SUPEROPERATORS IN NMR

A SUMMARY

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1. Introduction to State and Hilbert Spaces

Consider an NMR system of N spins, each spin with $I = 1/2$. Corresponding to this system, there will be a *function* or *state* space $\mathcal{F}_n$ of dimension $n = 2^N$. States of the system are represented as kets or functions $|\psi\rangle$ belonging to $\mathcal{F}_n$. However, for the case of nuclear spins, these functions happen to be only a mathematical abstraction. Strictly, $\mathcal{F}_n$ is spanned by a continuous basis. Unfortunately, in the present scenario of nuclear spins we are dealing with, no such basis exists and we have to look for alternative, discrete bases. So the kets are ***mapped*** into an n-dimensional Hilbert space which is a linear vector space. Again we assume our Hilbert space to be finite and discrete. The mapping is from $\mathcal{F}_n$ to $\mathcal{H}_n$. In (1), the $\longmapsto$ has been used in place of equality to signify this transformation.

$$\begin{aligned} |\psi\rangle &\longmapsto \sum_{i=1}^{n} c_i |i\rangle \\ &= \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{bmatrix} \end{aligned} \tag{1}$$

The coefficients c_i in (1) are the components of the n-dimensional vector and are given as:

$$c_i = \langle i| \left(\sum_{j=1}^{n} c_j |j\rangle \right) \tag{2}$$

The set of **vectors**, $\mathbb{S}_n = \{|j\rangle, j = 1, 2, \ldots, n\}$ forms a discrete, orthonormal basis, in the Hilbert space $\mathcal{H}_n$, simultaneously satisfying the two conditions given in (3).

$$\langle i|j\rangle = \delta_{ij} \tag{3a}$$

$$\sum_{i=1}^{n} |i\rangle\langle i| = \mathbb{1} \tag{3b}$$

Each vector in $\mathbb{S}_n$ has n components and there are n vectors in the set. A convenient choice for the basis vectors is:

$$\mathbb{S}_n = \left\{ \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{bmatrix}, \quad \dots \quad , \begin{bmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 1 \end{bmatrix} \right\} \tag{4}$$

In the vectorial representation of the basis set $\mathbb{S}_n$, the vector $|j\rangle$ has its j'th element as 1 and all other elements are 0's.

2. Operators over the Hilbert Space $\mathcal{H}_n$

An operator $\hat{O}$ acts over the Hilbert Space to transform the vector $|\psi\rangle \longmapsto \sum_{j=1}^{n} c_j|j\rangle$ into a new vector $\sum_{j=1}^{n} d_j|j\rangle \longleftarrow |\phi\rangle$. The small hat $\hat{}$ over the symbol O represents an operator in $\mathcal{H}_n$. (Once again, the $\longleftarrow$ and $\longmapsto$ represent a conceptual distinction between $\mathcal{F}_n$ and $\mathcal{H}_n$). Once we appreciate this difference, we can safely and consistently, represent vectors in the Hilbert space as kets $|\psi\rangle$'s. The action of the operator $\hat{O}$ over $\mathcal{H}_n$ is then given as:

$$\begin{aligned} \hat{O}|\psi\rangle &= |\phi\rangle \\ \Longrightarrow \hat{O}\sum_{j=1}^{n} c_j|j\rangle &= \sum_{j=1}^{n} d_j|j\rangle \\ \Longrightarrow \hat{O}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{bmatrix} &= \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ d_n \end{bmatrix} \end{aligned} \tag{5}$$

(5) also serves as a matrix equation, so there must be a matrix representation for $\hat{O}$ as well. Using the identities in (3), we can represent $\hat{O}$ as:

$$\begin{aligned} \hat{O} &= \Big(\sum_{i=1}^{n} |i\rangle\langle i|\Big)\, \hat{O}\, \Big(\sum_{j=1}^{n} |j\rangle\langle j|\Big) \\ &= \sum_{i=1}^{n}\sum_{j=1}^{n} \langle i|\hat{O}|j\rangle |i\rangle\langle j| \end{aligned} \tag{6}$$

In (6), $\langle i|\hat{O}|j\rangle$ represents the matrix element $\hat{O}_{ij}$ and the set of operators $|i\rangle\langle j|$ forms a basis set for the operator $\hat{O}$ in $\mathcal{H}_n$. The general matrix representation of an operator $\hat{O}$ could also be expressed in the form:

$$\hat{O} = \sum_{i,j=1}^{n} c_{ij} |i\rangle\langle j| \tag{7}$$

In (7), each of the indices i,j runs from 1 to n. So the basis set for the operator consists of n^2 elements:

$$\mathbb{S}'_{n^2} = \{|i\rangle\langle j|\}, i, j = 1, 2, \ldots, n \tag{8}$$

Different choices of the basis set for the operators in $\mathcal{H}_n$, $\mathbb{S}'_{n^2}$ is possible. Each of these choices would contain n^2 basis operators. The matrix representation of each of these, would in turn have n^2 independent elements.

