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CONCEPTS IN NUCLEAR SPIN DYNAMICS OF LIQUIDS. 3

(Presented by E. Lippmaa)

Nuclear Spin Dynamics (NSD) belongs to macroscopic physics and so the «classical doctrine» [1] applies to it very well, provided one uses a suitable quantity to describe the states of spin ensemble and a proper master equation which governs the time-evolution of these states. The success of the density matrix theory founded in earlier days of NMR [2-5], shows that it is possible to fulfil these demands. In this theory the states of the spin ensemble are described by the density operator of the molecular nuclear spin system. The possible states make up a continuous domain in the Cartesian Liouville Space and time-evolution is represented by a differentiable trajectory in this space. The master equation (the density matrix equation) includes (as special cases) both characteristic equations of quantum dynamics: the Liouville equation for adiabatically isolated spin systems (with the Schroedinger equation in the State Vector Space in the background) and the Pauli equation for the relaxation of populations of energy levels (with «quantum sprungs» between these levels in the background). Thus the density matrix theory turns out to be a working quantum theory which, in full agreement with Einstein's comments [6], accepts the «classical doctrine». In certain aspects NSD is indeed paradigmatic [7] for quantum theories of macroscopic phenomena. Nevertheless, if one attempts to derive the master equation on the basis of the first principles of the quantum theory, one meets with uncertainties. Moreover, the microscopic interpretation of the master equation depends upon which terms the other participants of NSD, the electromagnetic field and the molecular surroundings, are described in.

In the pioneering works mentioned above [2-5], the master equation was derived by combining quantum mechanical concepts with the principles of statistical physics. The so-called quantum mechanical theory [2-4] describes the states of the molecular surrounding of nuclear spins in terms of quantum theory, whereas the semiclassical theory [5] uses classical description. In spite of these differences, the mathematical form of the resulting master equation is in both theories essentially the same, though certain differences are present. However, it is the mathematical form of the master equation and not its microscopic interpretation, which predicts how the observed NMR signals depend upon the time evolution of an external magnetic field and also upon the values of chemical shifts and other NMR characteristics of substances under study. It is the task of NSD to give knowledge about these relationships and not about its microscopic background.

Therefore, it seems to be rational to consider the master equation as based on experimental findings of NMR spectroscopy, and to regard the problem of its microscopic interpretation as the task of a more general theory of liquid phenomena. Taking such a phenomenological point of view, one sets up a list of axioms which determine the mathematical form of the master equation unambiguously.

The present paper endeavours to bring such an axiomatic approach. The axioms listed below are ordered in growing degree of specificity, each axiom being followed by consequences it brings along. So, if some consequence of a more specific axiom disagrees with experiments, such an axiom can be omitted without disturbing the consequences of the foregoing axioms.

The notations of the foregoing papers of this series [8] are used throughout this work.

3. Master Equation. Axiomatic Approach

3.1. General physical concepts. We shall treat diamagnetic samples of molecular liquids in the form of dilute solutions of substances under study. A time-dependent external (classical) magnetic field is applied to the sample in order to interact with nuclear spins of the substance under study. The degrees of freedom of the sample other than the nuclear spins will be considered as composing a thermal bath the thermodynamic parameters of which are held constant. We take the time-evolution of the x-component of the vector of nuclear magnetization of the sample Eq. (2.62) for the observed NMR signal.

As a consequence of the molecular structure of the sample and of the statistical independence of molecules, we shall consider the nuclear spins under investigation as a Boltzmann statistical ensemble (spin ensemble) composed of molecular nuclear spin systems (of spin systems). The states of the spin ensemble will be specified by the density operator of a molecular nuclear spin system. However, from the macroscopic point of view P is a vector of the Cartesian Liouville Space (Sec. 1.1) which possesses the properties Eqs (2.57), (2.58), and which specifies the states of nuclear spins under study. Below we prefer to consider P as a vector of the corresponding Unitary Liouville Space (Sec. 1.1). We shall regard the observed NMR signal as a consequence of an underlying time-evolution $P(t) \in \mathbf{O}$, where $\dot{P}(t)$ is assumed to be a continuous, differentiable function of time.

