rangle \in \mathbf{C}$ $(m=1, 2, \ldots d)$. The latter form the moving A-basis in the State Vector Space **C**. One can introduce a unitary operator $D_N(t,0)$ such that

$$|a_m(t)\rangle=D_N(t,0)\,|a_m(0)\rangle. \tag{4.8}$$

This operator is the solution of a master equation like Eqs (1.32), (1.33), but a suitable hermitian operator $N(t)$ (the frequency operator) replaces $H(t)$ in this equation. Therefore, in general

$$N(t) \in \mathbf{su}(d); \quad D_N(t,0) \in \mathbf{SU}(d). \tag{4.9}$$

Now, the time-dependence of the corresponding moving A-basis in the Unitary Liouville Space **O** is described by the adjoint representation $\mathfrak{D}_N(t,0)$ Eq. (1.21) of $D_N(t,0)$:

$$A_{mn}(t)=\mathfrak{D}_N(t,0)A_{mn}(0) \tag{4.10}$$

The master equation for $\mathfrak{D}_N(t,0)$ is similar to Eqs (1.36), (1.37); but governed by the adjoint representation $\mathcal{N}(t)$ of $N(t)$.

We are now ready to enumerate general properties of the superoperator of relaxation. If $L \in \mathbf{O}$ is arbitrary, then $\mathfrak{R}(t)$ must be such that:

$$(\mathfrak{R}(t)L)^+=\mathfrak{R}(t)L^+, \tag{4.11}$$

$$\operatorname{tr}\mathfrak{R}(t)L=0, \tag{4.12}$$

$$\mathfrak{R}(t)P_0(t)=0, \tag{4.13}$$

$$(\mathfrak{R}(t)L, L)\leqslant 0, \tag{4.14}$$

$$\mathfrak{R}^0(t)^+=\mathfrak{R}^0(t), \tag{4.15}$$

$$[\mathcal{H}(t), \mathfrak{R}(t)]=0, \tag{4.16}$$

$$\mathfrak{R}^0(t)=\mathfrak{D}_N(t,0)\mathfrak{R}^0(0)\mathfrak{D}_N(t,0)^{-1}. \tag{4.17}$$

In Eq. (4.14) the sign of equality holds only in case $L \in \mathbf{O}_E$ or in case $\mathcal{R}(t)$ vanishes.

According to Eq. (4.12) knowledge of the induced superoperator of relaxation $\mathcal{R}^0(t)$ and of the vector $\mathcal{R}(t)I_0$ is sufficient to specify $\mathcal{R}(t)$. However, Eq. (4.13) allows to compute the vector $\mathcal{R}(t)I_0$ as long as $H(t)$ is given.

According to Eq. (4.15) $\mathcal{R}^0(t)$ is hermitian. This means that in $\mathbf{O}^0$ one can introduce an orthonormalized basis (the moving R—A-basis) which is composed of its eigenvectors. Due to Eq. (4.16) this basis can be chosen as follows.

$$\mathcal{R}^0(t)R_j(t) = -(1/\tau_j)R_j(t), \tag{4.18}$$

$$\mathcal{R}^0(t)A_{mn}(t) = -(1/\tau_{mn})A_{mn}(t). \tag{4.19}$$

In Eq. (4.18) the hermitian operators $R_j(t)$, $(j=1, 2, \dots d-1)$, are suitable superpositions

$$R_j(t) = \sum_m \langle m|R_j|m\rangle A_{mm}(t). \tag{4.20}$$

Since

$$R_j(t) = \mathcal{D}_N(t,0)R_j(0), \tag{4.21}$$

the coefficients of the expansion (4.20) are time-independent and real. Eq. (4.19): $m=n$, $(m, n=1, 2, \dots d)$.

In Eqs (4.18) (4.19) the positive real numbers τ_j and τ_{mn} are the longitudinal and transversal relaxation times, respectively. The values of these quantities and of the matrix elements $\langle m|R_j|m\rangle$ specify the superoperator $\mathcal{R}^0(t)$ relative to the moving A-basis, provided $\mathcal{H}(t)$ does not possess equal transition frequencies. In case these are present, Eq. (4.19) serves us for the definition of the moving R—A-basis.

