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V. SINIVEE

CONCEPTS IN NUCLEAR SPIN DYNAMICS OF LIQUIDS. 1

(*Presented by E. Lippmaa*)

The Density Matrix Theory founded by Bloch, Wangsness and Redfield [1–3] has been proved to be the only sound basis we have in Liquid NMR to explain phenomena and to generate ideas of new experimental methods. It has also stimulated similar theoretical developments in other branches of radiospectroscopy, in nonlinear optics and in quantum theory of irreversible processes. Thus, there is sufficient reason to develop Nuclear Spin Dynamics (NSD) as the theory of certain kind of natural phenomena in its own rights, although applications in NMR Spectroscopy are still in background.

The present series of papers is an attempt to give a brief but systematic explanation of mathematical and physical concepts needed in NSD of Liquids. General relationships between phenomena will be represented on a simple but sufficiently correct level. The usage of Lie groups and of their associated Lie algebras form the mathematical background of this treatment. Earlier work of the author on the use of unitary Lie groups in Adiabatic NSD [4,5] will be extended to the general case of irreversible NSD. In this, first, paper of this series we list the general mathematical concepts used throughout this work.

1. General mathematical concepts

1.1. Linear spaces. The general mathematical concepts we need to develop NSD are: unitary and cartesian linear (vector) spaces, linear operators on these spaces, Lie groups, Lie rings and their representations composed of linear operators [6].

Four different kinds of linear metric spaces will be used simultaneously: the 3-dimensional (cartesian) ordinary vector space **V**, the unitary State Vector Space **C**, the unitary space **O** composed of all linear operators on **C** (the Unitary Liouville Space), and the cartesian space **H** of all hermitian linear operators on **C** (the Cartesian Liouville Space). On each of these spaces we define linear operators; those defined on Liouville Spaces will be called superoperators [7]. Since linear operators on **C** are simultaneously vectors of Liouville Spaces, the dimensions of the spaces **C**, **O**, **H** are related by

$$\dim \mathbf{O} = \dim \mathbf{H} = (\dim \mathbf{C})^2. \tag{1.1}$$

Classical vectorial physical quantities, like the strength of the external magnetic field or the nuclear magnetization of the sample, are elements of the ordinary vector space **V**. Quantum mechanical quantities are elements of **C**, **O** and **H**. The state vector $|\psi\rangle \in \mathbf{C}$ specifies a pure quantum state of the molecular nuclear spin system (of the spin system), whereas the density operator $P \in \mathbf{H}$ describes a state of the statistical ensemble of spin systems embedded in the sample (of the spin ensemble). Since NSD is concerned only with macroscopic processes, the Liouville

Spaces rather than the State Vector Space is applied to describe time-evolution of the spin ensemble. The space **C** plays rather a purely mathematical role — we do not follow time-evolution of state vectors except in case of adiabatically isolated spin systems (of Adiabatic NSD). Since the principal quantum mechanical quantities are hermitian operators on **C**, the space **H** is the only Liouville Space we actually need. However, we shall use simultaneously the space **O** due to several mathematical advantages it promises. Of course, the vectors of **H** are simultaneously vectors of **O** and so are the superoperators on **H**. We use for such equivalent quantities a unified notation.

If $\dim \mathbf{C}=d$, we call the spin system a d-level system. So, a 4-level system can be a two-spin 1/2 system, but it could be also a single spin 3/2 system. However, if the d-level system is a many-spin system, its State Vector Space **C** as well as the Liouville Spaces can be presented as direct products of corresponding single spin spaces. Thus, in case of a two-spin system we have

$$\mathbf{C}=\mathbf{C}(1)\times\mathbf{C}(2), \tag{1.2}$$

$$\mathbf{O}=\mathbf{O}(1)\times\mathbf{O}(2), \tag{1.3}$$

$$\mathbf{H}=\mathbf{H}(1)\times\mathbf{H}(2), \tag{1.4}$$

where $\mathbf{C}(1)$ and $\mathbf{C}(2)$ denote the State Vector Spaces of single spins number 1 and 2, respectively. Similar notation is used in Eq. (1.3), (1.4) for Liouville Spaces.