The time-evolution $P(t) \in \mathbf{O}$ is controlled by interactions of spin systems. Taking the macroscopic point of view, we shall distinguish between coherent and stochastic interactions. Microscopically speaking, the coherent interactions are those which at each instant are the same for all members of the spin ensemble, the stochastic interactions are those which are different. Interaction of nuclear spins with external magnetic field as well as the coarse-grained time-scale averaged interaction of spin system with thermal bath, contribute to coherent interactions. From mathematical point of view both the coherent interactions and the stochastic ones are specified by interaction superoperators with definite properties, the latter being established by axioms. Specification of these interaction superoperators means specifying conditions of the experiment. This includes the specification of the substance under study, of the solvent and its thermodynamic state as well as the time-dependence of the external magnetic field.

The master equation given below will not depend upon the choice of the basis system of vectors of the space \mathbf{O} . In order to correlate the results of the general theory with the experiments, the interaction superoperators, the density operator, and the observable are to be represented in terms of a suitable I -basis (Sec. 2.2).

3.2. Axiomatics.

Axiom I.

The time-evolution $P(t) \in \mathbf{O}$ of an ensemble of d -level spin systems is governed by the first-order homogeneous differential equation

$$\frac{dP}{dt} = \mathfrak{V}(t)P, \quad (3.1)$$

where the interaction superoperator $\mathfrak{V}(t)$ is a general linear superoperator on space \mathbf{O} .

However, in Eq. (3.1), $\mathfrak{V}(t)$ must be such that the general properties of the density operator Eqs (3.2)—(3.4) are maintained as time proceeds.

$$P(t)^+ = P(t), \quad (3.2)$$

$$\text{tr } P(t) = 1, \quad (3.3)$$

$$(I_0, I_0) \leq (P(t), P(t)) \leq 1. \quad (3.4)$$

In Eq. (3.4) the notation $I_0 = (1/d)E \in \mathbf{O}_E$ has been introduced.

Axiom II.

In Eq. (3.1), $\mathfrak{V}(t)$ must be such that for every $\Delta(t)$ allowed by Eq. (3.4) the inequality

$$\frac{d}{dt} (\Delta(t), \Delta(t)) \leq 0 \quad (3.5)$$

is true. In Eq. (3.5), $\Delta(t)$ denotes the deviation operator

$$\Delta(t) = P(t) - P_s(t) \in \mathbf{O}^0, \quad (3.6)$$

and $P_s(t)$ is a particular solution of Eq. (3.1) chosen for reference (the reference trajectory). In Eq. (3.5), the sign of equality holds only in case of the special trajectory $\Delta(t) = 0$.

Axiom III.

Coherent interaction is specified by a hermitian operator $H(t) \in \mathbf{O}^0$, Eq. (1.27) (by the Hamiltonian) which is constructed by accepting the principle of classical analogy. The adjoint representation $\mathfrak{H}(t)$, Eq. (1.30), (the Superhamiltonian) of $H(t)$ is that part of $\mathfrak{V}(t)$ which describes the influence of coherent interactions, and which never vanishes.

The remaining part $\mathfrak{R}(t)$ of $\mathfrak{V}(t)$ (the superoperator of relaxation) specifies the influence of stochastic interactions.

Axiom IV.

The superoperator $\mathfrak{R}^0(t)$ induced in subspace $\mathbf{O}^0 \subset \mathbf{O}$ by $\mathfrak{R}(t)$ is hermitian

$$\mathfrak{R}^0(t)^+ = \mathfrak{R}^0(t). \quad (3.7)$$

Axiom V.

The thermal equilibrium state $P_0 \in \mathbf{O}$ of the spin ensemble is given by the Boltzmann Law

$$P_0 = (1/Z) \exp\left(-\frac{\hbar H_0}{kT}\right). \quad (3.8)$$

Axiom VI.

The Superhamiltonian $\mathfrak{H}(t)$ and the superoperator of relaxation commute with each other

$$[\mathfrak{H}(t), \mathfrak{R}(t)] = 0. \quad (3.9)$$

Axiom VII.

The supermatrix $\mathfrak{R}(t)$ calculated in terms of a (moving) A -basis which is composed of eigenvectors of $\mathfrak{H}(t)$, is time-independent.