Let us sum up. The interaction superoperator $\mathcal{H}(t)+\mathcal{R}(t)$, which governs a particular experiment, is a linear superoperator which transforms an hermitian operator into an hermitian one and traceless operator into a traceless one. The induced interaction superoperator is not an arbitrary superoperator with these properties, but a normal one, e. g. such whose antihermitian part $\mathcal{H}^0(t)$ and hermitian part $\mathcal{R}^0(t)$ commute with each other. $\mathcal{H}^0(t)$ is not an arbitrary antihermitian superoperator, but such which is the adjoint representation of an hermitian operator $H(t) \in \mathbf{su}(d)$. $\mathcal{R}^0(t)$ is restricted by the demand: its eigenvalues are time-independent and negative. The time-dependence of the common orthonormalized set of eigenvectors of $\mathcal{H}^0(t)$ and $\mathcal{R}^0(t)$ (of the R—A-basis) is described by the adjoint representation of an unitary operator $D_N(t,0) \in \mathbf{SU}(d)$.

Therefore, the significance of the Lie group $\mathbf{SU}(d)$ for the dynamics of a d-level spin system is twofold:

$$H(t) \in \mathbf{su}(d), \tag{4.22}$$

$$D_N(t,0) \in \mathbf{SU}(d). \tag{4.23}$$

4.2. Propagators. As shown in Sec. 3.3, the general solution of Eq. (4.1) can be described with the help of the propagator $\mathcal{L}(t,0)$ — a nonsingular linear superoperator the time-dependence of which is determined by the master equation

$$\frac{d\mathcal{L}(t,0)}{dt} = (\mathcal{H}(t)+\mathcal{R}(t))\mathcal{L}(t,0), \tag{4.24}$$

$$\mathcal{L}(0,0) = \mathcal{E}. \tag{4.25}$$

The narrowing of the manifold of the allowed interaction superoperators also cause restrictions to possible propagators. So, accepting Eqs (4.11), (4.12) and (4.14), one concludes that the propagator $\mathfrak{L}(t_2, t_1)$ is a nonsingular linear superoperator which possesses the following general algebraic properties.

$$(\mathfrak{L}L)^{+} = \mathfrak{L}L^{+}, \tag{4.26}$$

$$\operatorname{tr}(\mathfrak{L}L) = \operatorname{tr} L, \tag{4.27}$$

$$(\mathfrak{L}L, \mathfrak{L}L) \leqslant (L, L), \tag{4.28}$$

where $L \in \mathbf{O}$ is arbitrary. In Eq. (4.26) the sign of equality holds only in case $L \in \mathbf{O}_E$ or in case $\mathfrak{L}$ is unitary.

As a direct consequence of Eq. (4.28), we have

$$0 < \det \mathfrak{L} \leqslant 1. \tag{4.29}$$

It can be shown that propagators with the properties Eqs. (4.26), (4.27) belong to a subgroup of $\mathbf{GL}(d^2, \mathbf{C})$ — to the dynamical group. The interaction superoperators $\mathcal{K}(t)$ and $\mathcal{R}(t)$ belong to the infinitesimal ring of the dynamical group.

According to Eq. (4.27) $\mathbf{O}^0$ is an invariant subspace of all propagators. The superoperator $\mathfrak{L}^0(t_2, t_1)$ which is induced by the propagator $\mathfrak{L}(t_2, t_1)$ in subspace $\mathbf{O}^0$ will be called an induced propagator. Induced propagators describe general solutions of Eq. (4.3). The time-dependence of an induced propagator is determined by a master equation which is similar to Eq. (4.24) but with interaction superoperator replaced by the corresponding induced interaction superoperators.

The induced propagators belong to the induced dynamical group.

The following algebraic relationships between propagators and the corresponding induced propagators can be verified:

$$(\mathfrak{L}_1 \mathfrak{L}_2)^0 = \mathfrak{L}_1^0 \mathfrak{L}_2^0, \tag{4.30}$$

$$(\mathfrak{L}^{-1})^0 = (\mathfrak{L}^0)^{-1}, \tag{4.31}$$

$$(\mathfrak{L}^{+})^0 = (\mathfrak{L}^0)^{+}, \tag{4.32}$$

$$\det \mathfrak{L}^0 = \det \mathfrak{L}. \tag{4.33}$$

These equations establish a homomorphism between propagators and the corresponding induced propagators. In case one accepts Eq. (4.13), we have an isomorphism. For this reason we are mainly concerned with induced propagators.

Such propagators which possess also the property of Eq. (4.28) belong to the dynamical semigroup — a part of the dynamical group defined by Eqs (4.26) — (4.28). The corresponding induced propagators belong to the induced dynamical semigroup.

Semigroup means time-irreversibility of the dynamics as already explained in the preceding paper.

Adopting also the dynamical axioms III, IV, VI and VII, one gets a further reduction of the manifold of allowed propagators. This continuous manifold is embedded in the dynamical semigroup but does not form a subsemigroup.