The notation of a linear space means that its elements can be added as vectors and multiplied by real (cartesian space) or complex (unitary space) numbers. Linear transformations performed by linear operators also belong to the linear algebra of the linear space. If, in addition to these linear algebraic operations the scalar product between any two vectors is defined, one speaks of the metric of this space. We shall use spaces with cartesian metric (the spaces **V** and **H**) as well as with unitary metric (the spaces **C** and **O**). The linear operations and the scalar product are the main algebraic operations for the space **C**. In case of the space **O** there is a futher algebraic operation available — the matrix product between elements of this space considered as a linear operators on **C**. Thus, the elements of **O** form a matrix algebra [6]. Meanwhile, the scalar product between two elements of **O**, say **H** and **P**, is given in terms of matrix algebra as follows

$$u=(H,P)=\mathrm{tr}(HP^{+}), \tag{1.5}$$

where the cross stands for the hermitian conjugation. Especially, if H denotes the Hamiltonian and P, the density operator Eq. (1.5) gives the internal energy of the spin ensemble calculated per molecular spin system and in units of $\hbar=1$.

Eq. (1.2)—(1.4) bring a new algebraic operation — the direct product. There are direct products of vectors, of linear spaces, of linear operators and groups.

1.2. Lie rings. The space **H** is not closed with respect to matrix products between its elements, yet it is closed relative to linear operations in the domain of real numbers and relative to the Lie product given by

$$-i[H,P]=-i(HP-PH), \tag{1.6}$$

where H and P denote arbitrary hermitian operators on **C**. If the Lie products Eq. (1.6) are defined (in addition to linear operations) between the vectors of the linear space **H** of a d-level system, one speaks of the

Lie ring or Lie algebra $\mathbf{u}(d)$. Those operators $H \in \mathbf{H}$ which possess the property

$$\operatorname{tr} H = 0 \tag{1.7}$$

form the subspace $\mathbf{H}^0 \subset \mathbf{H}$ of traceless hermitian operators. This subspace is also closed relative to Lie products — it forms the Lie ring $\mathbf{su}(d)$, a subring of $\mathbf{u}(d)$.

It is worth mentioning that calculation of Lie products does not require, at all events, knowledge of the matrix products noted in Eq. (1.6). It is sufficient to choose a basis system of hermitian operators (a system of generators of the Lie algebra) which span the space $\mathbf{H}^0$ and between which the Lie products are given. The latter form the basic system of commutation relationships for the Lie algebra $\mathbf{su}(d)$.

Linear operators of the form λE, with λ a real number and E the unit operator on $\mathbf{C}$, constitute the 1-dimensional subspace $\mathbf{H}_E \subset \mathbf{H}$ which is orthogonal to $\mathbf{H}^0$. The operators $\lambda E \in \mathbf{H}_E$ commute with all other operators of the Lie ring $\mathbf{u}(d)$ — they are the Casimir operators of this ring. Decomposition of the space $\mathbf{H}$ into a direct sum of mutually orthogonal subspaces shown by Eq. (1.8)

$$\mathbf{H} = \mathbf{H}_E \dotplus \mathbf{H}^0 \tag{1.8}$$

reflects the location of vectors of the Lie ring $\mathbf{su}(d) = \mathbf{H}^0$ in the space $\mathbf{H} = \mathbf{u}(d)$. Note that

$$\dim \mathbf{H}^0 = d^2 - 1. \tag{1.9}$$

Lie rings possess representations composed of linear operators on suitable representation spaces [6]. If the space $\mathbf{H}^0$ is taken for the original (abstract) Lie ring $\mathbf{su}(d)$, then the traceless hermitian operators $H \in \mathbf{O}^0 \subset \mathbf{O}$ form such an (isomorphic) representation of $\mathbf{su}(d)$ on space $\mathbf{O}^0$. Linear operators of the form λE, with λ a complex number, constitute the 1-dimensional subspace $\mathbf{O}_E$ which is orthogonal to the subspace $\mathbf{O}^0$ of traceless linear operators on $\mathbf{C}$.