3.3. Group aspects. A general consequence of Eq. (3.1) is that one can associate with $\mathfrak{U}(t)$ a continuous manifold of time-dependent nonsingular superoperators (propagators) $\mathfrak{L}(t_2, t_1)$ which describe the time-evolution $P(t) \in \mathbf{O}$ as linear transformations from one instant t_1 to a following instant t_2

$$P(t_2) = \mathfrak{L}(t_2, t_1)P(t_1). \quad (3.10)$$

Especially, the infinitesimal transformation

$$P(t+\Delta t) = \mathfrak{L}(t+\Delta t, t)P(t) \quad (3.11)$$

is given by

$$\mathfrak{L}(t+\Delta t, t) = \mathfrak{E} + \Delta t \mathfrak{U}(t). \quad (3.12)$$

Since the product of two superoperators means two successive transformations, we have the following relationships between propagators

$$\mathfrak{L}(t_3, t_1) = \mathfrak{L}(t_3, t_2) \mathfrak{L}(t_2, t_1), \quad (3.13)$$

$$\mathfrak{L}(t_1, t_2)^{-1} = \mathfrak{L}(t_2, t_1); \quad (3.14)$$

$$\mathfrak{L}(0, 0) = \mathfrak{E}. \quad (3.15)$$

Eqs (3.13)—(3.15) say that the propagators belong to a Lie group (to the dynamical group) which at this point is the general linear group $\mathbf{GL}(d^2, \mathbf{C})$. Eq. (3.12) says that $\mathfrak{U}(t)$ must belong to the infinitesimal ring $\mathfrak{gl}(d^2, \mathbf{C})$ of the dynamical group (to the dynamical ring).

Since the trajectories $P(t)$ are smooth, only the bounded neighborhood of \mathfrak{E} can, actually, form the dynamical group. This means: $\mathfrak{L}(t_2, t_1)$ must be such that

$$\det \mathfrak{L}(t_2, t_1) > 0. \quad (3.16)$$

Now, the correspondence between a dynamical ring and a dynamical group becomes one-one.

In terms of propagators the general solution of the master equation (3.1) can be written as follows:

$$P(t) = \mathfrak{L}(t, 0)P(0). \quad (3.17)$$

Due to Eqs (3.13), (3.14), the knowledge of the propagator $\mathfrak{L}(t, 0)$ is sufficient to calculate any other transformation (3.10).

It is easy to show that the time-dependence of $\mathfrak{L}(t, 0)$ is governed by

$$\frac{d\mathfrak{L}(t, 0)}{dt} = \mathfrak{U}(t)\mathfrak{L}(t, 0). \quad (3.18)$$

Eqs (3.18), (3.15) establish the one-one correspondence

$$\mathfrak{U}(t) \leftrightarrow \mathfrak{L}(t, 0) \quad (3.19)$$

which shows how time-evolution $P(t) \in \mathbf{O}$ depends upon conditions of experiment as specified by $\mathfrak{U}(t)$. Since the dependence of $P(t)$ upon initial state $P(0)$ is soon included into the propagator, the main task of the theory is in setting up the correspondences Eq. (3.19), provided the propagator — language (the Group Approach in NSD) is used.

The statement: NSD is governed by the master equation (3.1) is equivalent to saying that $\mathbf{GL}(d^2, \mathbf{C})$ is the dynamical group of NSD. However, this statement turns out to be too broad. The axioms I—VII will set certain restrictions to superoperators $\mathfrak{U}(t)$ and, thus, also to propagators. Let us go on to these restrictions now.

3.4. Axiom I. The existence of a closed theory of NSD, regardless of other degrees of freedom of the sample, is itself a fundamental experimental fact the understanding of which is out of the theory of NSD. The same is true concerning statistical independence of molecular spin systems. So far both these assumptions have been accepted, the linearity axiom I is the most general one for NSD. The main theoretical argument for this axiom has been noted in Introduction: Eq. (3.1) includes in a direct way both characteristic equations of quantum dynamics, the Liouville equation and the Pauli equation. We shall clarify this point below. But now we proceed to restrictions which are due to Eqs (3.2)—(3.4).

