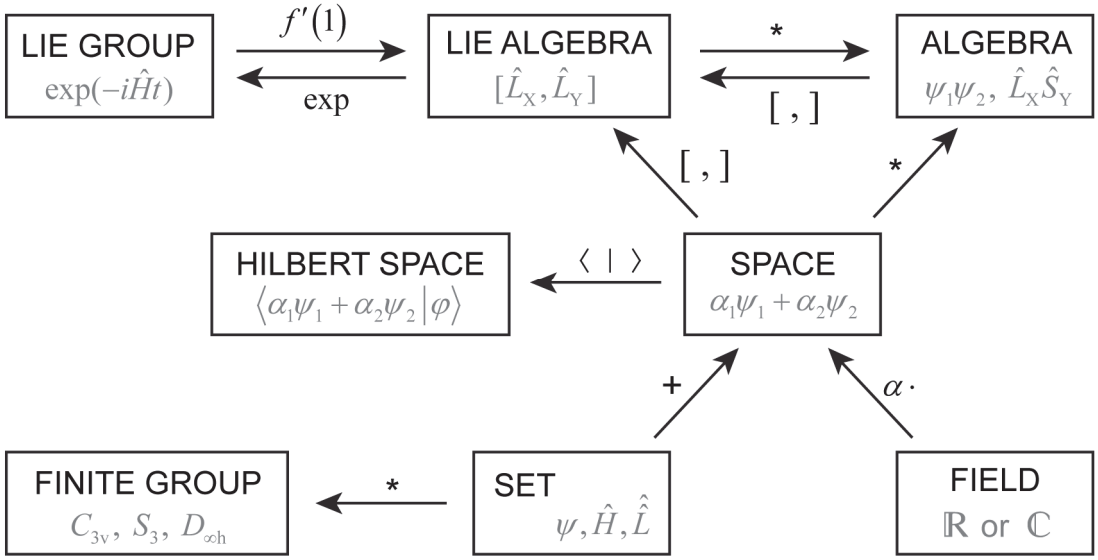
Module II, Lecture 01: Vector and Matrix Spaces

Much of the success of magnetic resonance spectroscopy and spin dynamics at large is due to the elegant mathematical structure of the corresponding quantum mechanical equations of motion. Lie algebraic arguments, in particular, are immensely powerful – the existence and structure of the Periodic Table of elements, for example, is a consequence of the properties of the rotation group.



The following lectures will be dealing with spaces, groups and algebras that appear in the spin dynamics context. We will not explore the properties of sets and fields (although they are of interest to mathematicians), but start with the first practically useful object in the hierarchy above – a space.

Function and operator spaces

Basic equations of motion (Schrödinger equation for wavefunctions and Liouville – von Neumann equation for density matrices) are linear with respect to the wavefunction and the density matrix, that is:

1. A sum of any two solutions is also a solution:

$$\begin{aligned}\frac{\partial}{\partial t}|\psi_{1,2}\rangle = -i\hat{H}|\psi_{1,2}\rangle \quad &\Rightarrow \quad \frac{\partial}{\partial t}\left(|\psi_1\rangle + |\psi_2\rangle\right) = -i\hat{H}\left(|\psi_1\rangle + |\psi_2\rangle\right)\\ \frac{\partial}{\partial t}\hat{\rho}_{1,2} = -i\left[\hat{H}, \hat{\rho}_{1,2}\right] \quad &\Rightarrow \quad \frac{\partial}{\partial t}\left(\hat{\rho}_1 + \hat{\rho}_2\right) = -i\left[\hat{H}, \hat{\rho}_1 + \hat{\rho}_2\right]\end{aligned} \tag{1}$$

2. Any solution multiplied by any complex scalar is also a solution:

$$\begin{aligned}\frac{\partial}{\partial t}|\psi\rangle = -i\hat{H}|\psi\rangle \quad &\Rightarrow \quad \frac{\partial}{\partial t}\left(\alpha|\psi\rangle\right) = -i\hat{H}\left(\alpha|\psi\rangle\right)\\ \frac{\partial}{\partial t}\hat{\rho} = -i\left[\hat{H}, \hat{\rho}\right] \quad &\Rightarrow \quad \frac{\partial}{\partial t}\left(\alpha\hat{\rho}\right) = -i\left[\hat{H}, \alpha\hat{\rho}\right]\end{aligned} \tag{2}$$

