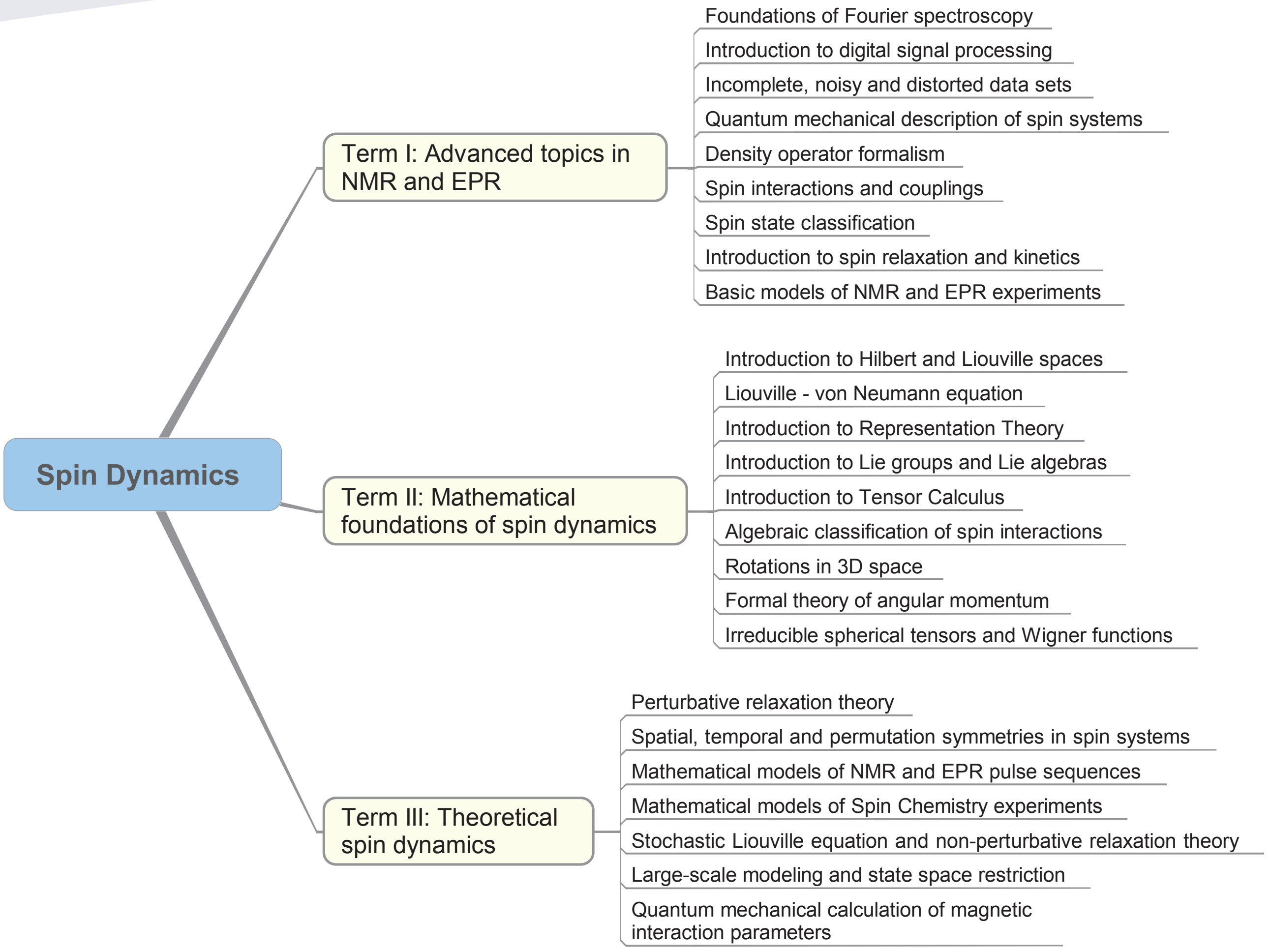
Spin Dynamics

Dr Ilya Kuprov
Oxford e-Research Centre



- **Spin Dynamics**
  - Term I: Advanced topics in NMR and EPR
    - Foundations of Fourier spectroscopy
    - Introduction to digital signal processing
    - Incomplete, noisy and distorted data sets
    - Quantum mechanical description of spin systems
    - Density operator formalism
    - Spin interactions and couplings
    - Spin state classification
    - Introduction to spin relaxation and kinetics
    - Basic models of NMR and EPR experiments
  - Term II: Mathematical foundations of spin dynamics
    - Introduction to Hilbert and Liouville spaces
    - Liouville - von Neumann equation
    - Introduction to Representation Theory
    - Introduction to Lie groups and Lie algebras
    - Introduction to Tensor Calculus
    - Algebraic classification of spin interactions
    - Rotations in 3D space
    - Formal theory of angular momentum
    - Irreducible spherical tensors and Wigner functions
  - Term III: Theoretical spin dynamics
    - Perturbative relaxation theory
    - Spatial, temporal and permutation symmetries in spin systems
    - Mathematical models of NMR and EPR pulse sequences
    - Mathematical models of Spin Chemistry experiments
    - Stochastic Liouville equation and non-perturbative relaxation theory
    - Large-scale modeling and state space restriction
    - Quantum mechanical calculation of magnetic interaction parameters

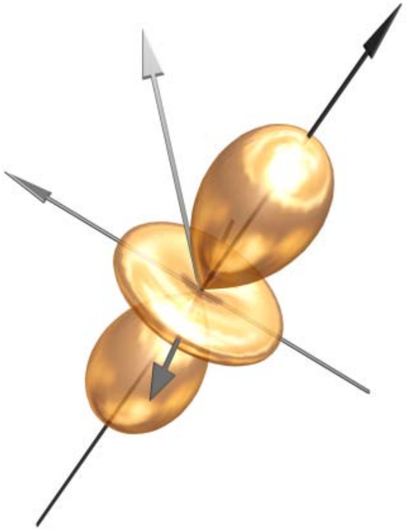
Spin Dynamics is a graduate level lecture course aimed at physicists and chemists working in the area of magnetic resonance spectroscopy or using NMR and EPR as part of their research.

Term I will provide the general physical and mathematical background of magnetic resonance, as well as an introduction to data processing and spin system analysis. Terms II and III will focus specifically on theoretical and computational aspects of spin dynamics.

Conference Room,
Oxford e-Research Centre,
7 Keble Road,
Oxford, OX1 3QG.

UNIVERSITY · OF · OXFORD

Fridays, 9:00-10:00
Starting 9 October 2009



> Experimental science is a combination of four basis vectors: *'this doesn't work'*, *'this is too expensive'*, *'this is broken'* and *'this has been done before'*.
>
> *Anonymous*
> *graduate student*

Lecture 3:
Basic angular momentum theory

Definition of angular momentum operators. Commutation relations. Raising and lowering operators. Eigenfunctions and eigenvalues of angular momentum operators.

Dr Ilya Kuprov, University of Oxford, 2009

Spin Dynamics, Lecture 3

Angular momentum theory is a vast topic (NMR, EPR, rotational spectroscopy, atomic orbitals, Lie groups, *etc*)…

Classical definition of angular momentum:

$$\vec{l} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_{\mathrm{x}} & p_{\mathrm{y}} & p_{\mathrm{z}} \end{vmatrix} = \begin{pmatrix} yp_{\mathrm{z}} - zp_{\mathrm{y}} \\ zp_{\mathrm{x}} - xp_{\mathrm{z}} \\ xp_{\mathrm{y}} - yp_{\mathrm{x}} \end{pmatrix}$$

(a conserved quantity, *solely* because of the isotropic nature of space)

angular momentum vector

Cartesian coordinates

linear momentum

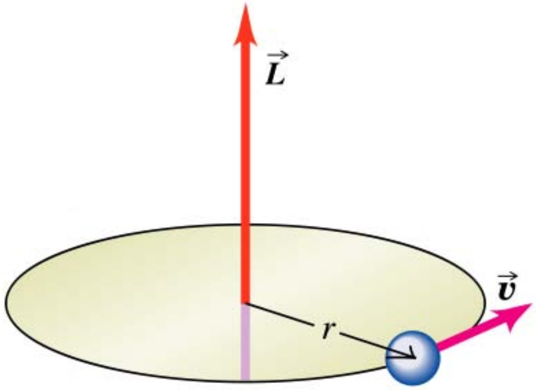
With the basic components coming from your physics course:

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}; \qquad \vec{p} = m\vec{v} = m\frac{\partial \vec{r}}{\partial t} = m\begin{pmatrix} v_{\mathrm{x}} \\ v_{\mathrm{y}} \\ v_{\mathrm{z}} \end{pmatrix} = \begin{pmatrix} p_{\mathrm{x}} \\ p_{\mathrm{y}} \\ p_{\mathrm{z}} \end{pmatrix}; \qquad \vec{u} \times \vec{v} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ u_{\mathrm{x}} & u_{\mathrm{y}} & u_{\mathrm{z}} \\ v_{\mathrm{x}} & v_{\mathrm{y}} & v_{\mathrm{z}} \end{vmatrix}$$

cross product

Spin Dynamics, Lecture 3

Physically, angular momentum corresponds to the "amount of spin" an object has and the direction of the *l* vector is perpendicular to the plane of spinning.



Quantum mechanical definition:

the *quantization rule* is to replace all physical quantities with their corresponding operators, therefore

Cartesian coordinates

$$\left.\begin{matrix} x & \rightarrow & \hat{x} \\ y & \rightarrow & \hat{y} \\ z & \rightarrow & \hat{z} \end{matrix}\right\}$$

Cartesian coordinate operators

components of the momentum vector

$$\left.\begin{matrix} p_x & \rightarrow & \hat{p}_x \\ p_y & \rightarrow & \hat{p}_y \\ p_z & \rightarrow & \hat{p}_z \end{matrix}\right\}$$

components of the momentum operator

Reminder:

$$\hat{p}_x = -i\hbar \,{}^{\partial}\!/_{\partial x}$$

$$\hat{p}_y = -i\hbar \,{}^{\partial}\!/_{\partial y}$$

$$\hat{p}_z = -i\hbar \,{}^{\partial}\!/_{\partial z}$$

After we apply this transformation to the classical definition of angular momentum, the following expressions emerge:

$$\vec{l} = \begin{pmatrix} yp_{\mathrm{z}} - zp_{\mathrm{y}} \\ zp_{\mathrm{x}} - xp_{\mathrm{z}} \\ xp_{\mathrm{y}} - yp_{\mathrm{x}} \end{pmatrix} \qquad \rightarrow \qquad \hat{\vec{l}} = \begin{pmatrix} \hat{y}\hat{p}_{\mathrm{z}} - \hat{z}\hat{p}_{\mathrm{y}} \\ \hat{z}\hat{p}_{\mathrm{x}} - \hat{x}\hat{p}_{\mathrm{z}} \\ \hat{x}\hat{p}_{\mathrm{y}} - \hat{y}\hat{p}_{\mathrm{x}} \end{pmatrix} = -i\hbar \begin{pmatrix} \hat{y}\,\partial/\partial z - \hat{z}\,\partial/\partial y \\ \hat{z}\,\partial/\partial x - \hat{x}\,\partial/\partial z \\ \hat{x}\,\partial/\partial y - \hat{y}\,\partial/\partial x \end{pmatrix}$$

In other words:

$$\hat{l}_{\mathrm{x}} = -i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right); \quad \hat{l}_{\mathrm{y}} = -i\hbar\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right); \quad \hat{l}_{\mathrm{z}} = -i\hbar\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right)$$

These are the standard expressions for the angular momentum operators (examinable).

The angular momentum vector corresponds to a vector operator with three components:

$$\hat{\vec{l}} = \vec{i}\hat{l}_{\mathrm{x}} + \vec{j}\hat{l}_{\mathrm{y}} + \vec{k}\hat{l}_{\mathrm{z}} = \begin{pmatrix} \hat{l}_{\mathrm{x}} \\ \hat{l}_{\mathrm{y}} \\ \hat{l}_{\mathrm{z}} \end{pmatrix}$$

Spin Dynamics, Lecture 3

Components of $\hat{\vec{l}}$ are observables, therefore the corresponding operators are Hermitian. An operator that will be important later is the momentum squared:

$$\hat{l}^2 = \hat{\vec{l}} \cdot \hat{\vec{l}} = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

Commutators

The following combination of operators occurs frequently enough to deserve a special name:

“commutator” ⟶ $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

Commutators of angular momentum operators occur quite frequently and it is important to be able to calculate them (examinable). Example:

$$\left[\hat{l}_x, \hat{l}_y\right] = \left[-i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right), -i\hbar\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right)\right] =$$

$$= -\hbar^2\left(\hat{y}\frac{\partial}{\partial z}\hat{z}\frac{\partial}{\partial x} - \hat{y}\frac{\partial}{\partial z}\hat{x}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\hat{z}\frac{\partial}{\partial x} + \hat{z}\frac{\partial}{\partial y}\hat{x}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial x}\hat{y}\frac{\partial}{\partial z} + \hat{z}\frac{\partial}{\partial x}\hat{z}\frac{\partial}{\partial y} + \hat{x}\frac{\partial}{\partial z}\hat{y}\frac{\partial}{\partial z} - \hat{x}\frac{\partial}{\partial z}\hat{z}\frac{\partial}{\partial y}\right) =$$

$$= \ldots = -\hbar^2\left(\hat{y}\frac{\partial}{\partial x} + \hat{y}\hat{z}\frac{\partial^2}{\partial x\partial z} + \hat{z}\hat{x}\frac{\partial^2}{\partial y\partial z} - \hat{y}\hat{z}\frac{\partial^2}{\partial x\partial z} - \hat{z}\hat{x}\frac{\partial^2}{\partial y\partial z} - \hat{x}\frac{\partial}{\partial y}\right) = -\hbar^2\left(\hat{y}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial y}\right) = i\hbar\hat{l}_z$$

Spin Dynamics, Lecture 3

Fortunately, the commutation relations can be tabulated as relatively simple general expressions (prove as an exercise):

$$[\hat{x},\hat{p}_{\mathrm{x}}]=i\hbar \qquad [\hat{y},\hat{p}_{\mathrm{y}}]=i\hbar \qquad [\hat{z},\hat{p}_{\mathrm{z}}]=i\hbar$$

$$[\hat{x},\hat{p}_{\mathrm{y}}]=[\hat{x},\hat{p}_{\mathrm{z}}]=\ldots=[\hat{z},\hat{p}_{\mathrm{y}}]=0$$

$$\left.\begin{aligned}[\hat{l}_{\mathrm{x}},\hat{l}_{\mathrm{y}}]&=i\hbar\hat{l}_{\mathrm{z}}\\ [\hat{l}_{\mathrm{y}},\hat{l}_{\mathrm{z}}]&=i\hbar\hat{l}_{\mathrm{x}}\\ [\hat{l}_{\mathrm{z}},\hat{l}_{\mathrm{x}}]&=i\hbar\hat{l}_{\mathrm{y}}\end{aligned}\right\}$$

may be generalized into one relation

$$[\hat{l}_i,\hat{l}_j]=i\hbar\varepsilon_{ijk}\hat{l}_k$$

$$\varepsilon_{ijk}=\begin{cases}1 \text{ for even } ijk \text{ permutation}\\ -1 \text{ for odd } ijk \text{ permutation}\\ 0 \text{ if } i=j \text{ or } j=k \text{ or } k=i\end{cases}$$

N.B.

$$\frac{\partial}{\partial z}\hat{z}\neq 1$$

$$\left(\frac{\partial}{\partial z}\hat{z}\right)\psi=\frac{\partial}{\partial z}\left(z\psi\right)=$$

$$=\psi+z\frac{\partial}{\partial z}\psi$$

Importantly, the total momentum operator commutes with its projections:

$$[\hat{l}^2,\hat{l}_{\mathrm{xyz}}]=0$$

meaning that they share the eigenvector systems.

Spin Dynamics, Lecture 3

Corollary: no two components of angular momentum can be specified precisely at the same time (lack of commutation leads to an uncertainty relation).

$$[\hat{l}_\mathrm{x},\hat{l}_\mathrm{y}]=i\hbar\hat{l}_\mathrm{z} \quad \Rightarrow \quad \Delta l_\mathrm{x}\Delta l_\mathrm{y}\geq\hbar/2$$

Corollary: both the square of angular momentum and one of its components can have a specific value simultaneously, since

$$[\hat{l}^2,\hat{l}_\mathrm{x}]=0; \quad [\hat{l}^2,\hat{l}_\mathrm{y}]=0; \quad [\hat{l}^2,\hat{l}_\mathrm{z}]=0$$

Based on this fact, we will introduce a labelling convention. A state would be labelled

$$\psi=\left|l,m\right\rangle \quad \text{if} \quad \hat{l}^2\psi=l\left(l+1\right)\hbar^2\psi \quad \text{and} \quad \hat{l}_\mathrm{z}\psi=m\hbar\psi$$

that is, if the state is an eigenstate of the momentum squared and its *z* projection with eigenvalues $l\left(l+1\right)\hbar^2$ and $m\hbar$ respectively.

In this new labelling convention

$$\hat{l}^2 \left| l,m \right\rangle = l\left(l+1\right)\hbar^2 \left| l,m \right\rangle \qquad \hat{l}_z \left| l,m \right\rangle = m\hbar \left| l,m \right\rangle$$

We shall skip the derivation for these equations (available in Atkins' Molecular Quantum Mechanics and similar textbooks).

Raising and lowering operators

Consider the following non-Hermitian operators

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y \qquad \hat{l}_- = \hat{l}_x - i\hat{l}_y$$

It is easy to see (exercise!) that

$$[\hat{l}^2, \hat{l}_\pm] = 0 \qquad [\hat{l}_+, \hat{l}_-] = 2\hbar\hat{l}_z \qquad [\hat{l}_z, \hat{l}_\pm] = \pm\hbar\hat{l}_\pm$$

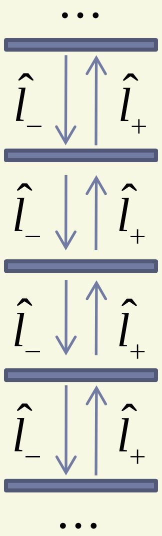
They are called "raising" and "lowering" because they raise and lower the *z*-projection quantum number *m*.

$$\hat{l}_z\hat{l}_\pm|l,m\rangle=\left([\hat{l}_z,\hat{l}_\pm]+\hat{l}_\pm\hat{l}_z\right)|l,m\rangle=\left([\pm\hbar\hat{l}_\pm+\hat{l}_\pm m\right)|l,m\rangle=(m\hbar\pm\hbar)\hat{l}_\pm|l,m\rangle$$

$$\hat{l}^2\hat{l}_\pm|l,m\rangle=\hat{l}_\pm\hat{l}^2|l,m\rangle=\hat{l}_\pm l(l+1)|l,m\rangle=l(l+1)\hat{l}_\pm|l,m\rangle$$

Eigenvalues

$\hat{l}^2$	$\hat{l}_z$
$l(l+1)\hbar^2$	$(m+2)\hbar$
$l(l+1)\hbar^2$	$(m+1)\hbar$
$l(l+1)\hbar^2$	$m\hbar$
$l(l+1)\hbar^2$	$(m-1)\hbar$
$l(l+1)\hbar^2$	$(m-2)\hbar$



Raising and lowering cannot be continued indefinitely:

$$\left\langle\hat{l}_x^2\right\rangle+\left\langle\hat{l}_y^2\right\rangle\geq 0$$

$$\langle l,m|\hat{l}_x^2+\hat{l}_y^2|l,m\rangle=\langle l,m|\hat{l}^2-\hat{l}_z^2|l,m\rangle$$

$$l(l+1)\hbar^2-m^2\hbar^2\geq 0 \quad\Rightarrow\quad |m|\leq\sqrt{l(l+1)}$$

Because the values of *m* are bounded on either side, there must be a state that cannot be raised any further and a state that cannot be lowered any further.

$$\hat{l}^2 \left| l, m_{\max} \right\rangle = l(l+1)\hbar^2 \left| l, m_{\max} \right\rangle; \qquad \hat{l}_z \left| l, m_{\max} \right\rangle = m_{\max}\hbar \left| l, m_{\max} \right\rangle$$

$$\hat{l}^2 \left| l, m_{\min} \right\rangle = l(l+1)\hbar^2 \left| l, m_{\min} \right\rangle; \qquad \hat{l}_z \left| l, m_{\min} \right\rangle = m_{\min}\hbar \left| l, m_{\min} \right\rangle$$

$$\hat{l}_+ \left| l, m_{\max} \right\rangle = 0; \qquad \hat{l}_- \left| l, m_{\min} \right\rangle = 0$$

Therefore

$$l(l+1)\hbar^2 = \left\langle l, m_{\max} \right| \hat{l}^2 \left| l, m_{\max} \right\rangle = \left\langle l, m_{\max} \right| \hat{l}_-\hat{l}_+ + \hat{l}_z^2 + \hbar\hat{l}_z \left| l, m_{\max} \right\rangle = \left(m_{\max}^2 + m_{\max} \right)\hbar^2$$

$$l(l+1)\hbar^2 = \left\langle l, m_{\min} \right| \hat{l}^2 \left| l, m_{\min} \right\rangle = \left\langle l, m_{\min} \right| \hat{l}_+\hat{l}_- + \hat{l}_z^2 - \hbar\hat{l}_z \left| l, m_{\min} \right\rangle = \left(m_{\min}^2 - m_{\min} \right)\hbar^2$$

Equating the two yields a quadratic equation with two solutions

$$m_{\max} = -m_{\min} \qquad\qquad m_{\max} = m_{\min} - 1$$

The second solution violates $m_{\max} > m_{\min}$ and is discarded. Solving the first equation for $m_{\max}$ yields

$$m_{\max} = -l - 1 \qquad\qquad m_{\max} = l$$

where the first solution violates the *m* bounds and is discarded. Finally

$$\hat{l}^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle \qquad \hat{l}_z|l,m\rangle = m\hbar|l,m\rangle$$

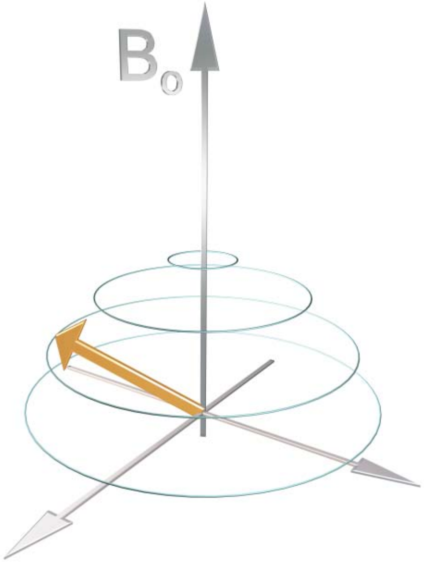
$$m = -l, -l+1, \;\dots\; , l-1, l$$

where *l* is either integer of half-integer. In the case of angular momentum *l* is always integer (a consequence of the quantization imposed by the periodic boundary condition). Half-integer values of *l* will make an appearance when we consider spin.

It can also be shown (DIY or look it up in Atkins) that

$$\hat{l}_\pm|l,m\rangle = \hbar\sqrt{l(l+1)-m(m\pm1)}\,|l,m\pm1\rangle$$

that is, the raising and lowering operators increase or decrease the projection quantum number by 1. It is easy to see that an attempt to raise the top state or lower the bottom state will lead to zero.



Let us place at the end of every chapter … the two letters used by the Roman judges when they did not understand a pleading: *N.L.* (*non liquet*) – it is not clear.

Voltaire

Lecture 4:
Semi-empirical description of spin

Spin as angular momentum. Semi-empirical theory of spin.
Coupling of angular momenta. Rules of vector addition for angular momenta.
Coupled and uncoupled representations. Clebsch-Gordan series.

Dr Ilya Kuprov, University of Oxford, 2009

Angular Momentum, Lecture 2

Why *semi-empirical* theory? We will be using the angular momentum analogy, but unlike *r p*, spin vanishes in the classical limit. Still, a correct theory can be constructed along the angular momentum lines.

Special properties of spin:

1. An intrinsic and unchanging property (e.g. *always* ½ for e^-).
2. Can take half-integer values (yet another weird QM effect).
3. Vanishes in the classical limit (i.e. when $h \to 0$).
4. In most cases yields a point magnetic dipole.

Quantum mechanical description of spin:

$$\psi(\vec{r},t) \;\to\; \begin{pmatrix} \psi(\vec{r},m=-1/2,t) \\ \psi(\vec{r},m=+1/2,t) \end{pmatrix}$$

spinors instead of wavefunctions

$$\psi(\vec{r},m,t) = \psi(\vec{r},t) \otimes \begin{pmatrix} C_{1/2}(t) \\ C_{-1/2}(t) \end{pmatrix} \qquad |\psi_S\rangle = \begin{pmatrix} C_{1/2}(t) \\ C_{-1/2}(t) \end{pmatrix}$$

"spin part"

Angular Momentum, Lecture 2

By analogy with angular momentum, spin *s* can have 2*s*+1 projections. $\left|\psi_{\mathrm{S}}\right\rangle$ is therefore a 2*s*+1 dimensional vector. For spin ½:

$$\left|\psi_{\mathrm{S}}\right\rangle=\begin{pmatrix} C_{1/2}(t) \\ C_{-1/2}(t) \end{pmatrix}$$

is an element of $\mathbb{C}_2$ vector space spanned by $\begin{pmatrix} 1 \\ 0 \end{pmatrix},\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

which should be eigenvectors of $\hat{S}^2$ and $\hat{S}_{\mathrm{Z}}$. Therefore

$$\hat{S}^2=\hbar^2\begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix} \qquad \hat{S}_{\mathrm{Z}}=\hbar\begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

Furthermore, they should be raised and lowered into each other, so

$$\hat{S}_{+}=\hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \hat{S}_{-}=\hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

For spins greater than ½ these matrices will have greater dimensions. Multi-gigabyte matrices are a common occurrence in current spin dynamics research.

Angular Momentum, Lecture 2

We will postulate the same commutation relations for spin as the ones we derived in the previous lecture for the angular momentum.

$$[\hat{S}_X,\hat{S}_Y]=i\hbar\hat{S}_Z \qquad [\hat{S}^2,\hat{S}_{XYZ}]=0 \qquad \hat{S}_X=\frac{\hat{S}_+ + \hat{S}_-}{2}$$

$$[\hat{S}_Z,\hat{S}_X]=i\hbar\hat{S}_Y \qquad \hat{S}_+=\hat{S}_X+i\hat{S}_Y$$

$$[\hat{S}_Y,\hat{S}_Z]=i\hbar\hat{S}_X \qquad \hat{S}_-=\hat{S}_X-i\hat{S}_Y \qquad \hat{S}_Y=\frac{\hat{S}_+ - \hat{S}_-}{2i}$$

The last two relations give us matrices for $\hat{S}_X$ and $\hat{S}_Y$ for spin ½:

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

The commutation relations above are easily verified by hand. The three matrices above are called *Pauli matrices*. They make an appearance whenever angular momentum does, *i.e.* in just about every area of physical chemistry and spectroscopy. The derivation above is known as *discrete (or matrix) representation of angular momentum operators*.