Eq. (3.2) says that the motion of spin ensemble can be described in terms of space \mathbf{H} (Sec. 1.1). This means:

$$\mathfrak{V}(t) \in \mathfrak{gl}(d^2, \mathbf{R}), \quad (3.20)$$

$$\mathfrak{L}(t, 0) \in \mathbf{GL}(d^2, \mathbf{R}), \quad (3.21)$$

$$\det \mathfrak{L}(t, 0) > 0. \quad (3.22)$$

If the motion is described in terms of space \mathbf{O} and an A -basis of this space is used, then the elements of, say, $\mathfrak{V}(t)$ are related by

$$\langle lk | \mathfrak{V}(t) | nm \rangle = \langle kl | \mathfrak{V}(t) | mn \rangle^*. \quad (3.23)$$

Eq. (3.3) says that $P(t)$ can be represented as follows:

$$P(t) = I_0 + M(t) \in \mathbf{O}, \quad (3.24)$$

where

$$M(t) \in \mathbf{O}^0. \quad (3.25)$$

Therefore, the $(d^2 - 1)$ -dimensional subspace $\mathbf{O}^0 \subset \mathbf{O}$ is a common invariant subspace of all superoperators $\mathfrak{V}(t)$ and $\mathfrak{L}(t, 0)$. It is an invariant subspace of motion. In mathematical terms this statement can be expressed as follows:

$$(\mathfrak{V}(t) I_0, I_0) = 0, \quad (3.26)$$

$$\mathfrak{V}(t) M \in \mathbf{O}^0, \quad (3.27)$$

$$(\mathfrak{L}(t, 0) I_0, I_0) = (I_0, I_0), \quad (3.28)$$

$$\mathfrak{L}(t, 0) M \in \mathbf{O}^0. \quad (3.29)$$

Some direct properties of superoperator $\mathfrak{V}(t)$ which are due to these equations are given by

$$\det \mathfrak{V}(t) = \det \mathfrak{V}(t) + = 0, \quad (3.30)$$

$$\mathfrak{V}(t) + I_0 = 0, \quad (3.31)$$

$$\sum_m \langle mm | \mathfrak{V}(t) | kk \rangle = 0. \quad (3.32)$$

It can be shown that superoperators \mathfrak{L} which possess the properties Eqs (3.28), (3.29) form a Lie subgroup in $\mathbf{GL}(d^2, \mathbf{R})$, whereas the superoperators \mathfrak{V} with the properties Eqs (3.26), (3.27) belong to the Lie ring of this subgroup.

If one considers only the transformations caused by $\mathfrak{V}(t)$ and $\mathfrak{L}(t, 0)$ in the invariant subspace \mathbf{O}^0 one gets the induced superoperators $\mathfrak{V}^0(t)$ and $\mathfrak{L}^0(t, 0)$, respectively. Eqs (3.33)—(3.35)

$$\mathfrak{V}^0(t) \in \mathfrak{gl}(d^2 - 1, \mathbf{R}), \quad (3.33)$$

$$\mathfrak{L}^0(t, 0) \in \mathbf{GL}(d^2 - 1, \mathbf{R}), \quad (3.34)$$

$$\det \mathfrak{L}^0(t, 0) > 0 \quad (3.35)$$

state that these induced superoperators belong to an induced dynamical ring and an induced dynamical group associated with linear transformations of the space \mathbf{O}^0 .

Making use of these induced superoperators, one can specify $\mathfrak{V}(t)$ by defining $\mathfrak{V}^0(t)$ and the vector $\mathfrak{V}(t)I_0$. Similarly, $\mathfrak{L}(t, 0)$ is specified by $\mathfrak{L}^0(t, 0)$ and $\mathfrak{L}(t, 0)I_0$.

Due to Eq. (3.3), the master equation for the deviation operator Eq. (3.6) is given by

$$\frac{d\Delta}{dt} = \mathfrak{V}^0(t)\Delta. \quad (3.36)$$

The induced propagator describes the general solution of Eq. (3.36)

$$\Delta(t) = \mathfrak{L}^0(t, 0)\Delta(0). \quad (3.37)$$

One concludes from Eq. (3.4): the allowed deviation operators are closed into a hypersphere defined by Eq. (3.38).

$$0 \leq (\Delta(t), \Delta(t)) \leq 1 - (I_0, I_0). \quad (3.38)$$

Due to the demands described by Eq. (3.38), only such $\mathfrak{L}^0(t, 0)$ allowed by Eq. (3.34) can be the induced propagator for which Eq. (3.39) is satisfied (for every $\Delta(0)$ permitted by Eq. (3.38))

$$0 \leq (\mathfrak{L}^0(t, 0)\Delta(0), \mathfrak{L}^0(t, 0)\Delta(0)) \leq 1 - (I_0, I_0). \quad (3.39)$$

The main consequence of Eq. (3.39) is: in general NSD turns out to be time-irreversible. Induced propagators allowed by Eq. (3.39) belong to a semigroup (to the dynamical semigroup) embedded in $\mathbf{GL}(d^2-1, \mathbf{R})$. If $\mathfrak{L}^0(t, 0)$ belongs to the dynamical semigroup and corresponds to $\mathfrak{V}^0(t)$, then $\mathfrak{L}^0(t, 0)^{-1}$ which describes the reversed motion, and corresponds to $-\mathfrak{V}^0(t)$ does not belong to this semigroup.