Hence, the formalism of our $\mathcal{H}_n$ is such that it is n-dimensional and is"inhabited" by kets that we represent by $n \times 1$ vectors. The operators over $\mathcal{H}_n$, operate on these kets and give kets (which are new vectors) as outputs. The operators are $n \times n$ matrices.

$$\widehat{Operatar}|ket\rangle = |newket\rangle \tag{9a}$$

$$|ket\rangle \xrightarrow{\widehat{Operator}} |newket\rangle \tag{9b}$$

3. The Liouville Space $\mathcal{L}_{n^2}$

Just as operators transform kets in $\mathcal{H}_n$, there must be some mathematical function that defines the transformation between operators ($\hat{A} \longmapsto \hat{B}$) in another higher-dimensional "superspace", $\mathcal{L}_{n^2}$. This is an n^2-dimensional space, called the *Liouvulle space*, a fact we shall soon convince ourselves of. The operands in $\mathcal{L}_{n^2}$ are operators and to maintain a level of uniformity with (9), we may stick to the habit of representing our operands as kets even in our new Liouville space $\mathcal{L}_{n^2}$. The mathematical map that acts on these operator kets is called a *superoperator* and is distinguished by a double hat over its symbol, like $\hat{\hat{S}}$.

$$\hat{\hat{S}}|\hat{A}\rangle = |\hat{B}\rangle \tag{10a}$$

$$|\hat{A}\rangle \xrightarrow{\hat{\hat{S}}} |\hat{B}\rangle \tag{10b}$$

The set of basis operators, $\mathcal{S}_{n^2}$ given in (8), has n^2 elements as each of the i and j indices runs from 1to n. The mapping from $\mathcal{H}_n$ to $\mathcal{L}_{n^2}$ involves a transformation of the kind:

$$|i\rangle\langle j| \longmapsto \langle i|\langle j| \equiv \langle ij| \tag{11}$$

If we *relabel* the two indices, i and j, each extending from 1to n, by a single index α, then α will extend from 1 to n^2. So, the basis set $\mathcal{S}_{n^2}$ in the Liouville space, becomes (from (8)):

$$\mathbb{S}'_{n^2} = \{|\alpha\rangle\}, \alpha = 1, 2, \ldots, n^2 \tag{12}$$

An example is given of the operator, $\hat{A} = \langle i|\hat{A}|j\rangle$ in a 3-dimensional Hilbert and a 9-dimensional Liouvulle Space:

In Hilbert Space $\mathcal{H}_n$:

$$\hat{A} = \begin{pmatrix} \langle 1|\hat{A}|1\rangle & \langle 1|\hat{A}|2\rangle & & \langle 1|\hat{A}|n\rangle \\ \langle 2|\hat{A}|1\rangle & \langle 2|\hat{A}|2\rangle & \ldots & \langle 2|\hat{A}|n\rangle \\ & \vdots & \ddots & \\ \langle n|\hat{A}|1\rangle & \langle n|\hat{A}|2\rangle & & \langle n|\hat{A}|n\rangle \end{pmatrix} \tag{13}$$

In Liouville Space $\mathcal{L}_{n^2}$:

$$\hat{A} \longmapsto \begin{bmatrix} \langle 1|\hat{A}|1\rangle \\ \langle 1|\hat{A}|2\rangle \\ \langle 1|\hat{A}|3\rangle \\ \vdots \\ \langle 1|\hat{A}|n\rangle \\ \langle 2|\hat{A}|1\rangle \\ \vdots \\ \langle n|\hat{A}|n\rangle \end{bmatrix} \tag{14a}$$