In order to get the adjoint representation of $\mathbf{su}(d)$ on $\mathbf{O}$, [6] we establish a one-one correspondence

$$H \to \mathcal{K} \tag{1.10}$$

between $H \in \mathbf{H}^0$ and antihermitian superoperators $\mathcal{K}$ on $\mathbf{O}$ as follows

$$\mathcal{K}L = -i[H, L]. \tag{1.11}$$

In Eq. (1.11) L denotes an arbitrary linear operator which runs through $\mathbf{O}$, whereas $H \in \mathbf{su}(d)$ is given and specifies the corresponding superoperator $\mathcal{K}$. Especially, if H denotes an Hamiltonian, then $\mathcal{K}$ denotes the corresponding Superhamiltonian.

If in Eq. (1.11) L denotes an arbitrary hermitian operator $L \in \mathbf{H}$, the superoperators $\mathcal{K}$ on $\mathbf{H}$ are antisymmetric. They form the adjoint representation of $\mathbf{su}(d)$ on $\mathbf{H}$.

The vectors of the space $\mathbf{V}$ constitute the Lie ring $\mathbf{so}(3)$, provided the ordinary vector product is considered as the Lie product. We choose the orthonormal laboratory coordinate system $\vec{e}_j \in \mathbf{V}$, $j = x, y, z$, traditionally: $\vec{e}_z$ is directed along the strong static magnetic field $\vec{b}_0$, $\vec{e}_x$ shows the direction of the receiver coil and $\vec{e}_y$ — that of the transmitter coil. The basis vectors are related by vector products:

$$[\vec{e}_x, \vec{e}_y] = \vec{e}_z \tag{1.12}$$

and cyclic permutations. Equation (1.12) forms the basic system of **so**(3).

An important for NSD isomorphic representation of **so**(3) on Liouville Spaces of single spin 1/2 systems is built-up as follows: one sets up the one-one correspondence

$$\vec{e}_j \leftrightarrow I_j, \qquad (j=x,y,z) \tag{1.13}$$

between the basis vectors of **V** and the corresponding single spin operators I_x, I_y, I_z. Since

$$-i[I_x, I_y]=I_z \tag{1.14}$$

and cyclic permutations, the single spin operators form the basis for a representation of **so**(3) on the space $\mathbf{H}^0$ or $\mathbf{O}^0$ of the single spin 1/2 system. Since

$$(I_j, I_k)=(1/2)\delta_{jk}, \qquad (j,k=x,y,z), \tag{1.15}$$

this basis is orthogonal yet not normalized. Using this representation, one gets such a one-one correspondence between ordinary vectors as

$$\vec{\omega}=\sum_j \omega_j \vec{e}_j \in \mathbf{V} \tag{1.16}$$

and single spin 1/2 hermitian operators

$$H=\sum_j \omega_j I_j \in \mathbf{H}^0 \tag{1.17}$$

so that the Lie algebraic relationships are the same in hoth spaces **V** and $\mathbf{H}^0$. Especially, if

$$\vec{\omega}=-\gamma\vec{b} \in \mathbf{V} \tag{1.18}$$

with $\vec{b}$ the strength of external magnetic field, γ the gyromagnetic ratio and $\vec{\omega}$ the Larmor vector, then Eq. (1.17) gives the Hamiltonian of the Zeemân interaction.

Note that the space $\mathbf{H}^0$ of a single spin 1/2 system is governed by the Lie algebra **su**(2). Thus, **so**(3) and **su**(2) are isomorphic.

1.3. Lie groups. The continuous manifold of regular linear operators which transform a linear space into itself, form a (linear) Lie group. Unitary Lie groups (e. g. composed of unitary operators) conserve the metric of unitary spaces, the orthogonal Lie groups conserve that of cartesian spaces. To each Lie group belongs a Lie ring (the infinitesimal ring of this group) the elements of which characterize infinitesimal transformations of the linear space. Knowledge of the Lie ring allows one to study common properties of operators of the associated Lie group [6].