3. A zero is a solution.

The sets of solutions to Schrödinger and LvN equations are therefore closed with respect to addition and multiplication by a complex scalar. Such sets are known in mathematics as *spaces* (of vectors, functions, operators, *etc.*). Generally speaking, any set V over a scalar field F is called a *space* if:

1. A binary addition operation is defined in V, such that

$$\forall a,b\in V\ \ \exists c\in V:\ a+b=c \tag{3}$$

2. A multiplication by a scalar (from the field F) is defined in V, such that

$$\forall \alpha\in F\ \ \forall a\in V\ \ \exists b\in V:\ \alpha a=b \tag{4}$$

3. The following properties hold:

$\forall a,b\in V\ \ a+b=b+a$	(commutativity of "+")
$\forall a,b,c\in V\ \ a+(b+c)=(a+b)+c$	(associativity of "+")
$\exists!0\in V:\ \ a+0=a\ \ \forall a\in V$	(unique zero element)
$\forall a\in V\ \ \exists!(-a):\ \ a+(-a)=0$	(unique opposite)
$\forall \alpha,\beta\in F\ \ \forall a\in V\ \ \alpha(\beta a)=(\alpha\beta)a$	(associativity of multiplication by scalars)
$\forall \alpha\in F\ \ \forall a,b\in V\ \ \alpha(a+b)=\alpha a+\alpha b$	(distributivity of multiplication by scalars)
$\forall \alpha,\beta\in F\ \ \forall a\in V\ \ (\alpha+\beta)a=\alpha a+\beta a$	(distributivity of multiplication by scalars)
$\exists!1\in F:\ \ 1a=a\ \ \forall a\in V$	(unique unit element in F)

It is easy to see that these properties are obeyed by vectors and matrices of any dimension, as well as by quantum mechanical operators and their commutation superoperators – in all cases a linear combination of elements of a set belongs to the same set: *e.g.* any linear combination of Hermitian operators is also a Hermitian operator.

Linear combinations, linear dependence and basis sets

An element $b\in V$ is called a *linear combination* of elements $a_1,\ldots,a_n\in V$ if such scalars $\alpha_1,\ldots,\alpha_n$ exist in the field F, that $b=\alpha_1a_1+\ldots+\alpha_na_n$. A system of elements $a_1,\ldots,a_n$ is called *linearly dependent* if

$$\alpha_1a_1+\ldots+\alpha_na_n=0 \tag{5}$$

for some $\alpha_i\in F$ that are not all zero. In practice this means that one of the elements $a_1,\ldots,a_n$ can be represented as a linear combination of others.

Theorem: let V be a space, $a_1,\ldots,a_n,b\in V$ and

$$b=\alpha_1a_1+\ldots+\alpha_na_n \tag{6}$$

where $\alpha_i\in F$. This expansion of b in terms of $a_1,\ldots,a_n$ is unique if and only if elements $a_1,\ldots,a_n$ are linearly independent. The proof is left as an exercise.

A *basis* of a set of elements is a linearly independent subset, such that all elements of the set can be represented as its linear combinations. The number of elements in the basis of a space is called space *dimension*. All basis sets of a given space have the same number of elements.

If $a_1,\ldots,a_n$ is a basis set of V, then every element $b\in V$ can be represented as

$$b=\sum_k\alpha_ka_k \tag{7}$$

This relation is called an *expansion* of element b in the basis $a_1,...,a_n$. This expansion is unique. Therefore, once a basis set is fixed, an element (of any nature) can be represented by a string of numbers $\alpha_1,...,\alpha_n$. Those are known as *expansion coefficients* or *coordinates*.

Subspaces, their sums and products

If V is a space over a field F and $L\subseteq V$, then L is called a *subspace* of V if

1. L is closed under addition: $\forall a,b\in L\;\; a+b\in L$
2. L is closed under multiplication by a scalar: $\forall a\in L\;\; \forall\alpha\in F\;\; \alpha a\in L$

A *sum* $L_1+...+L_n$ of subspaces $L_1,...,L_n$ of a space V is a set of all elements of the form $a=l_1+...+l_n$, where $l_k\in L_k$. Such a sum is also a subspace of V. A sum of L_i and L_j is called a *direct sum* and denoted $L_i\oplus L_j$ if the subspaces only have the zero element in common, *i.e.* $L_i\cap L_j=\{0\}$.

Theorem: the dimension of a sum of two subspaces is equal to the sum of their dimensions minus the dimension of their intersection. The proof is left as an exercise.