In (14a), we have used the same indices i *and* j as have been used in the Hilbert representation (13). We can adjoin these indices as in (11) and then relabel them as in (12), to obtain the following Liouville space representation of the operator $\hat{A}$:

$$\hat{A} \longmapsto |\hat{A}\rangle \equiv \begin{bmatrix} \langle 1|\langle 1|\hat{A} \\ \langle 1|\langle 2|\hat{A} \\ \langle 1|\langle 3|\hat{A} \\ \vdots \\ \langle 1|\langle n|\hat{A} \\ \langle 2|\langle 1|\hat{A} \\ \vdots \\ \langle n|\langle n|\hat{A} \end{bmatrix} \equiv \begin{bmatrix} \langle 1|\hat{A} \\ \langle 2|\hat{A} \\ \langle 3|\hat{A} \\ \vdots \\ \langle n|\hat{A} \\ \langle n+1|\hat{A} \\ \vdots \\ \langle n^2|\hat{A} \end{bmatrix} \tag{14b}$$

It would now be clear from (14b), that there will be n^2 components in the Liouville space representation of an operator. The basis set defined in (12) will also have n^2 basis operators. It is also easy to consider the fact that in the Liouville space, the operators are represented as $n^2 \times 1$ vectors, unlike their $n \times n$ matrix representations in the corresponding Hilbert space.

4. Superoperators over the Liouville Space $\mathcal{L}_{n^2}$

Now that we have obtained a ket representation of the operator in $\mathcal{L}_{n^2}$(14b), we are also expecting a matrix form for $\hat{\hat{S}}$ satisfying (10a). From inspection of (10b) and (14b), we can immediately write:

$$\hat{\hat{S}}|\hat{A}\rangle = |\hat{B}\rangle \tag{10b}$$

$$\Longrightarrow \begin{pmatrix} \langle 1|\hat{\hat{S}}|1\rangle & \langle 1|\hat{\hat{S}}|2\rangle & & \langle 1|\hat{\hat{S}}|n^2\rangle \\ \langle 2|\hat{\hat{S}}|1\rangle & \langle 2|\hat{\hat{S}}|2\rangle & \dots & \langle 2|\hat{\hat{S}}|n^2\rangle \\ & \vdots & \ddots & \\ \langle n^2|\hat{\hat{S}}|1\rangle & \langle n^2|\hat{\hat{S}}|2\rangle & & \langle n^2|\hat{\hat{S}}|n^2\rangle \end{pmatrix} \begin{bmatrix} \langle 1|\hat{A} \\ \langle 2|\hat{A} \\ \langle 3|\hat{A} \\ \vdots \\ \langle n|\hat{A} \\ \langle n+1|\hat{A} \\ \vdots \\ \langle n^2|\hat{A} \end{bmatrix} = \begin{bmatrix} \langle 1|\hat{B} \\ \langle 2|\hat{B} \\ \langle 3|\hat{B} \\ \vdots \\ \langle n|\hat{B} \\ \langle n+1|\hat{B} \\ \vdots \\ \langle n^2|\hat{B} \end{bmatrix} \tag{15}$$

Hence $\hat{\hat{S}}$ is represented in $\mathcal{L}_{n^2}$ by an $n^2 \times n^2$ matrix, having n^4 independent elements. The general element of $\hat{\hat{S}}$ is $\langle\gamma|\hat{\hat{S}}|\delta\rangle$, where the indices γ and δ each extend from 1 to n^2. Each of the indices γ , δ is obtained via transformation from the Hilbert space as specified in (11).

Several useful superoperators exist that describe transformation of operators in the NMR system. They help explain and understand processes like relaxation, diffusion and chemical processes, to name a few. We shall discuss some important basic examples of superoperators and briefly outline some of their properties. One important class comprises the *decomposable* superoperators.

5. Decomposable superoperators

Many operator transformation in the Liouville space can be formulated as:

$$|\hat{A}\rangle \longmapsto |\hat{M}\hat{A}\hat{N}\rangle \tag{16}$$

In fact *all* operator transformations can be described as:

$$|\hat{A}\rangle \longmapsto \sum_{k,l=1}^{q\geq 1} s_{kl}|\hat{M}_k\hat{A}\hat{N}_l\rangle \tag{17}$$

The corresponding superoperator equation for (17) is:

$$\hat{\hat{S}}|\hat{A}\rangle = \sum_{k,l=1}^{q\geq 1} s_{kl}|\hat{M}_k\hat{A}\hat{N}_l\rangle \tag{18}$$