Unitary operators D on the State Vector Space **C** of a d-level system form the Lie group $\mathbf{U}(d)$, those with $\det D=1$ compose its unimodular subgroup $\mathbf{SU}(d)$. The elements $D(\tau) \in \mathbf{SU}(d)$ can be considered as points of a (d^2-1)-dimensional Rieman space in which continuous smooth functions of a real parameter $\tau \geqslant 0$ describe curves which possess a common initial point $D(0)=E$ (the unit operator on **C**). The infinitesimal ring $\mathbf{su}(d)$ of this Lie group is composed of traceless hermitian operators like

$$I=i\left(\frac{dD(\tau)}{d\tau}\right)_{\tau=0} \tag{1.19}$$

which thus play the role of the tangent of the curve $D(\tau)$ at the initial point. All possible operators (1.19) constitute the Lie ring $\mathbf{su}(d)$ descri-

bed in Sec. 1.2. Infinitesimal unitary transformations ($\tau \to 0$) of space $\mathbf{C}$ are now given by

$$D(\tau) = E - i\tau I. \tag{1.20}$$

One can choose a set of (d^2-1) mutually orthogonal operators (1.19) associated with mutually orthogonal curves $D(\tau)$, which span the space $\mathbf{H}^0$ of the Lie ring $\mathbf{su}(d)$.

Lie groups and its Lie rings possess representations defined on other linear spaces (on representation spaces) [6]. The group algebraic and Lie algebraic relationships in a representation coincide with those in the original group or ring, respectively. The same is true for the relation (1.19) between a Lie group and its associated Lie ring.

Nuclear Spin Dynamics is especially interested in adjoint representations of Lie groups $\mathbf{SU}(d)$ and of its Lie rings $\mathbf{su}(d)$ on spaces $\mathbf{O}$ and $\mathbf{H}$ of a d-level system. If L denotes an arbitrary vector of $\mathbf{O}$ and $D \in \mathbf{SU}(d)$, then the unitary adjoint representation $\mathfrak{D}$ of D is given by

$$\mathfrak{D}L = DLD^{-1} \in \mathbf{O}, \tag{1.21}$$

where $\mathfrak{D}$ is a unimodular unitary superoperator on $\mathbf{O}$. If the correspondence

$$D \to \mathfrak{D} \tag{1.22}$$

defined by Eq. (1.21), is applied to all $D \in \mathbf{SU}(d)$, we have the unitary adjoint representation of $\mathbf{SU}(d)$.

If, on the other hand, the definition (1.21) is applied only to hermitian operators $L \in \mathbf{O}$, one gets the orthogonal adjoint representation of $\mathbf{SU}(d)$ on $\mathbf{H}$.

If $D = D(\tau)$, then $\mathfrak{D} = \mathfrak{D}_T$ and the superoperator

$$\mathfrak{I} = \left(\frac{d\mathfrak{D}(\tau)}{d\tau} \right)_{\tau=0} \tag{1.23}$$

is the adjoint representation of the operator (1.19). In case of unitary adjoint representation $\mathfrak{I}$ is antihermitian, whereas for orthogonal adjoint representation $\mathfrak{I}$ is asymmetric. In both cases the definition (1.23) is equivalent to the definition (1.11). Applying the correspondence

$$I \to \mathfrak{I} \tag{1.24}$$

defined by Eq. (1.11), (1.23) to all $I \in \mathbf{su}(d)$, one gets the adjoint representations of $\mathbf{su}(d)$ on $\mathbf{H}$ and $\mathbf{O}$.

1.4. Adiabatic Nuclear Spin Dynamics. The dynamics of an ensemble of adiabatically isolated d-level systems can be described in terms of Lie group $\mathbf{SU}(d)$ and Lie ring $\mathbf{su}(d)$.