Zeeman interaction

In classical physics the interaction energy between a point magnetic dipole and magnetic field is

$$E = -\vec{\mu} \cdot \vec{B}$$

If the magnetic field is along *z*-axis, this simplifies into

$$E = -\mu_{\mathrm{z}} B_{\mathrm{z}}$$

In quantum mechanics μ_{z} is replaced by $\gamma \hat{S}_{\mathrm{z}}$, resulting in

$$\hat{H} = -\gamma B \hat{S}_{\mathrm{z}} = -\omega \hat{S}_{\mathrm{z}}$$

The equation of motion for the observable corresponding to operator $\hat{A}$ has been derived in the Quantum Mechanics course

$$\frac{d \left\langle \hat{A} \right\rangle}{dt} = \frac{i}{\hbar} \left\langle [\hat{H}, \hat{A}] \right\rangle$$

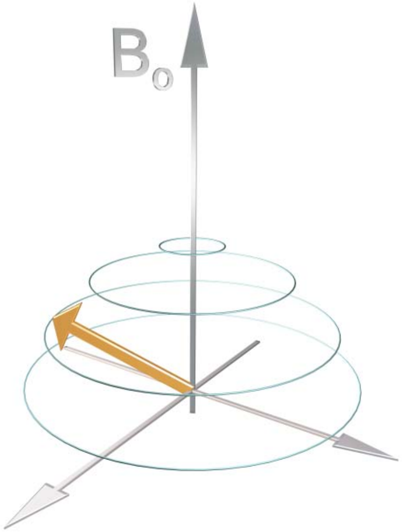
Computing the relevant commutators yields the following system of differential equations

Zeeman interaction

$$\frac{d}{dt}\langle S_x \rangle = \omega \langle S_y \rangle$$

$$\frac{d}{dt}\langle S_y \rangle = -\omega \langle S_x \rangle$$

$$\frac{d}{dt}\langle S_z \rangle = 0$$



If we assume that the initial polarization of spin was along the x-axis, that is

$$\langle S_x \rangle = 1; \qquad \langle S_y \rangle = 0; \qquad \langle S_z \rangle = 0;$$

the following solutions emerge:

$$\langle S_x \rangle (t) = \cos(\omega t)$$

$$\langle S_y \rangle (t) = \sin(\omega t)$$

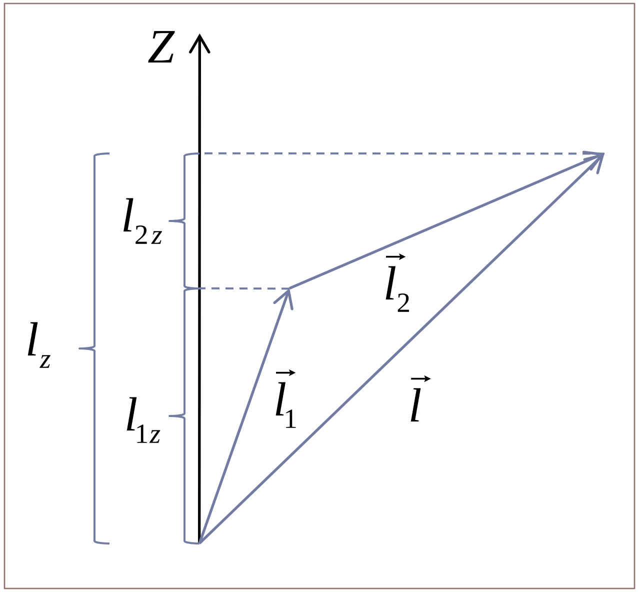
$$\langle S_z \rangle (t) = 0$$

The observed direction of spin precesses around the *z*-axis, *i.e.* along the direction of the applied magnetic field.

Angular Momentum, Lecture 2

Addition of angular momenta

In an interacting system, only the *total* angular momentum is conserved. If there are two or more particles bearing angular momentum and/or spin, we need a way to find the total momentum.



If the two subsystems are in states

$$|l_1, m_1\rangle \qquad |l_2, m_2\rangle$$

the total projection quantum number (as may be seen from the schematic on the left) is a simple sum:

$$M = m_1 + m_2$$

However, the *l* quantum numbers do require careful derivation, because their relations are not as straightforward.

$$\hat{l}_1^{\,2}|l_1, m_1\rangle = l_1(l_1+1)\hbar^2|l_1, m_1\rangle \qquad \hat{l}_2^{\,2}|l_2, m_2\rangle = l_2(l_2+1)\hbar^2|l_2, m_2\rangle$$

Angular Momentum, Lecture 2

We will only consider the classical argument here (the quantum mechanical derivation, called *highest weight construction*, will be given in Term 2).

$$\vec{l} = \vec{l}_1 + \vec{l}_2$$

$$l^2 = \left(\vec{l}_1 + \vec{l}_2\right)\cdot\left(\vec{l}_1 + \vec{l}_2\right) = l_1^2 + 2\vec{l}_1\cdot\vec{l}_2 + l_2^2 = l_1^2 + 2l_1 l_2\cos\varphi + l_2^2$$

but $-1 \le \cos\varphi \le 1,$ therefore

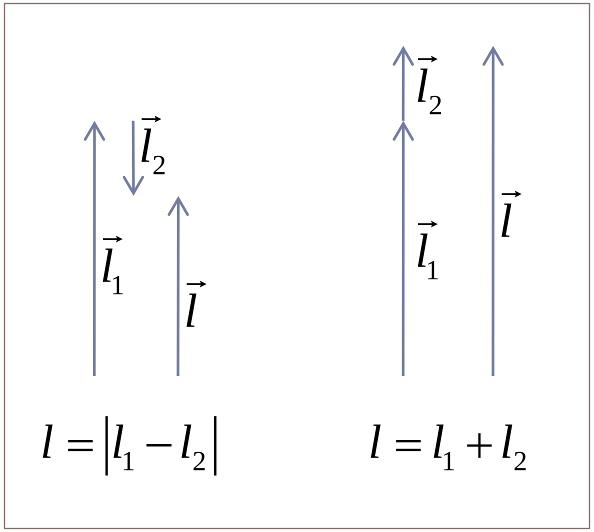
$$l_1^2 - 2l_1 l_2 + l_2^2 \le l^2 \le l_1^2 + 2l_1 l_2 + l_2^2$$

$$\left(l_1 - l_2\right)^2 \le l^2 \le \left(l_1 + l_2\right)^2$$

$$\left|l_1 - l_2\right| \le l \le l_1 + l_2$$

Very important result (momentum addition rules):

$$\boxed{\begin{aligned} m &= m_1 + m_2 \\ \left|l_1 - l_2\right| &\le l \le l_1 + l_2 \end{aligned}}$$



Angular Momentum, Lecture 2

Coupled basis construction

1. Start from the state with the highest projection

$$\left|l,l\right\rangle=\left|l_1,l_1\right\rangle\left|l_2,l_2\right\rangle$$

2. Sequentially apply lowering operators $\hat{L}_-=\hat{L}_{1-}+\hat{L}_{2-}$ to both sides

$$\sqrt{l\left(l+1\right)-l\left(l-1\right)}\left|l,l-1\right\rangle=$$

$$\sqrt{l_1\left(l_1+1\right)-l_1\left(l_1-1\right)}\left|l_1,l_1-1\right\rangle\left|l_2,l_2\right\rangle+\sqrt{l_2\left(l_2+1\right)-l_2\left(l_2-1\right)}\left|l_1,l_1\right\rangle\left|l_2,l_2-1\right\rangle$$

until the state with the lowest projection is reached.

3. Construct the orthogonal complement to the state with the next highest projection

$$\left|l-1,l-1\right\rangle=A\left|l_1,l_1-1\right\rangle\left|l_2,l_2\right\rangle+B\left|l_1,l_1\right\rangle\left|l_2,l_2-1\right\rangle$$

and apply sequential lowering until all $\left|l-1,m\right\rangle$ states are sampled.

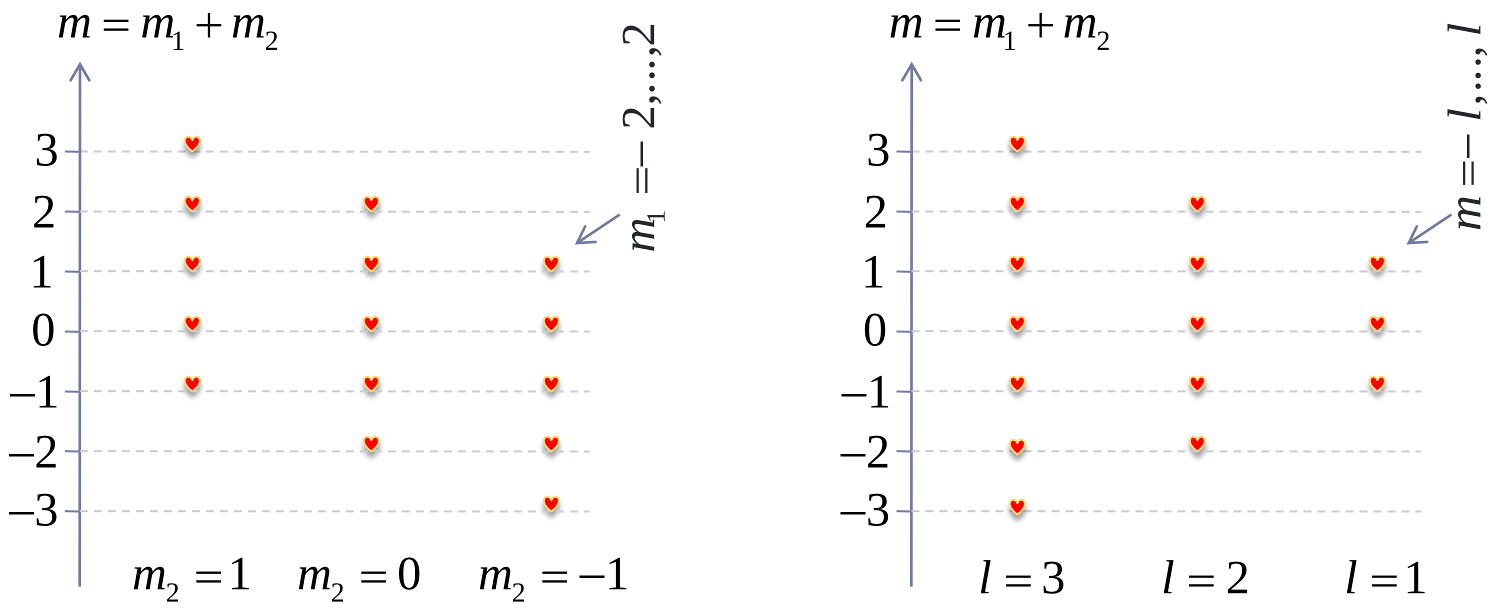
4. *Et cetera… (a rather tedious procedure)*

Angular Momentum, Lecture 2

The procedure can be generalized (*Clebsch-Gordan series*):

$$|l,m\rangle = \sum_{m_1,m_2} (-1)^{l_1-l_2+m}\sqrt{2l+1}\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix}|l_1,m_1\rangle|l_2,m_2\rangle$$

Schematic representation of angular momentum coupling

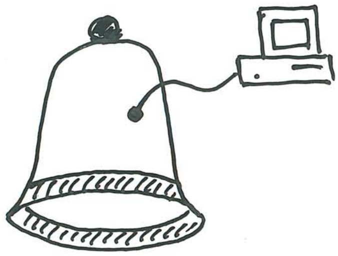


1. Foundations of Fourier spectroscopy

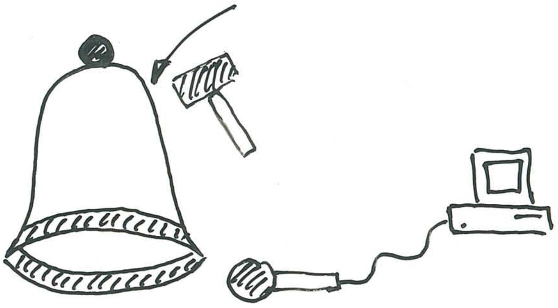
ⓐ Introduction

There are two ways of tuning a bell...

A



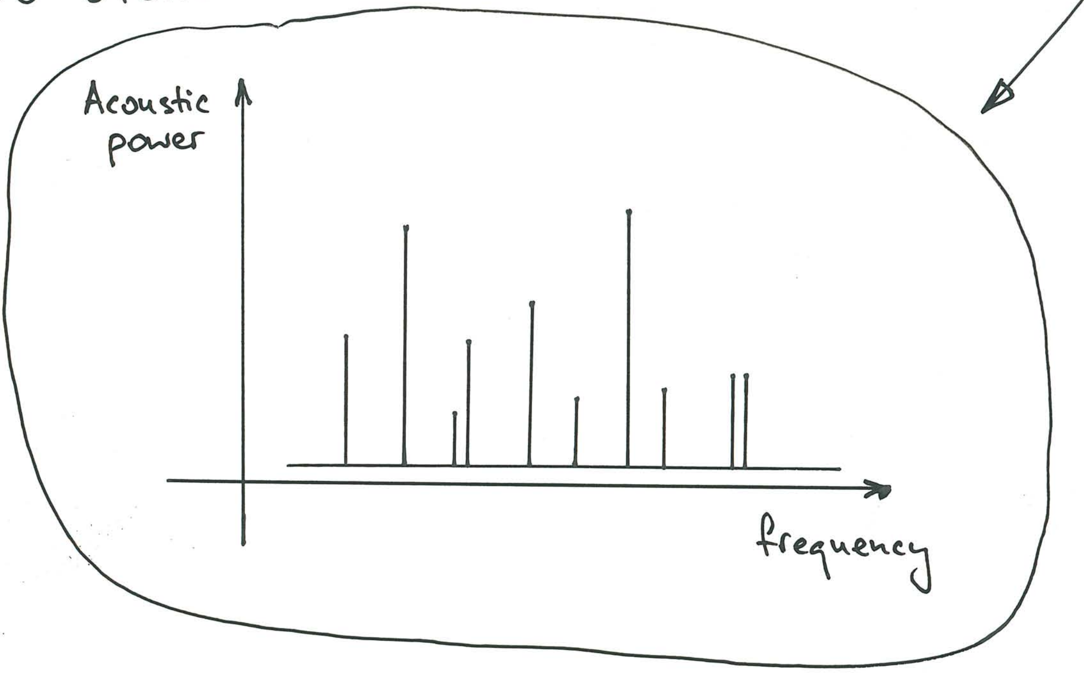
B



Check every frequency in turn, find those the bell resonates on.

Hit the bell with a hammer. Record the sound and determine the frequencies it contains. FAST!

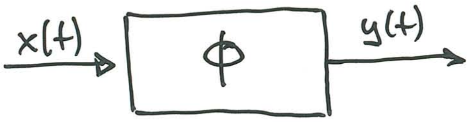
LONG STORY



Not just bells — many other physical systems behave like this. Why?

ⓑ Linear response theory

Consider a black box with an input and an output...



OR $y(t) = \Phi\{x(t)\}$

The system Φ is called <u>linear time-invariant</u> if :

1. $\Phi\{\alpha x_1(t) + \beta x_2(t)\} = \alpha \Phi\{x_1(t)\} + \beta \Phi\{x_2(t)\} = \alpha y_1(t) + \beta y_2(t)$

2. $\Phi\{x(t-t_0)\} = y(t-t_0)$

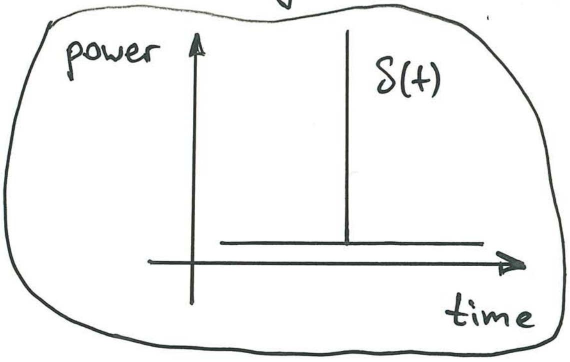
The input function $x(t)$ can be expanded in some basis set:

$$x(t) = \sum_k x_k g_k(t) \qquad \text{OR} \qquad x(t) = \int \chi(k)\, g(k,t)\, dk$$

Then the response to an arbitrary input function may be written in terms of responses to individual basis functions:

(*) $$y(t) = \Phi\{x(t)\} = \sum_k x_k \Phi\{g_k(t)\} = \int \chi(k) \Phi\{g(k,t)\} dk$$

Now, what does a hammer strike amount to? A very short and sharp peak — a delta-function.



A basic property of the delta-function (see your maths course) is:

$$\int_{-\infty}^{\infty} f(x)\, \delta(x-x_0)\, dx = f(x_0) \,,$$ therefore

$$x(t) = \int_{-\infty}^{\infty} x(\tau)\, \delta(\tau - t)\, d\tau .$$

After feeding this into our black box (Equation (*)), we get:

(**) $$y(t) = \Phi\{x(t)\} = \int_{-\infty}^{\infty} x(\tau)\, \Phi\{\delta(\tau - t)\}\, d\tau .$$

The function $h(t) = \Phi\{\delta(t)\}$ is called <u>pulse response</u> of the system.

From Equation (**), the response to <u>any</u> input function $x(t)$ can be calculated as:

$$y(t) = \int_{-\infty}^{\infty} x(\tau)\, h(\tau - t)\, d\tau .$$

This integral is known as a a <u>convolution integral</u>, and is often abbreviated as

$$y(t) = x(t) * h(t) .$$

$$\boxed{\begin{aligned} y(t) &= x(t) * h(t) \\ f(t) * g(t) &= \int_{-\infty}^{\infty} f(\tau)\, g(\tau - t)\, d\tau \\ h(t) &= \Phi\{\delta(t)\} \end{aligned}}$$

So, in some sense the pulse response $h(t)$ contains complete information about our linear time-invariant black box Φ and allows us to predict its response to an arbitrary input.

But what exactly is $h(t)$?

Let us try some spectroscopy on Φ. A linear system cannot shift frequencies (prove it!), therefore:

$$\Phi\{e^{i\omega t}\} = H(\omega) e^{i\omega t}$$

frequency response

On the other hand:

$$\Phi\{e^{i\omega t}\} = \int_{-\infty}^{\infty} e^{i\omega\tau} h(\tau - t)\, d\tau =$$

$$= \int_{-\infty}^{\infty} e^{i\omega(\tau + t)} h(\tau)\, d\tau = \left(\int_{-\infty}^{\infty} h(\tau) e^{i\omega\tau} d\tau \right) e^{i\omega t}$$

Putting the two together:

$$H(\omega) e^{i\omega t} = \int_{-\infty}^{\infty} h(\tau)\, e^{i\omega\tau} d\tau\; e^{i\omega t}. \qquad \text{Finally:} \quad H(\omega) = \int_{-\infty}^{\infty} h(\tau)\, e^{i\omega\tau} d\tau .$$

> So the frequency response (aka spectrum) of a linear time-invariant system is a Fourier transform of its pulse response (aka FID).

Nothing special about bells and NMR — all LTI systems behave like that. LTI is an appoximation — most systems are not perfectly linear and most pulses are not perfectly sharp.

ⓒ Properties of the Fourier transform

Definition

$$F_+\{f(t)\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t)\, e^{-i\omega t} dt$$

$$F_-\{f(t)\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t)\, e^{i\omega t} dt$$

(coefficients may vary, the definition on the left preserves the function norm)

As an exercise, demonstrate that $F_+\{F_-\{f(t)\}\} = F_-\{F_+\{f(t)\}\} = f(t)$

Linearity

$$F_\pm\{\alpha f(t) + \beta g(t)\} = \alpha F_\pm\{f(t)\} + \beta F_\pm\{g(t)\}$$

FT of a derivative

$$F_\pm\{f^{(k)}(t)\} = (\pm i\omega)^k F_\pm\{f(t)\}$$

Exercise: demonstrate that, for a one-sided Fourier transform, $f(0)$ makes an appearance.

Derivative of an FT

$$\left(F_\pm\{f(t)\}\right)^{(k)} = (\mp i)^k F_\pm\{t^k f(t)\}$$

Convolution theorem

$$f * g = \int_{-\infty}^{\infty} f(\tau)\, g(t-\tau)\, d\tau = F_-\{F_+\{f(t)\} F_+\{g(t)\}\} =$$

$$= F_+\{F_-\{f(t)\} F_-\{g(t)\}\}.$$

i.e. convolution in frequency domain amounts to multiplication in the time domain. This will be very useful when we get to window functions.

Wiener – Khinchin theorem

For the autocorrelation function of a random process $f(t)$:

$$C(t) = \int_{-\infty}^{\infty} f^*(\tau)\, f(t+\tau)\, d\tau = F_+\{|F_-\{f(t)\}|^2\}$$

(this is extremely useful in relaxation theory)

Power theorem

The Fourier transform, as defined above, is unitary, i.e.

$$\int_{-\infty}^{\infty} |F_\pm\{f(t)\}|^2 d\omega = \int_{-\infty}^{\infty} |f(t)|^2 dt$$

Discrete and 'fast' Fourier transform

For discrete data the integral can be represented by a sum:

$$\left(F_+\{f\}\right)_n = \frac{1}{N\sqrt{2\pi}} \sum_{k=0}^{N-1} f_k e^{-ikn/N}.$$

This sum has to be computed for every point in the spectrum, meaning that N^2 multiplications are required for a size N FT. That's a lot.

If $N = 2^n$, the FT can be broken down into smaller chunks yielding $N \log_2 N$ scaling. That is known as 'fast' Fourier transform.

2. Introduction to digital signal processing

ⓐ Sampling rate and digital resolution.

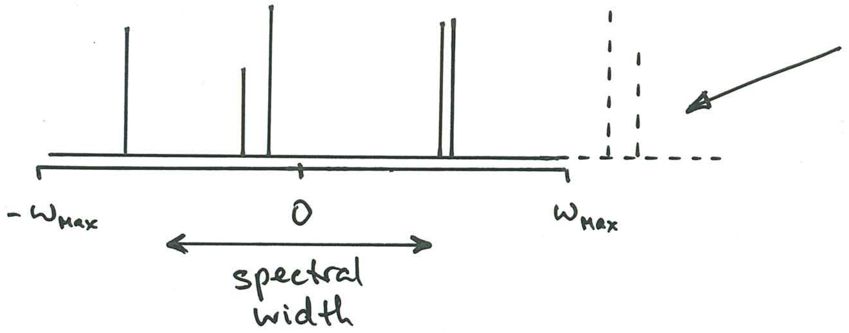
Sampling rate – number of points per unit time used to represent a continuous time-domain signal in a discrete form.

Digital resolution – number of points per unit frequency used to represent a frequency domain signal in a discrete form.

Nyquist condition : perfect reconstruction of the signal from the samples is possible if and only if the sampling rate exceeds two points per period of the fastest oscillation found in the signal.

Example : the correct digitization of an NMR spectrum located between 0 and 15kHz requires 30kHz sampling rate.

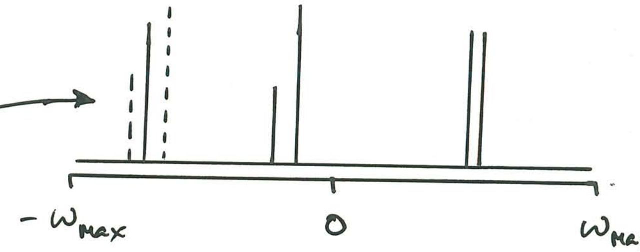
Violating the Nyquist condition is not a good idea!



signals outside the spectral width will be 'folded' inside it.

What would happen if we decide to oversample the signal instead?

Any signal has noise in it
More points → more unnecessary noise.



wrong position,
wrong order,
wrong phase.

Conclusion: the best possible sampling in almost any experiment is the Nyquist sampling.

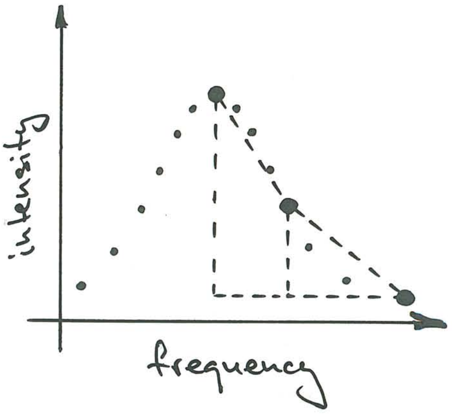
ⓑ Harmonic interpolation and zero filling

Padding the time-domain signal with zeros amounts to harmonic interpolation in the frequency domain:

Original spectrum: $\frac{1}{N\sqrt{2\pi}}\sum_{k=0}^{N-1} f_k e^{-ikn/N}$

Zero-filled FT : $\frac{1}{2N\sqrt{2\pi}}\sum_{k=0}^{N-1} f_k e^{-ikn/2N}$

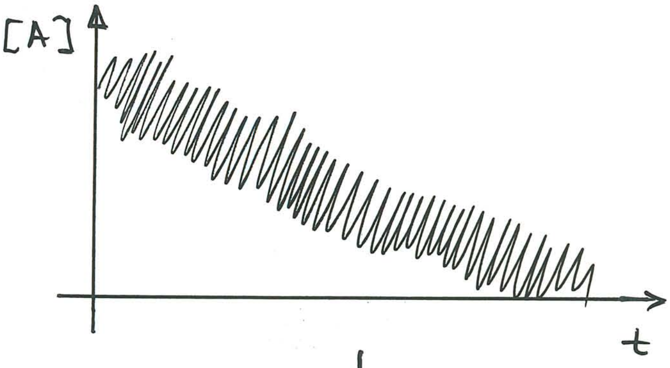
The frequency sampling step (digital resolution) became finer ⇒ more accurate quantification.



Sharp signals often require zero filling to be integrated accurately, particularly in multi-dimensional experiments.

ⓒ Band-pass filters

Imagine a chemical kinetics experiment with a large amount of signal integration noise...



The frequency of the signal we are interested in is clearly way lower than that of the noise.

Can we shut the noise off?