If $q = 1$ in (18), then $\hat{\hat{S}}$ is called a *decomposable* superoperator. $\hat{M}_k$ and $\hat{N}_l$ belong to the same *operator algebra* and are sometimes called the *generating* operators. Moreover, (18) indicates that all superoperators can be expressed as a sum of decomposable superoperators. Consider one such decomposable superoperator:

$$\hat{\hat{S}}|\hat{A}\rangle = |\hat{M}\hat{A}\hat{N}\rangle \tag{19}$$

We shall determine the relation of $\hat{\hat{S}}$ to the operators $\hat{M}$ *and* $\hat{N}$. We also need to answer the question: *how could we find $\hat{\hat{S}}$ once the Hilbert representations of $\hat{M}$ and $\hat{N}$ are known?* To answer this question, we shall work in the simpler and more familiar Hilbert space, and change to the Liouville space with the transformation specified in (11). This method will further clarify the relationship borne between the two spaces.

A general element of the matrix $\hat{M}\hat{A}\hat{N}$ in $\mathcal{H}_n$, $\langle i|\hat{M}\hat{A}\hat{N}|j\rangle$ is given as:

$$\begin{aligned}
\langle i|\hat{M}\hat{A}\hat{N}|j\rangle &= \sum_{r=1}^{n}\sum_{s=1}^{n}\langle i|\hat{M}|r\rangle\langle r|\hat{A}|s\rangle\langle s|\hat{N}|j\rangle \qquad \text{(from (3b))} && \text{(20a)}\\
&= \sum_{r=1}^{n}\sum_{s=1}^{n}\langle i|\hat{M}|r\rangle\langle s|\hat{N}|j\rangle\langle r|\hat{A}|s\rangle && \text{(20b)}\\
&= \sum_{r=1}^{n}\sum_{s=1}^{n}\langle i|\hat{M}|r\rangle\langle j|\hat{N}^{\dagger}|s\rangle\langle r|\hat{A}|s\rangle && \text{(20c)}
\end{aligned}$$

Transforming (20c) from the Hilbert to the Liouville space using (11), we obtain the following relation:

$$\langle ij|\hat{M}\hat{A}\hat{N}\rangle = \sum_{r=1}^{n}\sum_{s=1}^{n}\langle ij|\hat{\hat{S}}|rs\rangle\langle rs|\hat{A}\rangle \tag{20d}$$

Once again relabeling the indices as done in (12) and (14b):

$$\langle\beta|\hat{M}\hat{A}\hat{N}\rangle = \sum_{\alpha=1}^{n^2}\langle\beta|\hat{\hat{S}}|\alpha\rangle\langle\alpha|\hat{A}\rangle \tag{20e}$$

From (20d), we recognize $\hat{\hat{S}}$ as a *tetradic* that is indexed by four variables i,j,r and s, and from (20e) shows that this tetradic also has a matrix respresentation with only two indices α and β. The tetradic and matrix representations of the superoperators are hence isomorphic in the mathematical sense. Also by comparing (20c) and (20d), we can easily verify that the relation between the Liouville superoperator $\hat{\hat{S}}$ and the Hilbert operators $\hat{M}$ *and* $\hat{N}$ is one of a direct product:

$$\langle ij|\hat{\hat{S}}|rs\rangle \longleftarrow \langle i|\hat{M}|r\rangle\langle j|\hat{N}^{\dagger}|s\rangle \tag{21a}$$

$$\hat{\hat{S}} \equiv \hat{M} \otimes \hat{N}^{\dagger} \tag{21b}$$

In fact, (21b) serves as a useful prescription for writing down a superoperator for the operator transformations given in (19). For example, if $|\hat{A}\rangle$ transforms as $|\hat{A}\rangle \longmapsto |\hat{U}\hat{A}\hat{U}^{\dagger}\rangle$, then the superoperator affecting this transformation would be $\hat{\hat{S}} \equiv \hat{U} \otimes (\hat{U}^{\dagger})^{\dagger} = \hat{U} \otimes \hat{U}$.