For a direct sum of two subspaces, the following statements are equivalent:

1. $L_3=L_1\oplus L_2$
2. $L_1\cap L_2=\{0\},\;\; L_3=L_1+L_2$
3. $\dim(L_1)+\dim(L_2)=\dim(L_3),\;\; L_3=L_1+L_2$
4. $L_1=\mathrm{span}\{a_1,...,a_n\},\; L_2=\mathrm{span}\{b_1,...,b_m\}\;\Rightarrow\; L_3=\mathrm{span}\{a_1,...,a_n,b_1,...,b_m\}$

A *Cartesian product* of two spaces V_1 and V_2 is the set of all possible ordered pairs of elements, in which the first component belongs to V_1 and the second component belongs to V_2:

$$V_1\times V_2=\{(\varphi,\psi)\,|\,\varphi\in V_1,\psi\in V_2\} \tag{8}$$

The space of all linear combinations of such pairs with coefficients taken from the field F is called the *tensor product* of vector spaces:

$$V_1\otimes V_2=\left\{\sum_{ij}a_{ij}(\varphi_i,\psi_j)\,|\,\varphi_i\in V_1,\psi_j\in V_2\right\} \tag{9}$$

The pairs (φ,ψ), where φ belongs to the basis of V_1 and ψ belongs to the basis of V_2, are denoted $\varphi\otimes\psi$. The tensor product operation is distributive from both sides with respect to addition:

$$\begin{aligned}(\varphi_1+\varphi_2)\otimes\psi&=\varphi_1\otimes\psi+\varphi_2\otimes\psi\\ \varphi\otimes(\psi_1+\psi_2)&=\varphi\otimes\psi_1+\varphi\otimes\psi_2\end{aligned} \tag{10}$$

and associative with respect to multiplication by a scalar:

$$(c\varphi)\otimes\psi=\varphi\otimes(c\psi)=c(\varphi\otimes\psi),\qquad c\in F \tag{11}$$

Linear operators

Let V and W be spaces over the same field F and M be such a map from V to W that for any $\alpha\in F$ and any $a,b\in V$ the following is true:

$$M(\alpha a)=\alpha M(a)\qquad M(a+b)=M(a)+M(b) \tag{12}$$

Then M is called a *linear operator* (or *homomorphism*) and $M(a)$ is called the *image* of a in W. The relationships above are often abbreviated as $M: V \to W$.

Theorem: let V and W be spaces over the same field F, $\{a_1,...,a_n\}$ be a basis set of V and $\{b_1,...,b_n\}$ be a basis set of W. Then there is one and only one such linear operator M that $M(a_k) = b_k$ for all k. The proof is left as an exercise.

A linear operator performing a $M: V \to V$ map is called a *linear transformation* (or *automorphism*) of the space V. If V and W are spaces over the same field and M is a linear operator mapping V into W in a mutually unique and reversible way, then M is called an *isomorphism* and spaces V and W are called *isomorphous*.

Theorem: isomorphous spaces have the same dimension. The proof is left as an exercise.

Corollary: all *n*-dimensional spaces over a field F are isomorphous to F^n.

We would often abstract from the specific nature of the elements of the spaces we are dealing with and work with their images in $\mathbb{R}^n$ and $\mathbb{C}^n$, whose elements are n-vectors. The linear operators mapping one set of vectors into another would therefore become matrices. More precisely, if $A = \{a_1,...,a_n\}$ and $B = \{b_1,...,b_k\}$ are basis sets of spaces V and W and $M: V \to W$ is a linear operator, then a matrix $\mathbf{M}$ is called a *matrix representation* of M in the pair of basis sets A and B, if $\mathbf{M}|x\rangle = |y\rangle$, where $|x\rangle$ is an element from V, written as a column of coefficients in basis A and $|y\rangle$ is the image of $|x\rangle$ in W, written as a column of coefficients in basis B.