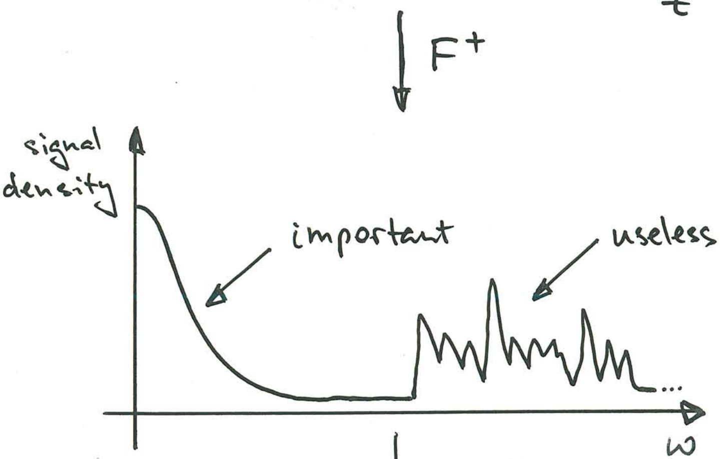
Let:

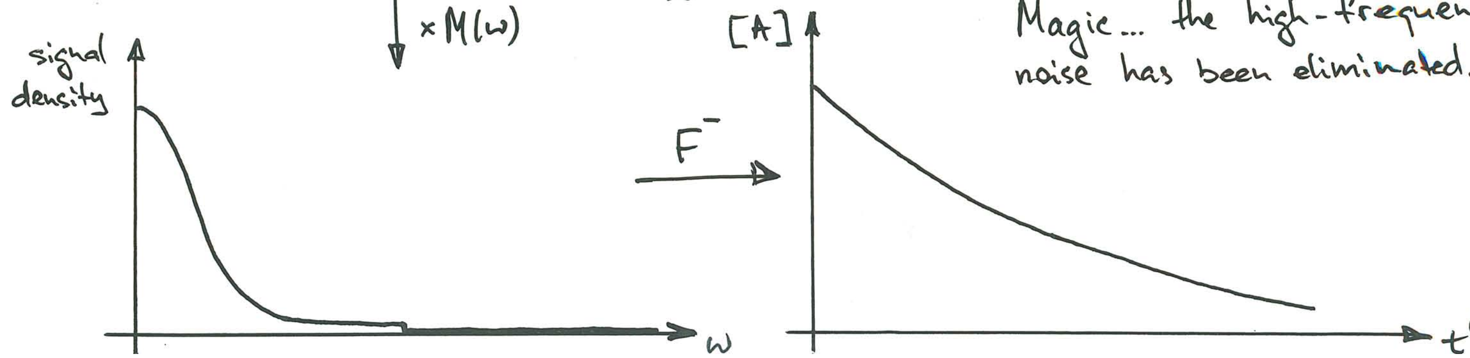
$$M(\omega) = \begin{cases} 0 & \text{for unwanted } \omega \\ 1 & \text{for desired } \omega \end{cases}$$

(magnitude transfer function)

Then $[A]^*(t) = F^-\{M(\omega)F^+\{[A](t)\}\}$

would have the undesired frequencies eliminated...





Magic... the high-frequency noise has been eliminated.

Despite their complicated appearance, band-pass filters are linear:

$$F^{+}\{f(t)\} = \frac{1}{N\sqrt{2\pi}} \sum_{k=0}^{N-1} f_k e^{-ikn/N} \Rightarrow \overrightarrow{F^{+}\{f(t)\}} = A\vec{f}\ \text{, where}$$

$$A_{nk} = \frac{1}{N\sqrt{2\pi}} e^{-ikn/N}. \quad \text{Similarly,} \quad [A^{-1}]_{nk} = \frac{1}{N\sqrt{2\pi}} e^{ikn/N}.$$

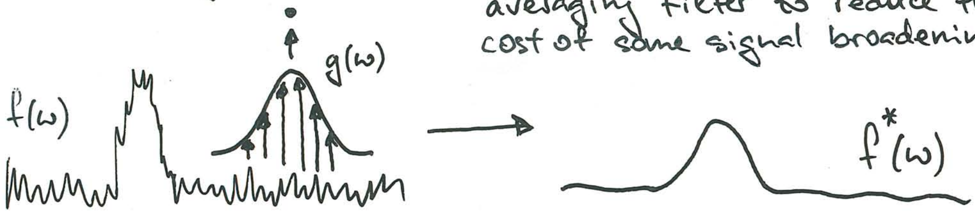
So, a discrete Fourier transform may be represented by a matrix acting on a vector of digitized data values.

Magnitude transfer function zeroing the unwanted frequencies may be represented by a diagonal matrix. Therefore:

$$f^{*}(t) = A^{-1} M A f(t) \text{, which is linear in } f(t).$$

ⓓ Convolution filters (aka window functions)

Let us try to smooth our frequency-domain signal using a local averaging filter to reduce the noise at the cost of some signal broadening...



Mathematically speaking, this is a convolution operation:

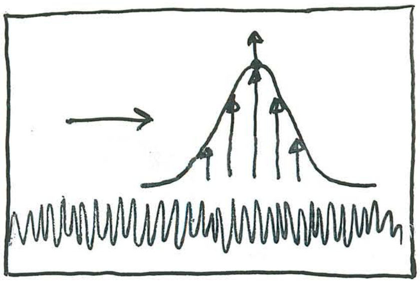
$$f^{*}(\omega) = \int_{-\infty}^{\infty} f(\nu)\cdot g(\omega-\nu)\, d\nu \qquad \text{OR} \qquad f^{*}(\omega) = f(\omega) * \underset{\swarrow\ \text{often a Lorentzian function.}}{g(\omega)}$$

We do know, however, that we could reverse-FT $f(\omega)$ and $g(\omega)$, multiply them and forward-FT the result (see Lecture 1).

What is the inverse FT of $f(\omega)$? The FID.

What is the inverse FT of the Lorentzian function $\frac{1}{1+\omega^2}$? $\underline{\underline{e^{-t}}}$

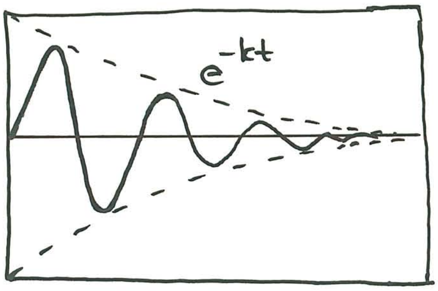
So...



Lorentzian smoothing convolution filter.

$$\Longleftrightarrow$$

FT



Exponential apodization.

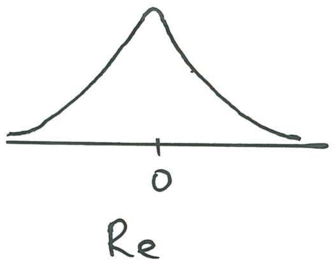
For didactic purposes, let us Fourier-transform an exponential decay...

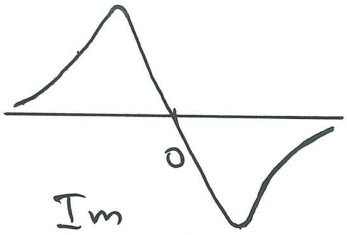
$$f(t) = e^{-t/T_2} \qquad f(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{-t/T_2} e^{-i\omega t}\, dt = \ldots = \frac{1}{\sqrt{2\pi}} \frac{1}{1/T_2 + i\omega} =$$

$$= \frac{1}{\sqrt{2\pi}} \left(\frac{1/T_2 - i\omega}{1/T_2^2 + \omega^2} \right).$$

Real part: $\frac{1}{\sqrt{2\pi}} \cdot \frac{1/T_2}{1/T_2^2 + \omega^2}$ – Lorentzian curve.

Imaginary part: $\frac{1}{\sqrt{2\pi}} \cdot \frac{-\omega}{1/T_2^2 + \omega^2}$ – "dispersion" curve.





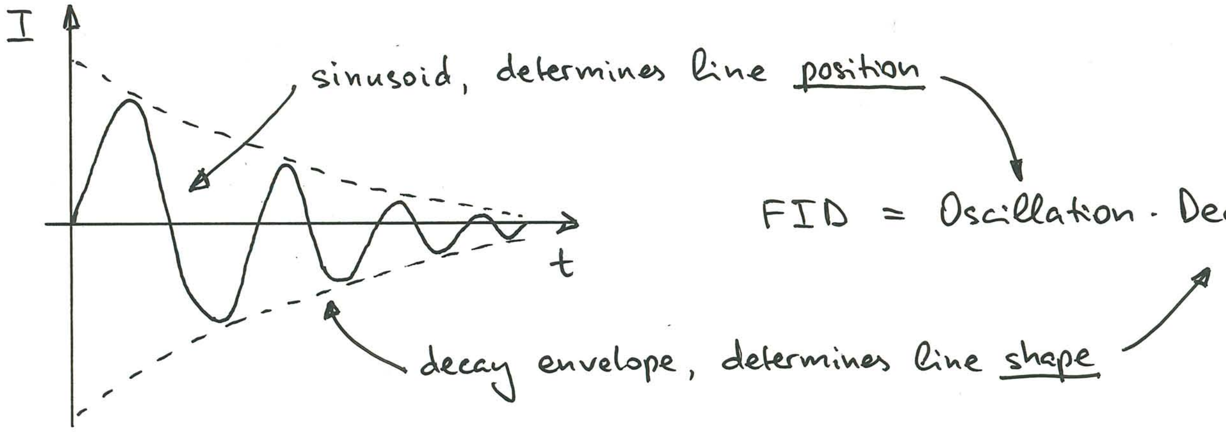
... so that's the standard line shape, positioned at zero.

Now let us Fourier-transform an exponential oscillation...

$$f(t) = e^{i\omega_0 t} \qquad f(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega_0 t} e^{-i\omega t}\, dt = \delta(\omega - \omega_0)$$

– delta-function at the peak position.

So, in the absence of FID decay all signals are infinitely sharp. It is the decay that gives lines their shape!



FID = Oscillation · Decay.

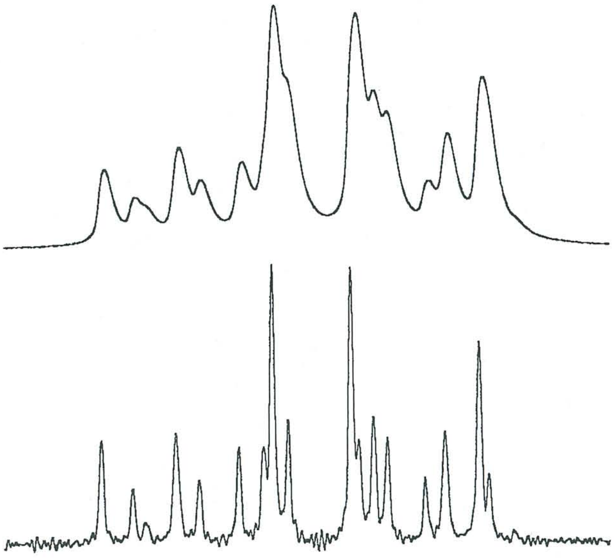
But the envelope is relatively easy to manipulate...

- exponential weighting: aka soft low-pass, speeds the decay up, makes signals broader, but reduces noise
- Lorentz-Gaussian transformation: replaces e^{-t/T_2} with $e^{-t^2/T_2'}$, makes signals narrower, but enhances the noise.

Etc, etc, there's a large number of window functions. All of them correspond to convolution filters in the frequency domain.

The window function choice mostly depends on S/N budget. You can trade some S/N for some resolution and vice versa.

ⓔ Reference deconvolution



In a poorly shimmed NMR magnet all signals are distorted in precisely the same way:

$$\underset{\substack{\uparrow \\ \text{experimental}}}{S_{exp}(\omega)} = \int_{-\infty}^{\infty} \underset{\substack{\uparrow \\ \text{ideal}}}{S_{id}(\omega')}\, \underset{\substack{\uparrow \\ \text{bloody shims.}}}{R(\omega-\omega')}\, d\omega'$$

But we know that in time domain:

$$S_{exp}(t) = S_{id}(t)\cdot R(t)$$

, so we could recover $S_{id}(t)$ if only we knew the envelope function $R(t)$. This is where the "reference" comes in. If we have an a priori standalone singlet (e.g. TMS) $s(\omega)$, then shifting it to zero and performing an inverse FT recovers the envelope:

$$R(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} s(\omega-\omega_0)\, e^{i\omega t}\, d\omega$$

If the desired envelope is $P(t)$, then the following transformation gets rid of the poor shimming:

$$S_{id}(\omega) = F^{+}\left\{ F^{-}\{S_{exp}(\omega)\}\cdot\left(F^{-}\{s(\omega-\omega_0)\}\right)^{-1} P(t)\right\}.$$

It should be noted that the S/N cost is often huge.

ⓕ Analytic representation and Hilbert transform

In most cases the real part of the spectrum is not independent from the imaginary part:

$$\mathrm{Im}(S(t)) = \mathrm{p.v.}\int_{-\infty}^{\infty} \mathrm{Re}(S(t))\, h(t-\tau)\, d\tau \;;\; h(t) = \frac{1}{\pi t}.$$

So, if you've digitized a spectrum from a 1960-es paper, you may still be able to phase it...

But what exactly is "phasing"? Remember that a Fourier transform of $e^{i\omega_0 t} e^{-t/T_2}$ is a complex-valued function:

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{1/T_2 + i(\omega-\omega_0)} = \underbrace{\frac{1}{\sqrt{2\pi}} \cdot \frac{1/T_2}{1/T_2^2 + (\omega-\omega_0)^2}}_{\text{"real"}} + \underbrace{\frac{1}{\sqrt{2\pi}} \cdot \frac{-i(\omega-\omega_0)}{1/T_2^2 + (\omega-\omega_0)^2}}_{\text{"imaginary"}} ;$$

A "phase" is an offset in the oscillatory part: $e^{i\omega t +} \; e^{-t/T_2}$.

φ may depend on ω, and often does.

Uniform phase shift comes from the spectrometer reference clock and may be corrected easily:

$$(*) \begin{cases} R = \text{"real"} \cdot \cos\varphi + \text{"imaginary"} \cdot \sin\varphi \\ I = -\text{"real"} \cdot \sin\varphi + \text{"imaginary"} \cdot \cos\varphi \end{cases}$$

Phase correction (manual or automatic) consists in finding such φ as would minimize the amount of dispersive signal in R.

Non-uniform phasing: when $\varphi = \varphi(\omega) = \varphi_0 + \varphi_1 \omega + \varphi_2 \omega^2 + \dots$

"orders"

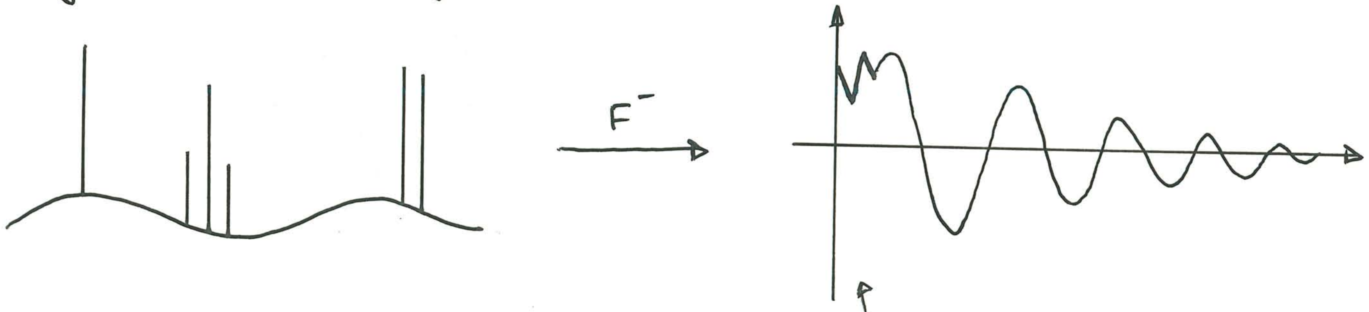
Equations (*) then need to be applied to each frequency point separately.

What would make the phase non-uniform? Usually a time shift in the FID:

$$f(t) \Rightarrow f(\omega) \qquad\qquad f(t-t_0) \Rightarrow e^{i\omega t_0} f(\omega)$$

⑨ Baseline matters

Most types of baseline distortions are very broad features, meaning that they are determined by just a few initial points in the FID...



spike at the start of the FID.

Ways to correct? Could fit some function in the frequency domain and subtract it out, but there is a better way...

So far so good... but what if a part of your data is not just distorted, but completely destroyed? It turns out that some cases are tractable.

(h) Linear prediction

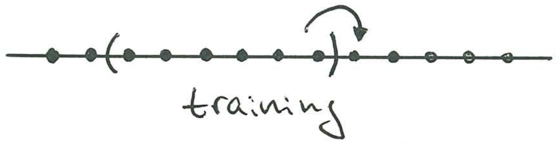
If we make a (reasonable) assumption that the future values of a discrete time-domain signal may be represented as a linear function of the past values, we get:

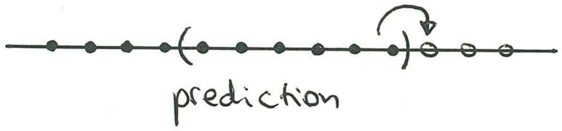
$$f(t_n) = \sum_{k=1}^{m} a_k f(t_{n-k}) \quad \leftarrow \text{a linear combination of } m \text{ past values with unknown coefficients } a_k.$$

The number of coefficients m determines prediction accuracy (the more, the better, but generally m > the number of distinct peaks expected in the spectrum). How to find the coefficients? From a so-called "training set".

Let us assume we already have 2m points (e.g. from experiment). Then

$$\Big\}_{l=1}^{m} \; f(t_{m+l}) = \sum_{k=1}^{m} a_k f(t_{m+l-k})$$





i.e. the known points give a system of linear equations for a_k.
(if this system is overdetermined, it is solved in a least squares sense)

Linear prediction is useful for:

→ dealing with most types of baseline distortions ("backward LP").

→ improving the resolution of data with unfinished FIDs as an alternative to zero filling ("forward LP").

→ eliminating point defects in the acquired data.

(i) Retrofitting

With very non-uniformly sampled data, a Fourier transform may be obtained in a least squares sense:

$$F^{+}\{f(t)\} = F^{+}\left(\min_{f(\omega)}\left\{\left\|f(t) - F^{-}\{f(\omega)\}\right\|^{2}\right\}\right)$$

N.B. non-uniformly sampled data is encountered more and more often – people are trying to save the spectrometer time.

where the norm is usually either the 2-norm or the ∞-norm, defined using the available data points.

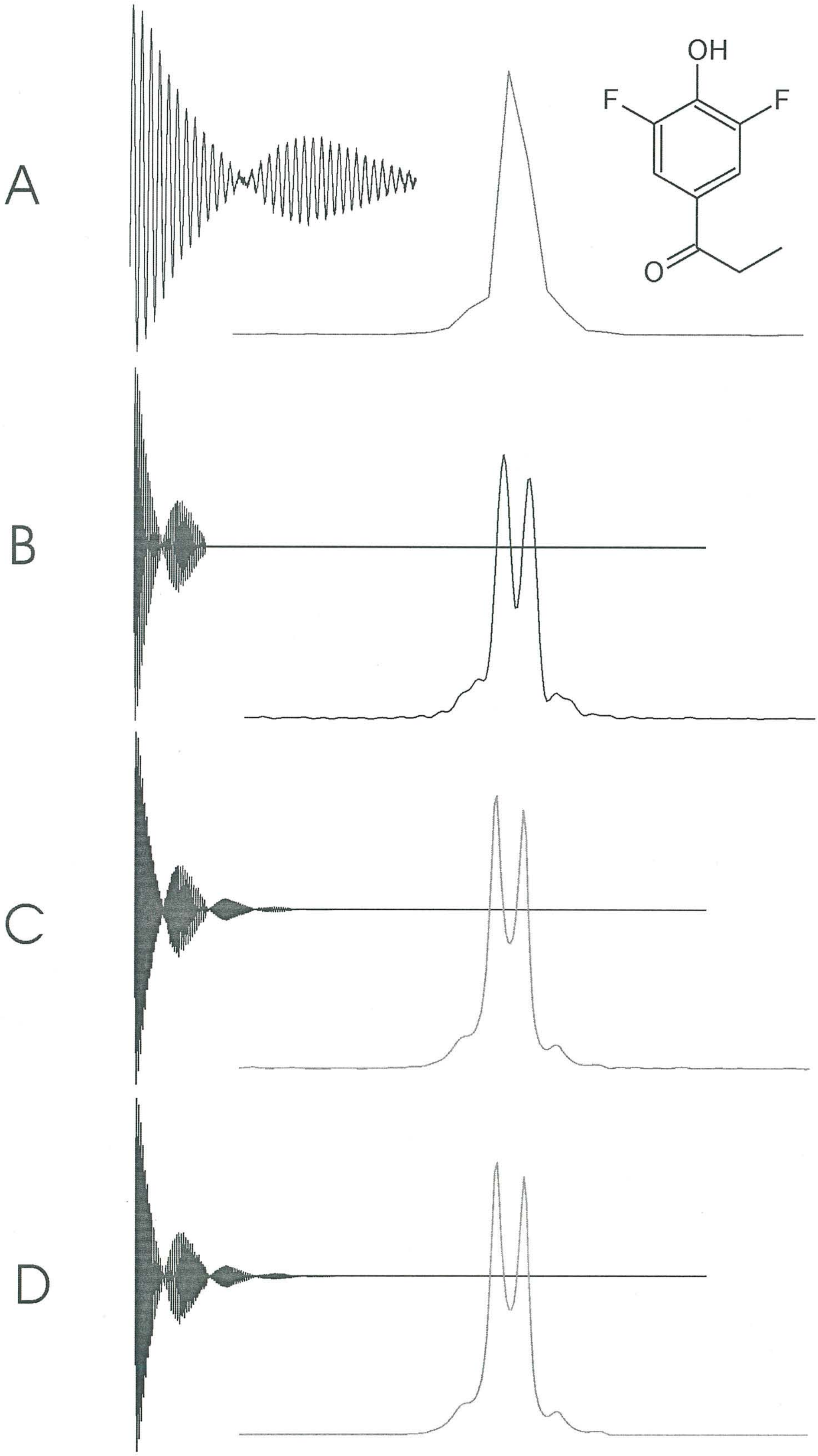


Fig. 3. Ways of obtaining sufficient digital resolution with deliberately or accidentally truncated set of data. (**A**) Original fid, ^{19}F signal of 3,5-difluoro-4-hydroxypropiophenone, one of my compounds. Spectral width is 12kHz – I had to include the signals of possible admixtures. The signal is useless, since I need relative doublet intensities. (**B**) Plain zero-filling and its result. (**C**) Linear prediction of the missing points and its result. (**D**) Ten-line ME spectrum reconstruction and the corresponding fid. Fid was obtained by inverse Fourier transform of the spectrum.

5. Spin Interactions and Couplings

ⓐ Types of interaction Hamiltonians.

The vast majority of spin systems only have three types of interactions:

→ Linear in spin: these come from a coupling to some external vectors (magnetic field, orbital angular momentum etc)

$$\hat{H} = \underset{\substack{\text{spin operators}\\ (\hat{S}_x, \hat{S}_y, \hat{S}_z)}}{\hat{\vec{S}}} \cdot \underset{\text{"interaction tensor"}}{A} \cdot \underset{\text{external vector}}{\vec{B}} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

(chemical shielding, g-tensor, spin-orbit coupling etc)

→ Bilinear in spin: these come from couplings between the spins. The mechanisms causing the coupling can vary a lot, but the algebraic form of the result is always the same:

$$\hat{H} = \underset{\substack{\text{first spin}\\ (\hat{S}_x\ \hat{S}_y\ \hat{S}_z)}}{\hat{\vec{S}}} \cdot \underset{\text{"interaction tensor"}}{A} \cdot \underset{\substack{\text{second spin}\\ (\hat{L}_x\ \hat{L}_y\ \hat{L}_z)}}{\hat{\vec{L}}} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix}$$

(scalar, dipolar, hyperfine, exchange etc)

→ Quadratic in spin: these are often caused indirectly by other interactions, but manifest themselves algebraically as coupling between a spin and itself:

$$\hat{H} = \hat{\vec{S}} \cdot \underset{\text{"interaction tensor"}}{A} \cdot \hat{\vec{S}} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$

spin operators $(\hat{S}_x\ \hat{S}_y\ \hat{S}_z)$

(quadrupolar interaction, zero-field splitting etc)

Higher order interactions do exist (e.g. in paramagnetic metal clusters), but they are extremely rare.

In most cases the matrix A is symmetric, meaning that its eigenvalues are real and its eigenvectors orthogonal.

Let A_{XX}, A_{YY}, A_{ZZ} be the eigenvalues of A. The interaction tensor A is called

isotropic if $A_{XX} = A_{YY} = A_{ZZ} = a$

axial if $A_{XX} = A_{YY} \neq A_{ZZ}$ Axiality $= A_{ZZ} - \frac{1}{2}(A_{XX} - A_{yy})$

rhombic if $A_{XX} \neq A_{YY} \neq A_{ZZ}$ Rhombicity $= A_{XX} - A_{yy}$

traceless if $A_{XX} + A_{YY} + A_{ZZ} = 0$

When the interaction tensor is isotropic, the Hamiltonians above acquire a particularly simple ("scalar") form:

$$\hat{H} = (\hat{S}_x \; \hat{S}_y \; \hat{S}_z)\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}\begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix} = a(\hat{S}_x\hat{L}_x + \hat{S}_y\hat{L}_y + \hat{S}_z\hat{L}_z)$$

"scalar coupling"

Scalar interactions also do not change under a rotation (hence the name)

$$\hat{\hat{R}}(\hat{A}) = \hat{R}\cdot A\cdot\hat{R}^{-1} = a\hat{R}\cdot\mathbb{1}\cdot\hat{R}^{-1} = a\mathbb{1} = A$$

More generally, every interaction tensor has three rotation invariants:

$I_A = \mathrm{Tr}(A) = A_{11} + A_{22} + A_{33}$ – determines the scalar part, survives rotational averaging.

$II_A = \frac{1}{2}\left(\mathrm{Tr}(A)^2 - \mathrm{Tr}(A^2)\right)$ – determines relaxation properties and powder patterns in solids.

$III_A = \det(A)$ – not used.

The following relation holds (DIY): $A^3 - I_A A^2 + II_A A - III_A \mathbb{1} = 0$.

ⓑ Experimentally encountered interactions

- J-coupling: bilinear coupling between two nuclear spins, 5–500 Hz, the anisotropy is often ignored.

The dominant contribution comes from the Fermi contact interaction with the electrons:

$$\hat{H}_{FC} = \frac{16\pi\beta\hbar}{3}\sum_{kn}\gamma_n\,\delta(\vec{r}_{kn})\,\hat{\vec{L}}_k\,\hat{\vec{S}}_n$$

Long-range scalar couplings often have point dipolar contributions:

$$\hat{H}_{DD} = 2\beta\hbar \sum_{kn}{}' \gamma_n \left(\frac{3(\vec{\hat{L}}_k \cdot \hat{\vec{r}}_{kn})(\hat{\vec{S}}_n \cdot \hat{\vec{r}}_{kn})}{r_{kn}^5} - \frac{(\vec{L}_k \cdot \vec{S}_n)}{r_{kn}^3} \right)$$

(in fact, $\hat{H}_{FC}$ is a consequence of $\hat{H}_{DD}$ when the finite size of the nucleus is taken into account)

The total J-coupling energy is computed in second order perturbation approximation:

$$E^{(2)} = -\sum_{n=1}^{\infty}{}' \frac{\langle 0 | \hat{H}_{FC} + \hat{H}_{DD} | n \rangle \langle n | \hat{H}_{FC} + \hat{H}_{DD} | 0 \rangle}{E_n - E_0} \qquad (*)$$

and then differentiated with respect to the magnetic moments of the nuclei in question:

$$J_{\underset{xyz}{ij}}^{\overset{\text{spins}}{(a,b)}} = \frac{\partial^2 E^{(2)}}{\partial \mu_i^{(a)} \partial \mu_i^{(b)}} .$$

The terms involving only $|0\rangle$ in Equation (*) are often called "diamagnetic" and are relatively easy to compute (only the ground state is required). The terms involving excitations ("paramagnetic") are a major computational nightmare.