3.5. Axiom II. According to this axiom, the norm $|\Delta(t)|$ diminishes monotonically as time proceeds. Therefore, if $t \rightarrow \infty$, then

$$P(t) \rightarrow P_s(t). \quad (3.40)$$

During time-evolution the whole family of trajectories Eq. (3.17) contracts into a single trajectory $P_s(t)$.

Calculations of the rate of changes of $|\Delta(t)|$ shows that due to axiom II, $\mathfrak{V}^0(t)$ must be a negatively definite superoperator

$$(\mathfrak{V}^0(t)\Delta(t), \Delta(t)) \leq 0. \quad (3.41)$$

Strictly speaking, Eq. (3.41) sets a demand concerning the hermitian part of $\mathfrak{V}^0(t)$ only. Axiom II states that this part must always exist and possess negative eigenvalues.

In case of relaxation processes (e. g. in case \mathfrak{V} does not depend upon time), the master equation (3.1) has a special time-independent solution P_0 into which the family of trajectories Eq. (3.17) collapses as time proceeds. We adopt the term thermal equilibrium state for P_0 . It is obvious that P_0 must be the unique solution of the algebraic equation

$$\mathfrak{V}P_0 = 0. \quad (3.42)$$

Eq. (3.30) guarantees that this solution exists. From uniqueness of P_0 we conclude:

$$\det \mathfrak{V}^0 \neq 0. \quad (3.43)$$

As it is shown above, the time-irreversibility of NSD is a consequence of Eq. (3.4). If one accepts only time-independent interaction superoperators, the Eqs (3.40), (3.41) will also be the consequences of axiom I only. However, in the more general case of time-dependent interaction superoperators, Axiom I permits oscillatory change of $|\Delta(t)|$, provided the time-dependence of $\mathfrak{V}^0(t)$ is chosen suitably. Our main theoretical argument for Axiom II goes as follows: the theory must be applicable for arbitrary time-dependence of $\mathfrak{V}(t)$.

3.6. Axioms III and IV. Axiom III guarantees that Adiabatic NSD described in Sec. 1.4 will be an integral part of NSD. If there were no stochastic interactions, the propagators would belong to the adjoint representation of $SU(d)$ and NSD would be time-reversible.

According to Axiom III,

$$\mathfrak{V}(t) = \mathfrak{H}(t) + \mathfrak{R}(t), \quad (3.44)$$

where $\mathfrak{H}(t)$ is the adjoint representation of a hermitian operator $H(t) \in \mathfrak{su}(d)$. This means, in particular, that

$$\mathfrak{H}(t)I_0 = 0, \quad (3.45)$$

$$\mathfrak{H}(t)^+ = -\mathfrak{H}(t), \quad (3.46)$$

$$\text{tr } \mathfrak{H}(t) = 0. \quad (3.47)$$

Due to Eq. (3.45), we have

$$\mathfrak{V}(t)I_0 = \mathfrak{R}(t)I_0. \quad (3.48)$$

Introducing this equation into Eqs (3.26), (3.27) and (3.30)—(3.32), one gets the list of general properties of $\mathfrak{R}(t)$. The superoperator $\mathfrak{R}(t)$ is specified by the induced superoperator $\mathfrak{R}^0(t)$ and by the vector $\mathfrak{R}(t)I_0$.

Now the Eq. (3.42) of thermal equilibrium is

$$(\mathfrak{H}_0 + \mathfrak{R})P_0 = 0. \quad (3.49)$$

Replacing in Eq. (3.49)

$$P_0 = I_0 + M_0, \quad (3.50)$$

we have

$$(\mathfrak{H}_0 + \mathfrak{R}^0)M_0 = -\mathfrak{R}I_0. \quad (3.51)$$

If P_0 is established postulatively, the vector $\mathfrak{R}I_0$ is uniquely determined by Eq. (3.51).