Hilbert spaces

The definition of space given above does not include any notion of distance or angle. To create those, a map must be introduced from pairs of elements into the field of complex scalars:

$$\langle\ |\ \rangle : (V \times V) \ \to\ \mathbb{C} \tag{13}$$

This map is called an *inner product* and a space equipped with this map is called a *Hilbert space* if:

1. $\forall \psi \in V \quad \langle\psi|\psi\rangle \geq 0$
2. $\forall \varphi,\psi \in V \quad \langle\varphi|\psi\rangle = \langle\psi|\varphi\rangle^*$
3. $\forall \varphi,\psi,\chi \in V \quad \forall \alpha,\beta \in \mathbb{C} \quad \langle\alpha\varphi+\beta\psi|\chi\rangle = \alpha\langle\varphi|\chi\rangle + \beta\langle\psi|\chi\rangle$
4. $\langle\psi|\psi\rangle = 0 \quad \Rightarrow \quad \psi = 0$
5. $\forall \varphi,\psi \in V \quad \sqrt{\langle\psi|\psi\rangle} + \sqrt{\langle\varphi|\varphi\rangle} \geq \sqrt{\langle\psi+\varphi|\psi+\varphi\rangle}$

These conditions are satisfied by a large variety of mathematical operations. In spaces of square-integrable functions encountered in quantum mechanics, the following inner product is commonly used:

$$\langle\varphi|\psi\rangle = \int_{-\infty}^{\infty} \varphi^*(x)\psi(x)\,dx \qquad \langle\varphi|\psi\rangle = \sum_n \varphi_n^*\psi_n \tag{14}$$

Where the integral is used in continuous representations and the sum over the elements of the corresponding vectors is used in discrete representations. If the functions depend on more than one argument, all continuous arguments are integrated over and all discrete arguments are summed over.

The inner product of an element with itself is known as the square of its *norm*. The norm inherits its definition from the inner product. For the inner product introduced in Equations (14), we have:

$$\left\|\psi\right\| = \sqrt{\left\langle\psi\middle|\psi\right\rangle} = \left(\int_{-\infty}^{\infty}\psi^{*}\left(x\right)\psi\left(x\right)dx\right)^{1/2} = \left(\int_{-\infty}^{\infty}\left|\psi\left(x\right)\right|^{2}dx\right)^{1/2}$$
$$\left\|\psi\right\| = \sqrt{\left\langle\psi\middle|\psi\right\rangle} = \left(\sum_{n}\psi_{n}^{*}\psi_{n}\right)^{1/2} = \left(\sum_{n}\left|\psi_{n}\right|^{2}\right)^{1/2} \tag{15}$$

with the same extension to the case where the functions depend on multiple continuous and discrete arguments: all continuous arguments are integrated over and all discrete arguments are summed over.

The presence of the inner product operation in Hilbert spaces allows us to move between continuous and discrete representations. If V is an n-dimensional space of continuous square-integrable functions and $\left\{\left|\varphi_{k}\right\rangle\right\}$ is an *orthonormal basis set* of V:

$$\forall\left|\psi\right\rangle\in V \quad \left|\psi\right\rangle = \sum_{k}\psi_{k}\left|\varphi_{k}\right\rangle \quad \left\|\varphi_{k}\right\| = 1 \quad \left\langle\varphi_{k}\middle|\varphi_{n}\right\rangle = \delta_{kn} \tag{16}$$

the space of the expansion coefficient vectors $\left\{\psi_{k}\right\}$ is a subspace of $\mathbb{C}^{n}$ and is called a discrete representation of V in $\mathbb{C}^{n}$. The connection between the continuous and the discrete versions of the inner product for a pair of functions is easily established:

$$\left|\psi\right\rangle = \sum_{k}\psi_{k}\left|\varphi_{k}\right\rangle \qquad \left|\chi\right\rangle = \sum_{k}\chi_{k}\left|\varphi_{k}\right\rangle$$
$$\left\langle\psi\middle|\chi\right\rangle = \int_{-\infty}^{\infty}\psi^{*}\left(x\right)\chi\left(x\right)dx = \sum_{mk}\psi_{m}^{*}\chi_{k}\int_{-\infty}^{\infty}\varphi_{m}^{*}\left(x\right)\varphi_{k}\left(x\right)dx = \sum_{mk}\psi_{m}^{*}\chi_{k}\delta_{mk} = \sum_{k}\psi_{k}^{*}\chi_{k} \tag{17}$$

It is easy to see that quantum mechanical wavefunctions and state vectors belong to Hilbert spaces of various dimensions. Discrete representations are often preferred because digital computers are better adapted to multiplying vectors and matrices than to performing analytical transformations.