- Inter-nuclear dipolar coupling: just a point dipole coupling between nuclei. An example of traceless interaction.

$$\hat{H}_{DD} = -\frac{\mu_0}{4\pi}\hbar \sum_{i>k}{}' \gamma_i \gamma_k \left(\frac{3(\hat{\vec{L}}_i \cdot \vec{r}_{ik})(\hat{\vec{L}}_k \cdot \vec{r}_{ik})}{r_{ik}^5} - \frac{(\hat{\vec{L}}_i \cdot \hat{\vec{L}}_k)}{r_{ik}^3} \right) =$$

$$= -\frac{\mu_0}{4\pi}\hbar \sum_{i>k}{}' \frac{\gamma_i \gamma_k}{r_{ik}^5} \left(\hat{L}_x^{(i)} \; \hat{L}_y^{(i)} \; L_z^{(i)} \right) .$$

$$\cdot \begin{pmatrix} r_{ik}^2 - 3(x - x_k)^2 & 3(x_i - x_k)(y_i - y_k) & 3(x_i - x_k)(z_i - z_k) \\ 3(y_i - y_k)(x_i - x_k) & r_{ik}^2 - 3(y_i - y_k)^2 & 3(y_i - y_k)(z_i - z_k) \\ 3(z_i - z_k)(x_i - x_k) & 3(z_i - z_k)(y_i - y_k) & r_{ik}^2 - 3(z_i - z_k) \end{pmatrix} \begin{pmatrix} \hat{L}_x^{(k)} \\ \hat{L}_y^{(k)} \\ \hat{L}_z^{(k)} \end{pmatrix} .$$

It is easy to see that the trace is zero. A slightly more complicated argument (DIY) would demonstrate that rhombicity is also zero.

- Hyperfine interaction: electron-nuclear bilinear coupling with two principal components.

  - Fermi contact coupling (we saw it above), thankfully to just the ground state:

$$\langle 0|\hat{H}_{FC}|0\rangle = \sum_i a_i\, \hat{\vec{L}}\cdot\hat{\vec{S}}_i \,; \qquad a_i = \frac{8\pi}{3}\cdot\frac{g_e}{g_0}\cdot g_i\beta_i\underbrace{(\rho_i^{\alpha}-\rho_i^{\beta})}$$

space wavefunction

over nuclei

electron

nucleus

spin density at the nucleus

  - electron-nuclear dipolar coupling (same as the inter-nuclear, but with an integral over the electron distribution):

nuclei

electron

$$\langle 0|\hat{H}_{DD}|0\rangle = -\frac{\mu_0}{4\pi}\hbar\gamma_e\sum_i \gamma_i \int_V \left(\frac{3(\hat{\vec{L}}\cdot\vec{r}_{iL})(\hat{\vec{S}}_i\cdot\vec{r}_{iL})}{r_{iL}^5} - \frac{(\hat{\vec{L}}\cdot\hat{\vec{S}}_i)}{r_{iL}^3}\right)\rho(r)\,dV$$

spin density

It is easy to see that the FC component is isotropic and the DD component is traceless. Unlike the inter-nuclear case, however, the DD component of HFC often has non-zero rhombicity.

- Inter-electron dipolar coupling: between non-overlapping electrons looks much the same as inter-nuclear, except for the double integral over electron distributions:

$$\langle 0|\hat{H}_{DD}|0\rangle = -\frac{\mu_0\hbar\gamma_e^2}{4\pi}\iint_{V_1 V_2}\left(\frac{3(\hat{\vec{L}}\cdot\vec{r}_{12})(\hat{\vec{S}}\cdot\vec{r}_{12})}{r_{12}^5} - \frac{(\hat{\vec{L}}\cdot\hat{\vec{S}})}{r_{12}^3}\right)\rho_1(r_1)\rho_2(r_2)\,dV_1\,dV_2$$

(N.B.: $\mathrm{Tr}\neq 0$, $\mathrm{Ax}\neq 0$, $\mathrm{Rh}\neq 0$.)

assuming that $\mathrm{sup}(\rho_1)\cap\mathrm{sup}(\rho_2)=\varnothing$. If that's not the case, the total spin needs to be considered, and we get...

- Zero-field splitting:

$$\hat{H}_{ZFS} = \hat{\vec{S}}\cdot D\cdot\hat{\vec{S}}$$

electron spin operators written in the total electron spin basis, $l \geq 1$.

3x3 symmetric traceless tensor.

This is a notoriously difficult parameter to compute. The brave may wish to read Frank Neese's recent work.

- Two-electron exchange interaction: the non-classical part of Coulomb interaction that happens to depend on spin.

According to the fermion symmetry constraint, a pair of electrons can be in four possible states:

$$\varphi_1(x_1)\begin{cases}\alpha\\ \beta\end{cases} \qquad \frac{1}{\sqrt{2}}\left(\varphi_1(x_1)\varphi_2(x_2)+\varphi_2(x_1)\varphi_1(x_2)\right)(\alpha\beta-\beta\alpha) \quad - \text{"singlet"}$$

$$\Longrightarrow$$

$$\varphi_2(x_2)\begin{cases}\alpha\\ \beta\end{cases} \qquad \frac{1}{\sqrt{2}}\left(\varphi_1(x_1)\varphi_2(x_2)-\varphi_2(x_1)\varphi_1(x_2)\right)\begin{cases}\alpha\alpha\\ (\alpha\beta+\beta\alpha)\\ \beta\beta\end{cases} \quad - \text{"triplet"}$$

The Coulomb interaction energy is different for the singlet and triplet states:

$$\frac{1}{2}\int\left(\varphi_1(r_1)\varphi_2(r_2)+\varphi_2(r_1)\varphi_1(r_2)\right)\frac{1}{r_{12}}\left(\varphi_1^*(r_1)\varphi_2^*(r_2)+\varphi_2^*(r_1)\varphi_1^*(r_2)\right)dV_1\,dV_2 =$$

$$= \int|\varphi_1(r_1)|^2\frac{1}{r_{12}}|\varphi_2(r_2)|^2\,dV_1\,dV_2 + \int\varphi_1(r_1)\varphi_2^*(r_1)\frac{1}{r_{12}}\varphi_2(r_2)\varphi_1^*(r_2)\,dV_1\,dV_2.$$

$$\frac{1}{2}\int\left(\varphi_1(r_1)\varphi_2(r_2)-\varphi_2(r_1)\varphi_1(r_2)\right)\frac{1}{r_{12}}\left(\varphi_1^*(r_1)\varphi_2^*(r_2)-\varphi_2^*(r_1)\varphi_1^*(r_2)\right)dV_1\,dV_2 =$$

$$= \int|\varphi_1(r_1)|^2\frac{1}{r_{12}}|\varphi_2(r_2)^2|\,dV_1\,dV_2 - \int\varphi_1(r_1)\varphi_2^*(r_1)\frac{1}{r_{12}}\varphi_2(r_2)\varphi_1^*(r_2)\,dV_1\,dV_2$$

The difference is $2J$, where

$$J = \int\varphi_1(r_1)\varphi_2^*(r_1)\frac{1}{r_{12}}\varphi_2(r_2)\varphi_1^*(r_2)\,dV_1\,dV_2 \quad \text{- exchange integral.}$$

Because singlet and triplet happen to be eigenstates of isotropic coupling, the resulting Hamiltonian is simply

$$\hat{H}_{ex} = -J\,\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2 ,$$ sometimes with minor anisotropies due to more complicated mechanisms.

Note the close relationship to inter-electron dipolar coupling and ZFS. In practice, it is not possible to tell apart the genuine exchange coupling from the isotropic component of the non-point dipolar coupling.

$\Rightarrow$ the only reliable classification is algebraic!

- Quadrupolar interaction: nuclei with spin greater than 1/2 are not spherical (e.g. ^{14}N is an ellipsoid) and the resulting dipole moment is rigidly glued to the spin ⇒ electrostatic interaction induces a spin interaction.

quadrupole moment

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar}\, \hat{\vec{L}}\cdot A \cdot \hat{\vec{L}}$$

total spin

electric field

$$A_{ij} = \frac{\partial E_i}{\partial x_j} = \frac{\partial^2 \varphi}{\partial x_i \partial x_j}$$

electrostatic potential.

Poisson's equation constrains the quadrupolar interaction tensor to be traceless (DIY). QI is relatively easy to compute with DFT.

- Chemical shielding: coupling of the nuclear spin, via its associated magnetic dipole moment, to an external magnetic field.

The magnetic field at the nucleus contains the contribution from the applied field and from the electronic structure perturbation produced by that field:

$$\vec{B} = \vec{B}_0 + \vec{B}_{ind}$$

to a good appoximation the induced field is a linear function of the applied one, meaning that

$$\vec{B} = \vec{B}_0 + \delta \vec{B}_0 \;; \qquad E = -\vec{\mu}\cdot\vec{B} = -\vec{\mu}(\mathbb{1}+\delta)\vec{B}_0 \;;$$

chemical shielding tensor (3×3)

$$\hat{H} = \hat{\vec{L}} \cdot A \cdot \vec{B}_0$$

The components of A are usually computed as derivatives

$$\delta_{ij} = -\frac{\partial^2 E}{\partial \mu_i \partial B_j}$$

of the total molecular energy calculated using perturbation theory. In the presence of a magnetic field $\hat{\vec{p}} \longrightarrow \hat{\vec{p}} + q\vec{A}$, therefore

vector potential

The vector potential (see your Magnetism course) due to the external field and a single magnetic dipole positioned at the origin is:

$$\vec{A} = \frac{1}{2}\vec{B}\times\vec{r} + \frac{\mu_0}{2\pi}\cdot\frac{\vec{\mu}\times\vec{r}}{r^3},$$

so the resulting Hamiltonian is

$$\hat{H} = \sum_i \frac{(\hat{\vec{p}} + q\vec{A})^2}{2m_i} + \hat{V} \longleftarrow \text{all the usual electrostatic interactions}$$

After defining $\hat{H}_1 = \hat{H} - \sum_i \frac{p_i^2}{2m_i} - \hat{V}$, the perturbation theory correction to the energy becomes:

$$\Delta E = \langle 0|\hat{H}_1|0\rangle + \sum_{n=1}^{\infty} \frac{\langle 0|H_1|n\rangle\langle n|H_1|0\rangle}{E_0 - E_n}$$

↑ "diamagnetic" part, only depends on the ground state, easy to compute.

← "paramagnetic" part, involves excitations, notoriously difficult, particularly if small denominators are present.

Ab initio calculation of chemical shielding is a big trade (Term III).

- g-tensor: coupling of the electron spin, via its associated magnetic dipole moment, to an external magnetic field.

Much the same algebra as above:

$$\hat{H} = \hat{\vec{L}}\cdot A\cdot\vec{B}_0 \, ; \qquad g_{ik} = \frac{1}{\mu_B}\cdot\frac{\partial^2 E}{\partial\mu_i\,\partial B_k}$$

with the only difference in that $\hat{H}_1$ perturbation Hamiltonian contains contributions from the spin-orbit coupling.

<u>Bottom line</u>: the physical nature of the interactions listed above is very complicated. However, the only thing that determines their behaviours in a spin dynamics simulation is their algebraic type (linear, bilinear, quadratic) and eigenvalue behaviour (isotropic, axial, rhombic, traceless).

6. Wavefunction formalism for spin dynamics simulations.

This is based on standard quantum mechanics. Starting from TDSE:

$$|\psi(0)\rangle = \psi_0 \;; \qquad \left.\frac{\partial|\psi(t)\rangle}{\partial t}\right|_{t=0} = -i\hat{H}|\psi(0)\rangle ; \qquad \frac{\partial^2|\psi(t)\rangle}{\partial t^2} = (-i\hat{H})^2|\psi(0)\rangle$$

and so on. Therefore, the Taylor expansion of $|\psi(t)\rangle$ around $t=0$ is

$$|\psi(t)\rangle = |\psi(0)\rangle + \left.\frac{\partial|\psi(t)\rangle}{\partial t}\right|_{t=0} t + \frac{1}{2}\left.\frac{\partial^2|\psi(t)\rangle}{\partial t^2}\right|_{t=0} t^2 + \ldots =$$

$$= \sum_{n=0}^{\infty} \frac{(-i\hat{H})^n}{n!} t^n |\psi(0)\rangle = e^{-i\hat{H}t}|\psi(0)\rangle$$ – the famous exponential solution.

Therefore $\langle A\rangle(t) = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|e^{i\hat{H}t}\hat{A}e^{-iHt}|\psi(0)\rangle$ and this, in principle, solves the problem in full generality. If $\hat{H}$ is time-dependent, it may be shown that

$$|\psi(t)\rangle = \lim_{N\to\infty}\left\{\prod_{k=0}^{N} e^{-i\hat{H}(t_k)(t_{k+1}-t_k)}|\psi(0)\rangle\right\} ; \quad t_k = \frac{kt}{N} .$$

In other words, for sufficiently fine discrete time stepping, the piecewise-constant approximation to $\hat{H}(t)$ is good enough.

One is often interested in computing the Fourier transform of this trace:

$$\frac{\partial|\psi(t)\rangle}{\partial t} = -i\hat{H}|\psi(t)\rangle \xRightarrow{F^+} \int_0^{\infty}\frac{\partial|\psi(t)\rangle}{\partial t}e^{-i\omega t}\,dt =$$

$$= e^{-i\omega t}|\psi(t)\rangle\Big|_0^{\infty} + i\omega\int_0^{\infty}e^{-i\omega t}|\psi(t)\rangle\,dt = i\omega|\psi(\omega)\rangle - |\psi(0)\rangle =$$

$$= -i\hat{H}|\psi(\omega)\rangle .$$

$$\boxed{i(\hat{H} + \hat{\mathbb{1}}\omega)|\psi(\omega)\rangle = |\psi(0)\rangle}$$

The frequency domain Schrödinger equation (time-independent $\hat{H}$ only)

In most cases $\hat{H} + \hat{\mathbb{1}}\omega$ matrix is invertible, so

$$|\psi(\omega)\rangle = -i(\hat{H} + \hat{\mathbb{1}}\omega)^{-1}|\psi(0)\rangle .$$ Damping may sometimes be required to eliminate the singularities.

So $\langle A(\omega)\rangle = \langle \psi(0)|(\hat{H}+\hat{\mathbb{1}}\omega-\hat{\mathbb{1}}ir)^{-1} A (\hat{H}+\mathbb{1}\omega+\hat{\mathbb{1}}ir)^{-1}|\psi(0)\rangle$

where r is the regularization (line broadening) factor.

A somewhat older approach (inspired by the way the early instruments operated) is based on time-dependent perturbation theory.

To first order in TDPT, the transition rate under a given perturbation is

$$W = 2\pi\hbar\,|V_{fi}|^2 = 2\pi\hbar\,\langle \text{final}|\hat{V}|\text{initial}\rangle$$

with the following transition frequencies:

$$\omega = \frac{1}{\hbar}\Delta E = \frac{1}{\hbar}\left(\langle \text{final}|\hat{H}|\text{final}\rangle - \langle \text{initial}|\hat{H}|\text{initial}\rangle\right).$$

where $|\text{initial}\rangle$ and $|\text{final}\rangle$ are some eigenvectors of $\hat{H}$.

Imagine now a spectrometer applying an oscillating magnetic field in X direction. Its absorption would be proportional to W and it will be absorbed at the frequencies given above. The perturbation affects all spins and is therefore

$$\hat{V} = \sum_i \hat{L}_x^{(i)}.$$

So the recipe is:

Time-dependent QM	TDPT
1. Find the initial state $\|\psi(0)\rangle$	1. Find what it is your instrument observes and find the corresponding operator $\hat{V}$.
2. For every time interval Δt compute $e^{-i\hat{H}(t)\Delta t}$ and multiply it into the wavefunction that emerged from the previous step.	2. Diagonalize the Hamiltonian
3. The result is $\|\psi(t)\rangle$, use it to compute the observables of your choice.	3. For every pair of eigenvectors, compute W and ω.
	4. Draw a stick spectrum and use some broadening transform on it.
GOOD PRACTICE (though better methods exist)	SOMEWHAT STALE

- An example of time-dependent solution

For a single spin in a magnetic field $\hat{H} = \omega \hat{S}_z$, $\frac{\partial}{\partial t}|\psi\rangle = -i\omega S_z|\psi\rangle$.

The solution is

$$|\psi(t)\rangle = e^{-i\omega\hat{S}_z t}|\psi(0)\rangle \quad \text{where}$$

$$e^{-i\omega S_z t} = \sum_{=0}^{\infty} \frac{(-i\omega t)^n}{n!}\hat{S}_z^n = \sum_{n=0}^{\infty}\frac{(-i\omega t)^n}{n!}\begin{pmatrix} (1/2)^n & 0 \\ 0 & (-1/2)^n \end{pmatrix} =$$

$$= \begin{pmatrix} \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-i\omega t}{2}\right)^n & 0 \\ 0 & \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i\omega t}{2}\right)^n \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}.$$

So the general solution is

$$|\psi(t)\rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}|\psi(0)\rangle.$$ Looking at the specific initial conditions:

→ $|\psi(0)\rangle$ along z axis

$$|\psi(0)\rangle = |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|\psi(t)\rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix}$$

$$\langle S_x\rangle = \langle\psi|\hat{S}_x|\psi\rangle = \langle S_y\rangle = \langle\psi|\hat{S}_y|\psi\rangle = 0$$

$\langle S_z\rangle = \langle\psi|S_z|\psi\rangle = \frac{1}{2}$ – the magnetization stays along z.

→ $|\psi(0)\rangle$ somewhere in the XY plane

The initial state $|\psi(0)\rangle = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$ may be shown to correspond to

$$\langle\psi(0)|\hat{S}_z|\psi(0)\rangle = \langle\psi(0)|\hat{S}_y|\psi(0)\rangle = 0$$

$\langle\psi(0)|\hat{S}_x|\psi(0)\rangle = \frac{1}{2}$ – along the X axis

$$|\psi(t)\rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} 1/ \\ 1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2} \end{pmatrix} .$$

$$\langle\psi|S_z|\psi\rangle = 0$$

$$\left.\begin{aligned} \langle\psi|\hat{S}_x|\psi\rangle &= \dots = \tfrac{1}{2}\cos(\omega t) \\ \langle\psi|\hat{S}_y|\psi\rangle &= \dots = -\tfrac{1}{2}\sin(\omega t) \end{aligned}\right\} \text{ the familiar circular oscillation.}$$

- An example of time-independent solution.

Consider a "strongly coupled" two-spin system with

$$\hat{H} = \omega_I \hat{I}_z + \omega_S \hat{S}_z + J(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y + \hat{I}_z\hat{S}_z) = (\text{DIY}) =$$

$$= \omega_I \hat{I}_z + \omega_S \hat{S}_z + J\left(\hat{I}_z\hat{S}_z + \tfrac{1}{2}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+)\right).$$

Basis: $\{|\alpha\rangle, |\beta\rangle\} \otimes \{|\alpha\rangle, |\beta\rangle\} = \{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}.$

$\hat{H}|\alpha\alpha\rangle = \dots = \left(\frac{\omega_I + \omega_S}{2} + \frac{J}{4}\right)|\alpha\alpha\rangle$ – eigenfunction already

$$\left.\begin{aligned} \hat{H}|\alpha\beta\rangle &= \dots = \left(\frac{\omega_I - \omega_S}{2} - \frac{J}{4}\right)|\alpha\beta\rangle + \underline{J}\,|\beta\alpha\rangle \\ \hat{H}|\beta\alpha\rangle &= \dots = \left(\frac{\omega_S - \omega_I}{2} - \frac{J}{4}\right)|\beta\alpha\rangle + \frac{J}{2}|\alpha\beta\rangle \end{aligned}\right\} \text{ need to orthogonalize these.}$$

$\hat{H}|\beta\beta\rangle = \dots = \left(-\frac{\omega_I + \omega_S}{2} + \frac{J}{4}\right)|\beta\beta\rangle$ – eigenfunction already

Inside the $\{|\alpha\beta\rangle, |\beta\alpha\rangle\}$ subspace:

$$\hat{H} = \begin{pmatrix} \frac{\omega_I - \omega_S}{2} - \frac{J}{4} & \frac{J}{2} \\ \frac{J}{2} & \frac{\omega_S - \omega_I}{2} - \frac{J}{4} \end{pmatrix}$$

The eigenvalues are:
$$\lambda = -\frac{J}{4} \pm \frac{\sqrt{J^2 + (\omega_I - \omega_S)^2}}{2}$$

So the four energy levels are:

$$\lambda_1 = \frac{\omega_I+\omega_S}{2} + \frac{J}{4}$$

$$\lambda_2 = -\frac{J}{4} + \frac{\sqrt{J^2+(\omega_I-\omega_S)^2}}{2}$$

$$\lambda_3 = -\frac{J}{4} - \frac{\sqrt{J^2+(\omega_I-\omega_S)^2}}{2}$$

$$\lambda_4 = -\frac{\omega_I+\omega_S}{2} + \frac{J}{4}$$

And the energies of the four possible single spin flip (multi-spin flips are forbidden) are:

$$\underbrace{\frac{\omega_I+\omega_S}{2}}_{\text{fundamental frequency}} \pm \underbrace{\frac{J\pm\sqrt{J^2+(\omega_I-\omega_S)^2}}{2}}_{\text{splitting.}}$$

Unitary state mixing in a two-level system is isomorphous to rotations and we will use this to write compact expressions for the two "difficult" eigenvectors:

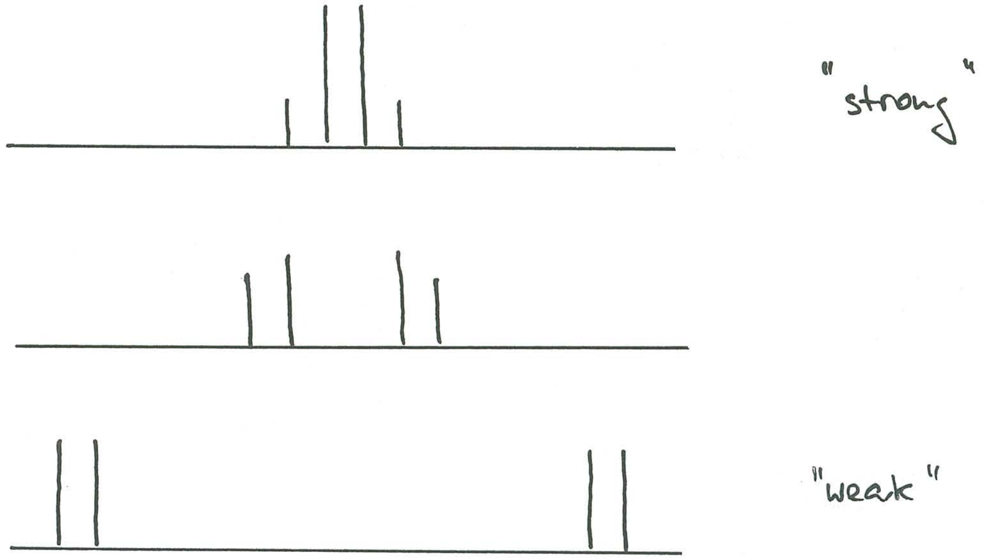
$$\left.\begin{aligned} |2\rangle &= \cos\varphi\,|\alpha\beta\rangle + \sin\varphi\,|\beta\alpha\rangle \\ |3\rangle &= -\sin\varphi\,|\alpha\beta\rangle + \cos\varphi\,|\beta\alpha\rangle \end{aligned}\right\} \text{a very useful way of representing two-state mixing.}$$

where $$\operatorname{tg}\varphi = \frac{J}{(\omega_I-\omega_S)-\sqrt{J^2+(\omega_I-\omega_S)^2}};$$

Finally, computing transition moments:

$$|\langle 1|\hat{I}_-|3\rangle|^2 = |\langle 2|I_-|4\rangle|^2 = \cos^2\varphi$$

$$|\langle 1|I_-|2\rangle|^2 = |\langle 3|I_-|4\rangle|^2 = \sin^2\varphi$$



7. Density operator formalism

We saw above that the Schrodinger equation

$$\frac{\partial\psi}{\partial t}=-\frac{i}{\hbar}\hat{H}\psi \quad\Leftrightarrow\quad \frac{\partial}{\partial t}|\psi\rangle=-\frac{i}{\hbar}\hat{H}|\psi\rangle \tag{1}$$

yields a simple and straightforward general solution of the form

$$|\psi\rangle=\exp\left[-\frac{i}{\hbar}\hat{H}t\right]|\psi_0\rangle \tag{2}$$

(possibly with time-ordered exponentials if the Hamiltonian is time-dependent). Solutions for a single spin were trivial to obtain. What about 10^{23} spins? We need to update our mathematics a bit...

For a single quantum system with a wavefunction $|\psi\rangle$ we will introduce something called ‘the density operator’:

$$\hat{\rho}(t)=|\psi\rangle\langle\psi| \tag{3}$$

It is an operator because it can act upon a wavefunction and return another wavefunction:

$$\hat{\rho}|\varphi\rangle=|\psi\rangle\langle\psi|\varphi\rangle=a|\psi\rangle, \qquad a=\langle\psi|\varphi\rangle \tag{4}$$

We can find the equation of motion for $\hat{\rho}(t)$ from the definition:

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\rho}(t)&=\frac{\partial}{\partial t}\left(|\psi\rangle\langle\psi|\right)=\left(\frac{\partial}{\partial t}|\psi\rangle\right)\langle\psi|+|\psi\rangle\left(\frac{\partial}{\partial t}\langle\psi|\right)=\left\{\begin{matrix}\text{use Schrodinger}\\ \text{equation}\end{matrix}\right\}\\ &=-\frac{i}{\hbar}\hat{H}|\psi\rangle\langle\psi|+\frac{i}{\hbar}|\psi\rangle\langle\psi|\hat{H}=-\frac{i}{\hbar}\hat{H}\hat{\rho}+\frac{i}{\hbar}\hat{\rho}\hat{H}=-\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]\end{aligned} \tag{5}$$

therefore

$$\frac{\partial}{\partial t}\hat{\rho}=-\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right] \tag{6}$$

(*Liouville – von Neumann equation*). But why do we need this, why not stay with the wavefunction? Two reasons:

1. $|\psi\rangle$ does not survive the ensemble average, whereas $|\psi\rangle\langle\psi|$ does:

$$\overline{|\psi\rangle}=\frac{1}{2\pi}\int_0^{2\pi}e^{i\varphi}|\psi\rangle d\varphi=0, \qquad \overline{|\psi\rangle\langle\psi|}=\frac{1}{2\pi}\int_0^{2\pi}e^{i\varphi}|\psi\rangle\langle\psi|e^{-i\varphi}d\varphi=|\psi\rangle\langle\psi| \tag{7}$$

2. $|\psi\rangle$ becomes unacceptably large for 10^{23} spins, whereas the above mentioned ensemble average provides a serviceable substitute to the explicit description for $|\psi\rangle\langle\psi|$.