According to Eq. (3.44), the induced interaction superoperator decomposes as follows

$$\mathfrak{V}^0(t) = \mathfrak{H}(t) + \mathfrak{R}^0(t), \quad (3.52)$$

where the special label for induced Superhamiltonian has been dropped.

If now Axiom IV is also accepted, we conclude: the antihermitian part of $\mathfrak{V}^0(t)$ specifies coherent interaction, whereas the hermitian part $\mathfrak{R}^0(t)$ is due to stochastic interactions. The latter cause the irreversible character of NSD. This is shown by Eq. (3.53)

$$(\mathfrak{R}^0(t)\Delta(t), \Delta(t)) < 0 \quad (3.53)$$

which now replaces Eq. (3.41). Meanwhile, the eigenvalues of $\mathfrak{R}^0(t)$ do not vanish, but must be negative real numbers (possibly, time-dependent).

Due to Axiom IV, $\mathfrak{V}^0(t)$ is not an arbitrary element of the Lie ring $\mathfrak{gl}(d^2 - 1, \mathbf{R})$ but such whose antihermitian part is the adjoint representation of a hermitian operator and whose hermitian part is negatively definite.

3.7. Axiom V. This fundamental axiom incorporates the relationships of the equilibrium statistical physics into the framework of NSD. At the same time the Pauli equation is introduced into NSD.

The Boltzmann Law Eq. (3.8) establishes for the state of thermal equilibrium

$$P_0 = \sum_m^0 \pi_{mm} A_{mm} \in \mathbf{O}_A \quad (3.54)$$

the unitary orientation of P_0 , so that

$$\mathcal{K}_0 P_0 = 0 \quad (3.55)$$

and the distribution of equilibrium populations

$$\pi_{hk}^0 / \pi_{mm}^0 = \exp(\hbar\omega_{mk}^0 / kT). \quad (3.56)$$

Due to Eq. (3.55), the algebraic equations (3.49), (3.51), (3.43) must be replaced by

$$\mathcal{R} P_0 = 0, \quad (3.57)$$

$$\mathcal{I}^0 M_0 = -\mathcal{R} I_0, \quad (3.58)$$

$$\det \mathcal{R}^0 \neq 0. \quad (3.59)$$

In terms of the A -basis, Eq. (3.57) is represented by the homogeneous system of algebraic equations

$$\sum_{m \neq k} (\Gamma_{km} \pi_{mm}^0 - \Gamma_{mk} \pi_{kk}^0) = 0, \quad (3.60)$$

where the notation

$$\Gamma_{mk} = \langle mm | \mathcal{R} | kk \rangle \quad (3.61)$$

has been used and Eq. (3.32) was utilized. The solution of Eq. (3.60) is given by

$$\pi_{kk}^0 / \pi_{mm}^0 = \Gamma_{km} / \Gamma_{mk}. \quad (3.62)$$

The comparison of Eqs (3.56) and (3.62) force to conclude: \mathcal{R} must be such that

$$\Gamma_{km} / \Gamma_{mk} = \exp(\hbar\omega_{mk}^0 / kT). \quad (3.63)$$

By definition, the master equation (3.1) for relaxation

$$\frac{dP}{dt} = (\mathcal{K}_0 + \mathcal{R})P \quad (3.64)$$

is governed by time-independent interaction superoperators \mathcal{K}_0 and \mathcal{R} . According to Axiom V, Eq. (3.64) must possess the special solution Eq. (3.8). This is possible only in case of independence of longitudinal and transversal relaxation. \mathcal{R} must be such that the space \mathbf{O} decomposes into a direct sum of two invariant subspaces of the superoperator \mathcal{R} :

$$\mathbf{O} = \mathbf{O}_A \dot{+} \mathbf{O}_\perp. \quad (3.65)$$

In Eq. (3.65), the d -dimensional subspace \mathbf{O}_A is spanned by A_{mm} but A_{mn} ($m \neq n$), span the $d(d-1)$ -dimensional subspace \mathbf{O}_\perp . If not stated otherwise, the A -basis refers to \mathcal{K}_0 . Now, \mathcal{R} also decomposes into a similar direct sum

$$\mathcal{R} = \mathcal{R}_A \dot{+} \mathcal{R}_\perp. \quad (3.66)$$

The equation of relaxation (3.64) splits into two independent equations, the equation of longitudinal relaxation

$$\frac{dP_A}{dt} = \mathcal{R}_A P_A \quad (3.67)$$

and the equation of transversal relaxation

$$\frac{dP_{\perp}}{dt} = (\mathcal{K}_0 + \mathcal{R}_{\perp})P_{\perp} \quad (3.68)$$

In Eqs (3.67), (3.68) we used the decomposition of $P(t)$ into two components: $P_A(t) \in \mathbf{O}_A$ and $P_{\perp}(t) \in \mathbf{O}_{\perp}$.

