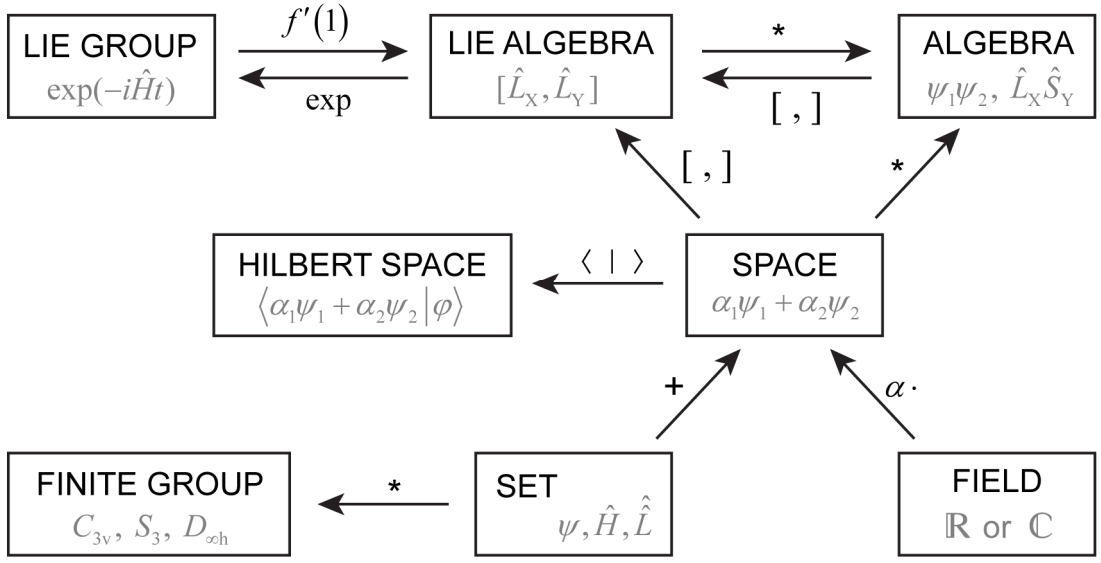
Module II, Lecture 02: Groups and Algebras

Before we proceed to introduce groups and algebras, it is useful to review the diagram from the previous lecture and note that we have now fully explored the part dealing with spaces and Hilbert spaces.



Rigorous definitions are given below, but for overview purposes the relationship between spaces, groups and algebras can be illustrated on spin operators:

Space: operators and their linear combinations. Norm and inner product optionally defined. No products between operators or inverse operators.

Group: operators, their products and inverses. All operators must be invertible. No linear combinations, norms, inner products or multiplication by scalars.

Algebra: operators, their linear combinations, products and functions. Norm and scalar product optionally defined.

The set of quantum mechanical operators, as conventionally viewed by physicists, is therefore an algebra consisting of a space of operators with their superposition used as product. Certain sets of operators (notably matrix exponentials) are groups under that product. The scalars come from $\mathbb{R}$ or $\mathbb{C}$.

Semigroups and groups

A set G equipped with an associative binary product $*: G\times G \to G$ is called a *semigroup* if it is closed under that binary product:

$$\forall g,h \in G \quad gh \in G \tag{1}$$

If additionally the following relations hold in G:

1. $\exists! e \in G: \quad \forall g \in G \quad eg = g$ (there exists a unique unit element)
2. $\forall g \in G \quad \exists! g^{-1} \in G: \quad gg^{-1} = e$ (for every element there exists a unique inverse)

Then the set is called a *group*. The elements of G need not commute, but if they do, the group is called *Abelian*. The number of elements in the group is called the *order of the group*. A subset of G which is itself a group is called a *subgroup* of G. Two groups G and H are called *isomorphous* if there exists a one-to-one correspondence $\varphi: G \to H$ such that $\forall g_1, g_2 \in G,\ \varphi(g_1 g_2) = \varphi(g_1)\varphi(g_2)$.

Examples of groups commonly encountered in spin dynamics include:

1. The set of all time propagators $\exp(-i\hat{\hat{H}}t)$ under a static Hamiltonian $\hat{H}$. It is called the *propagator group* of $\hat{H}$. The properties listed above are easy to demonstrate – a product of any two propagators is also a propagator:

$$\forall e^{-i\hat{\hat{H}}t_1}, e^{-i\hat{\hat{H}}t_2} \in G \qquad e^{-i\hat{\hat{H}}t_1} e^{-i\hat{\hat{H}}t_2} = e^{-i\hat{\hat{H}}(t_1+t_2)} \in G \tag{2}$$

   there is a unit propagator that does nothing:

$$\exists! \hat{\hat{E}} \in G: \qquad \forall e^{-i\hat{\hat{H}}t} \in G \qquad \hat{\hat{E}} e^{-i\hat{\hat{H}}t} = e^{-i\hat{\hat{H}}t} \tag{3}$$

   And for every propagator there is a unique inverse that takes the system back in time:

$$\forall e^{-i\hat{\hat{H}}t} \in G \qquad \exists! \left[e^{-i\hat{\hat{H}}t} \right]^{-1} = e^{i\hat{\hat{H}}t} \in G: \qquad e^{-i\hat{\hat{H}}t} e^{i\hat{\hat{H}}t} = \hat{\hat{E}} \tag{4}$$

   Because the Hamiltonian commutes with itself, this is an Abelian group. If relaxation is present, the propagators do not, in general, have a unique inverse – the set of all time propagators under a Liouvillian that includes relaxation is therefore a semigroup.