So what is this $|\psi\rangle\langle\psi|$ construct? A matrix of sorts, with diagonal elements

$$\langle i|\psi\rangle\langle\psi|i\rangle=\left|\langle\psi|i\rangle\right|^2=\left|c_i\right|^2=p_i \tag{8}$$

giving the populations of the basis wavefunctions $|i\rangle$ and off-diagonal elements describing some ongoing transitions between them. When operating under the ensemble averaging, the off-diagonal elements describe collective coherent behaviour of particles in the ensemble and for that reason are called 'coherences'.

Interestingly, the density operator is idempotent:

$$\hat{\rho}^2=|\psi\rangle\langle\psi|\psi\rangle\langle\psi|=|\psi\rangle\langle\psi|=\hat{\rho} \tag{9}$$

The equation of motion for the density operator, just as the original Schrodinger equation, has a "simple" general solution:

$$|\psi\rangle=\exp\left[-\frac{i}{\hbar}Ht\right]|\psi_0\rangle \quad \Rightarrow \quad |\psi\rangle\langle\psi|=\exp\left[-\frac{i}{\hbar}\hat{H}t\right]|\psi_0\rangle\langle\psi_0|\exp\left[\frac{i}{\hbar}\hat{H}t\right] \tag{10}$$

$$\hat{\rho}(t)=\exp\left[-\frac{i}{\hbar}\hat{H}t\right]\hat{\rho}(t)\exp\left[\frac{i}{\hbar}\hat{H}t\right] \tag{11}$$

The equations for the observables follow in a similar way from Schrodinger formalism:

$$\langle A\rangle=\langle\psi|\hat{A}|\psi\rangle=\sum_{ij}\psi_i^*A_{ij}\psi_j=\sum_{ij}\left(\psi_i^*\psi_j\right)A_{ij}=\sum_{ij}\rho_{ij}^*A_{ij}=\sum_{ij}\rho_{ji}A_{ij}=Tr\left(\hat{\rho}\hat{A}\right) \tag{12}$$

$$\langle A\rangle=Tr\left(\hat{\rho}\hat{A}\right) \tag{13}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle A\rangle&=\mathrm{Tr}\left(\frac{\partial}{\partial t}\hat{\rho}\hat{A}\right)=\mathrm{Tr}\left(-\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]\hat{A}\right)=-\frac{i}{\hbar}\mathrm{Tr}\left(\hat{H}\hat{\rho}\hat{A}-\hat{\rho}\hat{H}\hat{A}\right)\\&=-\frac{i}{\hbar}\mathrm{Tr}\left(\hat{\rho}\hat{A}\hat{H}-\hat{A}\hat{\rho}\hat{H}\right)=\frac{i}{\hbar}\mathrm{Tr}\left(\hat{\rho}\left[\hat{H},\hat{A}\right]\right)=\frac{i}{\hbar}\left\langle\left[\hat{H},\hat{A}\right]\right\rangle\end{aligned} \tag{14}$$

$$\frac{\partial}{\partial t}\langle A\rangle=\frac{i}{\hbar}\left\langle\left[\hat{H},\hat{A}\right]\right\rangle \tag{15}$$

So the density matrix can, particularly in analytical calculations, be eliminated from the picture and the central role shifted to commutators.

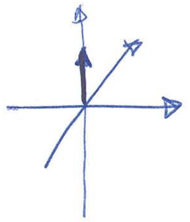
ⓕ Product operator formalism

We saw above that the density matrix can be eliminated from the equations of motion and the problem reformulated as

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{i}{\hbar}\langle[\hat{H};\hat{A}]\rangle, \qquad (*)$$

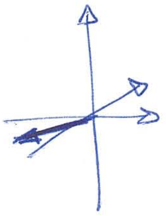
where $\hat{A}$ is the operator of the physical observable we are interested in. It turns out that simple rules can be formulated based on this equation, and they are much easier to use. But before that...

Classification of spin states



- longitudinal single-spin orders : L_z; S_z etc

- longitudinal multi-spin orders : $2L_zS_z$; $4L_zM_zS_z$ etc
  (also known as "entanglements" – the state of one spin is conditional upon the state of the other)



- transverse single-spin orders : L_x; S_y; L_+ etc
  (also known as "single quantum coherences")

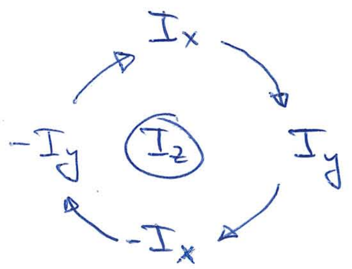
- transverse multi-spin orders : L_xL_y; L_+S_- etc
  (known as "zero-" and "multiple-quantum coherences")

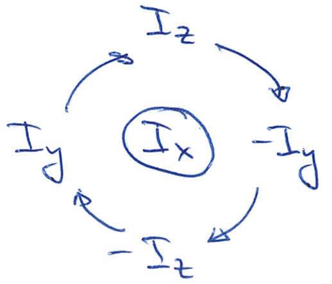
- mixed orders : $2L_zS_+$ etc.

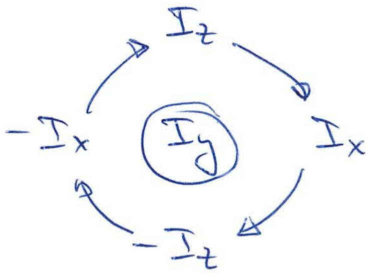
These states interconvert and evolve under the Hamiltonian $\hat{H}$ according to equation (*). After we do the math, the following rules emerge:

$$\left.\begin{aligned} I_x &\xrightarrow{\omega I_z} I_x\cos(\omega t)+I_y\sin(\omega t)\\ I_y &\xrightarrow{\omega I_z} I_y\cos(\omega t)\quad I_x\sin(\omega t)\\ I_z &\xrightarrow{\omega I_z} I_z \end{aligned}\right| \longleftarrow \text{free precession rules.}$$

The rules can be summarized in the following diagrams:



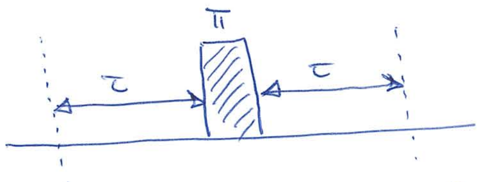




Thus, for example, under a pulse:

$$I_z \xrightarrow{\omega I_x} -I_y \sin(\omega t) + I_z \cos(\omega t) \xrightarrow{\omega t = \pi/2} -I_y$$

Example 1: spin echo.



(meant to "refocus" the frequency differences due to chemical shift)

- Initial state: $I_x + S_x$
- After the first τ period under the Zeeman interaction $(\omega_1 I_z + \omega_2 S_z)$:

$$I_x \xrightarrow{\omega_1 I_z + \omega_2 S_z} I_x \cos(\omega_1 \tau) + I_y \sin(\omega_1 \tau)$$
$$S_x \xrightarrow{\omega_1 I_z + \omega_2 S_z} S_x \cos(\omega_2 \tau) + S_y \sin(\omega_2 \tau)$$

the two signals are out of sync with each other.

- After the π_x pulse:

$$I_x \cos(\omega_1 \tau) + I_y \sin(\omega_1 \tau) \xrightarrow{\pi I_x} I_x \cos(\omega_1 \tau) - I_y \sin(\omega_1 \tau)$$
$$S_x \cos(\omega_2 \tau) + S_y \sin(\omega_2 \tau) \xrightarrow{\pi S_x} S_x \cos(\omega_2 \tau) - S_y \sin(\omega_2 \tau)$$

- After the second τ period:

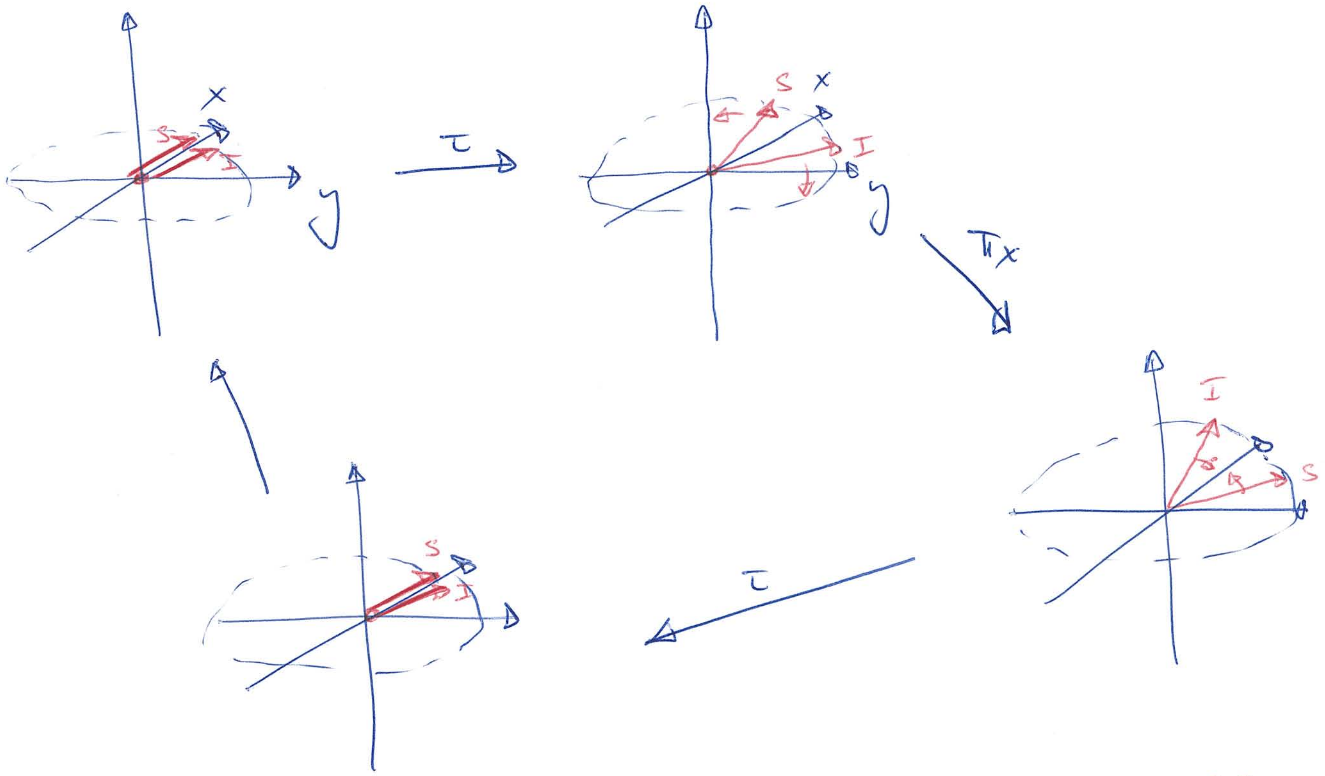
$$I_x \cos(\omega_1 \tau) - I_y \sin(\omega_1 \tau) \xrightarrow{\omega_1 I_z + \omega_2 S_z} \big(I_x \cos(\omega_1 \tau) + I_y \sin(\omega_1 \tau)\big) \cos(\omega_1 \tau) -$$
$$-\big(I_y \cos(\omega_1 \tau) - I_x \sin(\omega_1 \tau)\big) \sin(\omega_1 \tau) =$$
$$= I_x\big(\cos^2(\omega_1 \tau) + \sin^2(\omega_1 \tau)\big) = I_x$$

Similarly:

$$S_x \cos(\omega_2 \tau) - S_y \sin(\omega_2 \tau) \xrightarrow{\omega_1 I_z + \omega_2 S_z} \dots \longrightarrow S_x,$$

so the chemical shifts have been refocussed and we are back to $I_x + S_x$.

A pictorial representation may be helpful in visualizing what's going on:



Scalar couplings (J-coupling or hyperfine coupling) require a different set of rules:

$$\begin{tikzcd}
 & I_x \arrow[dr, bend left] & \\
-2I_yS_z \arrow[ur, bend left] & I_zS_z & 2I_yS_z \arrow[dl, bend left] \\
 & -I_x \arrow[ul, bend left] &
\end{tikzcd}
\qquad
\begin{tikzcd}
 & I_y \arrow[dr, bend left] & \\
2I_xS_z \arrow[ur, bend left] & I_zS_z & -2I_xS_z \arrow[dl, bend left] \\
 & -I_y \arrow[ul, bend left] &
\end{tikzcd}$$

For example: $I_x \xrightarrow{\pi J I_z S_z} I_x \cos(\pi J t) + 2I_yS_z \sin(\pi J t)$.

Two-spin order is generated as a result.

<u>Example 2: coherence transfer experiment</u>

It is sometimes necessary to move magnetization from one spin to another. This is useful if the second spin has low sensitivity, e.g. in a $^1H - ^{15}N$ pair.

Assuming that both nuclei have zero offset (to be lifted later):

$$H_z \xrightarrow{(\pi/2)_y^H} H_x$$

$$H_x \xrightarrow{\pi J H_z N_z} H_x \cos(\pi J t) + 2 H_y N_z \sin(\pi J t)$$

Choosing $t = \frac{1}{2J}$: $H_x \cos(\pi/2) + 2H_yN_z \sin \pi/2 = 2H_yN_z$

$$2H_yN_z \xrightarrow{(\pi/2)_x^H} 2H_zN_z \xrightarrow{(\pi/2)_y^N} 2H_zN_x$$

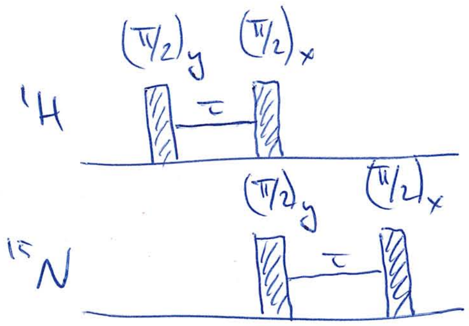
$$2H_zN_x \xrightarrow{\pi J H_z N_z} 2H_zN_x \cos(\pi J t) + N_y \sin(\pi J t)$$

Choosing $t = \frac{1}{2J}$: $2H_zN_x \cos(\pi/2) + N_y \sin(\pi/2) = N_y$

$$N_y \xrightarrow{(\pi/2)_x} N_z$$

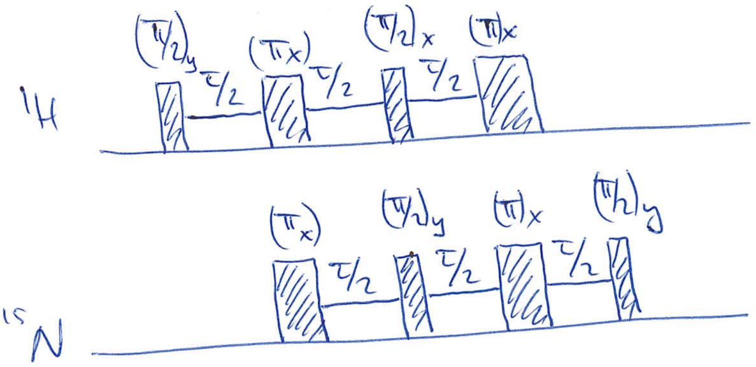
All together: $H_z \rightarrow \rightarrow \dots \rightarrow \rightarrow N_z$ - the magnetization has been moved across from ^1H to ^{15}N.

The event sequence that we used has the following schematic representation:



$\tau = \frac{1}{2J}$

We may, however, need to refocus the offsets, because $\omega_H \neq \omega_N$. Inserting the π-pulses into the sequence yields:



It is easy to demonstrate that the J-coupling is unaffected by simultaneous π-pulses on both nuclei, but cancels out if only one nucleus is π-pulsed:

$$H_x \xrightarrow{\pi J H_z N_z} H_x \cos(\pi J t) + 2H_yN_z \sin(\pi J t) \xrightarrow{\pi_x^{H,N}} H_x \cos(\pi J t) + \\ + 2H_yN_z \sin(\pi J t)$$

because $H_y \xrightarrow{\pi_x^H} -H_y$ and $N_z \xrightarrow{\pi_x^N} -N_z$ so $(-)^2 = (+)$.

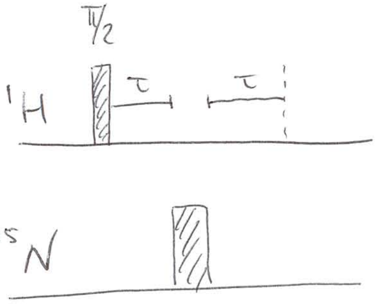
However:

$$\begin{tikzcd}[column sep=small]
H_x \arrow[r, "\pi J H_z N_z"] & H_x\cos(\pi J t) + 2H_yN_z\sin(\pi J t) \arrow[dl, "\pi_x^H"'] \arrow[dr, "\pi_x^N"] & \\
H_x\cos(\pi J t) - 2H_yN_z\sin(\pi J t) & \textcircled{=} & H_x\cos(\pi J t) - 2H_yN_z\sin(\pi J t)
\end{tikzcd}$$

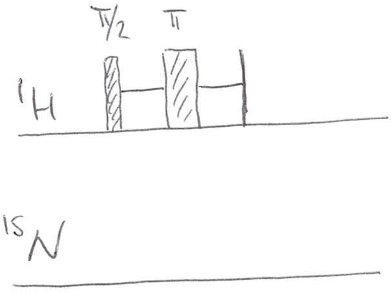
$$H_x\cos(\pi J t) - 2H_yN_z\sin(\pi J t) \xrightarrow{\pi J H_z N_z} \left(H_x\cos(\pi J t) + 2H_yN_z\sin(\pi J t)\right)\times$$

$$\times\cos(\pi J t) + \left(-2H_yN_z\cos(\pi J t) + H_x\sin(\pi J t)\right)\sin(\pi J t) = H_x\left(\cos^2(\dots) + \sin^2(\dots)\right) = H_x.$$

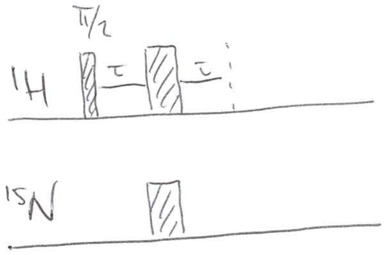
So... to eliminate the effect of <u>weak</u> J-coupling, put a π-pulse in the middle of the evolution period



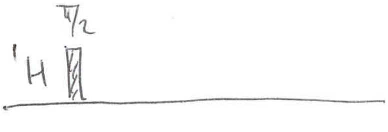
- keep ¹H offset, refocus J-coupling



- refocus ¹H offset, refocus J-coupling



- refocus ¹H offset, keep J-coupling



- keep ¹H offset, keep J-coupling.

The processes above critically require the J coupling to have the $L_z S_z$ form. What about the rest of it, i.e. $(L_x S_x + L_y S_y)$?

Detailed analysis (Term 3) shows that for heteronuclear spin pairs

$$L_x S_x + L_y S_y + L_z S_z \cong L_z S_z \quad \text{(weak J-coupling limit)}$$

However, for homonuclear spin pairs (like $^1H - ^1H$) the scalar coupling has all three terms and in general cannot be perfectly refocussed.

Example 3: pulsed field gradients

A PFG is a distortion of the B_0 field introduced deliberately and in a carefully controlled way. Its effect is to make the Zeeman frequency position dependent. Let us look at the effect:

Pulse sequences are never perfect and let us assume that we have a bit of N_x admixed to N_z at the end of Example 2. This admixture would lead to stray signals and is best eliminated. How?

Under standard Zeeman interaction:

$$N_z + \alpha N_x \xrightarrow{\omega_N t} N_z + \alpha\left(N_x \cos(\omega_N t) + N_y \sin(\omega_N t)\right)$$

Under PFG the Zeeman frequency ω_N becomes position-dependent:

$\omega_N = \omega_0 + kz$ in the case of a z-gradient. therefore

$$N_z + \alpha N_x \xrightarrow[PFG]{\omega_N t} N_z + \alpha\left(N_x \cos[(\omega_0 + kz)t] + N_y \sin([\omega_0 + kz]t)\right)$$

The NMR coil, however, detects the entire sample, so the integral has to be taken over the z coordinate:

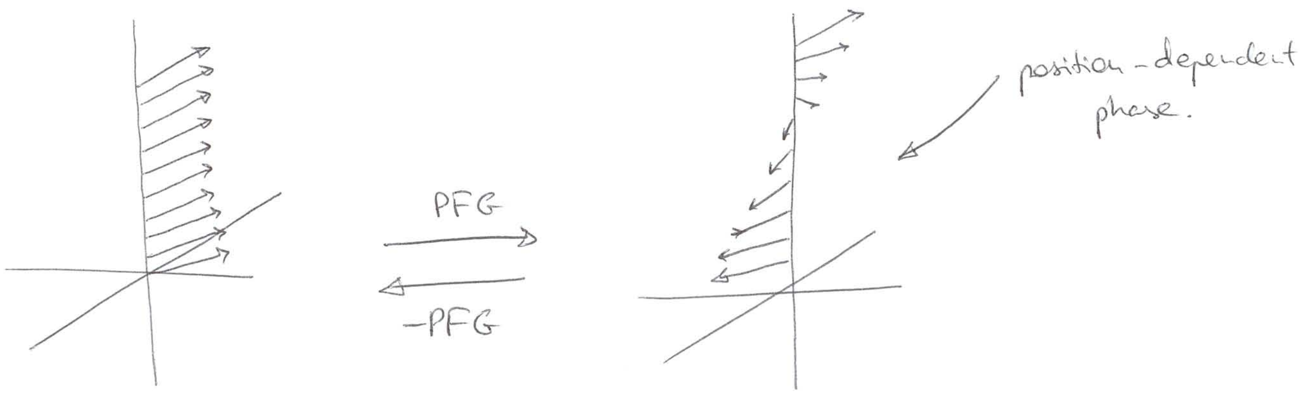
$$\frac{1}{L}\int_{-L/2}^{L/2} \left\{ N_z + \alpha\left(N_x \cos[(\omega_0 + kz)t] + N_y \sin[(\omega_0 + kz)t]\right)\right\} dz =$$

$$= N_z + \alpha N_x \frac{1}{L}\int_{-L/2}^{L/2} \cos[(\omega_0 + kz)t]\,dz + \alpha N_y \int_{-L/2}^{L/2} \sin[(\omega_0 + kz)t]\,dz = \dots =$$

$$= N_z + \alpha N_x \frac{2\cos(\omega_0 t)\sin\left(\frac{kLt}{2}\right)}{kLt} + \alpha N_y \frac{2\sin(\omega_0 t)\sin\left(\frac{kLt}{2}\right)}{kLt}, \text{ so the}$$

transverse terms get suppressed if $kLt \gg 1$, meaning that either a strong gradient needs to be applied for a short time, or a week gradient needs to be applied for a long time (L is usually a constant).

The effect of a gradient can be visuelized in the following way:



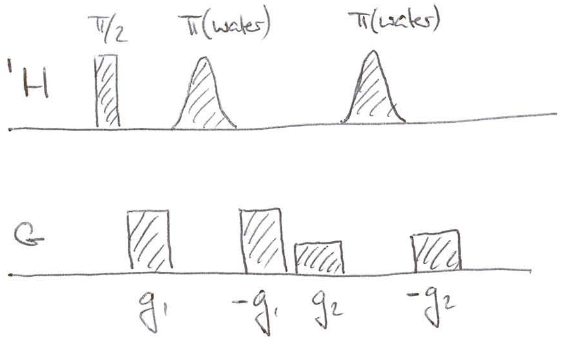
As the intuitive picture above suggests, the effect of a PFG can be reversed by reversing the current in the PFG coil:

$$N_z + \alpha N_x \xrightarrow{PFG} N_z + \alpha(N_x \cos(kzt) + N_y \sin(kzt)) \xrightarrow{-PFG}$$

$$\longrightarrow N_z + \alpha\{(N_x \cos(-kzt) + N_y \sin(-kzt))\cos(kzt) + \\ + (N_y \cos(-kzt) - N_x \sin(-kzt))\sin(kzt)\} =$$

$$= N_z + \alpha N_x(\cos^2(kzt) + \sin^2(kzt)) = N_z + \alpha N_x .$$

Example 4: DPFGSE water suppression



Double pulsed field gradient spin echo (DPFGSE) sequence can selectively suppress water to a factor of over 50000 : 1.

Millimolar concentrations can typically be observed with a 100M water signal completely eliminated.

$$H_z^S + H_z^{H_2O} \xrightarrow{\pi/2} H_x^S + H_x^{H_2O} \xrightarrow[g_1]{PFG} H_x^S(\circlearrowright) + H_x^{H_2O}(\circlearrowright) \xrightarrow{\pi^{H_2O}}$$

$$\longrightarrow H_x^S(\circlearrowright) + H_x^{H_2O}(\circlearrowleft) \xrightarrow[-g_1]{PFG} H_x^S + H_x^{H_2O}(\circledcirc) \xrightarrow{repeat} H_x^S + H_x^{H_2O}(\circledcirc) .$$

Lecture 10: algebraic foundations of spin dynamics

a) Vector spaces

A set V over a scalar field F is called a *vector space* if:

1. A binary addition operation is defined in V, such that $\forall a,b\in V \;\; \exists c\in V,\; a+b=c$ (*n.b.* this need not be the usual "+" operation).
2. A multiplication by a scalar (from the field F) is defined, such that $\forall\alpha\in F \;\; \forall a\in V \;\; \exists b\in V,\; \alpha a=b$.
3. The following properties hold:

$\forall a,b\in V \;\; a+b=b+a$	(commutativity)
$\forall a,b,c\in V \;\; a+(b+c)=(a+b)+c$	(associativity)
$\exists! 0\in V \;\; a+0=a \;\; \forall a\in V$	(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)
$\forall\alpha\in F \;\; \forall a,b\in V \;\; \alpha(a+b)=\alpha a+\alpha b$	(distributivity)
$\forall\alpha,\beta\in F \;\; \forall a\in V \;\; (\alpha+\beta)a=\alpha a+\beta a$	(distributivity)
$\exists! 1\in F \;\; \forall a\in V \;\; 1a=a$	(unique unit element in F)

Elements of V are called *vectors* and elements of F are called *scalars*. Vector b is called a *linear combination* of vectors $a_1,...,a_n$ if such scalars $\alpha_1,...,\alpha_n$ exist in F, that $b=\alpha_1 a_1+...+\alpha_n a_n$. A system of vectors $a_1,...,a_n$ is called *linearly dependent* if one of those vectors can be represented as a linear combination of others.