Now, Eq. (3.67) is the Pauli equation of relaxation of populations of energy levels. Indeed, by introducing the expansion

$$P(t) = \sum_m \sum_n \pi_{mn}(t) A_{mn} \in \mathbf{O} \quad (3.69)$$

into Eq. (3.67), we get the original form [9] of the Pauli equation

$$\frac{d\pi_{hk}}{dt} = \sum_{m \neq k} (\Gamma_{km}\pi_{mm} - \Gamma_{mk}\pi_{hk}). \quad (3.70)$$

The Pauli equation (3.70) can be interpreted in terms of an independent model due to Pauli [9]. We adopt the term «theory of quantum transitions» for this model. According to this theory, only the discrete set of eigenstates $|a_m\rangle \in \mathbf{C}$ of H_0 is considered as allowed for spin systems. Relaxation is due to transitions which occur between these allowed states and which are governed by a statistical law. Assuming that the transition probabilities Eq. (3.61) do not depend upon time, one gets the Pauli equation [9].

At this point it is illuminating to discuss energy exchange between spin ensemble and its surroundings. For this we define the internal energy of the spin ensemble calculated per molecule and in units $\hbar=1$, as follows:

$$u(t) = (P(t), H(t)). \quad (3.71)$$

According to Eq. (3.71), the rate of energy exchange is given by

$$\frac{du}{dt} = \frac{dq}{dt} + \frac{d\omega}{dt}, \quad (3.72)$$

where

$$\frac{dq}{dt} = \left(\frac{dP}{dt}, H(t) \right) = (\mathcal{R}(t)P(t), H(t)) \quad (3.73)$$

gives the rate of energy exchange between spin ensemble and thermal bath (energy exchange in the form of heat), and

$$\frac{d\omega}{dt} = \left(P(t), \frac{dH}{dt} \right) \quad (3.74)$$

gives the rate of energy exchange between spin ensemble and time-dependent external magnetic field (energy exchange in the form of work).

In case of relaxation processes only heat exchange occurs. Calculation of the rate of heat exchange Eq. (3.73) on the basis of the Pauli equation (3.70), gives

$$\frac{dq}{dt} = (\mathcal{R}_A P_A(t), H_0) = \sum_{m>k} \sum (\Gamma_{mk}\pi_{hk} - \Gamma_{km}\pi_{mm}) \omega_{mk}^0. \quad (3.75)$$

The interpretation of Eq. (3.75) in terms of exchange of energy quanta ω_{mk}^0 is obvious. Note that Eq. (3.60) satisfies the principle of detailed balance [10]. Though there is not net heat exchange in the state of thermal equilibrium, one can interpret Eq. (3.75) in this case as expressing the balance of opposite heat flows.

The theory of quantum transitions can be used in order to introduce quantum statistics and the concept of photon. One can explain the effects of incoherent irradiation, but the whole domain of the so-called coherent phenomena are out of the scope of the theory of quantum transitions.

3.8. Axioms VI and VII. Eq. (3.9) was established in Bloch's paper [4]. It emphasizes the idea that all time-dependence of the interaction superoperator is induced by the external magnetic field. Time-dependent magnetic field causes time-dependence of $H(t)$ and $\mathcal{K}(t)$. In general $\mathcal{K}(t)$ has time-dependent eigenvalues $\omega_{mn}(t)$ as well as eigenvectors $A_{mn}(t)$ (the moving A -basis of \mathbf{O}). Due to Axiom VI, the moving A -basis spans an orthogonal set of (moving) common invariant subspaces of superoperators $\mathcal{K}(t)$ and $\mathcal{R}(t)$. According to Axiom VII, there is no dependence of $\mathcal{R}(t)$ upon $\omega_{mn}(t)$. Thus the master equation

$$\frac{dP}{dt} = (\mathcal{K}(t) + \mathcal{R}(t))P \quad (3.76)$$

predicts the same law of motion relative to the moving A -basis as the equation of relaxation (3.64) relative to the usual A -basis, provided an infinitesimal time interval is considered. The supermatrix \mathcal{R} measured in relaxation experiment is (according to Axiom VII) the same as the supermatrix $\mathcal{R}(t)$ in Eq. (3.76), provided the latter is assigned to the moving A -basis.