2. The set of all possible permutations of several identical spins in a spin system. This group is not Abelian because the order of permutations does affect the result. The *permutation group* of n objects is usually denoted S_n.

3. Symmetry groups encountered in electronic structure theory and crystallography. All finite point groups describing molecular symmetry are subgroups of S_n for some n.

4. Automorphism groups of Hilbert spaces. It is easy to see that the set of all invertible linear operators acting on the wavefunction space of a physical system is a group.

The definitions of group and semigroup given above are too general for our purposes, and in the treatment below we shall therefore work specifically with groups of quantum mechanical operators and superoperators, which will inherit the norm and inner product from the corresponding space. The broadest of such groups – the group made by the set of all invertible $N \times N$ matrices over a field F together with matrix multiplication – is called the *general linear group* $GL(N,F)$. In the treatment below we shall also assume $F = \mathbb{C}$ or $F = \mathbb{R}$.

Discrete and finite groups

For a given element $g \in G \subset GL(N)$ and any positive $\varepsilon \in \mathbb{R}$, the set of all operators h such that

$$\|g - h\| < \varepsilon \tag{5}$$

is called the *ε-neighbourhood* of g. If every element of the group G has an ε-neighbourhood in $GL(N)$ that does not contain other elements of G, the group G is called *discrete*. In other words, the operators of a discrete group are placed in $GL(N)$ separately and can be enumerated. If a group has a finite number of elements, it is called a *finite* group. All other groups are *infinite*.

Examples of finite groups include permutation groups and point groups describing molecular symmetry. Crystallographic symmetry groups are discrete, but infinite, because they contain an infinite number of distinct crystal cell translation symmetry operations.

Continuous groups

A group G is called *continuous* or *Lie group* if it is also a differentiable manifold, that is, if each operator $g \in G$ has an ε-neighbourhood with the following property:

> There exists an operator-valued function $g(t_1,...,t_k)$ of k variables, which is continuous within the $|t_i| < \varepsilon$ cube, defines all operators within the ε-neighbourhood of g and has different values for different parameters $(t_1,...,t_k)$.

Such a function is called the *parameterization* of the group around g. It can be shown that the number of variables k is uniquely determined by the group. It is called the *dimension* of the group, and the group itself is called *k-parametric*.

In spin dynamics, Lie groups mostly arise in the context of three-dimensional rotations and time evolution. We will encounter the following Lie groups:

- *General linear group*, $GL(N)$ – of invertible $N \times N$ matrices.
- *Special linear group*, $SL(N)$ – of invertible $N \times N$ matrices with $\det = 1$.
- *Unitary group*, $U(N)$ – of unitary $N \times N$ matrices.
- *Orthogonal group*, $O(N)$ – of orthogonal $N \times N$ matrices.
- *Special unitary group*, $SU(N)$ – of unitary $N \times N$ matrices with $\det = 1$.
- *Special orthogonal group*, $SO(N)$ – of orthogonal $N \times N$ matrices with $\det = 1$.

In particular, $SU(2)$ is the group of transformations of the wavefunction space of a single spin-1/2 particle and $SO(3)$ is the group of three-dimensional rotations in real space.

Group actions, orbits and stabilizers

The spin system trajectory under a given Hamiltonian:

$$\left|\hat{\rho}(t)\right\rangle = e^{-i\hat{H}t}\left|\hat{\rho}(0)\right\rangle \tag{6}$$

shares the parameter (time) with the propagator group. The system trajectory may therefore be viewed as sequential application of every element of the propagator group to the initial state of the system.

More formally, if G is a group of operators acting on a set A, then the *group action* by G on A is a map $G: A \to A$, that is, $a \to g(a)$, where $a \in A$, $g \in G$. In non-Abelian groups, a *left* and a *right* action may be defined in the obvious way.

A subset B of the set A is called *invariant* under the action by G if $\{gb \,|\, b \in B, g \in G\} \subseteq B$ and *fixed* under G if $gb = b$ for all $g \in G$ and $b \in B$.

If G is a group of operators acting on a set A, then the *group orbit* of an element $a \in A$ is the subset of A to which a may be moved by the action of elements of G:

$$Ga = \{ga \,|\, g \in G\} \tag{7}$$

Therefore, the spin system trajectory $\hat{\rho}(t)$ is the propagator group orbit of the initial state $\hat{\rho}(0)$. The orbits are equivalence classes on A under the following equivalence relation:

$$x \sim y \quad \text{if} \quad \exists g \in G: \qquad gx = y \tag{8}$$

The set of orbits of all elements of A forms a *partition* of A, that is, distinct orbits never intersect. If A is a space, then different orbits belong to different subspaces of A. The set of all orbits of A under the action of group G is called the *quotient* or the *orbit space* of the action and denoted A/G.

The subset of G leaving a particular point $a \in A$ invariant is a subgroup of G. It is called the *stabilizer subgroup* G_a of a:

$$G_a = \{g \in G \mid ga = a\} \tag{9}$$

If all stabilizers are trivial, the group action $G : A \to A$ is called *free*. In the spin dynamics context the action by the propagator group is rarely free due to the existence of the conservation laws.

Conjugacy classes and centres

Two elements $a, b \in G$ are called *conjugate* if $\exists g \in G,\ gag^{-1} = b$. The set of all elements of the form gag^{-1} with $g \in G$ is called the *conjugacy class* of a:

$$Cl(a) = \{gag^{-1} \mid g \in G\} \tag{10}$$

Each element of a group can belong to just one conjugacy class. Two conjugacy classes of a group are either identical, or disjoint – the group is *partitioned* into conjugacy classes. It is obvious that the identity element always forms its own class and the number of classes in Abelian groups is equal to the order of the group. The number of elements in each conjugacy class is a divisor of the group order and the number of unique (up to a similarity transformation) irreducible representations of a group is equal to the number of conjugacy classes.