Superoperator spaces

The set of matrices of a given dimension satisfies the definition of a space given in the previous lecture – it is closed under addition and multiplication by a scalar. It is also associative, commutative and distributive in both operations. The matrices populating this space accomplish a linear transformation (*aka endomorphism*) of some vector space V, and their space is therefore denoted $\mathrm{End}\left(V\right)$. Invertible endomorphisms are called *automorphisms* and the corresponding subspace is denoted $\mathrm{Aut}\left(V\right)$.

Because $\mathrm{End}\left(V\right)$ is itself a space, we can also consider the space of its linear transformations $\mathrm{End}\left(\mathrm{End}\left(V\right)\right)$, the elements of which would be linear maps between matrices. Because matrices populating $\mathrm{End}\left(V\right)$ are known as *operators* in quantum mechanics, the elements of $\mathrm{End}\left(\mathrm{End}\left(V\right)\right)$ are known as *superoperators*, a simple example being the Hamiltonian commutation superoperator that transforms $\mathrm{End}\left(V\right)$ by commuting its elements with the Hamiltonian.

Theorem: the space $M_{N}\left(F\right)$ of all $N\times N$ matrices over a field F is N^{2} dimensional. More generally, a space of endomorphisms of an N-dimensional space is N^{2}-dimensional. The proof is left as an exercise.

Corollary: the space of all linear operators $M:\mathbb{C}^N\rightarrow\mathbb{C}^N$ is isomorphous to $\mathbb{C}^{N^2}$.

Corollary: the space of all linear superoperators $L:M_N\left(\mathbb{C}\right)\rightarrow M_N\left(\mathbb{C}\right)$ is isomorphous to $\mathbb{C}^{N^4}$.

We can conclude that the space of all operators acting on a given space is itself a space with the square of the dimension of the original space. The space of all superoperators transforming the operators that act on a given space have the dimension that is the fourth power of the dimension of the original space. The space of all endomorphisms of $\mathbb{C}^N$ (often with the superoperator space implicitly defined as well) is colloquially known in spin dynamics as the *Liouville space*. In principle, further layers of endomorphisms (*hyperoperators, etc.*) are possible, but they currently have only limited use in spin dynamics.

Every superoperator in $M_{N^2}\left(\mathbb{C}\right)$ can be expressed as:

$$\hat{\hat{P}}\hat{\rho}=\sum_{nk}p_{nk}\hat{S}_n\hat{\rho}\hat{S}_k\qquad\qquad\hat{S}_n,\hat{S}_k\in M_N\left(\mathbb{C}\right)\tag{18}$$

but such a representation is not in practice convenient because of the computational overhead associated with double-sided matrix multiplication and storage of sparse matrix stacks. In practical calculations the density matrix is usually stretched column-wise into a vector and a representation of the superoperator is computed in the resulting vector space.

Theorem: the matrix representation of a superoperator $\hat{\hat{C}}$ accomplishing two-sided multiplication $\hat{\hat{C}}\hat{\rho}=\hat{A}\hat{\rho}\hat{B}$ is $\hat{\hat{C}}\left|\hat{\rho}\right\rangle=\left[B^{\mathrm{T}}\otimes A\right]\left|\hat{\rho}\right\rangle$, in which the vector representation of the density matrix $\left|\hat{\rho}\right\rangle$ is obtained by stretching the original matrix $\hat{\rho}$ vertically column-wise.

Proof: in the indexed notation for the corresponding matrices we have:

$$\left[\hat{\hat{C}}\hat{\rho}\right]_{ij}=\left[\hat{A}\hat{\rho}\hat{B}\right]_{ij}=\sum_{kn}A_{ik}\rho_{kn}B_{nj}=\sum_{kn}\left(A_{ik}B_{nj}\right)\rho_{kn}\tag{19}$$

After replacing pairs of indices k,n and i,j with single indices (N is matrix dimension):

$$\begin{array}{lll}r=N\left(j-1\right)+i & \Rightarrow & i=r\left(\mathrm{mod}\,N\right),\quad j=r(\mathrm{div}\,N)+1\\ s=N\left(n-1\right)+k & \Rightarrow & k=s\left(\mathrm{mod}\,N\right),\quad n=s(\mathrm{div}\,N)+1\end{array}\tag{20}$$

we get the expression for the matrix elements of $\hat{\hat{C}}$ in the stretched representation:

$$\left[\hat{\hat{C}}\hat{\rho}\right]_r=\sum_s C_{rs}\rho_s,\qquad C_{N(j-1)+i,N(n-1)+k}=A_{ik}B_{nj}=A_{ik}B_{jn}^{\mathrm{T}}\tag{21}$$

We can now inspect the entries of the resulting matrix $\hat{\hat{C}}$. It appears to have multiple $N\times N$ cells, enumerated by j,n indices. Each cell, enumerated by i,k indices, appears to be a copy of $\hat{A}$ multiplied by B_{jn}^{T}. This is the structure of the Kronecker product $B^{\mathrm{T}}\otimes A$.