In Adiabatic NSD time-evolution of the state vector $|\psi(t)\rangle \in \mathbf{C}$ is determined by the Schroedinger equation

$$i\frac{d|\psi\rangle}{dt} = H(t)|\psi\rangle, \tag{1.25}$$

whereas the motion of the density operator $P(t) \in \mathbf{H}$ is governed by the Liouville equation [8, 9]

$$\frac{dP}{dt} = \mathfrak{K}(t)P. \tag{1.26}$$

In Eq. (1.25), (1.26) $H(t)$ denotes the Hamiltonian (in units $\hbar = 1$) and $\mathfrak{K}(t)$ is the corresponding Superhamiltonian. As a rule,

$$H(t) = H_0 + H_E(t), \tag{1.27}$$

where the time-independent part H_0 includes (time-averaged) internal interactions of the spin system as well as its interactions with the strong static magnetic field $\vec{b}_0$. The time-dependent part $H_E(t)$ (the excitation) is usually due to time-dependent external magnetic field $\vec{b}_E(t)$ (the Zeeman excitation) which is weak in the sence

$$|\vec{b}_E(t)| \ll |\vec{b}_0|. \tag{1.28}$$

As a rule, the Hamiltonian (1.27) satisfies Eq. (1.7). Thus

$$H(t) \in \mathbf{su}(d), \tag{1.29}$$

whereas the Superhamiltonian

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_E(t) \tag{1.30}$$

belongs to the adjoint representation of $\mathbf{su}(d)$.

An alternative way in Adiabatic NSD is in use of time-dependent unitary operators $D(t,0) \in \mathbf{SU}(d)$ (of propagators) which describe the general solution of Eq. (1.25) [4]

$$|\psi(t)\rangle = D(t,0)\,|\psi(0)\rangle \tag{1.31}$$

the time-dependence of the propagator is governed by the equations

$$i\frac{dD}{dt} = H(t)D, \tag{1.32}$$

$$D(0,0) = E, \tag{1.33}$$

which establish the one-one correspondence

$$H(t) \leftrightarrow D(t,0). \tag{1.34}$$

The general solution of the Liouville equation (1.26)

$$P(t) = \mathfrak{D}(t,0)P(0) \tag{1.35}$$

is described by propagators $\mathfrak{D}(t,0)$ on $\mathbf{H}$ or $\mathbf{O}$ the time-dependence of which is determined by the equations

$$\frac{d\mathfrak{D}}{dt} = \mathcal{H}(t)\mathfrak{D}, \tag{1.36}$$

$$\mathfrak{D}(0,0) = \mathcal{E}, \tag{1.37}$$

where $\mathcal{E}$ denotes the unit superoperator. If $D(t,0) \in \mathbf{SU}(d)$, then $\mathfrak{D}(t,0)$ belongs to the adjoint representation of the dynamical group $\mathbf{SU}(d)$, whereas $\mathcal{H}(t)$ belongs to the adjoint representation of the dynamical ring $\mathbf{su}(d)$. Note that Eq. (1.31), (1.35) describe a family of trajectories associated with a continuous manifold of experimental situations rather than a concrete one. Since the dependence of motion upon initial state is soon incorporated in the propagator, one can concern oneself with the establishment of the correspondence (1.34). In order to solve Eq. (1.32), (1.33), one can apply, say, the local approach studied by Magnus [10] or the global approach proposed by Wei and Norman [11]. However, it is the main purpose of the Group Approach in NSD [4, 5] to use the theory of Lie groups in order to set up a classification of dynamical relationships based on group structure and group representations.

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Academy of Sciences of the Estonian SSR,
Institute of Chemical Physics and Biophysics

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V. SINIVEE

VEDELIKE TUUMASPINNIDE DÜNAAMIKA PÕHIMÕISTEID. 1

Käesoleva artikliga alustatud töödetsükli eesmärk on vedelike tuumaspinnide dünaamika põhimõistete ja põhimiste seoste süstemaatiline esitus. Esimeses artiklis on vaadeldud kasutatavaid matemaatilisi mõisteid.

В. СИНИВЕЭ

ОСНОВНЫЕ ПОНЯТИЯ В ЯДЕРНОЙ СПИНОВОЙ ДИНАМИКЕ ЖИДКОСТЕЙ. 1

Задача данной серии работ — систематическое изложение основных понятий и соотношений в ядерной спиновой динамике жидкостей. В первой статье рассмотрены основные применяемые математические понятия.