6. The Liouville-Von Neumann (LV) Equation

The Liouville-Von Neumann **LV** Equation is written as:

$$\frac{d\sigma(t)}{dt} = -i\,[\hat{H}(t), \sigma(t)] \tag{22}$$

The solution of the **LV** Equation, explaining the time-dependence of the spin density matrix σ(t) is given as:

$$\sigma(t) = \hat{U}\sigma(0)\hat{U}^{\dagger} \tag{23}$$

where $\hat{U}$ is the suitable *propagator*:

$$\hat{U}(t) = \prod_{t} exp\,(-i\int_{t_1}^{t_2} \hat{H}(t')\,dt') \tag{24}$$

where $\prod_{t}$ is the appropriate *Dyson time-ordering* operator. Writing (23) in the Liouville space:

$$|\sigma(t)\rangle = \hat{\hat{U}}\,|\sigma(0)\rangle \tag{25a}$$

$$\Longrightarrow \hat{\hat{U}} = \hat{U} \otimes \hat{U} \tag{25b}$$

(25a) can be regarded as a *motion* equation, relating the density matrix at a time t to the initial density matrix at $t = 0$. Likewise, $\hat{\hat{U}}$ is called the *finite time displacement superoperator*.

The **LV** Equation (22), could also be written in superoperator form as:

$$\frac{d}{dt}|\sigma(t)\rangle = -i\,\hat{\hat{L}}\,|\sigma(t)\rangle \tag{26}$$

The superoperator $\hat{\hat{L}}$ is defined using the following linear map:

$$\begin{aligned}\hat{\hat{L}}\,|\sigma(t)\rangle =&|[\hat{H}(t),\sigma(t)]\rangle \\ =&|\hat{H}(t)\sigma(t)\rangle - |\sigma(t)\hat{H}(t)\rangle\end{aligned} \tag{27}$$

Clearly $\hat{\hat{L}}$ is a *commutation superoperator*. It is termed the *Liouvillian*. Associated with any operator $\hat{A}$ in $\mathcal{H}_n$, we can write a corresponding commutation superoperator $\hat{\hat{A}}$ in $\mathcal{L}_{n^2}$. For example, corresponding to the NMR angular momentum operator $\hat{I}_x$ there will be a superoperator, $\hat{\hat{I}}_x$. The relation between an arbitrary $\hat{A}$ and its associated commutation superoperator $\hat{\hat{A}}$ is given as:

$$\hat{\hat{A}} \equiv \hat{A} \otimes \mathbb{1}_n - \mathbb{1}_n \otimes \hat{A}^\dagger \tag{28}$$

In (28), $\mathbb{1}_n$ is the n-order identity matrix in the n-dimensional Hilbert space. As a numerical example, we may consider the construction of the superoperator $\hat{\hat{I}}_z$ in accordance with (28). For the single spin case:

$$\begin{aligned}\hat{\hat{I}}_z \equiv& \hat{I}_z \otimes \mathbb{1}_2 - \mathbb{1}_2 \otimes \hat{A}_z^\dagger \\ =&\frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \otimes \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} - \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \otimes \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \\ =&\frac{1}{2}\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\end{pmatrix} - \frac{1}{2}\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\end{pmatrix} \\ =&\begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}\end{aligned} \tag{29}$$

We can also express $\hat{\hat{L}}$ in the form analogous to (28) and by additionally noting that $\hat{H}$ is hermitian:

$$\begin{aligned}\hat{\hat{L}} \equiv& \hat{H} \otimes \mathbb{1}_n - \mathbb{1}_n \otimes \hat{H}^\dagger \\ =& \hat{H} \otimes \mathbb{1}_n - \mathbb{1}_n \otimes \hat{H}\end{aligned} \tag{30}$$

Commutation superoperators like the Liouvillian $\hat{\hat{L}}$ could also be expressed as the difference of the *left* and *right* superoperators, $\hat{\hat{L}}_L$ amd $\hat{\hat{L}}_R$, defined as follows:

$$\hat{\hat{L}} = \hat{\hat{L}}_L - \hat{\hat{L}}_R \tag{31a}$$

$$\hat{\hat{L}}_L \equiv \hat{H} \otimes \mathbb{1}_n \implies \hat{\hat{L}}_L|\sigma(t)\rangle = |\hat{H}\sigma(t)\rangle \tag{31b}$$

$$\hat{\hat{L}}_R \equiv \mathbb{1}_n \otimes \hat{H} \implies \hat{\hat{L}}_R|\sigma(t)\rangle = |\sigma(t)\hat{H}\rangle \tag{31c}$$

A useful property of the left and right superoperators is that they always commute. With an arbitrary operator $|A\rangle$, we can show that:

$$\begin{aligned}
[\hat{\hat{L}}_L, \hat{\hat{L}}_R]|\hat{A}\rangle =& \hat{\hat{L}}_L\hat{\hat{L}}_R|\hat{A}\rangle - \hat{\hat{L}}_R\hat{\hat{L}}_L|\hat{A}\rangle \\
=& |\hat{H}\hat{A}\hat{H}\rangle - |\hat{H}\hat{A}\hat{H}\rangle \\
=& \mathbb{0}
\end{aligned} \tag{32}$$