Corollary: the matrix representation of a commutation superoperator $\hat{\hat{L}}\equiv[\hat{H},\,]$ acting on a stretched (column-wise linear indexing of elements) matrix space $M_N\left(\mathbb{C}\right)$ is given by $\hat{\hat{L}}=\hat{E}\otimes\hat{H}-\hat{H}^{\mathrm{T}}\otimes\hat{E}$, where $\hat{E}$ is a unit matrix in $M_N\left(\mathbb{C}\right)$.

One often encountered situation in which commutation superoperators appear is the transformation from the double-sided to the single-sided time propagation:

$$\hat{\rho}(t+\Delta t)=e^{-i\hat{H}\Delta t}\hat{\rho}(t)e^{i\hat{H}\Delta t}=e^{-i\hat{\hat{H}}\Delta t}\hat{\rho}(t)=$$
$$=\left[\sum_{n=0}^{\infty}\frac{(-i\Delta t)^n}{n!}\hat{\hat{H}}^n\right]\hat{\rho}=\sum_{n=0}^{\infty}\frac{(-i\Delta t)^n}{n!}[\hat{H},[\hat{H},[...[\hat{H},\hat{\rho}]]]] \tag{22}$$

where $\hat{\hat{H}}=[\hat{H},\ ]$ denotes a commutation superoperator such that $\hat{\hat{H}}\hat{\rho}=[\hat{H},\hat{\rho}]=\hat{H}\hat{\rho}-\hat{\rho}\hat{H}$. Another useful practical consequence of the theorem above is the expression for the exponential of a commutation superoperator:

$$\exp\left(\hat{L}\otimes\hat{E}+\hat{E}\otimes\hat{S}\right)=\exp\left(\hat{L}\right)\otimes\exp\left(\hat{S}\right)$$
$$\Downarrow \tag{23}$$
$$\exp\left[-i\left(\hat{E}\otimes\hat{H}-\hat{H}^{\mathrm{T}}\otimes\hat{E}\right)t\right]=\exp\left(i\hat{H}^{\mathrm{T}}t\right)\otimes\exp\left(-i\hat{H}t\right)$$

which avoids the computationally expensive exponentiation of an $N^2\times N^2$ matrix and improves the memory footprint of the time propagator calculation.

Matrix scalar products

The set of $N\times N$ matrices (or, equivalently, the set of all linear transformations of an N-dimensional vector space) satisfies the definition of a space given in the previous lecture – it is closed under addition and multiplication by a scalar. It is also associative, commutative and distributive in both operations. To make $M_N(\mathbb{C})$ into a Hilbert space, an inner product must be defined with the following properties:

1. $\forall\hat{L}\in M_N(\mathbb{C})\quad\left\langle\hat{L}\middle|\hat{L}\right\rangle\geq 0$
2. $\forall\hat{L},\hat{S}\in M_N(\mathbb{C})\quad\left\langle\hat{L}\middle|\hat{S}\right\rangle=\left\langle\hat{S}\middle|\hat{L}\right\rangle^*$
3. $\forall\hat{L},\hat{S},\hat{I}\in M_N(\mathbb{C})\quad\forall\alpha,\beta\in\mathbb{C}\quad\left\langle\hat{L}\middle|\alpha\hat{S}+\beta\hat{I}\right\rangle=\alpha\left\langle\hat{L}\middle|\hat{S}\right\rangle+\beta\left\langle\hat{L}\middle|\hat{I}\right\rangle$
4. $\forall\hat{L}\in M_N(\mathbb{C})\quad\left\langle\hat{L}\middle|\hat{L}\right\rangle=0\ \Rightarrow\ \hat{L}=0$
5. $\forall\hat{L},\hat{S}\in M_N(\mathbb{C})\quad\left\|\hat{L}\right\|+\left\|\hat{S}\right\|\geq\left\|\hat{L}+\hat{S}\right\|,\qquad\left\|\hat{L}\right\|=\sqrt{\left\langle\hat{L}\middle|\hat{L}\right\rangle}$