The *centre* $Z(G)$ of a group G is the set of elements that commute with every element of G:

$$Z(G) = \{z \in G \mid \forall g \in G,\ zg = gz\} \tag{11}$$

It is easy to see that the centre is an Abelian subgroup of G. A group with only the identity element in the centre is called *centreless*.

Algebras

A vector space A over a field F equipped with a binary product $* : A \times A \to A$ is called an *algebra*, if:

1. $\forall a, b \in A \quad ab \in A$ (the space is closed under the product)
2. $\forall a, b, c \in A \quad (a+b)c = ac + bc$ (the binary product is left-distributive)
3. $\forall a, b, c \in A \quad a(b+c) = ab + ac$ (the binary product is right-distributive)
4. $\forall a, b \in A,\ \forall \alpha, \beta \in F \quad (\alpha a)(\beta b) = (\alpha\beta)(ab)$ (multiplication by a scalar is associative)

Note that there is no requirement for the binary product to be associative and no requirement for a unit element or a unique inverse to exist. The set all of spin operators, along with their superpositions and linear combinations, is therefore an algebra. Subalgebras are defined in the usual way.

An algebra inherits basis sets (and the metric, if it exists) from the parent space. Each element of an algebra thus has a unique expansion *via* the elements of the chosen basis set:

$$a = \sum_n \alpha_n e_n \qquad b = \sum_k \beta_k e_k \tag{12}$$

where $\{e_k\}$ is the basis set. In particular, this is true for products of basis elements:

$$e_n e_k = \sum_m c_{nkm} e_m \tag{13}$$

Therefore, the expansion coefficients for the product of any two elements:

$$ab = \sum_{nk} \alpha_n \beta_k e_n e_k = \sum_{nkm} \alpha_n \beta_k c_{nkm} e_m = \sum_m \gamma_m e_m, \qquad \gamma_m = \sum_{nk} \alpha_n \beta_k c_{nkm} \tag{14}$$

are completely determined by the expansion coefficients of the operands and the array of *structure coefficients* c_{nkm}. The structure coefficients uniquely define the algebra. Basis sets with simple structure relations (for example, Gaussian functions and spherical harmonics in Quantum Chemistry) are valuable because they facilitate computationally efficient implementations of many practical operations.

Lie algebras

A vector space $\mathfrak{a}$ over a field of complex numbers (this is not strictly necessary, but is dictated by physics) equipped with a binary operation $[\cdot,\cdot]: \mathfrak{a} \times \mathfrak{a} \to \mathfrak{a}$ (a *Lie bracket*), is called a *Lie algebra*, if:

1. $\forall a,b,c \in \mathfrak{a} \quad \forall \alpha,\beta \in \mathbb{C}$ $\quad [\alpha a + \beta b, c] = \alpha[a,c] + \beta[b,c]$ $\quad [a, \alpha b + \beta c] = \alpha[a,b] + \beta[a,c]$ (the bracket is bilinear)
2. $\forall a,b \in \mathfrak{a} \quad [a,b] = -[b,a]$ (the bracket is antisymmetric)
3. $\forall a,b,c \in \mathfrak{a} \quad [[a,b],c] + [[b,c],a] + [[c,a],b] = 0$ (*Jacobi identity* holds)
4. (mathematics) $\forall a,b \in \mathfrak{a} \quad [a,b] \in \mathfrak{a}$ (space is closed under $[\cdot,\cdot]$)
4. (physics) $\forall a,b \in \mathfrak{a} \quad i[a,b] \in \mathfrak{a}$ (space is closed under $i[\cdot,\cdot]$)

In the context of quantum mechanics it is often the case that the space in question is of Hermitian operators, which correspond to physical observables. It is easy to see, however, that the commutator of two Hermitian operators $[\hat{a},\hat{b}]$ is anti-Hermitian. This is inconvenient and for this reason the definition commonly used in physical sciences includes the i term in Condition 4 – writing the commutation operation as $[\hat{a},\hat{b}] = i\hat{c}$ ensures that $\hat{c}$ is also a Hermitian operator. The convenience of the physicists' formulation is particularly evident from Liouville – von Neumann's equation.

Two Lie algebras $\mathfrak{a}_1$ and $\mathfrak{a}_2$ over a field F are called *isomorphous*, if there exists a one-to-one map $\varphi: \mathfrak{a}_1 \to \mathfrak{a}_2$, such that

1. $\forall a,b \in \mathfrak{a}_1 \quad \varphi(a+b) = \varphi(a) + \varphi(b)$
2. $\forall a \in \mathfrak{a}_1 \ \forall \alpha \in F \quad \varphi(\alpha a) = \alpha \varphi(a)$
3. $\forall a,b \in \mathfrak{a}_1 \quad \varphi([a,b]) = [\varphi(a), \varphi(b)]$