4.3. Zeeman exited spin dynamics. Up to now we have discussed the General NSD in which $H(t)$ could be an arbitrary trajectory in the $(d^2 - 1)$ dimensional Cartesian Liouville Space $\mathbf{H}^0 = \mathbf{su}(d)$. However, in the NMR Spectroscopy of isotropic liquids the time-dependence of Hamiltonians is usually due to Zeeman interaction of spin systems with an alternating external magnetic field. Thus, for a typical substance under study the manifold of possible time-dependent Hamiltonians is only 3-dimensional. In this Zeeman excited NSD the manifold of possible interaction superoperators and propagators is drastically reduced. The operators $D_N(t,0)$ introduced in Sec. 4.1, will now belong to a subgroup $\mathbf{G}_Z$ of $\mathbf{SU}(d)$ only (to the Zeeman subgroup).

The time-dependence of the external magnetic field

$$\vec{b}(t) = b(t)\vec{k}(t) \in \mathbf{V} \tag{4.34}$$

can be due to its alternating strength $b(t)$, that is of the Larmor frequency

$$\omega_L(t) = \gamma b(t); \tag{4.35}$$

but also due to changes of its direction $\vec{k}(t) \in \mathbf{V}$. It is useful to describe the latter as rotation $C_N(t,0)$ in the ordinary vector space:

$$\vec{k}(t) = C_N(t,0)\vec{k}(0). \tag{4.36}$$

The operator of rotation $C_N(t,0)$ is specified by the direction $\vec{n}$ of the axis of right-hand rotation and by the rotation angle ψ

$$C_N(t,0) = C(\vec{n}(t), \psi(t)) \in \mathbf{SO}(3). \tag{4.37}$$

In order to describe the time-dependence of Hamiltonians caused by the magnetic field Eq. (4.34), let us first define a special unitary representation $D_N(t,0)$ of the rotation operator Eq. (4.37) in the State Vector Space $\mathbf{C}$ and the corresponding adjoint representation $\mathfrak{D}_N(t,0)$ in the Unitary Liouville Space $\mathbf{O}$

$$C(\vec{n},\psi) \rightarrow D(\vec{n},\psi) \rightarrow \mathfrak{D}(\vec{n},\psi). \tag{4.38}$$

For this we establish a one-one correspondence between the directions $\vec{n} \in \mathbf{V}$, the respective total spin operators I_n and the total superspin operators $\mathfrak{I}_n$

$$\vec{n} \leftrightarrow I_n \leftrightarrow \mathfrak{I}_n; \tag{4.39}$$

as has already been discussed in Sec. 1.2 and in Sec. 1.3.
Now, in Eq. (4.38) we have

$$D(\vec{n},\psi) = \exp(-i\psi I_n) \in \mathbf{G}_Z, \tag{4.40}$$

$$\mathfrak{D}(\vec{n},\psi) = \exp(\psi \mathfrak{I}_n). \tag{4.41}$$

If $\vec{n}$ or/and ψ are time-dependent, the corresponding operators in Eqs (4.40), (4.41) are also time-dependent. In this case we use notations $D_N(t,0)$ and $\mathfrak{D}_N(t,0)$, respectively.

Note that I_n belongs to the 3-dimensional Lie subring $\mathbf{g}_z$ spanned by total spin operators I_x, I_y and I_z. The unitary operators Eq. (4.40) belong to the corresponding Lie subgroup $\mathbf{G}_z \subset \mathbf{SU}(d)$ (to the Zeeman group) — a special unitary representation of $\mathbf{SO}(3)$ in the space $\mathbf{C}$.

In terms of this representation the time-dependence of the total spin operator $I_k(t)$ that corresponds to the direction $\vec{k}(t)$ of the magnetic field, is given by

$$I_k(t) = \mathfrak{D}_N(t,0) I_k(0) \in \mathbf{g}_z. \tag{4.42}$$

Now, Zeeman excited Nuclear Spin Dynamics of isotropic liquids is defined by the following restriction set up on the Hamiltonians

$$[H(t), I_k(t)] = 0. \tag{4.43}$$

Eq. (4.43) states that the Hamiltonian is axially symmetric relative to the direction of the external magnetic field. This statement is based on the understanding that the external magnetic field is the only force in NMR which can induce anisotropy in an originally isotropic liquid. It is also assumed that, due to sufficiently short correlation times of stochastic molecular motions, this axially symmetric anisotropy is able to follow changes of the magnetic field.

Let us turn to the main consequences of Eq. (4.43).

The axial symmetry of the Hamiltonian causes the same symmetry of the quasistatic state Eq. (4.4)

$$[P_0(t), I_k(t)] = 0. \tag{4.44}$$

However, as far as a strong static magnetic field is present, we have

$$\hbar\omega_L(t)/kT \ll 1. \tag{4.45}$$

Eq. (4.45) justifies the use of the following expression

$$P_0(t) = I_0 - (\hbar\omega_L(t)/dkT)\, I_k(t) \tag{4.46}$$

as a good approximation for the quasi-static process.