We ware now interested in establishing a relationship between the time-displacement superoperator $\hat{\hat{U}}$ given in (25a) and the Liouvillian $\hat{\hat{L}}$ in $\mathcal{L}_{n^2}$ and the hermitian Hamiltonian operator $\hat{H}$ in $\mathcal{H}_n$. Let us briefly digress and look into a scenario in which an operator $\hat{A}$ in the Liouvulle space is acted upon by two superoperators, $\hat{\hat{S}}_2 = \hat{M}_2 \otimes \hat{N}_2$ and $\hat{\hat{S}}_1 = \hat{M}_1 \otimes \hat{N}_1$:

$$\begin{aligned}
(\hat{M}_2 \otimes \hat{N}_2)(\hat{M}_1 \otimes \hat{N}_1)|\hat{A}\rangle &= (\hat{M}_2 \otimes \hat{N}_2)|\hat{M}_1\hat{A}\hat{N}_1^\dagger\rangle \\
&= |\hat{M}_2\hat{M}_1\hat{A}\hat{N}_1^\dagger\hat{N}_2^\dagger\rangle \\
&= |\hat{M}_2\hat{M}_1\hat{A}(\hat{N}_2\hat{N}_1)^\dagger\rangle \\
&= \hat{M}_2\hat{M}_1 \otimes \hat{N}_2\hat{N}_1|\hat{A}\rangle \\
\implies (\hat{M}_2 \otimes \hat{N}_2)(\hat{M}_1 \otimes \hat{N}_1) &= \hat{M}_2\hat{M}_1 \otimes \hat{N}_2\hat{N}_1
\end{aligned} \tag{33}$$

We must also convince ourselves of the unitarity property of the time-displacement superoperator. Considering a time-independent Hamiltonian in (24), with only one term in the time-ordered product, the propagator $\hat{U}(t) = \hat{U}$ will be unitary, $\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \mathbb{1}_n$ in the Hilbert space. Using the unitarity of the Hilbert propagators $\hat{U}$, we can write the following relations in the Liouville space:

$$\begin{aligned}
|\hat{A}\rangle = \; |\hat{U}^\dagger\hat{U}\hat{A}\hat{U}\hat{U}^\dagger\rangle &= |\hat{U}^\dagger(\hat{U}\hat{A}\hat{U})\hat{U}^\dagger\rangle \\
&\equiv (\hat{U}^\dagger \otimes \hat{U}^\dagger)|\hat{U}\hat{A}\hat{U}\rangle \\
&\equiv (\hat{U}^\dagger \otimes \hat{U}^\dagger)(\hat{U} \otimes \hat{U})|\hat{A}\rangle \\
&\equiv \hat{\hat{U}}^\dagger\hat{\hat{U}}|\hat{A}\rangle \qquad\qquad \text{from (25b)} \\
\implies \hat{\hat{U}}^\dagger\hat{\hat{U}} &= \mathbb{1}_{n^2}
\end{aligned} \tag{34}$$

Starting with $|\hat{U}\hat{U}^\dagger\hat{A}\hat{U}^\dagger\hat{U}\rangle$, we can also show that $\hat{\hat{U}}\hat{\hat{U}}^\dagger = \mathbb{1}_{n^2}$ and so $\hat{\hat{U}}$ must be unitary superoperator. We must however, keep in mind, that unitarity of the time-displacement superoperator is guaranteed only if (24) can be written in piecewise-constant form, such as:

$$\hat{U} = \prod_k exp\,(-i\hat{H}_k\,\Delta t_k) \tag{35a}$$

with the additional constraint that:

$$[\hat{H}_k, \hat{H}_{k'}] = \mathbb{0} \tag{35b}$$

In (35a), the $\hat{H}_k$'s are time-independent within each interval Δt_k. The time-displacement super-operators for this particular case of time-independent, commuting propagators form a group under multiplication.