A finite set of operators $\{e_1,\ldots,e_N\}$ from a Lie algebra $\mathfrak{a}$ is called a *basis*, if every operator in $\mathfrak{a}$ can be represented as a linear combination of $\{e_1,\ldots,e_N\}$:

$$\forall a \in \mathfrak{a} \quad a = \sum_{k=1}^{N} \alpha_k e_k \tag{15}$$

Importantly, when an algebra is defined over a specific field of scalars, it is the coefficients of such linear combinations that come from that field, but not necessarily the matrices. If the basis is linearly independent the expansion above is unique. For a commutator of two basis set elements, we get:

$$\left[e_k, e_m\right] = i\sum_n c_{kmn} e_n \tag{16}$$

The coefficients c_{kmn} are known as the *structure constants* of the Lie algebra. They are determined by the choice of the basis set. In the practical simulation context, the structure constants can often be obtained analytically. They allow the calculation of commutators without recourse to any specific representations:

$$\left[a, b\right] = \sum_{km} \alpha_k \beta_m \left[e_k, e_m\right] = i\sum_{kmn} \alpha_k \beta_m c_{kmn} e_n \tag{17}$$

From the definition of the commutator and from Jacobi identity it is easy to demonstrate that:

$$c_{kmn} = -c_{mkn}, \qquad c_{kkn} = 0, \qquad \sum_p \left(c_{kmp} c_{pnq} + c_{mnp} c_{pkq} + c_{nkp} c_{pmq}\right) = 0 \quad \forall q \tag{18}$$

Commonly encountered Lie algebras include:

1. $\mathfrak{gl}_n$ – the Lie algebra of all linear operators. The most popular basis set is composed of matrices b^{ij} with a single unit element in i-th row and j-th column: $\left[b^{ij}\right]_{pq} = \delta_{pi}\delta_{qj}$. Therefore, for the commutator of two such matrices:

$$\begin{gathered}\left[\left[b^{ij}, b^{nk}\right]\right]_{pq} = \left[b^{ij}b^{nk} - b^{nk}b^{ij}\right]_{pq} = \sum_r \left[b^{ij}\right]_{pr}\left[b^{nk}\right]_{rq} - \sum_r \left[b^{nk}\right]_{pr}\left[b^{ij}\right]_{rq} = \\ = \sum_r \delta_{ip}\delta_{jr}\delta_{nr}\delta_{kq} - \sum_r \delta_{np}\delta_{kr}\delta_{ir}\delta_{jq} = \delta_{ip}\delta_{jn}\delta_{kq} - \delta_{np}\delta_{ki}\delta_{jq} = \delta_{jn}\left[b^{ik}\right]_{pq} - \delta_{ki}\left[b^{nj}\right]_{pq} \\ \left[b^{ik}, b^{lm}\right] = \delta_{im}b^{lk} - \delta_{lk}b^{im}\end{gathered} \tag{19}$$

2. $\mathfrak{sl}_n$ – the Lie algebra of all traceless linear operators. One of the most convenient basis sets is *Okubo matrices*, for which:

$$\begin{gathered}a^{ik} = b^{ik} - \frac{1}{N}\delta_{ik}\left(b^{11} + \ldots + b^{NN}\right) \\ \left[a^{ik}, a^{lm}\right] = \sum_{rs}\left(\delta_{im}\delta_{lr}\delta_{sk} - \delta_{lk}\delta_{ir}\delta_{sm}\right)a^{rs}\end{gathered} \tag{20}$$

3. $\mathfrak{u}_n$ – the Lie algebra of all Hermitian operators. We could choose the basis matrices to be Hermitian linear combinations of one-element matrices b^{ij}:

$$b^{kk}, \quad b^{nk} + b^{kn}, \quad i\left(b^{nk} - b^{kn}\right) \tag{21}$$

but it is often convenient to use an *external basis set*, such as b^{ij} themselves, which does belong to a larger algebra, but still generates $\mathfrak{u}_n$ because $\mathfrak{u}_n \subset \mathfrak{gl}_n$. Convenient internal generators for $\mathfrak{u}_2$, originally proposed by Wolfgang Pauli, are

$$\hat{e} = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}, \qquad \hat{\sigma}_1 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \qquad \hat{\sigma}_2 = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \qquad \hat{\sigma}_3 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{22}$$

4. $\mathfrak{su}_n$ – the Lie algebra of all traceless Hermitian operators. One of the possible internal generator sets may be obtained by forming Hermitian linear combinations of Okubo matrices:

$$a^{kk}, \quad a^{nk} + a^{kn}, \quad i\left(a^{nk} - a^{kn}\right) \tag{23}$$

In the case of $n = 2$, if a matrix is traceless, the unit matrix $\hat{E}$ does not appear in its expansion. Therefore, the $\left\{\sigma_1, \sigma_2, \sigma_3\right\}$ Pauli matrices are internal generators of $\mathfrak{su}_2$.

Exponential map

Let us analyse the properties of exponentials of the matrices belonging to one of the algebras described above. It is easy to prove the following statements:

1. $\det\left[e^a\right]=e^{\mathrm{Tr}[a]}$
2. For any matrix a, e^a is an invertible operator and its inverse is e^{-a}.
3. If $[a,b]=0$, then $e^{a+b}=e^a e^b$.
4. For any operator $a\in\mathfrak{gl}_n$, $e^{a^\dagger}=\left[e^a\right]^\dagger$.
5. If a is Hermitian, then e^{ia} is unitary, and if a is traceless, then $\det\left[e^{ia}\right]=1$.