There are infinitely many binary operations that would satisfy these conditions, but the only inner product that matches naturally the calculus of probabilities inherent in quantum mechanics is:

$$\left\langle\hat{L}\middle|\hat{S}\right\rangle=\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{S}\right) \tag{24}$$

where the dagger denotes the conjugate-transpose operation. All the properties listed above may be proven by direct inspection:

- $\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{L}\right)=\sum_{kn}\left[\hat{L}^{\dagger}\right]_{nk}L_{kn}=\sum_{kn}L_{kn}^{*}L_{kn}=\sum_{kn}\left|L_{kn}\right|^2\geq 0$, and only $=0$ if all $L_{nk}=0$
- $\mathrm{Tr}\left[\hat{L}^{\dagger}\left(\alpha\hat{S}+\beta\hat{I}\right)\right]=...=\alpha\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{S}\right)+\beta\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{I}\right)$
- $\left\|\hat{L}+\hat{S}\right\|^2=\left\|\hat{L}\right\|^2+\left\|\hat{S}\right\|^2+\left\langle\hat{L}\middle|\hat{S}\right\rangle+\left\langle\hat{S}\middle|\hat{L}\right\rangle\leq\left\|\hat{L}\right\|^2+\left\|\hat{S}\right\|^2+2\left\|\hat{L}\right\|\left\|\hat{S}\right\|=\left(\left\|\hat{L}\right\|+\left\|\hat{S}\right\|\right)^2$

Note that the matrix scalar product, as it is defined above, transforms into a vector scalar product if a matrix is stretched column-wise into a vector:

$$\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{S}\right)=\sum_{nk}L_{nk}^{*}S_{nk}=\sum_{n}L_{n}^{*}S_{n} \tag{25}$$

if the matrices are re-indexed linearly as $\{n,k\}\rightarrow\{n\}$. This matrix stretching is used a lot in spin dynamics to construct matrix representations of superoperators. Another important point is that the calculation of the trace scalar product does not actually require a matrix-matrix multiplication, which has an $O\left(N^3\right)$ cost with the matrix dimension as well as irregular memory access patterns – it may instead be calculated using the Hadamard product, which is defined as follows:

$$\hat{L}\circ\hat{S}=\sum_{nk}L_{nk}S_{nk}\qquad\Rightarrow\qquad\mathrm{Tr}\left(\hat{L}^{\dagger}\hat{S}\right)=\sum_{nk}L_{nk}^{*}S_{nk}=\hat{L}^{*}\circ\hat{S} \tag{26}$$

where the star denotes element-wise conjugation. In the dense case the Hadamard product requires $O\left(N^2\right)$ multiplications, and in the sparse case only $O\left(\min\left\{N_{\mathrm{NZ}}\left(\hat{L}\right),N_{\mathrm{NZ}}\left(\hat{S}\right)\right\}\right)$ – the cost is linear in the number of non-zero elements.

Inner products on the space of superoperators and further up the hierarchy may be defined in a similar way – the previous space is mapped onto a vector space by stretching its matrices, which generates a matrix representation of the current space. At that point, the inner product may be defined as above. The table below gives a summary of such scalar products for the three Hilbert spaces encountered in practical spin dynamics simulations.

Name	Continuous representation	Continuous scalar product	Discrete representation	Discrete scalar product
Superoperator space	superoperators	$\sum_{\hat{M}}\left\langle\hat{M}\middle\vert\hat{\hat{P}}^{\dagger}\hat{\hat{Q}}\middle\vert\hat{M}\right\rangle$	$n^2\times n^2$ matrices	$\mathrm{Tr}\left(P^{\dagger}Q\right)$
Liouville space	operators, density matrices	$\sum_{\varphi}\left\langle\varphi\middle\vert\hat{M}^{\dagger}\hat{K}\middle\vert\varphi\right\rangle$	$n\times n$ matrices	$\mathrm{Tr}\left(M^{\dagger}N\right)$
Hilbert space	wavefunctions	$\int\varphi^{*}(x)\psi(x)dx$	n-vectors	$\sum_{n}\varphi_n^{*}\psi_n$