The explicit dependence of the time-displacement superoperator on the Liouvillian and the corresponding Hamiltonians is explored below:

$$\begin{aligned}
|\sigma(t)\rangle = \hat{\hat{U}}|\sigma(0)\rangle &= exp(-i\hat{\hat{L}}t/\hbar)|\sigma(0)\rangle && (36)\\
&= exp(-i(\hat{\hat{L}}_L - \hat{\hat{L}}_R)t/\hbar)|\sigma(0)\rangle && \text{from (31a)}\\
&= exp(-i\hat{\hat{L}}_L t/\hbar)\,exp(i\hat{\hat{L}}_R t/\hbar)|\sigma(0)\rangle && \text{from (32)}\\
&\equiv exp(-i\hat{H}t/\hbar)\sigma(0)\,exp(i\hat{H}t/\hbar) && \text{in the Corresponding Hilbert Space}
\end{aligned}$$

This result is consistent with (23) showing that the superoperator for the motion of the spin density operator in the Liouville space is indeed $\hat{\hat{U}} = exp(-i\hat{\hat{L}}t/\hbar)$.

(25a) conveniently formulates the motion of the spin density operator in the Liouville space, but in the associated **LV** Equation, (22), we notice that the operator $\hat{H}$ carries an additional significance of acting as an *energy* operator as well. We need recourse to a corresponding energy superoperator $\hat{\hat{E}}$ in the higher dimensional Liouville space. We define $\hat{\hat{E}}$ through the anti-commutation superoperator:

$$\begin{aligned}
\hat{\hat{E}}|\sigma(t)\rangle &= \frac{1}{2}|[\hat{H}(t), \sigma(t)]_+\rangle\\
&= \frac{1}{2}(|\hat{H}(t)\sigma(t)\rangle + |\sigma(t)\hat{H}(t)\rangle)
\end{aligned} \tag{37}$$

Like all superoperators, $\hat{\hat{E}}$ can also be expressed as a sum of decomposable superoperators:

$$\hat{\hat{E}} \equiv \frac{1}{2}(\hat{H}\otimes \mathbb{1}_n + \mathbb{1}_n \otimes \hat{H}) \qquad \hat{H}^\dagger = \hat{H} \tag{38}$$

The energy superoperator directly returns the hamiltonian from the relation:

$$|\hat{H}\rangle = \hat{\hat{E}}|\mathbb{1}\rangle \tag{39}$$

Following the definition of Frobenius, we can introduce a *metric* into the Liouville space, by defining the scalar product of two operators, $\hat{A}$ and $\hat{B}$ as:

$$\langle \hat{A} | \hat{B} \rangle \equiv Tr(\hat{A}^{\dagger} \hat{B}) \tag{40}$$

where the R.H.S. in 40 corresponds to the trace traditionally defined in the Hilbert space. As an example of the use of this metric in $\mathcal{L}_{n^2}$, we can immediately write:

$$\langle \mathbb{1} | exp(-i\hat{H}/kT) \rangle \equiv Tr(exp(-i\hat{H}/kT)) \tag{41}$$

Using (39) and (41), we can easily write the partition function Z in terms of the energy superoperator:

$$Z = \langle \mathbb{1} | exp(-i\hat{\hat{E}}/kT) | \mathbb{1} \rangle \tag{42}$$

Starting from a density matrix $\sigma(0)$ as in (36), we can also evaluate the expectation value of any operator $\hat{A}$ at a subsequent time t, using the time-displacement superoperator and the definition of the scalar product in the Liouville space:

$$\langle \hat{A} \rangle (t) = Tr(\hat{A}\sigma(t)) \qquad \text{in } \mathcal{H}_n \tag{43a}$$

$$\langle \hat{A} \rangle (t) = \langle \hat{A}^{\dagger} | \sigma(t) \rangle \qquad \text{in } \mathcal{L}_{n^2} \tag{43b}$$

$$= \langle \hat{A}^{\dagger} | \hat{\hat{U}} | \sigma(0) \rangle \qquad \text{from (36)} \tag{43c}$$

The superoperator, therefore, turms out to be a very comprehensive and compact mathematical object with many useful quantities flowing from its natural definition. The superiority of (43) over its traditional Hilbert space counterpart, $\langle \hat{A} \rangle (t) = Tr(\hat{A}\hat{U}(t,0)\sigma(0)\hat{U}^{\dagger}(t,0))$, is immediately evident, through the linear dependence of the density operator on the superoperator in the Liouville space, compared to the non-linear dependence of the former on the Hilbert space Hamiltonian. In the case of piecewise constant Hamiltonians in $\mathcal{H}_n$, $\hat{H}_1, \hat{H}_2, \ldots$, we would need to both pre and post multiply the density operator with the appropriate propagators, $\hat{U}_1, \hat{U}_2, \ldots$, followed by a trace operation. However, a superoperator $\hat{\hat{U}}$ constructed using (33), only needs to be pre-multiplied to the initial density operator, as done in (43c).