It therefore appears that the exponentials of the matrices inhabiting the algebras listed above satisfy the definition of a Lie group – they are invertible and continuous with respect to the coefficients of the linear combinations in the parent algebra. More specifically, we have seen above that a Lie algebra can be parameterized by a set of N basis operators $\{e_k\}$ and coefficients α_k and the following relation provides a map between the group and the algebra:

$$\begin{gathered}a(\alpha_1,\ldots,\alpha_N)=\sum_{k=1}^{N}\alpha_k e_k\in\mathfrak{a},\qquad \alpha_1,\ldots,\alpha_N\in\mathbb{C}\\ g(\alpha_1,\ldots,\alpha_N)=\exp[iA]=\exp\left[i\sum_{k=1}^{N}\alpha_k e_k\right]=\sum_{n=1}^{\infty}\frac{1}{n!}\left(i\sum_{k=1}^{N}\alpha_k e_k\right)^n\in G\end{gathered}\tag{24}$$

In the physics context, the most common form of a matrix exponential is $\exp(ia)$. Under this definition of the exponential map, the following correspondence holds (the fields refer to linear combination coefficients inside the algebras that parameterize the corresponding groups):

Lie group	Dimension	Matrices in the group	Lie algebra	Matrices in the algebra
$GL(n,\mathbb{C})$	$2n^2$	invertible	$\mathfrak{gl}_n(\mathbb{C})$	all
$GL(n,\mathbb{R})$	n^2	real, invertible	$\mathfrak{gl}_n(\mathbb{R})$	imaginary
$SL(n,\mathbb{C})$	$2n^2-2$	invertible, $\det=1$	$\mathfrak{sl}_n(\mathbb{C})$	traceless
$SL(n,\mathbb{R})$	n^2-1	real, invertible, $\det=1$	$\mathfrak{sl}_n(\mathbb{R})$	imaginary, traceless
$SO(n,\mathbb{R})$	$n(n-1)/2$	real, invertible, orthogonal	$\mathfrak{so}_n(\mathbb{R})$	imaginary, Hermitian
$U(n,\mathbb{R})$	n^2	invertible, unitary	$\mathfrak{u}_n(\mathbb{R})$	Hermitian
$SU(n,\mathbb{R})$	n^2-1	invertible, unitary, $\det=1$	$\mathfrak{su}_n(\mathbb{R})$	Hermitian, traceless

Adjoint action

In the same way as the group operation defines an action of the group on itself, the Lie bracket may be used to define an action by an algebra on itself. Given an element a of a Lie algebra $\mathfrak{a}$, the *adjoint ac-*

tion of a on $\mathfrak{a}$ is an endomorphism $\mathrm{ad}_a : \mathfrak{a} \to \mathfrak{a}$ with $\mathrm{ad}_a(b) = [a,b]$. In spin dynamics language, the adjoint action by an operator $\hat{a}$ corresponds to the action by the commutation superoperator induced by $\hat{a}$: $\mathrm{ad}_{\hat{a}}\left(\hat{b}\right) = \hat{\hat{a}}\hat{b} = [\hat{a},\hat{b}]$.

Adjoint action defines a representation of a Lie algebra (it is called the *adjoint representation*) because the adjoint actions satisfy the same commutation relations as the original operators:

$$\left[\mathrm{ad}_a, \mathrm{ad}_b\right](c) = \left(\mathrm{ad}_{[a,b]}\right)(c) \quad \Leftrightarrow \quad \left([\hat{\hat{L}}, \hat{\hat{S}}]\right)\hat{\rho} = \hat{\hat{M}}\hat{\rho},\ \hat{M} = \left[\hat{L}, \hat{S}\right] \tag{25}$$

It is easy to see from the definition that the adjoint representation corresponds to the transformation between Hilbert and Liouville space formalisms in spin dynamics:

$$\begin{gathered}\frac{\partial}{\partial t}\hat{\rho}(t) = -\mathrm{i}[\hat{H}(t), \hat{\rho}(t)] = -\mathrm{i}\hat{\hat{H}}(t)\hat{\rho}(t) \qquad \hat{\hat{H}}(t) = \mathrm{ad}\hat{H}(t) = [\hat{H}(t),\ \ ] \\ \exp\left(-\mathrm{i}\hat{\hat{H}}t\right)\hat{\rho} = \exp\left(-\mathrm{i}\hat{H}t\right)\hat{\rho}\exp\left(\mathrm{i}\hat{H}t\right)\end{gathered} \tag{26}$$

The adjoint representation (*aka* Liouville space) is very convenient because time propagation is accomplished by a *one-sided* multiplication operation on a column vector, rather than *two-sided* multiplication on a matrix – this facilitates many analytical calculations.

Matrix representations of groups and algebras

Because calculations are typically performed on digital computers, it is in practice convenient to work with matrix representations of operators (rather than, for example, their differential forms). An *N-dimensional matrix representation* of a group G is a map $P : G \to GL(N)$, such that:

$$\forall g, h \in G \qquad P(gh) = P(g)P(h) \tag{27}$$

and a unit operator in G is represented by a unit matrix in $GL(N)$. Some loss of information may occur under this map. In this regard, group representations can be:

- *Faithful:* when P is an isomorphism, that is, different elements of G are mapped into different elements of $GL(N)$. A common example of a faithful representation is the one commonly used in quantum mechanics: if G is a group of operators on a Hilbert space and $\{|\varphi_k\rangle\}$ is an orthonormal basis of that space, then the set of matrices with the following elements:

$$\left[P(g)\right]_{nk} = \langle\varphi_n|g|\varphi_k\rangle \tag{28}$$

  where $g \in G$, is a faithful representation of the group G.

- *Regular*: a faithful representation that uses the group itself as a basis (this is possible because G is able to act on itself by multiplication). If we define $\Delta^{(i)}_{jk}$ such that $g_i g_j = \Delta^{(i)}_{jk} g_k$, then the matrix corresponding to the regular representation of g_i is $\left[P(g_i)\right]_{jk} = \Delta^{(i)}_{jk}$. The dimension of the regular representation is equal to the order of the group.