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

$$b=\alpha_1 a_1+...+\alpha_n a_n$$

This expansion of b in terms of $a_1,...,a_n$ is unique if and only if vectors $a_1,...,a_n$ are linearly independent. Proof: DIY.

Clearly, a lot of problems would appear in quantum mechanics if such expansions are not guaranteed to be unique because the coefficients $\alpha_1,...,\alpha_n$ are related to measurement probabilities. We do therefore want our vector systems to be linearly independent whenever possible. A *basis* of a vector system is a linearly independent subsystem, such that all vectors of the system can be represented as its linear combinations. The number of vectors in the basis of a vector space is called vector space *dimension*. All basis sets of a given vector space are of the same size.

If $a_1,...,a_n$ is a basis set of V, then every element of V can be represented as

$$b=\sum_k \alpha_k a_k$$

This relation is called an *expansion* of vector b in the basis $a_1,...,a_n$. This expansion is unique. Therefore, once a basis set is fixed, a vector (of any nature) can be represented by a string of numbers

$\alpha_1,...,\alpha_n$. Those are known as *expansion coefficients* or *coordinates*. Note that we do not yet have any means of finding them.

If V is a vector space over F and $L \subseteq V$, then L is called a *subspace* of V if the following conditions hold:

1. $0 \in L$
2. $\forall a,b \in L \;\; a+b \in L$
3. $\forall a \in L \;\; \forall \alpha \in F \;\; \alpha a \in L$

A *sum* $L_1 + ... + L_n$ of subspaces $L_1,...,L_n$ of a vector space V is a set of all vectors 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 is called a *direct sum* if $L_i \cap L_j = \{0\}$.

Theorem: the dimension of a sum of two subspaces is equal to the sum of their dimensions minus the dimension of their intersection. Proof: DIY.

For a direct sum, 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. $L_1 = \operatorname{span}\{a_1,...,a_n\}, \; L_2 = \operatorname{span}\{b_1,...,b_m\} \;\; \Rightarrow \;\; L_3 = \operatorname{span}\{a_1,...,a_n,b_1,...,b_m\}$

Examples of vector spaces: numbers, vectors, matrices, functions, bank accounts etc. A very large number of different sets have the basic properties of vector spaces. Their other properties may differ, but they do share the properties listed above.

b) Linear operators

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

$$\psi(\alpha a) = \alpha \psi(a) \qquad \psi(a+b) = \psi(a) + \psi(b)$$

Then ψ is called a *linear operator* (or *homomorphism*) and $\psi(a)$ is called the *image* of a in W.

Theorem: let V and W be vector 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 ψ that $\psi(a_k) = b_k$. Proof: DIY.

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

Theorem: isomorphous vector spaces have the same dimension. Proof: DIY.

Corollary: all *n*-dimensional vector spaces over $\mathbb{F}$ are isomorphous to $\mathbb{F}^n$.

We shall henceforth abstract from the actual nature of the vector spaces we are dealing with and work with their images in $\mathbb{R}^n$ and sometimes $\mathbb{C}^n$.

Let $A=\{a_1,...,a_n\}$ and $B=\{b_1,...,b_n\}$ be basis sets of vector spaces V and W and $\psi: V \to W$ be a linear operator. Matrix M is called a *matrix of operator* ψ if $Mx = y$, where x is a vector from V, written as a column of coefficients in basis A and y is the image of x in W, written as a column of coefficients in basis B.

c) Hilbert spaces

In the discussion so far we did not define any metrics – there was no notion of length or angle and no systematic way of constructing operator matrices. Defining a metric on a vector space produces an object called *Hilbert space*. In the treatment below we will assume that the elements of the original vector space were functions and reduce the level of abstraction with the purpose of moving the discussion closer to the practical context of quantum mechanics. We will need a vector space with the following operations defined:

1. Multiplication by a scalar (already there): $\forall \alpha \in F \quad \forall a \in V \quad \exists b \in V, \ \alpha a = b$
2. Addition and subtraction (already there): $\forall a,b \in V \quad (a \pm b) \in V$
3. So-called *inner* or *scalar product* (new): $P:(V \otimes V) \to \mathbb{C}$ with the following properties:
   a) $\forall f \in V \quad (f,f) \geq 0$
   b) $\langle g|f\rangle = \langle g|f\rangle^*$
   c) $\langle \alpha f + \beta g|h\rangle = \alpha\langle f|h\rangle + \beta\langle g|h\rangle$
   d) $\langle f|f\rangle = 0 \quad \Rightarrow \quad f = 0$
   e) $\sqrt{\langle f|f\rangle} + \sqrt{\langle g|g\rangle} \geq \sqrt{\langle f+g|f+g\rangle}$

In $\mathbb{C}^n$, as you likely remember, the scalar product was defined as $\langle x|y\rangle = \Sigma_k x_k^* y_k$, $\sqrt{\langle x|x\rangle}$ was the “length”, the “angle” between two vectors was defined as $\cos\varphi = \langle x|y\rangle \big/ \sqrt{\langle x|x\rangle\langle y|y\rangle}$ and “orthogonal” vectors had $\langle x|y\rangle = 0$. In a (generally infinite-dimensional) Hilbert space of functions of (for now) one real argument we can use generalizations of these definitions to the case where the k index is continuous:

$$\|f\| = \sqrt{\langle f|f\rangle} = \left(\int_{-\infty}^{\infty} f^*(x) f(x)\, dx\right)^{1/2} = \left(\int_{-\infty}^{\infty} |f(x)|^2\, dx\right)^{1/2} \quad - \quad \text{"norm"}$$

$$\langle f|g\rangle = \int_{-\infty}^{\infty} f^*(x) g(x)\, dx \quad - \quad \text{"scalar product"}$$

If the functions depend on more than one argument, all continuous arguments are integrated over and all discrete arguments are summed over the domain on which the functions are defined. The Hilbert space of all square-integrable functions with the conditions above satisfied forms the foundation of quantum theory, because wavefunctions live in it.

Because the notion of norm and orthogonality are now defined, we can define an *orthonormal basis set* to be a basis set $\{\varphi_k\}$ for which

$$\forall f \in V \quad f = \sum_k f_k \varphi_k \quad \|\varphi_k\| = 1 \quad \langle \varphi_k | \varphi_n \rangle = \delta_{kn}$$

When a suitable basis set is fixed, the Hilbert space admits a *discrete representation*:

$$f = \sum_k f_k \varphi_k \qquad f \Leftrightarrow \{f_k\}$$

A scalar product gets discretized as well:

$$f = \sum_k f_k \varphi_k \qquad g = \sum_k g_k \varphi_k$$

$$\langle f | g \rangle = \int_{-\infty}^{\infty} f^*(x) g(x) dx = \sum_{nk} f_n^* g_k \int_{-\infty}^{\infty} \varphi_n^*(x) \varphi_k(x) dx = \sum_{nk} f_n^* g_k \delta_{nk} = \sum_k f_k^* g_k$$

There is thus a direct correspondence between the continuous scalar product (integral) and the discrete one (sum).

Lecture 11: algebraic foundations of spin dynamics

d) Operator and superoperator spaces

The elements of metric vector spaces need not be vectors. Let us define a *matrix space*.

1. Multiplication by a scalar is defined in the usual way. If M is a matrix, then αM is also a matrix.
2. Addition and subtraction require all matrices in our space to have the same dimension.
3. Scalar product $\langle \cdot | \cdot \rangle$ and norm $\|\cdot\|$ need special care. We should have:
   a) $\langle M | M \rangle \geq 0$
   b) $\langle M | K \rangle = \langle K | M \rangle^*$
   c) $\langle M | \alpha N + \beta K \rangle = \alpha \langle M | N \rangle + \beta \langle M | K \rangle$
   d) $\langle M | M \rangle = 0 \quad \Rightarrow \quad M = 0$
   e) $\|M\| + \|K\| \geq \|M + K\|$

The following scalar product satisfies all these conditions:

$$\langle M | K \rangle = \mathrm{Tr}\left(M^\dagger K\right)$$

Proofs:

- $\mathrm{Tr}\left(M^\dagger M\right) = \sum_{nk} M^\dagger_{nk} M_{kn} = \sum_{nk} M^*_{kn} M_{kn} = \sum_{nk} \left|M_{kn}\right|^2 \geq 0$, and only $= 0$ if all $M_{nk} = 0$
- $\mathrm{Tr}\left[M^\dagger \left(\alpha N + \beta K\right)\right] = \ldots = \alpha \mathrm{Tr}\left(M^\dagger N\right) + \beta \mathrm{Tr}\left(M^\dagger K\right)$
- $\|M + K\|^2 = \|M\|^2 + \|K\|^2 + (M, K) + (K, M) \leq \|M\|^2 + \|K\|^2 + 2\|M\|\|K\| = \left(\|M\| + \|K\|\right)^2$

Theorem: the space $M_n(\mathbb{F})$ of all $n \times n$ matrices over $\mathbb{F}$ is n^2 dimensional. Proof: DIY.

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

Corollary: the space of all linear superoperators $L : M_n(\mathbb{C}) \to M_n(\mathbb{C})$ is isomorphous to $\mathbb{C}^{n^4}$.

That is, the space of all operators acting on a given vector space is itself a vector space with the square of the dimension of the original space. The space of all superoperators transforming the operators that act on a given vector space have the dimension that is the fourth power of the dimension of the original vector space. The space of all automorphisms of $\mathbb{C}^n$ (often with the superoperator space implicitly defined as well) is colloquially known as the *Liouville space* in spin dynamics.

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:

$$Tr\left(M^\dagger K\right) = \sum_{nk} M^*_{nk} K_{nk} = \sum_{n} M^*_n K_n$$

if the matrices are re-indexed linearly as $\{n, k\} \to \{n\}$. This matrix stretching is used a lot in spin dynamics to construct matrix representations of superoperators.

We can now sketch the “hierarchy” of spaces:

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

In principle, further layers of automorphisms (*hyperoperators etc*) are possible, but they currently have only limited use in spin dynamics.

Superoperators are often introduced via *commutators* and *commutation superoperators*:

$$\hat{\hat{L}} \equiv [\hat{L}, \ ] \qquad \hat{\hat{L}} \hat{\rho} = [\hat{L}, \hat{\rho}] = \hat{L} \hat{\rho} - \hat{\rho} \hat{L} .$$

Not every superoperator in $M_{n^2}(\mathbb{C})$ can be expressed as a commutation superoperator (because $M_n(\mathbb{C})$ is much smaller) but every superoperator in $M_{n^2}(\mathbb{C})$ can be expressed as

$$\hat{\hat{P}} \hat{\rho} = \sum_{jk} p_{jk} \hat{M}_j \hat{\rho} \hat{M}_k \qquad \hat{M}_k \in M_n(\mathbb{C})$$

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

Proof: we can write the commutation superoperator via right and left *multiplication superoperators*

$$\hat{\hat{L}} = \hat{\hat{H}}^{\mathrm{L}} - \hat{\hat{H}}^{\mathrm{R}} \qquad \hat{\hat{H}}^{\mathrm{L}} \hat{\rho} = \hat{H} \hat{\rho} \qquad \hat{\hat{H}}^{\mathrm{R}} \hat{\rho} = \hat{\rho} \hat{H}$$

and look for the matrix elements of those superoperators first. In the *standard basis* (of matrices with a single “1” somewhere in the matrix), those would be

$$\left[\hat{\hat{H}}^{\mathrm{L}}\right]_{ij} = \mathrm{Tr}\left(\hat{\rho}^{(i)\dagger} \hat{H} \hat{\rho}^{(j)}\right) \qquad \left[\hat{\hat{H}}^{\mathrm{R}}\right]_{ij} = \mathrm{Tr}\left(\hat{\rho}^{(i)\dagger} \hat{\rho}^{(j)} \hat{H}\right)$$

Cyclical permutation under the trace yields

$$\left[\hat{\hat{H}}^{\mathrm{L}}\right]_{ij} = \mathrm{Tr}\left(\hat{H} \hat{\rho}^{(j)} \hat{\rho}^{(i)\dagger}\right) = \sum_{nk} H_{nk} \left[\hat{\rho}^{(j)} \hat{\rho}^{(i)\dagger}\right]_{kn} = \sum_{nk} H_{nk} \delta_{i(\mathrm{mod}\,N),n} \delta_{j(\mathrm{mod}\,N),k} \delta_{i(\mathrm{div}\,N),j(\mathrm{div}\,N)} = \left[\hat{H} \otimes E\right]_{ij}$$

$$\left[\hat{\hat{H}}^{\mathrm{R}}\right]_{ij} = \mathrm{Tr}\left(\hat{H} \hat{\rho}^{(i)\dagger} \hat{\rho}^{(j)}\right) = \sum_{nk} H_{nk} \left[\hat{\rho}^{(i)\dagger} \hat{\rho}^{(j)}\right]_{kn} = \sum_{nk} H_{nk} \delta_{i(\mathrm{mod}\,N),j(\mathrm{mod}\,N)} \delta_{n,j(\mathrm{div} N)} \delta_{k,i(\mathrm{div} N)} = \left[E \otimes \hat{H}^{\mathrm{T}}\right]_{ij}$$

e) Common basis sets

For a spin S it is natural to *represent* the different projection states by vectors pointing along different coordinates:

$$|S,S\rangle=\begin{pmatrix}1\\0\\0\\\vdots\\0\end{pmatrix};\qquad |S,S-1\rangle=\begin{pmatrix}0\\1\\0\\\vdots\\0\end{pmatrix};\qquad \ldots\qquad |S,-S\rangle=\begin{pmatrix}0\\0\\0\\\vdots\\1\end{pmatrix};$$

This provides a basis for the Hilbert space of the spin itself. The basis for the automorphism space can be constructed using Kronecker products. In general:

$$\hat{M}=\sum_{m_1,m_2}a_{m_1,m_2}|S,m_1\rangle\langle S,m_2|$$

So, the basis (known as *projector basis*, because it is composed of projection operators) is composed of Kronecker products of the Hilbert space basis vectors, for example:

$$|S,S\rangle\langle S,S-1|=\begin{pmatrix}1 & 0 & 0 & \cdots & 0\end{pmatrix}\otimes\begin{pmatrix}0\\1\\0\\\vdots\\0\end{pmatrix}=\begin{pmatrix}0 & 0 & 0 & \cdots & 0\\1 & 0 & 0 & \cdots & 0\\0 & 0 & 0 & \cdots & 0\\\vdots & \vdots & \vdots & \ddots & 0\\0 & 0 & 0 & 0 & 0\end{pmatrix}$$

Projector basis (also known as *polarization basis*) is rarely used, because its elements do not obey common spin system symmetries and are not Hermitian matrices or close relatives thereof.

A much more popular basis set uses spin operators (augmented by the identity matrix) as a basis set for the operator space and the eigenvectors of σ_Z as a basis set for the wavefunction space. For example, for spin-1/2 we have:

$$\left\{\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix},\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix},\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix},\begin{pmatrix}0 & -1\\1 & 0\end{pmatrix}\right\}$$

which are proportional to $\hat{E}$, $\hat{S}_Z$, $\hat{S}_X$ and $\hat{S}_Y$. This is known as *Pauli basis*.

Other basis sets (single-transition, shift, and IST) will be introduced after the Lie theory segment, because they are formulated as generators for certain transformation groups.

Lecture 12: algebraic foundations of spin dynamics

f) Groups

A system of operators $G:\mathbb{C}^n \to \mathbb{C}^n$ is called a *group* if:

1. $\forall g,h \in G \;\; gh \in G$ (G is closed with respect to operator multiplication)
2. $\exists! e \in G \;\; \forall g \in G \;\; eg = g$ (there exists a unique unit element in G)
3. $\forall g \in G \;\; \exists! g^{-1} \in G,\; gg^{-1} = e$ (for every element in G there exists a unique inverse in G)

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

<u>Exercise:</u> demonstrate that, for a time-independent Liouvillian superoperator $\hat{\hat{L}}$, the set of all propagators $\exp(-i\hat{\hat{L}}t)$ is an Abelian group. This group is called the *propagator group* of $\hat{\hat{L}}$.

<u>Exercise:</u> demonstrate that the set of all symmetry operations of a benzene ring is a non-Abelian group.

By selecting a basis set $\{|\varphi_k\rangle\}$ in $\mathbb{C}^n$ and computing the matrix elements $\langle\varphi_n|g|\varphi_k\rangle$ for all g in G, we can obtain a *matrix representation* for the group G. Because the operators are required in the definition above to be invertible, the group would be represented with invertible matrices.

<u>Exercise:</u> demonstrate that the set of all invertible operators acting on $\mathbb{C}^n$ is a non-Abelian group. This group is called $GL(n,\mathbb{C})$. Prove that all elements of $GL(n,\mathbb{C})$ have a non-zero determinant, and that any matrix representation of any group must be a subgroup of $GL(n,\mathbb{C})$ for some n.

Let $g \in GL(n,\mathbb{C})$, $\{|\varphi_k\rangle\}$ be the basis in $\mathbb{C}^n$ and $\hat{g}$ be the matrix of g in that basis. For any positive ε, the set H of all operators h such that

$$\left\|\hat{g} - \hat{h}\right\| < \varepsilon$$

is called the *ε-neighbourhood* of g. If every element of a group G has an ε-neighbourhood in $GL(n,\mathbb{C})$ that does not contain other elements of G, the group G is called *discrete*. The operators of a discrete group are placed in $GL(n,\mathbb{C})$ separately and can be enumerated. Point groups describing molecular symmetry belong to this category. If a group has a finite number of elements, it is called a *finite* group. All other groups are *infinite*.

A group G is called *continuous* or *Lie group* if each operator $g \in G$ has an ε-neighbourhood with the following property:

> There exists a matrix-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 (or a system of functions, if we are looking at matrix elements) 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*.

Examples of Lie groups (over $\mathbb{C}$):

- *General linear group*, $GL(n)$ – the group of all invertible operators on $\mathbb{C}^n$, dimension $2n^2$. All groups listed below are subgroups of $GL(n)$.
- *Special linear group*, $SL(n)$ – the group of all invertible operators with a determinant equal to 1. Dimension $2n^2 - 2$.
- *Unitary group*, $U(n)$ – the group of all unitary operators, dimension n^2.
- *Orthogonal group*, $O(n)$ – real subgroup of $U(n)$, dimension $n(n-1)/2$.
- *Special unitary group*, $SU(n)$ – intersection of $SL(n)$ and $U(n)$, the group of all unitary operators with a determinant equal to 1. Dimension $n^2 - 1$. These groups play a central role in spin dynamics and particle physics.
- *Special orthogonal group*, $SO(n)$ – intersection of $SL(n)$ and $O(n)$, the group of all orthogonal operators with a determinant equal to 1. Dimension $n(n-1)/2$. These groups describe rotations.

Examples of discrete groups:

- All *point groups* encountered in molecular quantum chemistry and crystallography, with the exception of groups containing an infinite-order symmetry axis ($\mathrm{C}_{\infty\mathrm{v}}$, $\mathrm{D}_{\infty\mathrm{h}}$ and such like, those have Lie subgroups).
- *Permutation group* of n objects, usually denoted S_n. All finite point groups describing molecular symmetry are subgroups of S_n for some n.

g) Group representations

As we saw above, after a basis set is fixed in the Hilbert space, the space of operators acquires a matrix representation. However, the $g_{nk} = \langle \varphi_n | g | \varphi_k \rangle$ representation commonly used in quantum mechanics is not the only one possible.

A *k-dimensional representation* of a group G is a homomorphism $P : G \to GL(k)$, such that

$$\forall g, h \in G \quad P(gh) = P(g)P(h)$$

and a unit operator in G is represented by a unit matrix in $GL(k)$. A representation is called *unitary*, if the image of P is in $U(k)$. Some specific examples are:

- *Faithful representation:* when P is an isomorphism, that is, different elements of G are mapped into different elements of $GL(n)$.
- *Trivial representation:* all elements of G are mapped into the unit matrix. Interestingly, this very uninformative construction is known and loved in chemistry under the name of the "fully symmetric irreducible representation".
- *Scalar representation:* let a representation of each $g \in G$ be a determinant of its faithful representation. This representation is always Abelian, even though the original group might not have been.

Let P be a k-dimensional representation of G and let the representation space $\mathbb{C}^k$ have a decomposition into a direct sum of subspaces $\mathbb{C}^k = \mathbb{C}^{k_1} \oplus \ldots \oplus \mathbb{C}^{k_s}$, such that the individual subspaces $\mathbb{C}^{k_i}$ are invariant under the operators representing the elements of G. It can then be said that 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 $\mathbb{C}^{k_i}$ and their direct sum is used as the basis of $\mathbb{C}^k$, 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 the same group G in $\mathbb{C}^k$ and $\mathbb{C}^l$. The Kronecker products of operators of the form $P(g) \otimes Q(g),\ g \in G$ defined on $\mathbb{C}^k \otimes \mathbb{C}^l$ are another representation of G, because

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

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

Two representations P and Q are called *equivalent*, if they have the same dimension and there is a bijective map (similarity transformation) taking one into the other:

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

Let P be a representation of a group G in $\mathbb{C}^k$. If $\mathbb{C}^k$ 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*.

Lecture 13: algebraic foundations of spin dynamics

h) Lie algebras

For any two operators A and B acting on $\mathbb{C}^n$ we can define their *commutator* (also known as *Lie product*) – an operator defined as

$$[A,B]=AB-BA$$

Commutators have several obvious properties:

- $[A,B]=-[B,A]$ (*anticommutativity*)
- $[[A,B],C]+[[B,C],A]+[[C,A],B]=0$ (*Jacobi identity*)
- $[[A,B],C]\neq[A,[B,C]]$ (lack of associativity)

A set of operators A on $\mathbb{C}^n$ is called a *Lie algebra*, if

1. A is an *algebra*, that is, a vector space equipped with (and closed under) a bilinear matrix product operation.
2. $\forall A,B\in\mathrm{A}\quad \frac{1}{i}\left[A,B\right]\in\mathrm{A}$, that is, A is also closed under commutation.

The reason for the $1/i$ term is physical – most physically interesting operators are Hermitian and writing the commutation operation as $[A,B]=iC$ ensures that C is also a Hermitian operator.

Two Lie algebras A_1 and A_2 are *isomorphous*, if there exists a bijective map $\varphi:\mathrm{A}_1\to\mathrm{A}_2$, such that

1. $\forall A,B\in\mathrm{A}_1\quad \varphi\left(A+B\right)=\varphi\left(A\right)+\varphi\left(B\right)$
2. $\forall A\in\mathrm{A}_1\quad \forall\lambda\in\mathbb{R}\quad \varphi\left(\lambda A\right)=\lambda\varphi\left(A\right)$
3. $\forall A,B\in\mathrm{A}_1\quad \varphi\left(\frac{1}{i}\left[A,B\right]\right)=\frac{1}{i}\left[\varphi\left(A\right),\varphi\left(B\right)\right]$

A finite set of operators $\{L_1,...,L_s\}$ from a Lie algebra A is called a *generating set*, if every operator in A can be represented as a linear combination of $\{L_1,...,L_s\}$ with real coefficients:

$$\forall A\in\mathrm{A}\qquad A=\sum_{k=1}^{s}a_kL_k$$

Here and below we will assume that the generating set is linearly independent, which guarantees the uniqueness of the expansion above. Expanding a commutator of two generators, we have

$$\frac{1}{i}\left[L_k,L_m\right]=\sum_{j=1}^{s}c_{km}^{j}L_j$$

The coefficients c_{km}^{j} are known as the *structure constants*. They are specific to each choice of generators and allow the calculation of commutators without recourse to any specific matrix representations:

$$\frac{1}{i}\left[A,B\right]=\frac{1}{i}\sum_{km}a_kb_m\left[L_k,L_m\right]=\sum_{kmj}a_kb_mc_{km}^{j}L_j$$

Exercise: given the properties of the commutators listed above, demonstrate that

- $c^j_{km} = -c^j_{mk}$
- $c^j_{kk} = 0$
- $\sum_l \left(c^l_{ik} c^q_{lp} + c^l_{kp} c^q_{li} + c^l_{pi} c^q_{lk} \right) = 0$

Examples of Lie algebras

1. $AGL(n,\mathbb{C})$ – an algebra of *all* operators in $\mathbb{C}^n$. The most popular generator 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:

$$\left[[B^{ij},B^{nk}]\right]_{pq} = \left[B^{ij}B^{nk} - B^{nk}B^{ij}\right]_{pq} = \sum_r \left[B^{ij}\right]_{pr}\left[B^{nk}\right]_{rq} - \sum_r \left[B^{nk}\right]_{pr}\left[B^{ij}\right]_{rq} =$$

$$= \sum_r \delta_{ip}\delta_{jr}\delta_{nr}\delta_{kq} - \sum_r \delta_{np}\delta_{kr}\delta_{ir}\delta_{jq} = \delta_{ip}\delta_{jn}\delta_{kq} - \delta_{np}\delta_{ki}\delta_{jq} = \delta_{jn}\left[B^{ik}\right]_{pq} - \delta_{ki}\left[B^{nj}\right]_{pq}$$

$$[B^{ik},B^{lm}] = \delta_{im}B^{lk} - \delta_{lk}B^{im}$$

2. $ASL(n,\mathbb{C})$ – an algebra of all traceless operators in $\mathbb{C}^n$. One of the most convenient generator sets is *Okubo matrices*, for which:

$$A^{ik} = B^{ik} - \frac{1}{n}\delta_{ik}\left(B^{11} + \ldots + B^{nn}\right)$$

$$[A^{ik},A^{lm}] = \left(\delta_{im}\delta_{lr}\delta_{sk} - \delta_{lk}\delta_{ir}\delta_{sm}\right)A^{rs}$$

The other one is irreducible spherical tensors, but we will get to those after we deal with the rotation group in the next lecture.