7. Eigenvalues of the Liouvillian Superoperator

In the Hilbert space, the Hamiltonian operator $\hat{H}$ will be diagonal in its own eigenbasis. Let $|a\rangle$, $|b\rangle$, ... be the eigenkets of $\hat{H}$ with eigenvalues $\hbar\omega_a$, $\hbar\omega_b$, ... The eigenkets of the Liouvillian $\hat{\hat{L}}$ in the Liouville space will be of the form $||a\rangle\langle b|\rangle$ with eigenvalues involving the differences of frequencies such as $\hbar(\omega_a - \omega_b)$. So $\hat{\hat{L}}$ must also be diagonal in the basis spanned by

$||a\rangle\langle b|\rangle$. Furthermore, for a hermitian Hamiltonian with real eignevalues, the eigenvalues of the corresponding $\hat{\hat{L}}$ will also be real.

$$Let\ \hat{H}|a\rangle = \hbar\omega_a|a\rangle \tag{44a}$$

$$and\ \hat{H}|b\rangle = \hbar\omega_b|b\rangle \tag{44b}$$

Then the eigenvalues of $\hat{\hat{L}}$ are shown to be:

$$\begin{aligned}
\hat{\hat{L}}||a\rangle\langle b|\rangle &\equiv |(\hat{H}\otimes\mathbb{1})|a\rangle\langle b| - (\mathbb{1}\otimes\hat{H})|a\rangle\langle b|\rangle \qquad \text{from (30)} \\
&\equiv |\hat{H}(|a\rangle\langle b|)\mathbb{1} - \mathbb{1}(|a\rangle\langle b|)\hat{H}\rangle \\
&\equiv |\hbar\omega_a|a\rangle\langle b| - |a\rangle(\hbar\omega_b\langle b|)\rangle \\
&\equiv \hbar(\omega_a-\omega_b)||a\rangle\langle b|\rangle
\end{aligned} \tag{45}$$

$\hat{\hat{L}}$ will clearly be diagonal in the basis spanned by these operator kets, $\{||a\rangle\langle b|\rangle\}$. We consider a simple example similar to a 1-spin NMR system. Writing the Hamiltonian $\hat{H}$ in (44) in the basis $\{|a\rangle,|b\rangle\}$, we get the following diagonal form:

$$\hat{H} = \frac{\hbar}{2}\begin{pmatrix} \omega_a & 0 \\ 0 & \omega_b \end{pmatrix} \tag{46a}$$

whereas for the case of a single spin in the laboratory frame, $\omega_a = \omega_0$ and $\omega_b = -\omega_0$. Expressing the Liouvillian corresponding to (46a) in the $\{||a\rangle\langle b|\rangle\} = \{||0\rangle\langle 0|\rangle, ||0\rangle\langle 1|\rangle, ||1\rangle\langle 0|\rangle, ||1\rangle\langle 1|\rangle\}$ basis:

$$\hat{\hat{L}} = \frac{\hbar}{2} \quad \begin{array}{c c} \begin{array}{cccc} ||0\rangle\langle 0|\rangle & ||0\rangle\langle 1|\rangle & ||1\rangle\langle 0|\rangle & ||1\rangle\langle 1|\rangle \end{array} & \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \omega_a-\omega_b & 0 & 0 \\ 0 & 0 & -(\omega_a-\omega_b) & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} & \begin{array}{c} ||0\rangle\langle 0|\rangle \\ ||0\rangle\langle 1|\rangle \\ ||1\rangle\langle 0|\rangle \\ ||1\rangle\langle 1|\rangle \end{array} \end{array} \tag{46b}$$

The Liouvillian in (46b) is also diagonal. The eigenvalue corresponding to $||a\rangle\langle a|\rangle$ is 0, which is doubly degenerate for the 1-spin example. This degeneracy does not appear in the corresponding Hilbert space. Generalizing this to higher-spin systems, the eigenvalue 0 is always degenerate and corresponds to the stationary states of the system.

The superpropagator corresponding to $\hat{\hat{L}}$ is:

$$\hat{\hat{U}}(t,0) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \exp(-it(\omega_a-\omega_b)\hbar/2) & 0 & 0 \\ 0 & 0 & exp(it(\omega_a-\omega_b)\hbar/2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{46c}$$

8. References

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