- *Lossy:* a representation in which two or more elements of G are mapped into the same element of $GL(N)$. Some properties and relations between the elements of the group may survive, others would be lost.

- *Scalar:* a lossy representation in which each $g \in G$ is mapped into the determinant of its faithful representation. This representation is always Abelian.
- *Trivial:* a lossy representation in which all elements of G are mapped into the unit matrix.

Two representations P and Q of the same group G are called *equivalent*, if they have the same dimension and there is a similarity transformation taking one into the other:

$$\forall g \in G \quad Q(g) = W^{-1} P(g) W \tag{29}$$

All representations of finite groups are equivalent to unitary representations.

Let P be a N-dimensional matrix representation of G and let the representation space $\mathbb{C}^N$ have a decomposition into a direct sum of subspaces $\mathbb{C}^N = \mathbb{C}^{N_1} \oplus \ldots \oplus \mathbb{C}^{N_S}$, such that the individual subspaces $\mathbb{C}^{N_i}$ are invariant under the operators representing the elements of G. Then the representation $P = P_1 \oplus \ldots \oplus P_S$ is a *direct sum of representations* $P_1, \ldots, P_S$. If a basis is selected in each of the subspaces $\mathbb{C}^{N_i}$ and their direct sum is used as the basis of $\mathbb{C}^N$, the matrices of P acquire a block-diagonal form, with individual blocks corresponding to individual representations in the direct sum.

Let P and Q be representations of G in $\mathbb{C}^N$ and $\mathbb{C}^K$ respectively. The Kronecker products of matrices of the form $P(g) \otimes Q(g)$ defined on $\mathbb{C}^N \otimes \mathbb{C}^K$ are another representation of G, because

$$\begin{gathered} P(gh) \otimes Q(gh) = P(g)P(h) \otimes Q(g)Q(h) = \\ = \left[P(g) \otimes Q(g)\right]\left[P(h) \otimes Q(h)\right] \end{gathered} \tag{30}$$

this representation is called a *direct product of representations* P and Q.

A matrix representation P of a group G in $GL(N)$ is said to be *reducible* if it can be cast by some similarity transformation into the following form:

$$P(g) = \begin{pmatrix} P_1(g) & X(g) \\ 0 & P_2(g) \end{pmatrix} \quad \forall g \in G \tag{31}$$

where $P_1(g)$, $P_2(g)$ and $X(g)$ are blocks of the matrix $P(g)$. A representation is *fully reducible* if it can be transformed into a direct sum of representations of lower dimension:

$$P(g) = \begin{pmatrix} P_1(g) & 0 & 0 \\ 0 & P_2(g) & 0 \\ 0 & 0 & \cdots \end{pmatrix} = P_1(g) \oplus P_2(g) \oplus \ldots \tag{32}$$

If $\mathbb{C}^N$ does not contain any subspaces other than itself that are invariant with respect to all the operators in P, the representation P is called *irreducible*. Any representation of a finite group is either irreducible or fully reducible. For infinite groups, if a representation is unitary and reducible, then it is fully reducible.

A very general orthogonality relation (known as the *great orthogonality theorem*) exists between two unitary irreducible matrix representations P_a and P_b of a group G:

$$\frac{\sqrt{N_a N_b}}{N_G} \sum_{g \in G} \left[P_a(g)\right]^*_{jk} \left[P_b(g)\right]_{lm} = \delta_{ab} \delta_{jl} \delta_{km} \tag{33}$$

where N is the order of the group and n_a, n_b are dimensions of the two representations. In other words, if the representation matrices are stacked on top of one another like a deck of cards on a table, the columns of the two stacks are orthogonal for different representations.

Characters

The *character* of a matrix representation P of a group element is the trace of the corresponding matrix:

$$\chi_P(g) = \mathrm{Tr}\left[P(g)\right] = \sum_k \left[P(g)\right]_{kk} \tag{34}$$

The *character of a representation* is an ordered set of characters of the individual elements of the group (usually written as a row vector). Trace is invariant under similarity transformation:

$$\mathrm{Tr}\left[W^{-1}P(g)W\right] = \mathrm{Tr}\left[WW^{-1}P(g)\right] = \mathrm{Tr}\left[P(g)\right] \tag{35}$$

meaning that all equivalent representations have the same characters. From the definition of a conjugacy class it also follows that all members of a conjugacy class have the same character. After computing the traces of the matrices on the left hand side of the great orthogonality theorem, we get:

$$\begin{gathered}
\sum_{jklm}\left(\frac{\sqrt{N_a N_b}}{N_G}\sum_{g\in G}\left[P_a(g)\right]^*_{jk}\left[P_b(g)\right]_{lm}\right)\delta_{jk}\delta_{lm} = \sum_{jklm}\delta_{ab}\delta_{jl}\delta_{km}\delta_{jk}\delta_{lm} \\
\Downarrow \\
\sum_{km}\left(\frac{\sqrt{N_a N_b}}{N_G}\sum_{g\in G}\left[P_a(g)\right]^*_{kk}\left[P_b(g)\right]_{mm}\right) = \sum_{km}\delta_{ab}\delta_{km} \\
\Downarrow \\
\frac{1}{N_G}\sum_{g\in G}\left[\left(\sum_k\left[P_a(g)\right]^*_{kk}\right)\left(\sum_m\left[P_b(g)\right]_{mm}\right)\right] = \delta_{ab} \\
\Downarrow \\
\frac{1}{N_G}\sum_{g\in G}\chi^*_{P_a}(g)\chi_{P_b}(g) = \delta_{ab}
\end{gathered} \tag{36}$$

That is, characters of different irreducible representations are orthogonal as vectors (this is known as the *little orthogonality theorem*). A *character table* is a table of characters for all unique (up to a similarity transformation) irreducible representations of the group. For the common example of S_3 group (*aka* C_{3v} – the symmetry group of NH_3 molecule) we have:

	E	**C_3(120°)**	**C_3(240°)**	**σ_1**	**σ_2**	**σ_3**
A_1	1	1	1	1	1	1
A_2	1	1	1	–1	–1	–1
E	2	–1	–1	0	0	0

It is easy to see that the lines of this table are orthogonal as vectors. Character tables for all commonly encountered groups are tabulated in the literature.