Normalization-commutation dilemma

In Hilbert spaces it is usually convenient to work with orthonormalized basis sets. It is easy to see, however, that the matrices that obey the angular momentum commutation relations:

$$\hat{S}_{\mathrm{X}}=\begin{pmatrix}0 & 1/2\\ 1/2 & 0\end{pmatrix}\qquad\hat{S}_{\mathrm{Y}}=\begin{pmatrix}0 & -i/2\\ i/2 & 0\end{pmatrix}\qquad\hat{S}_{\mathrm{Z}}=\begin{pmatrix}1/2 & 0\\ 0 & -1/2\end{pmatrix} \tag{27}$$
$$[\hat{S}_{\mathrm{X}},\hat{S}_{\mathrm{Y}}]=i\hat{S}_{\mathrm{Z}}\qquad[\hat{S}_{\mathrm{Z}},\hat{S}_{\mathrm{X}}]=i\hat{S}_{\mathrm{Y}}\qquad[\hat{S}_{\mathrm{Y}},\hat{S}_{\mathrm{Z}}]=i\hat{S}_{\mathrm{X}}$$

are orthogonal, but do not have unit norms. Furthermore, their norm is different for different total spin:

$$\left\|\hat{S}_{\mathrm{Z}}^{(1/2)}\right\|=1/\sqrt{2},\qquad\left\|\hat{S}_{\mathrm{Z}}^{(1)}\right\|=\sqrt{2},\qquad\left\|\hat{S}_{\mathrm{Z}}^{(3/2)}\right\|=\sqrt{5},\qquad\ldots \tag{28}$$

If an attempt is made to normalize them, the commutation relations get broken. This is a delicate situation – as we shall see later, commutation relations are more valuable than the normalization. For this

reason, most operator basis sets in magnetic resonance simulations are not normalized and this fact has to be accounted for during basis transformations and the calculation of observables.

Common basis sets

The choice of a basis set for a given simulation is dictated entirely by the physical nature of the system – a well-chosen set of basis operators must be invariant under the greatest possible number of interactions in the system, so as to minimize the amount of dynamics that a numerical simulation has to account for. Clearly, the best possible basis set from this point of view would be composed of eigenoperators of the Hamiltonian commutation superoperator $\hat{\hat{H}}$:

$$\hat{\hat{H}}\hat{S}_k = \left[\hat{H}, \hat{S}_k\right] = h_k \hat{S}_k \tag{29}$$

because such a basis is invariant under the action of $\hat{\hat{H}}$. For practical reasons (the expense of diagonalizing $\hat{\hat{H}}$) this basis is not usually available. Still, basis sets that are invariant under specific parts of $\hat{\hat{H}}$ are known.

Hamiltonians of high-field NMR and ESR experiments are dominated by Zeeman interactions, and so the best basis sets should be composed of operators that are invariant under the commutation with $\hat{L}_Z$. In the simple case of a collection of spin-1/2 particles, these are direct products of

$$\hat{S}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \hat{S}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_Z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \qquad \hat{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{30}$$

and in the more complicated case of a collection of particles of arbitrary spin these operators are generalized (see the rotations lecture) into irreducible spherical tensors.

A similar basis set (and the default choice in most everyday calculations) is composed of direct products of Pauli matrices and (in the case of high-spin particles) their powers:

$$\hat{S}_X = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \qquad \hat{S}_Y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \qquad \hat{S}_Z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \qquad \hat{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{31}$$

These matrices are particularly convenient as building blocks of spin Hamiltonians, because they correspond directly to the Cartesian projections of spin and observable magnetization.

In the total spin representation, the different spin-projection states $|l,m\rangle$ are mutually orthogonal and it is therefore natural to represent them by vectors pointing along different coordinates:

$$|l,l\rangle = \begin{pmatrix} 1 & 0 & \ldots & 0 \end{pmatrix}^T, \qquad |l,l-1\rangle = \begin{pmatrix} 0 & 1 & \ldots & 0 \end{pmatrix}^T, \qquad \cdots \quad |l,-l\rangle = \begin{pmatrix} 0 & 0 & \ldots & 1 \end{pmatrix}^T \tag{32}$$

In the individual spin representation, the basis sets can be built for individual spins and then crossed together using Kronecker products. The basis for the operator space can then be built as:

$$\hat{S} = \sum_{l_1,l_2,m_1,m_2} a^{l_1,l_2}_{m_1,m_2} |l_1,m_1\rangle\langle l_2,m_2|$$

This basis is known as *projector basis* or *polarization basis*. It is not in practice convenient because its elements do not obey common spin system symmetries are not invariant under any component of practically encountered Hamiltonians.