3. $AU(n,\mathbb{C})$ – an algebra of all Hermitian operators in $\mathbb{C}^n$. We could choose the generators to be Hermitian linear combinations of one-element matrices B^{ij}:

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

but it is often convenient to use an *external generator set*, such as B^{ij} themselves, which does belong to a larger algebra, but still generates $AU(n,\mathbb{C})$ because $AU(n,\mathbb{C}) \subset AGL(n,\mathbb{C})$. Generators for $AU(2)$, originally proposed by Wolfgang Pauli, are

$$\varepsilon = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\qquad \sigma_1 = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\qquad \sigma_2 = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\qquad \sigma_3 = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

4. $ASU(n,\mathbb{C})$ – an algebra of all traceless Hermitian operators in $\mathbb{C}^n$. One of the possible internal generator sets may be obtained by forming Hermitian linear combinations of Okubo matrices:

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

In the case of $n = 2$, if a matrix is traceless, ε does not appear in its expansion. Therefore, the $\{\sigma_1,\sigma_2,\sigma_3\}$ Pauli matrices are the generators of $ASU(2)$.

i) Exponential map

Let us analyze the properties of matrix exponentials of the matrices belonging to one of the algebras described above. The proof of the following statements is left as an exercise:

- $\det\left(e^{A}\right)=e^{\mathrm{Tr}(A)}$
- for any operator $A\in AGL(n,\mathbb{C})$, e^{A} is an invertible operator and its inverse is e^{-A}
- if $[A,B]=0$, then $e^{A+B}=e^{A}e^{B}$
- $e^{A^{\dagger}}=\left(e^{A}\right)^{\dagger}$
- if A is Hermitian, then e^{iA} is unitary
- if A is traceless, then $\det\left(e^{iA}\right)=1$

We have seen above that a Lie algebra can be parameterized by a set of N generators X_k and real-valued coefficients θ_k:

$$A=\sum_{k=1}^{N}X_k\theta_k$$

Because an exponential of A always has an inverse and depends in a continuous way on θ_k, the set of exponentials of all matrices in a Lie algebra generated by N linearly independent generators is an N-parametric Lie group, and the following relation provides a map between the elements of the group and the elements of its algebra:

$$\exp:\mathrm{A}\to G$$

$$A\left(\vec{\theta}\right)=\sum_{k=1}^{N}X_k\theta_k,\quad A\left(\vec{\theta}\right)\in\mathrm{A},\quad \vec{\theta}\in\mathbb{R}^{N}$$

$$g\left(\vec{\theta}\right)=\exp\left[iA\left(\vec{\theta}\right)\right]=\exp\left[i\sum_{k=1}^{N}X_k\theta_k\right]=\sum_{n=1}^{\infty}\frac{1}{n!}\left(i\sum_{k=1}^{N}X_k\theta_k\right)^{n},\quad \mathrm{g}\left(\vec{\theta}\right)\in G$$

It may be shown (exercise), that the following correspondence holds (hence the names):

Lie group	**Dimension**	**Matrices in the group**	**Lie algebra**	**Matrices in the algebra**
$GL(n,\mathbb{C})$	$2n^2$	invertible	$AGL(n,\mathbb{C})$	all
$GL(n,\mathbb{R})$	n^2	real, invertible	$AGL(n,\mathbb{R})$	imaginary
$SL(n,\mathbb{C})$	$2n^2-2$	invertible, $\det=1$	$ASL(n,\mathbb{C})$	traceless
$SL(n,\mathbb{R})$	n^2-1	real, invertible, $\det=1$	$ASL(n,\mathbb{R})$	imaginary, traceless
$SO(n)$	$n(n-1)/2$	real, invertible, orthogonal	$ASO(n)$	imaginary, Hermitian
$U(n)$	n^2	invertible, unitary	$AU(n)$	Hermitian
$SU(n)$	n^2-1	invertible, unitary, $\det=1$	$ASU(n)$	Hermitian, traceless

Lecture 14: SO(3) – rotation group in three dimensions

$SO(3)$ is a *special orthogonal group* in three dimensions. It consists of all linear transformations of $\mathbb{R}^3$ that leave the scalar product invariant and have a determinant of +1. It is a subgroup of the full orthogonal group $O(3)$, which also includes inversions.

Elements of $SO(3)$ are related by the exponential map to their infinitesimal generators in $ASO(3)$, which is a Lie algebra of all imaginary Hermitian matrices, for example:

$$\begin{pmatrix} \cos\varphi & 0 & -\sin\varphi \\ 0 & 1 & 0 \\ \sin\varphi & 0 & \cos\varphi \end{pmatrix} = \exp\left[i \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \varphi \right]$$

Because every rotation can be decomposed into a combination of three rotations around the coordinate axes, $SO(3)$ is a triparametric Lie group with the following generators for its representation in $\mathbb{R}^3$:

$$E_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \qquad E_2 = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \qquad E_3 = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

This is not the only representation however, and we would be particularly interested in representations of $SO(3)$ with operators transforming functions defined in $\mathbb{R}^3$ rather than $\mathbb{R}^3$ itself.

Consider an infinitesimal action of an element of $SO(3)$ generated by E_3 on a function $f(x,y,z)$ defined in $\mathbb{R}^3$:

$$\begin{aligned} x' &= x\cos\varphi - y\sin\varphi \\ y' &= x\sin\varphi + y\cos\varphi \\ z' &= z \end{aligned}$$

$$f(x',y',z') = f(x',y',z')\Big|_{\varphi=0} + \frac{\partial f(x',y',z')}{\partial\varphi}\bigg|_{\varphi=0} \varphi + O(\varphi^2)$$

$$\frac{\partial f}{\partial\varphi} = \frac{\partial f}{\partial x'}\frac{\partial x'}{\partial\varphi} + \frac{\partial f}{\partial y'}\frac{\partial y'}{\partial\varphi} + \frac{\partial f}{\partial z'}\frac{\partial z'}{\partial\varphi} = x\frac{\partial f}{\partial y} - y\frac{\partial f}{\partial x} = i\hat{L}_Z f(x,y,z)$$

So the infinitesimal generator of rotation in the XY plane appears to be the good old $\hat{L}_Z$ angular momentum operator. Similar calculations may be carried out for YZ and XZ planes (exercise) with the very important result that *any coordinate system rotation in* $\mathbb{R}^3$ *may be represented by*

$$\hat{R}(\alpha,\beta,\gamma) f(x,y,z) = e^{i\hat{L}_X\alpha} e^{i\hat{L}_Y\beta} e^{i\hat{L}_Z\gamma} f(x,y,z)$$

$$\hat{L}_X = -i\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right); \quad \hat{L}_Y = -i\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right); \quad \hat{L}_Z = -i\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right)$$

that is, *the angular momentum operators are the generating set of the* $ASO(3)$ *Lie algebra corresponding to the* $SO(3)$ *Lie group of rotations*.

With this in place, our (quite extensive) knowledge of the properties of the angular momentum operators is presented in a different light. The commutation relations between angular momentum operators

$$[\hat{L}_{\mathrm{X}}, \hat{L}_{\mathrm{Y}}] = i\hat{L}_{\mathrm{Z}} \qquad [\hat{L}_{\mathrm{Y}}, \hat{L}_{\mathrm{Z}}] = i\hat{L}_{\mathrm{X}} \qquad [\hat{L}_{\mathrm{Z}}, \hat{L}_{\mathrm{X}}] = i\hat{L}_{\mathrm{Y}}$$

are now identified as structure relations of $ASO(3)$ and their central role in the angular momentum theory is explained by the fact that they define $ASO(3)$ completely.

The separate role played by $\hat{L}^2$ is due to the fact that it does not belong to $ASO(3)$, since only the Lie bracket is defined in a Lie algebra, but not products of $\{\hat{L}_{\mathrm{X}}, \hat{L}_{\mathrm{Y}}, \hat{L}_{\mathrm{Z}}\}$. To introduce $\hat{L}^2$, we need to define an object called *universal enveloping algebra* $U(A)$ of a Lie algebra A – an algebra of all products as well as Lie brackets of the generators. Clearly, $\hat{L}^2 = \hat{L}_{\mathrm{X}}^2 + \hat{L}_{\mathrm{Y}}^2 + \hat{L}_{\mathrm{Z}}^2$ does belong to $U(ASO(3))$ and is, in fact, a *Casimir operator* of $U(ASO(3))$, since it commutes with all generators. It is also clear that we are in most cases (and certainly when dealing with spins greater than 1/2) working with $U(ASO(3))$ when we build angular momentum Hamiltonians.

Because rotations play a fundamental role in the preparation of spin system Hamiltonians, we are interested in families of functions and operators left invariant by the elements of $SO(3)$. It may be demonstrated (exercise) that subspaces that are invariant with respect to $\hat{L}^2$ are also invariant with respect to $\{\hat{L}_{\mathrm{X}}, \hat{L}_{\mathrm{Y}}, \hat{L}_{\mathrm{Z}}\}$ and therefore any rotation. We are therefore looking for eigenfunctions (or, more precisely, invariant subspaces in the space of all well-behaved functions on $\mathbb{R}^3$) of $\hat{L}^2$.

$$\hat{L}^2 f(r,\theta,\varphi) = \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] f(r,\theta,\varphi) = l(l+1) f(r,\theta,\varphi)$$
$$f(r,\theta+2\pi,\varphi) = f(r,\theta,\varphi)$$
$$f(r,\theta,\varphi+2\pi) = f(r,\theta,\varphi)$$

where we called the eigenvalue $l(l+1)$ for reasons which would become clear in a moment. Solving the spherical Legendre equation and demonstrating that the following functions are the solution

$$f_l(r,\theta,\varphi) = \sum_{m=-l}^{l} a_m(r) Y_{lm}(\theta,\varphi)$$

($a_m(r)$ are arbitrary functions of distance) is left as an exercise. We can take advantage of the fact that

$$[\hat{L}^2, \hat{L}_{\mathrm{Z}}] = 0 \qquad \hat{L}_{\mathrm{Z}} Y_{lm}(\theta,\varphi) = m Y_{lm}(\theta,\varphi)$$

to classify functions further by projection of the angular momentum on Z-axis, but this is not strictly necessary. What is important is that *spherical harmonics of a given rank span an $SO(3)$-invariant subspace of the space of all functions of θ,φ*. Because matrix representations of the rotation operators for each value of l in $Y_{lm}(\theta,\varphi)$ are irreducible (prove it as an exercise), the spherical harmonics of different ranks form basis sets for different irreducible representations (irreps) of $SO(3)$. From a practical point of view this means that any spherical harmonic is transformed by any rotation into a linear combination of spherical harmonics of the same rank – the ranks never get mixed.

Spherical harmonics may be transformed into Cartesian coordinates, and this Cartesian representation corresponds to linear combinations of coordinates that form basis sets of different irreps of $SO(3)$.

l	m	$Y_{lm}(\theta,\varphi)$	$Y_{lm}(x,y,z)$	$\hat{T}_m^{(l)}$
0	0	$1/\sqrt{4\pi}$	$1/\sqrt{4\pi}$	$\hat{E}$
1	−1	$\sqrt{3/8\pi}e^{-i\varphi}\sin\theta$	$\sqrt{3/8\pi}(x-iy)/r$	$\left(1/\sqrt{2}\right)\hat{L}_-$
1	0	$\sqrt{3/4\pi}\cos\theta$	$\left(\sqrt{3/4\pi}\right)z/r$	$\hat{L}_Z$
1	1	$-\sqrt{3/8\pi}e^{i\varphi}\sin\theta$	$-\sqrt{3/8\pi}(x+iy)/r$	$-\left(1/\sqrt{2}\right)\hat{L}_+$
2	−2	$\sqrt{15/32\pi}e^{-2i\varphi}\sin^2\theta$	$\sqrt{15/32\pi}\left(x-iy\right)^2/r^2$	$(1/2)\hat{L}_-^2$
2	−1	$\sqrt{15/8\pi}e^{-i\varphi}\sin\theta\cos\theta$	$\sqrt{15/8\pi}\left(x-iy\right)z/r^2$	$(1/2)\left(\hat{L}_Z\hat{L}_-+\hat{L}_-\hat{L}_Z\right)$
2	0	$\sqrt{5/16\pi}\left(3\cos^2\theta-1\right)$	$\sqrt{5/16\pi}\left(2z^2-x^2-y^2\right)/r^2$	$\sqrt{\frac{2}{3}}\left(\hat{L}_Z^2-\frac{1}{4}\left(\hat{L}_+\hat{L}_-+\hat{L}_-\hat{L}_+\right)\right)$
2	1	$-\sqrt{15/8\pi}e^{i\varphi}\sin\theta\cos\theta$	$-\sqrt{15/8\pi}\left(x+iy\right)z/r^2$	$-(1/2)\left(\hat{L}_Z\hat{L}_++\hat{L}_+\hat{L}_Z\right)$
2	2	$\sqrt{15/32\pi}e^{2i\varphi}\sin^2\theta$	$\sqrt{15/32\pi}\left(x+iy\right)^2/r^2$	$(1/2)\hat{L}_+^2$

The operators obtained by replacing the Cartesian coordinates with Cartesian angular momentum operators are known as *irreducible spherical tensor operators* (IST). Single-spin ISTs are listed in the table above, but two-spin ISTs:

$$\begin{aligned}
\hat{T}_2^{(2)}(L,S) &= +\frac{1}{2}\hat{L}_+\hat{S}_+ \\
\hat{T}_1^{(2)}(L,S) &= -\frac{1}{2}\left(\hat{L}_Z\hat{S}_++\hat{L}_+\hat{S}_Z\right) \\
\hat{T}_0^{(2)}(L,S) &= +\sqrt{\frac{2}{3}}\left(\hat{L}_Z\hat{S}_Z-\frac{1}{4}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)\right) \\
\hat{T}_{-1}^{(2)}(L,S) &= +\frac{1}{2}\left(\hat{L}_Z\hat{S}_-+\hat{L}_-\hat{S}_Z\right) \\
\hat{T}_{-2}^{(2)}(L,S) &= +\frac{1}{2}\hat{L}_-\hat{S}_-
\end{aligned}$$

are also useful for setting up coupling tensor rotations. Because of their common group theoretical heritage, spherical harmonics and ISTs have common rotation properties:

$$\hat{\hat{R}}(\alpha,\beta,\gamma)\hat{T}_m^{(l)} = \sum_{m'=-l}^{l}\hat{T}_{m'}^{(l)}\mathfrak{D}_{m',m}^{(l)}(\alpha,\beta,\gamma)$$

$$\hat{\hat{R}}(\alpha,\beta,\gamma)Y_{lm}(\theta,\varphi) = \sum_{m'=-l}^{l}Y_{lm'}(\theta,\varphi)\mathfrak{D}_{m',m}^{(l)}(\alpha,\beta,\gamma)$$

The $\mathfrak{D}_{m',m}^{(l)}(\alpha,\beta,\gamma)$ coefficients in the equations above are known as *Wigner functions* and the corresponding matrices as *Wigner rotation matrices*. We will be using them a lot.

Lecture 15: spatial rotations in spin systems

Interaction tensor anisotropy parameters

1. Anisotropy + asymmetry (“Haeberlen notation”)

$$\sigma_{\mathrm{Iso}} = \frac{1}{3}\left(\sigma_{\mathrm{XX}} + \sigma_{\mathrm{YY}} + \sigma_{\mathrm{ZZ}}\right)$$

$$\Delta\sigma = \sigma_{\mathrm{ZZ}} - \frac{1}{2}\left(\sigma_{\mathrm{XX}} + \sigma_{\mathrm{YY}}\right) \quad \text{or} \quad \zeta = \sigma_{\mathrm{ZZ}} - \sigma_{\mathrm{Iso}}$$

$$\eta = \frac{3}{2}\frac{\sigma_{\mathrm{YY}} - \sigma_{\mathrm{XX}}}{\Delta\sigma} = \frac{\sigma_{\mathrm{YY}} - \sigma_{\mathrm{XX}}}{\zeta}$$

The eigenvalues are assumed to be ordered as

$$\left|\sigma_{\mathrm{ZZ}} - \sigma_{\mathrm{Iso}}\right| \geq \left|\sigma_{\mathrm{XX}} - \sigma_{\mathrm{Iso}}\right| \geq \left|\sigma_{\mathrm{YY}} - \sigma_{\mathrm{Iso}}\right|$$

This definition has an obvious singularity when $\Delta\sigma = 0$ and suffers from an axis switching problem because eigenvalues are ordered explicitly. An alternative ordering of eigenvalues, known as “Mehring notation”, is

$$\sigma_{\mathrm{XX}} \leq \sigma_{\mathrm{YY}} \leq \sigma_{\mathrm{ZZ}}$$

2. Span + skew (“Maryland notation”)

$$\sigma_{\mathrm{Iso}} = \frac{1}{3}\left(\sigma_{\mathrm{XX}} + \sigma_{\mathrm{YY}} + \sigma_{\mathrm{ZZ}}\right)$$

$$\Omega = \sigma_{\mathrm{ZZ}} - \sigma_{\mathrm{XX}} \qquad \kappa = \frac{3}{2}\frac{\sigma_{\mathrm{Iso}} - \sigma_{\mathrm{YY}}}{\Omega}$$

with eigenvalues in Mehring order. These parameters give a physically intuitive picture of shielding powder patterns, but are not well adapted for the description of rotations.

3. Axiality + rhombicity (spherical tensor notation)

$$Ax = 2\sigma_{\mathrm{ZZ}} - \left(\sigma_{\mathrm{XX}} + \sigma_{\mathrm{YY}}\right) \qquad Rh = \sigma_{\mathrm{XX}} - \sigma_{\mathrm{YY}}$$

with eigenvalues in Mehring order. This notation is very well adapted for the description of rotations, because axiality and rhombicity are the natural coefficients in the irreducible spherical tensor expansion of spin interactions.

Interaction tensor rotations

When a molecule rotates, spins *do not rotate*. They get translated in space, but their projections on the lab frame axes stay the same. The anisotropic interactions, however, do rotate, because in most cases they are determined by the electronic structure and the angles that the distance vectors make with the applied magnetic field. In principle, a straightforward sine + cosine rotation matrix would often suffice:

$$\hat{R}\left(\hat{\vec{L}} \cdot A \cdot \hat{\vec{S}}\right) = \hat{\vec{L}} \cdot \left(R^{-1}AR\right) \cdot \hat{\vec{S}}$$

in which the rotation matrix R can be written as a sequence of rotations around the three laboratory frame axes:

$$R(\alpha,\beta,\gamma)=\begin{pmatrix}\cos\alpha & -\sin\alpha & 0\\ \sin\alpha & \cos\alpha & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\cos\beta & 0 & -\sin\beta\\ 0 & 1 & 0\\ \sin\beta & 0 & \cos\beta\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\gamma & -\sin\gamma\\ 0 & \sin\gamma & \cos\gamma\end{pmatrix}$$

and many simulation codes use it. It is, however, analytically cumbersome and completely blocks all attempts at performing relaxation theory treatment. We do therefore need a more regular way of describing rotations. The most popular conventions include:

- Euler angles convention A
  1. rotate about the Z axis through an angle α $(0\ldots 2\pi)$
  2. rotate about the new Y axis through an angle β $(0\ldots\pi)$
  3. rotate about the new Z axis through an angle γ $(0\ldots 2\pi)$

  This is a very inconvenient sequence because the reference frame drifts with the object.

- Euler angles convention B
  1. rotate about the Z axis through an angle γ $(0\ldots 2\pi)$
  2. rotate about the Y axis through an angle β $(0\ldots\pi)$
  3. rotate about the Z axis through an angle α $(0\ldots 2\pi)$

  This convention is more convenient and easier to visualize. the angles involved are the same and the two conventions accomplish identical rotations.

  Euler angles (in any convention) are notoriously difficult to convert into. They have been criticized because they are not a valid parameterization of $SO(3)$, since the generators corresponding to the Euler angles do not obey the required commutation relations. It is easy to see that the infinitesimal generators of

$$R(\alpha,\beta,\gamma)=\begin{pmatrix}\cos\alpha & -\sin\alpha & 0\\ \sin\alpha & \cos\alpha & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\cos\beta & 0 & -\sin\beta\\ 0 & 1 & 0\\ \sin\beta & 0 & \cos\beta\end{pmatrix}\begin{pmatrix}\cos\gamma & -\sin\gamma & 0\\ \sin\gamma & \cos\gamma & 0\\ 0 & 0 & 1\end{pmatrix}$$

  do not commute in the right way – the commutator of the first and the third one yields zero instead of the second generator. In practice this leads to nasty singularities: $\beta=0$ and $\beta=\pi$ points are singular, meaning that the differential equations involving Euler angles run into analytical and numerical difficulties. In general, while it is usually possible to translate Euler angles into more regular conventions (angle-axis, eigensystem, quaternions *etc*), it is not easy to go back.

- Angle-axis parameterization

  Any rotation may be defined in terms of a unit vector and an angle of rotation around that vector. This may be shown to be a correct parameterization of the rotation group and all singularities associated with Euler angles disappear in this approach. It also has the benefit of being easy to visualize.

- Quaternions (Euler-Rodriguez parameters)

  An obscure, but sometimes useful convention in which a rotation is defined by four parameters $\{a,b,c,d\}$, such that $a^2+b^2+c^2+d^2=1$ and

$$\begin{pmatrix} a+di & b+ci \\ -b+ci & a-di \end{pmatrix}$$

  is a family of generators of $SU(2)$. The quaternion representation is most easily obtained from angle-axis parameters:

$$\begin{aligned} a &= n_{\mathrm{X}}\sin(\theta/2) & b &= n_{\mathrm{Y}}\sin(\theta/2) \\ c &= n_{\mathrm{Z}}\sin(\theta/2) & d &= \cos(\theta/2) \end{aligned}$$

- DCM (directional cosine matrix, *aka* eigensystem)

  An explicit 3x3 matrix performing the rotation in question, i.e. $R^{-1}AR$. Usually results from the instrumental readout. DCM is also the matrix of eigenvectors (columns) of the tensor in question. Applying R to a vector rotates the vector into the eigensystem of the tensor.

- Cayley-Klein parameters

  A surprisingly useful convention with four parameters $\{\alpha,\beta,\gamma,\delta\}$ satisfying

$$\begin{gathered} |\alpha|^2+|\gamma|^2=1 \qquad |\alpha|^2+|\beta|^2=1 \qquad |\beta|^2+|\delta|^2=1 \\ \alpha^*\beta-\gamma^*\delta=0 \qquad \alpha\delta-\beta\gamma=1 \qquad \beta=-\gamma^* \qquad \delta=\alpha^* \end{gathered}$$

  CK parameters provide a straightforward link between DCMs and Wigner matrices, which is very useful in practical calculations, where the former are usually given and the latter are usually necessary.

$$R=\begin{pmatrix} \frac{1}{2}\left(\alpha^2-\gamma^2+\delta^2-\beta^2\right) & \frac{i}{2}\left(\gamma^2-\alpha^2+\delta^2-\beta^2\right) & \gamma\delta-\alpha\beta \\ \frac{i}{2}\left(\alpha^2+\gamma^2-\delta^2-\beta^2\right) & \frac{1}{2}\left(\alpha^2+\gamma^2+\delta^2+\beta^2\right) & -i\left(\alpha\beta-\gamma\delta\right) \\ \beta\delta-\alpha\gamma & i\left(\alpha\gamma-\beta\delta\right) & \alpha\delta+\beta\gamma \end{pmatrix}$$

Wigner functions can be computed using any of these conventions. The “grand coffee table book” (*Varshalovich, Moskalev, Khersonskii, Quantum Theory of Angular Momentum, World Scientific, 1988*) contains all the necessary tables. It is advisable to use Mathematica because the relations in the book are given in their most general form and are not always easy to evaluate.

Summary: setting up an anisotropic interaction

1. Get the eigenvalues and compute the following quantities:

$$Ax=2\sigma_{\mathrm{ZZ}}-\left(\sigma_{\mathrm{XX}}+\sigma_{\mathrm{YY}}\right) \qquad Rh=\sigma_{\mathrm{XX}}-\sigma_{\mathrm{YY}}$$

2. Determine the orientation parameters of the tensor in any of the conventions listed above.

3. Use the literature tables (*Varshalovich, Moskalev, Khersonskii, Quantum Theory of Angular Momentum, World Scientific, 1988*) or Mathematica to compute Wigner functions from your orientation parameters.

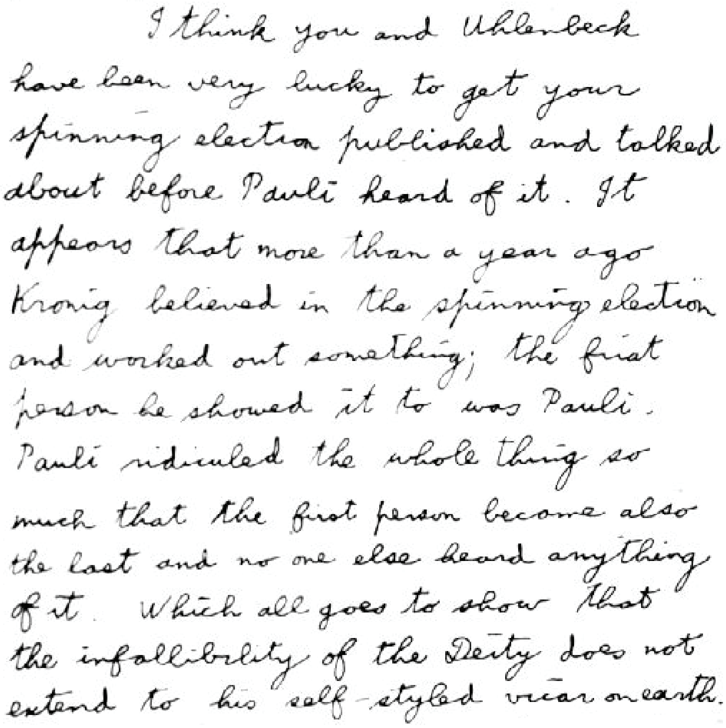
4. $$\begin{aligned}\hat{\hat{R}}\left(\hat{\vec{L}}\cdot\mathbf{A}\cdot\hat{\vec{S}}\right) &= \frac{Rh}{2}\sum_{m=-2}^{2}\hat{T}_{2,m}\left(L,S\right)\mathfrak{D}^{(2)}_{m,-2}+\frac{Rh}{2}\sum_{m=-2}^{2}\hat{T}_{2,m}\left(L,S\right)\mathfrak{D}^{(2)}_{m,2}+\frac{Ax}{\sqrt{6}}\sum_{m'=-2}^{2}\hat{T}_{2,m}\mathfrak{D}^{(2)}_{m,0}\\ &= \sum_{m=-2}^{2}\hat{T}_{2,m}\left(L,S\right)\Phi_{m}; \qquad \Phi_{m}=\frac{Rh}{2}\left(\mathfrak{D}^{(2)}_{m,-2}+\mathfrak{D}^{(2)}_{m,2}\right)+\frac{Ax}{\sqrt{6}}\mathfrak{D}^{(2)}_{m,0}\end{aligned}$$

   The same applies to $\vec{B}\cdot\mathbf{A}\cdot\hat{\vec{S}}$ and $\hat{\vec{S}}\cdot\mathbf{A}\cdot\hat{\vec{S}}$, with different $\hat{T}_{2,m}$ operators (see the previous lecture).

Lecture 16: SU(2) group of spin

Historical notes

A number of experimental observations reported in 1920-es have led to a conjecture that the electron has an intrinsic magnetic moment that is distinct from the one associated with its orbital motion. The intrinsic magnetic moment hypothesis yielded a satisfactory explanation of the anomalous Zeeman effect, of the fine structure of atomic spectra of alkali metals and of some other observations. In 1925, Uhlenbeck and Goudsmit proposed an explanation for this magnetic moment, suggesting that the electron has an intrinsic angular momentum, which they called *spin*.



I think you and Uhlenbeck have been very lucky to get your spinning electron published and talked about before Pauli heard of it. It appears that more than a year ago Kronig believed in the spinning electron and worked out something; the first person he showed it to was Pauli. Pauli ridiculed the whole thing so much that the first person became also the last and no one else heard anything of it. Which all goes to show that the infallibility of the Deity does not extend to his self-styled vicar on earth.