Applications of finite groups to spin dynamics

Character tables are useful for the construction of *symmetry-adapted linear combinations* (SALCs) of basis functions or operators. SALCs span subspaces that are invariant under the action of the operators of the group. Because the Hamiltonian commutes with the system symmetry operators, the same subspaces are also invariant under the Hamiltonian, which is therefore block-diagonal in the SALC basis. Hamiltonian block-diagonalization can save significant computational resources in practical calculations – each block can be simulated separately and it is often the case that some blocks are unpopulated in the initial condition and can therefore be dropped altogether.

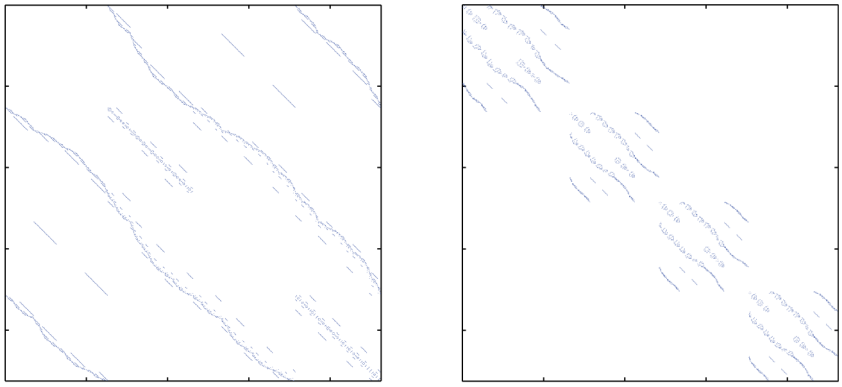


Figure 1. Non-zero pattern of the Hamiltonian commutation superoperator of a radical pair with four equivalent protons before (left) and after (right) symmetrisation of the basis set under the largest Abelian subgroup of S_4. Only one of the resulting blocks is populated in typical simulations.

The symmetry "blocks" correspond to conservation laws within the physical system. A simulation instance that started off in a specific invariant subspace of the symmetry operator would stay there indefinitely. As the common laboratory jargon puts it, "the states of different symmetry do not interact".

For discrete groups SALCs are given by the following equations:

$$\psi_k^{(\Gamma)} = \frac{1}{N}\sum_{g\in G}\chi_g^{(\Gamma)} g\left(\psi_k\right) \qquad \hat{O}_k^{(\Gamma)} = \frac{1}{N}\sum_{g\in G}\chi_g^{(\Gamma)} g\left(\hat{O}_k\right) \tag{37}$$

where N is the normalization constant, the summation is carried over the individual elements g of the symmetry group G, $\chi_g^{(\Gamma)}$ is the character of irreducible representation Γ of the group element g, and $g(O_k)$ is the result of the action by that group element on the basis operator $\hat{O}_k$.

For spin operators, the group action $g:\{\hat{O}_k\}\rightarrow\{\hat{O}_k\}$ is an endomorphism of the system state space that amounts to permutation of the order of the direct product components of $\{O_k\}$. An example is given below for the *group action table* of C_{3v} on proton spin operators of NH_3:

Operator	E	$C_3(120°)$	$C_3(240°)$	σ_1	σ_2	σ_3
$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{E}$
$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$
$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$
$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{E}\otimes\hat{L}_Z\otimes\hat{E}$	$\hat{L}_Z\otimes\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{E}\otimes\hat{L}_Z$

Liouville space symmetry treatment

In many practical cases, only one irreducible representation needs to be simulated in Liouville space – the one with all characters equal to unity, otherwise known as $\mathrm{A}_{1\mathrm{g}}$, otherwise known as Σ_{g}^{+}, or the 'fully symmetric' irreducible representation. This difference in symmetry behavior of Hilbert and Liouville spaces may be illustrated on a two-spin system – while the singlet state wavefunction does change sign under spin permutation in Hilbert space:

$$\hat{P}_{12}\left(\left|\alpha\beta\right\rangle-\left|\beta\alpha\right\rangle\right)=\left|\beta\alpha\right\rangle-\left|\alpha\beta\right\rangle=-\left(\left|\alpha\beta\right\rangle-\left|\beta\alpha\right\rangle\right) \tag{38}$$

its representation in Liouville space does not:

$$\hat{P}_{12}\left(\left|\alpha\beta\right\rangle-\left|\beta\alpha\right\rangle\right)\left(\left\langle\alpha\beta\right|-\left\langle\beta\alpha\right|\right)\hat{P}_{12}^{\dagger}=\left(\left|\alpha\beta\right\rangle-\left|\beta\alpha\right\rangle\right)\left(\left\langle\alpha\beta\right|-\left\langle\beta\alpha\right|\right) \tag{39}$$