A more important consequence of Eqs (4.43), (4.16) is given by

$$[\mathcal{H}(t), \mathfrak{I}_k(t)] = [\mathfrak{R}(t), \mathfrak{I}_k(t)] = 0. \tag{4.47}$$

Since the change of the external magnetic field is the only cause of time-dependence of the Superhamiltonian as well of the superoperator of relaxation; the moving A-basis on **O** turns out to be composed of eigenvectors of the superspin operator $\mathfrak{I}_k(t)$. Accordingly,

$$I_k(t)\,|a_m(t)\rangle = \mu_m |a_m(t)\rangle, \tag{4.48}$$

$$\mathfrak{I}_k(t) A_{mn}(t) = -i\mu_{mn} A_{mn}(t). \tag{4.49}$$

The eigenvalues μ_m are mostly degenerate and can take either integer values or the half-integer ones. However, in any case

$$\mu_{mn} = \mu_m - \mu_n = 0, \pm 1, \pm 2, \ldots . \tag{4.50}$$

Every adjoint representation of an unitary representation of **SO**(3) in the space **O** will be a tensorial representation. Since NMR refers to macroscopic phenomena which can only be described in terms of the Liouville Space (but not in terms of the State Vector Space), there is no reason to speak of the «spinor character» of these phenomena [6].

In case of Zeeman excited NSD, the unitary operator $D_N(t, 0)$ introduced in Sec. 4.1. is given by Eq. (4.40), its adjoint representation $\mathfrak{D}_N(t, 0)$ — by Eq. (4.41), respectively. The corresponding frequency operator $N(t) \in \mathbf{g}_z$ and its adjoint representation $\mathcal{N}(t)$ are given by

$$N(t) = -\nu(t) I_n(t), \tag{4.51}$$

$$\mathcal{N}(t) = -\nu(t)\mathfrak{I}_n(t), \tag{4.52}$$

where

$$\nu(t) = d\psi(t+\Delta t, t)/d\Delta t \tag{4.53}$$

refers to the infinitesimal operator $D_N(t+\Delta t, t)$.

In case of Zeeman excited NSD the spectra of eigenvalues $\nu_m(t)$ of the operator $N(t)$ and the spectra of eigenvalues $-i\nu_{mn}(t)$ of $\mathcal{N}(t)$ are equidistant:

$$\nu_m(t) = -\mu_m \nu(t), \tag{4.54}$$

$$\nu_{mn}(t) = \nu_m(t) - \nu_n(t) = -\mu_{mn} \nu(t). \tag{4.55}$$

In terms of any A-basis that refer to a Hamiltonian with the property Eq. (4.43), the Lie ring $\mathbf{g}_z$ is embedded in a subspace spanned by such A_{mn} for which the «selection rules»

$$\mu_{mn} = 0, \pm 1, \tag{4.56}$$

hold.

In summary: in the case of Zeeman excited NSD Eq. (4.9) is replaced by

$$N(t) \in \mathbf{g}_z; \quad D_N(t, 0) \in \mathbf{G}_z. \tag{4.57}$$

To this equation, which explains the importance of the Zeeman representation of **SO**(3), one must add the following

$$M_x \in \mathbf{g}_z \tag{4.58}$$

in which M_x denotes the observable operator of the nuclear magnetic moment Eq. (2.56). Notice that matrix elements of this operator are subject to the selection rules Eq. (4.56).

It is one of the aims of this series to show that by approximate description of resonant Zeeman excitation, different unitary representations of **SO**(3) (single resonance experiments) and of its direct products (multiple resonance) are useful in the systematics of resonances.

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VEDELIKE TUUMASPINNIDE DÜNAAMIKA PÕHIMÕISTED. 4

Tuumaspinnide dünaamika aksioomid seavad piiravaid tingimusi võimalikele interaktsiooni superoperaatoritele ja propagaatoritele. Viimaste hulk kitseneb veelgi seetõttu, et hamiltoniaanide ajalise sõltuvuse põhjuseks on ainult väline vahelduv magnetväli.

В. СИНИВЕЭ

ОСНОВНЫЕ ПОНЯТИЯ В ЯДЕРНОЙ СПИНОВОЙ ДИНАМИКЕ ЖИДКОСТЕЙ. 4

Аксиомы ядерной спиновой динамики устанавливают ряд ограничений на возможные супероператоры взаимодействия и на соответствующие им пропагаторы. Множество этих супероператоров суживается и в дальнейшем в силу того обстоятельства, что временная зависимость гамильтонианов обусловлена только внешним магнитным полем.