Let us turn to transversal relaxation. In this case Axiom VI states

$$[\mathcal{K}_0, \mathcal{R}] = 0. \quad (3.77)$$

Because of Eq. (3.77), one can choose in subspace \mathbf{O}_\perp an A -basis which is composed of common eigenvectors of superoperators \mathcal{K}_0 and \mathcal{R}^0

$$(\mathcal{K}_0 + \mathcal{R}^0)A_{mn} = -\left(\frac{1}{\tau_{mn}} + i\omega_{mn}^0\right)A_{mn}. \quad (3.78)$$

In Eq. (3.78) the transversal relaxational time τ_{mn} must be a positive number, otherwise Eq. (3.53) is not satisfied. Moreover, from Eq. (3.23) we conclude

$$\tau_{nm} = \tau_{mn}. \quad (3.79)$$

Expanding $P(t)$ in terms of the A -basis as shown by Eq. (3.69), one easily gets the solution of Eq. (3.68):

$$\pi_{mn}(t) = \pi_{mn}(0) \exp\left(-\left(\frac{1}{\tau_{mn}} + i\omega_{mn}^0\right)t\right). \quad (3.80)$$

Therefore, the NMR signal Eq. (2.62) is given by the superposition

$$\langle M_x \rangle = \sum_{m \neq n} \langle m | P(0) | n \rangle \langle n | M_x | m \rangle \exp\left(-\left(\frac{1}{\tau_{mn}} + i\omega_{mn}^0\right)t\right), \quad (3.81)$$

provided H_0 possess the axial symmetry

$$\mathcal{K}_0 I_z = 0. \quad (3.82)$$

This latter supposition is correct in case of isotropic liquids as well as in case of nematic solvents. Due to Eq. (3.82), only the one-quantum transitions contribute to the signal. The Fourier transform of the signal Eq. (3.81) gives the FID FT NMR spectrum.

Note that according to the theory of quantum transitions $P(t) \in \mathbf{O}_A$. Therefore, by this theory no FID NMR signal is observable.

The induced propagator for relaxation is given by

$$\mathcal{L}^0(t, 0) = \exp(t\mathcal{K}_0) \exp(t\mathcal{R}^0), \quad (3.83)$$

provided Axiom IV is correct. In order to obtain the vector $\mathcal{L}(t, 0)I_0$, it is sufficient to use Eq. (3.84)

$$\mathcal{L}(t, 0)P_0 = P_0. \quad (3.84)$$

The author inclines to conclude: if Eq. (3.77) is sufficiently correct, then so must also be Eq. (3.9).

It is likely that Eq. (3.77) is an approximation which premises certain degree of weakness of the influence of stochastic interactions as compared with this of coherent interaction. However, in case this precondition is not correct the choice of a new more symmetric H_0 avoids the breakdown of Eq. (3.77). In the extreme case of very strong relaxation, H_0 contains only Zeeman interaction with a static magnetic field. In case this is also not sufficient, only the phenomena of magnetic relaxation are observed.

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V. SINIVEE

VEDELIKE TUUMASPINNIDE DÜNAAMIKA PÕHIMÕISTEID. 3

Artiklis on antud tuumaspinnide dünaamika põhivõrrandi aksiomaatiline põhjendus. Selleks on püstitatud rida aksiome, mis väljendavad kõige üldisemaid katselisi tõdesid TMR-spektroskoopias ja milledest järeldub tuumaspinnide dünaamika põhivõrrand.

V. СИНИВЕЕ

ОСНОВНЫЕ ПОНЯТИЯ В ЯДЕРНОЙ СПИНОВОЙ ДИНАМИКЕ ЖИДКОСТЕЙ. 3

Изложено аксиоматическое обоснование квантовокинетического уравнения ядерной спиновой динамики. Установлен набор аксиом, которые выражают наиболее общие опытные закономерности ЯМР-спектроскопии и следствием которых является квантовокинетическое уравнение.