More generally, any symmetry-adapted Hilbert space wavefunction belonging to an irrep other than the fully symmetric one

$$\hat{P}\left|\psi\right\rangle=e^{i\varphi}\left|\psi\right\rangle,\qquad\varphi\in\mathbb{R} \tag{40}$$

is going to have a fully symmetric representation in Liouville space because

$$\hat{P}\left|\psi\right\rangle\left\langle\psi\right|\hat{P}^{\dagger}=e^{i\varphi}\left|\psi\right\rangle\left\langle\psi\right|e^{-i\varphi}=\left|\psi\right\rangle\left\langle\psi\right| \tag{41}$$

Therefore irreducible representations other than $\mathrm{A}_{1\mathrm{g}}$ get "symmetrized" into $\mathrm{A}_{1\mathrm{g}}$ during the Hilbert to Liouville space transformation. It also often the case that system evolution in Liouville space stays confined to $\mathrm{A}_{1\mathrm{g}}$. In the most general case, the evolution is governed by the following equation:

$$\frac{\partial\hat{\rho}}{\partial t}=-i\hat{\hat{H}}\hat{\rho}+\hat{\hat{K}}\hat{\rho}+\hat{\hat{R}}\left(\hat{\rho}-\hat{\rho}_{\mathrm{eq}}\right) \tag{42}$$

where $\hat{\rho}$ is the density matrix, $\hat{\rho}_{\mathrm{eq}}$ is the equilibrium density matrix, $\hat{\hat{H}}$ is the Hamiltonian commutation superoperator, $\hat{\hat{K}}$ is the chemical kinetics and spatial diffusion superoperator and $\hat{\hat{R}}$ is the relaxation superoperator obtained using one of the available relaxation theories. The Hamiltonian commutation superoperator $\hat{\hat{H}}=[\hat{H},\cdot]=\hat{E}\otimes\hat{H}^{\mathrm{T}}-\hat{H}\otimes\hat{E}$, where $\hat{E}$ is the identity operator, inherits the symmetry of the Hamiltonian which commutes with the symmetry group, meaning that $\hat{\hat{H}}\in\mathrm{A}_{1\mathrm{g}}$. If the user declared some spins "equivalent" in a system undergoing chemical reactions, they must be transported as such in any chemical process, meaning that, by definition, $\hat{\hat{K}}\in\mathrm{A}_{1\mathrm{g}}$. The initial state of the system is either thermodynamic equilibrium, which inherits the $\mathrm{A}_{1\mathrm{g}}$ symmetry of the Hamiltonian *via*

$$\hat{\rho}_{\mathrm{eq}}=\frac{\exp\left[-\hat{H}/k_{\mathrm{B}}T\right]}{\mathrm{Tr}\left(\exp\left[-\hat{H}/k_{\mathrm{B}}T\right]\right)} \tag{43}$$

or a user-supplied non-equilibrium state, which is fully symmetric by definition with respect to the spins that the user declared equivalent. The case of the relaxation superoperator is somewhat more involved. In the case of the Redfield superoperator

$$\hat{\hat{R}}\left(\hat{\rho}-\hat{\rho}_{\mathrm{eq}}\right)=\int_{0}^{\infty}\overline{[\hat{H}_{1}(0),[e^{i\hat{H}_{0}\tau}\hat{H}_{1}(\tau)e^{-i\hat{H}_{0}\tau},\hat{\rho}-\hat{\rho}_{\mathrm{eq}}]]}\,\mathrm{d}\tau \tag{44}$$

Under the assumption that the stochastic part $\hat{H}_{1}(t)$ of the Hamiltonian obeys the system symmetry, the entire double commutation superoperator on the right hand side inherits the symmetry of $\hat{H}_{0}$ and

$\hat{H}_1(t)$, which is A_{1g}. Noting that the direct product of any number of fully symmetric irreps is itself a fully symmetric irrep completes the proof. In summary, in symmetric systems with symmetric initial conditions the symmetry would not be broken spontaneously because all events and operators affecting it belong to A_{1g}.

Symmetry treatment for NMR and ESR systems

For any transformation to be a "symmetry", it is a requirement that the corresponding superoperator leaves the Hamiltonian unchanged. Examples include label permutations on identical spins:

$$\begin{gathered}\hat{H}=\omega\hat{S}_{Z}^{(1)}+\omega\hat{S}_{Z}^{(2)}+\omega\hat{S}_{Z}^{(3)}+\pi J\hat{L}_{Z}\left(\hat{S}_{Z}^{(1)}+\hat{S}_{Z}^{(2)}+\hat{S}_{Z}^{(3)}\right)= \\ =\omega\hat{S}_{Z}^{(2)}+\omega\hat{S}_{Z}^{(1)}+\omega\hat{S}_{Z}^{(3)}+\pi J\hat{L}_{Z}\left(\hat{S}_{Z}^{(2)}+\hat{S}_{Z}^{(1)}+\hat{S}_{Z}^{(3)}\right)\end{gathered} \tag{45}$$

but only in the case where the coupling structure (including tensor eigenvalues and eigenvectors) to any external spins is similarly invariant. This is often the case in liquid-state ESR spectroscopy, where all nuclei with similar hyperfine coupling constants can be declared equivalent under the full permutation group. The same applies to methyl and isopropyl groups in liquid-state NMR.

Situations where the Hamiltonian is invariant under simultaneous label permutations of groups of spins that are not related by simple permutation symmetry must be treated on a case-by-case basis. In particular, in solid state simulations the permutation symmetry can be applied *if and only if* the nuclei have identical interaction tensors to the same partner spins. It must be demonstrated that the Hamiltonian is indeed invariant under all group operations, the group action table must be built for each element of the basis set and multiplied into the character table to get the symmetry-adapted basis.