Part of a letter by L.H. Thomas to Samuel Goudsmit (25 March 1926).

This proposal faced serious difficulties. It contradicted the notion of elementary particle as a "point" object – as previously understood, a particle could not "rotate". The spin hypothesis did not fit into Schrödinger's wavefunction formalism either – the experiment by Stern and Gerlach suggested that an electron in a magnetic field can only have two "spin states", which meant that the corresponding operator must have *exactly two* eigenfunctions. Because angular momentum was assumed to be involved, the spin operators had to come from some representation of $SO(3)$. It is easy to see, however (see your angular momentum course), that the irreps of $SO(3)$ have dimensions of $2j+1$. So j had to be set to a fractional value, meaning that the resulting space had a bizarre physical interpretation (a wavefunction that changes sign upon a 360-degree rotation). It became obvious that the spin state of the system had to be represented by a vector from a space that is *different* from the Schrödinger wavefunction space.

Introducing SU(2)

Ironically (see the letter above), such a space was constructed by Pauli, who suggested that the discrete spin variable be introduced into the wavefunction as a separate coordinate

$$\psi(x,y,z) \quad \to \quad \psi(x,y,z,\sigma), \qquad \sigma = 1,2,3\ldots$$

and the infinite-dimensional Hilbert space of wavefunctions be crossed with a $(2j+1)$-dimensional spin space (elements of this space became known as *spinors*):

$$\mathbb{C}^{\infty} \quad \to \quad \mathbb{C}^{2j+1} \otimes \mathbb{C}^{\infty}$$

with some angular momentum type operators defined on $\mathbb{C}^{2j+1}$. It may be demonstrated (exercise) that the following families of $(2j+1)\times(2j+1)$ matrices satisfy the structure relations of $ASO(3)$

$$\hat{L}_{\mathrm{X}}^{1/2}=\frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Y}}^{1/2}=\frac{1}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Z}}^{1/2}=\frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$\hat{L}_{\mathrm{X}}^{1}=\frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Y}}^{1}=\frac{1}{\sqrt{2}}\begin{pmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Z}}^{1}=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}$$

$$\hat{L}_{\mathrm{X}}^{3/2}=\begin{pmatrix}0 & \sqrt{\frac{3}{2}} & 0 & 0\\ \sqrt{\frac{3}{2}} & 0 & 2 & 0\\ 0 & 2 & 0 & \sqrt{\frac{3}{2}}\\ 0 & 0 & \sqrt{\frac{3}{2}} & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Y}}^{3/2}=\begin{pmatrix}0 & -\sqrt{\frac{3}{2}}i & 0 & 0\\ \sqrt{\frac{3}{2}}i & 0 & -2i & 0\\ 0 & 2i & 0 & -\sqrt{\frac{3}{2}}i\\ 0 & 0 & \sqrt{\frac{3}{2}}i & 0\end{pmatrix},\quad \hat{L}_{\mathrm{Z}}^{3/2}=\begin{pmatrix}\frac{3}{2} & 0 & 0 & 0\\ 0 & \frac{1}{2} & 0 & 0\\ 0 & 0 & -\frac{1}{2} & 0\\ 0 & 0 & 0 & -\frac{3}{2}\end{pmatrix}$$

etc, but that they do not, in fact, generate $SO(3)$ under the $\exp(i\hat{L})$ map because they are not purely imaginary (remember from Lecture 13 that only real coefficients are allowed in linear combinations – the field over which the original matrix space was defined is $\mathbb{R}$). It turns out (exercise) that the group they do generate is $SU(2)$ and they themselves are generator sets for irreducible representations of $ASU(2)$.

ASU(2) and its universal enveloping algebra

In practical calculations one often finds that having just the generators as the basis set and just the Lie bracket multiplication is not sufficient – extra operators are required, such as non-Hermitian raising and lowering operators $\hat{L}_{\pm}=\hat{L}_{\mathrm{X}}\pm i\hat{L}_{\mathrm{Y}}$, as well as powers of the generators, which do not belong to $ASU(2)$. The operator describing nuclear quadrupolar interaction, for example

$$\hat{H}_{\mathrm{Q}}=\frac{3e^2qQ}{4L(2L-1)\hbar}\left\{\left(\hat{L}_{\mathrm{Z}}^2-\frac{1}{3}\hat{L}^2\right)+\frac{\eta}{3}\left(\hat{L}_{\mathrm{X}}^2-\hat{L}_{\mathrm{Y}}^2\right)\right\}$$

contains powers of the generators or, equivalently, powers of the raising and lowering operators, which behave differently for different representations:

$$\left(\hat{L}_{\mathrm{Z}}^{1/2}\right)^2=\frac{1}{4}\hat{E},\quad \left(\hat{L}_{\pm}^{1/2}\right)^2=0$$

$$\left(\hat{L}_{\mathrm{Z}}^{1}\right)^2=\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 1\end{pmatrix},\quad \left(\hat{L}_{+}^{1}\right)^2=\begin{pmatrix}0 & 0 & 2\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix},\quad \left(\hat{L}_{-}^{1}\right)^2=\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 2 & 0 & 0\end{pmatrix},\quad \left(\hat{L}_{\pm}^{1}\right)^3=0$$

The higher the rank of the representation, the higher the *nilpotency index* of $\hat{L}_{\pm}$ (incidentally, this explains indirectly why spin-1/2 systems never have quadrupole interactions). The *external generators* $\hat{L}_{\pm}$, their various powers as well as the *Casimir operator* $\hat{L}^2$ live in the *universal enveloping algebra* of $ASU(2)$, which is obtained by equipping $ASU(2)$ with a binary matrix product.

Multi-spin systems: direct products and Cartan decomposition

Because the state vector space of a multi-spin system is a direct product of state spaces of individual spins, the algebra of operators acting on the state space of a multi-spin system is a direct product of single-spin operator algebras.

Two-spin system: $U\left(ASU(2)\right)\otimes U\left(ASU(2)\right)$

This is an instructive special case. In a spin-1/2 representation, the direct product algebra has 16 basis operators:

	$\hat{E}$	$\hat{S}_{\mathrm{X}}$	$\hat{S}_{\mathrm{Y}}$	$\hat{S}_{\mathrm{Z}}$
$\hat{E}$	$\hat{E}\otimes\hat{E}$	$\hat{E}\otimes\hat{S}_{\mathrm{X}}$	$\hat{E}\otimes\hat{S}_{\mathrm{Y}}$	$\hat{E}\otimes\hat{S}_{\mathrm{Z}}$
$\hat{L}_{\mathrm{X}}$	$\hat{L}_{\mathrm{X}}\otimes\hat{E}$	$\hat{L}_{\mathrm{X}}\otimes\hat{S}_{\mathrm{X}}$	$\hat{L}_{\mathrm{X}}\otimes\hat{S}_{\mathrm{Y}}$	$\hat{L}_{\mathrm{X}}\otimes\hat{S}_{\mathrm{Z}}$
$\hat{L}_{\mathrm{Y}}$	$\hat{L}_{\mathrm{Y}}\otimes\hat{E}$	$\hat{L}_{\mathrm{Y}}\otimes\hat{S}_{\mathrm{X}}$	$\hat{L}_{\mathrm{Y}}\otimes\hat{S}_{\mathrm{Y}}$	$\hat{L}_{\mathrm{Y}}\otimes\hat{S}_{\mathrm{Z}}$
$\hat{L}_{\mathrm{Z}}$	$\hat{L}_{\mathrm{Z}}\otimes\hat{E}$	$\hat{L}_{\mathrm{Z}}\otimes\hat{S}_{\mathrm{X}}$	$\hat{L}_{\mathrm{Z}}\otimes\hat{S}_{\mathrm{Y}}$	$\hat{L}_{\mathrm{Z}}\otimes\hat{S}_{\mathrm{Z}}$

Similarly, the spin-1 representation would have 64 basis operators, *etc*. In practical calculations of multi-spin systems $\hat{A}\otimes\hat{B}$ is often abbreviated $\hat{A}\hat{B}$, but only if the symbols used for the operators for the two spins are different.

Definition: let G be a real semi-simple Lie algebra. A *Cartan decomposition* of G is a direct sum $G = P\oplus Q$, the terms in which satisfy the commutation relations

$$[Q,Q]\subset Q, \qquad [P,Q]=P, \qquad [P,P]\subset Q$$

For the two-spin system described above, it is easy to check (exercise) that

$$Q=\operatorname{span}\left\{\hat{L}_{\mathrm{X}},\hat{L}_{\mathrm{Y}},\hat{L}_{\mathrm{Z}},\hat{S}_{\mathrm{X}},\hat{S}_{\mathrm{Y}},\hat{S}_{\mathrm{Z}}\right\}$$

$$P=\operatorname{span}\left\{\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{X}},\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{Y}},\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{Z}},\hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{X}},\hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{Y}},\hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{Z}},\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{X}},\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Y}},\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}\right\}$$

meaning that the Q term in the Cartan decomposition is responsible for observables and RF pulses, whereas the P term is responsible for all spin-spin couplings. Every sub-algebra of P is Abelian (exercise).

Definition: the maximal Abelian subalgebra H of P is called a *Cartan subalgebra* of the pair (P,Q).

In the case of the two-spin system, the Cartan sub-algebra is one-dimensional and is generated by the close relatives of the Casimir operator:

$$H=\operatorname{span}\left\{\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{X}},\hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{Y}},\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}\right\}$$

Actions, orbits and stabilizers

Definition: 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, $a\to g\left(a\right)$, where $a\in A,\ g\in G$.

In spin dynamics context, an example of a group action would be an action of the elements of the propagator group on the system state vector, taking it forward or backward in time.

Definition: given an element g of a Lie algebra G, the *adjoint action* of g on G is an endomorphism $\mathrm{ad}_g : G \to G$ with $\mathrm{ad}_g\left(h\right) = [g,h]$.

In other words, the adjoint action by g corresponds to the action by the commutation superoperator induced by g.

Definition: an *orbit* Ga of an element a in a set A acted upon by a group G is the set of all elements that a is transformed into, that is:

$$Ga = \left\{ g\left(a\right) \mid g \in G \right\}.$$

The orbits induced by Lie groups are continuous with respect to the group parameters. In the case where G is the propagator group and A is the state space if the spin system, the orbits of the general form $\exp(-i\hat{\hat{L}}t)\hat{\rho}$ are known as *system trajectories*. The set of all orbits of A under the action by G is called the *orbit space*.

A subset $B \subset A$ is called *invariant under* G if

$$\forall b \in B \;\; \forall g \in G \;\; g\left(b\right) \in B$$

and *fixed under* G if

$$\forall b \in B \;\; \forall g \in G \;\; g\left(b\right) = b.$$

For every specific element $a \in A$, the *stabilizer subgroup* G_a of a is a set of all elements in G that leave a fixed:

$$G_a = \left\{ g \in G \mid g\left(a\right) = a \right\}$$

Lecture 17: strong, weak and secular coupling

Interaction representation

Because Zeeman interactions commonly encountered in magnetic resonance are fairly large (from MHz to THz in practically encountered magnets), it is usually inconvenient to propagate the spin system using the full Liouvillian

$$G\left(\hat{\rho}_0\right)=\left\{e^{-i\hat{\hat{L}}t}\hat{\rho}_0,\ t\in[0,\infty)\right\},\qquad G\left(\hat{\rho}_0\right)=\left\{\hat{\rho}_0,\hat{\hat{P}}\hat{\rho}_0,\hat{\hat{P}}^2\hat{\rho}_0,\ldots\right\};\qquad \hat{\hat{P}}=e^{-i\hat{\hat{L}}\Delta t}$$

because the time step required to correctly sample the system trajectory is extremely small (microseconds to picoseconds) on the time scale of the simulation (seconds). The following transformation (called *interaction representation transformation* or *rotating frame transformation*) is often applied to get rid of the large Zeeman terms in Liouville space:

$$\frac{\partial\hat{\rho}\left(t\right)}{\partial t}=-i\left(\hat{\hat{L}}_0+\hat{\hat{L}}_1\right)\hat{\rho}\left(t\right)$$

$$\hat{\sigma}\left(t\right)=e^{i\hat{\hat{L}}_0 t}\hat{\rho}\left(t\right)\qquad \hat{\hat{L}}_1^{\mathrm{D}}\left(t\right)=e^{i\hat{\hat{L}}_0 t}\hat{\hat{L}}_1 e^{-i\hat{\hat{L}}_0 t}\qquad \frac{\partial\hat{\sigma}\left(t\right)}{\partial t}=-i\hat{\hat{L}}_1^{\mathrm{D}}\left(t\right)\hat{\sigma}\left(t\right)$$

and similarly in Hilbert space:

$$\frac{\partial\hat{\rho}\left(t\right)}{\partial t}=-i[\hat{H}_0+\hat{H}_1,\hat{\rho}\left(t\right)]$$

$$\hat{\sigma}\left(t\right)=e^{i\hat{H}_0 t}\hat{\rho}\left(t\right)e^{-i\hat{H}_0 t}\qquad \hat{H}_1^{\mathrm{D}}\left(t\right)=e^{i\hat{H}_0 t}\hat{H}_1 e^{-i\hat{H}_0 t}\qquad \frac{\partial\hat{\sigma}\left(t\right)}{\partial t}=-i[\hat{H}_1^{\mathrm{D}}\left(t\right),\hat{\sigma}\left(t\right)]$$

with the result that the “large and simple” term $\hat{\hat{L}}_0=ad\hat{H}_0$ formally disappears from the equation and the “small and complicated” term $\hat{\hat{L}}_1=ad\hat{H}_1$ acquires a time dependence by virtue of the fact that it becomes wrapped in unitary propagators. This would, in principle, allow us to focus on the complicated dynamics prescribed by $\hat{\hat{L}}_1$.

If we remember that $SO\left(3\right)$ is a subgroup of $SU\left(2\right)$, then we could say that the transformation above is a (perhaps complicated) rotation. In the case where $\hat{\hat{L}}_0$ is Zeeman interaction, the interaction representation transformation does actually amount to a simple rotation in the physical sense (remember that $\exp\left(-i\hat{L}_Z\varphi\right)$ rotates the system by an angle φ in the XY plane), hence the “rotating frame” term. The case where interaction representation is invoked with respect to all Zeeman interactions in the system is not easy to visualize and is best approached as a formal unitary transformation.

Secular parts of spin interactions

Because of its ubiquity, the case of interaction representation transformation with respect to the high-field Zeeman Hamiltonian deserves special attention. Certain types of interactions commute with $\hat{L}_Z$, and therefore $\exp\left(-i\hat{L}_Z t\right)$, and are unaffected by the interaction representation transformation:

$$[\hat{L}_\mathrm{Z},\hat{L}_\mathrm{Z}\hat{S}_\mathrm{Z}]=[\hat{S}_\mathrm{Z},\hat{L}_\mathrm{Z}\hat{S}_\mathrm{Z}]=0,\qquad [\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z},\hat{L}_\mathrm{X}\hat{S}_\mathrm{X}+\hat{L}_\mathrm{Y}\hat{S}_\mathrm{Y}+\hat{L}_\mathrm{Z}\hat{S}_\mathrm{Z}]=0$$

Note (exercise) that the scalar coupling does not commute with $\hat{L}_\mathrm{Z}$ and $\hat{S}_\mathrm{Z}$ individually. In general, the irreducible spherical tensor basis is very convenient in that it is ordered with respect to this commutation property:

$$[\hat{L}_\mathrm{Z},\hat{T}_{lm}(L)]=m\hat{T}_{lm}(L),\qquad [\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z},\hat{T}_{lm}(L,S)]=m\hat{T}_{lm}(L,S)$$

meaning that

$$\begin{gathered}
e^{i\omega\hat{L}_\mathrm{Z}t}\hat{T}_{lm}(L)e^{-i\omega\hat{L}_\mathrm{Z}t}=e^{-im\omega t}\hat{T}_{lm}(L)\\
e^{i\omega\left(\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z}\right)t}\hat{T}_{lm}(L,S)e^{-i\omega\left(\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z}\right)t}=e^{-im\omega t}\hat{T}_{lm}(L,S)
\end{gathered}$$

Consider the rotating frame transformation of the irreducible spherical tensor expansion of a fairly typical Hamiltonian of a coupled two-spin system:

$$\begin{aligned}
&\hat{H}=\left[\omega\hat{L}_\mathrm{Z}+\omega\hat{S}_\mathrm{Z}\right]+\left[\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)\right]\\
&\hat{H}_0=\omega\hat{L}_\mathrm{Z}+\omega\hat{S}_\mathrm{Z}\\
&\hat{H}_1=\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)
\end{aligned}$$

The “big” Hamiltonian contains the carrier Zeeman frequencies, the “small one” has the offsets and the coupling. After the interaction representation transformation we have:

$$\begin{aligned}
\hat{H}_1^\mathrm{D}(t)&=e^{i\omega\left(\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z}\right)t}\left[\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)\right]e^{-i\omega\left(\hat{L}_\mathrm{Z}+\hat{S}_\mathrm{Z}\right)t}\\
&=\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+\sum_{m=-2}^{2}a_me^{-i\omega mt}\hat{T}_{2m}(L,S)\\
&=\left[\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+a_0\hat{T}_{2,0}(L,S)\right]+\sum_{m\neq0}a_me^{-i\omega mt}\hat{T}_{2m}(L,S)
\end{aligned}$$

We have two kinds of terms in the resulting rotating frame Hamiltonian – the time-independent terms in square brackets and the very rapidly oscillating (MHz to THz) terms under the sum. The *secular approximation* (dating back to Kepler, no less) states that the effect of the rapidly oscillating terms can be ignored, because they average to zero on the time scale of the evolution under the time-independent terms (kHz). We therefore have:

$$\hat{H}_1^\mathrm{D}=\omega_1\hat{L}_\mathrm{Z}+\omega_2\hat{S}_\mathrm{Z}+a_0\hat{T}_{2,0}(L,S)$$

meaning that the troublesome terms vanish from the Hamiltonian and the time-domain simulation can be carried out with a fairly leisurely sub-millisecond time step with the additional benefit of not having the double-quantum and mixed terms ($\hat{L}_+\hat{S}_+$, $\hat{L}_\mathrm{Z}\hat{S}_+$ etc) around.

Weak coupling limit

The secular Hamiltonian derived in the previous section still contains quite a few terms:

$$\hat{H}_1^{\mathrm{D}} = \omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}} + a_0 \sqrt{\frac{2}{3}} \left(\hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} - \frac{1}{4} \left(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ \right) \right)$$

we could get greedy and observe that in heteronuclear spin systems the difference in Zeeman frequencies ω_1 and ω_2 is still very large. We could apply a second interaction representation transformation (or amend the original one), with respect to the rest of the Zeeman Hamiltonian:

$$\begin{aligned}
\hat{H} &= \left[\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}} \right] + a_0 \sqrt{\frac{2}{3}} \left(\hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} - \frac{1}{4} \left(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ \right) \right) \\
\hat{H}_0 &= \omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}} \\
\hat{H}_1 &= a_0 \sqrt{\frac{2}{3}} \left(\hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} - \frac{1}{4} \left(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ \right) \right)
\end{aligned}$$

It is easy to demonstrate (exercise) that

$$\begin{gathered}
[\hat{L}_{\mathrm{Z}}, \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}}] = [\hat{S}_{\mathrm{Z}}, \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}}] = 0 \\
[\hat{L}_{\mathrm{Z}}, \hat{L}_+ \hat{S}_-] = -[\hat{S}_{\mathrm{Z}}, \hat{L}_+ \hat{S}_-] = \hat{L}_+ \hat{S}_- \\
[\hat{L}_{\mathrm{Z}}, \hat{L}_- \hat{S}_+] = -[\hat{S}_{\mathrm{Z}}, \hat{L}_- \hat{S}_+] = -\hat{L}_- \hat{S}_+
\end{gathered}$$

$$\begin{aligned}
e^{i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} e^{-i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} &= \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} \\
e^{i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} \hat{L}_+ \hat{S}_- e^{-i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} &= e^{-i(\omega_1 - \omega_2)t} \hat{L}_+ \hat{S}_- \\
e^{i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} \hat{L}_- \hat{S}_+ e^{-i\left(\omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}\right)t} &= e^{i(\omega_1 - \omega_2)t} \hat{L}_- \hat{S}_+
\end{aligned}$$

and so the second interaction representation transformation yields:

$$\hat{H}_1^{\mathrm{D}} = a_0 \sqrt{\frac{2}{3}} \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}} - a_0 \sqrt{\frac{1}{6}} \left(e^{-i(\omega_1 - \omega_2)t} \hat{L}_+ \hat{S}_- + e^{i(\omega_1 - \omega_2)t} \hat{L}_- \hat{S}_+ \right)$$

In the cases where the frequency difference $\omega_1 - \omega_2$ is large (that is, in high-field heteronuclear systems), it is permissible to ignore the rapidly oscillating second term, yielding a particularly simple *weak coupling* form for the interaction:

$$\hat{H}_1^{\mathrm{D}} = a_0 \sqrt{\frac{2}{3}} \hat{L}_{\mathrm{Z}} \hat{S}_{\mathrm{Z}}$$

Summary

System	Low-field	High-field homonuclear	High-field heteronuclear
Approximation available	*none*	*secular coupling*	*weak coupling*

Lecture 18: perturbative relaxation theories

Time-dependent perturbation theory

Consider the Schrödinger equation with a very complicated time-dependent Hamiltonian

$$\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{H}(t)\left|\psi(t)\right\rangle,$$

for which, however, we only require a short-time (strictly speaking, $t \ll \left\|\hat{H}\right\|^{-1}$ condition guarantees convergence) solution. We could reasonably say that, to a first approximation, the wavefunction barely changes within that interval, so our initial condition $\left|\psi(0)\right\rangle$ would yield a decent approximation to the wavefunction on the right hand side:

$$\left|\psi_0(t)\right\rangle = \left|\psi(0)\right\rangle \qquad \frac{\partial}{\partial t}\left|\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{H}(t)\left|\psi(0)\right\rangle.$$

We could integrate this equation to obtain a (hopefully) slightly better approximation to the wavefunction, because time dependence of the Hamiltonian is now explicitly factored in:

$$\left|\psi_1(t)\right\rangle = \left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t \hat{H}(t')\left|\psi(0)\right\rangle dt'.$$

We could plug this (hopefully) better wavefunction back into the original Schrödinger equation obtain an even better approximation:

$$\frac{\partial}{\partial t}\left|\psi_2(t)\right\rangle = -\frac{i}{\hbar}\hat{H}(t)\left|\psi(0)\right\rangle + \left(\frac{i}{\hbar}\right)^2 \hat{H}(t)\int_0^t \hat{H}(t')\left|\psi(0)\right\rangle dt',$$

$$\left|\psi_2(t)\right\rangle = \left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t \hat{H}(t')\left|\psi(0)\right\rangle dt' + \left(\frac{i}{\hbar}\right)^2 \int_0^t \hat{H}(t')\int_0^{t'} \hat{H}(t'')\left|\psi(0)\right\rangle dt'' dt'.$$

If we keep taking this procedure forward, we get the following iteration rule for the increasingly more accurate approximations to the solution:

$$\left|\psi_{k+1}(t)\right\rangle = \left|\psi_k(t)\right\rangle - \frac{i}{\hbar}\int_0^t \hat{H}(t')\left|\psi_k(t')\right\rangle dt'.$$

This procedure is known as *time-dependent perturbation theory (TDPT)*. It is not specific to quantum mechanics and can be used with many linear and non-linear PDEs provided that they can be integrated with respect to time in a straightforward way. Interaction representation with respect to strong static interactions is very advantageous, because it significantly lowers the norm of the Hamiltonian and therefore improves the convergence of the iterative procedure.

Bloch-Redfield-Wangsness (BRW) relaxation theory

Also known as *Redfield theory*, this is perhaps the most successful perturbative spin relaxation theory, widely used (and at times abused, because it can apparently tolerate limited excursions outside of its formal validity range) in all areas of Spin Dynamics. We start with the Liouville - von Neumann equation for the state vector in Liouville space:

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -i\left(\hat{\hat{L}}_0 + \hat{\hat{L}}_1(t)\right)\hat{\rho}(t), \qquad \hat{\hat{L}} = \mathrm{ad}\hat{H} = [\hat{H},\cdot]$$

where the time-dependent "noisy" term $\hat{\hat{L}}_1(t)$ (containing interaction anisotropies modulated by random molecular motion and rotation) is assumed to have a zero ensemble average and a small norm:

$$\overline{\hat{\hat{L}}_1(t)} = 0 \qquad \left\|\hat{\hat{L}}_1(t)\right\| \ll \left\|\hat{\hat{L}}_0\right\|$$

We will now move into the interaction representation with respect to the static part of the Liouvillian $\hat{\hat{L}}_0$ and perform a second-order TDPT treatment. The interaction representation transformation amounts to

$$\hat{\sigma}(t) = e^{i\hat{\hat{L}}_0 t}\hat{\rho}(t) \qquad \hat{\hat{L}}_1^{\mathrm{D}}(t) = e^{i\hat{\hat{L}}_0 t}\hat{\hat{L}}_1(t)e^{-i\hat{\hat{L}}_0 t}$$

after which the original LvN equation becomes:

$$\frac{\partial\hat{\sigma}(t)}{\partial t} = -i\hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\sigma}(t)$$

Formal integration and re-substitution yields a differential equation that looks similar to the second-order TDPT approximation:

$$\frac{\partial\hat{\sigma}(t)}{\partial t} = -i\hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\sigma}(0) - \int_0^t \hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\hat{L}}_1^{\mathrm{D}}(\tau)\hat{\sigma}(\tau)\,d\tau,$$

but a careful examination would reveal that this equation is still formally exact, because we have not plugged the initial condition into the integral, but rather the exact (and yet unknown) interaction representation state vector.

At this point the approximations start. If we perform the ensemble averaging on the previous equation, the first term on the right hand side would vanish because

$$\overline{\hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\sigma}(0)} = e^{i\hat{\hat{L}}_0 t}\,\overline{\hat{\hat{L}}_1(t)}\,e^{-i\hat{\hat{L}}_0 t}\hat{\sigma}(0) = 0$$

and we are left with

$$\frac{\partial\overline{\hat{\sigma}(t)}}{\partial t} = -\int_0^t \overline{\hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\hat{L}}_1^{\mathrm{D}}(\tau)\hat{\sigma}(\tau)}\,d\tau$$

We can now use the rotational factorization derived in the previous lectures and take advantage of the fact that it completely hides the details of the interactions within the spin system, leaving only the overall molecular rotation explicit:

$$\hat{\hat{L}}_1(t) = \sum_{km} \mathfrak{D}^{(2)}_{km}(t)\,\hat{\hat{Q}}_{km} = \sum_{km} \mathfrak{D}^{(2)*}_{km}(t)\,\hat{\hat{Q}}^{\dagger}_{km}$$

$$\frac{\partial \overline{\hat{\sigma}(t)}}{\partial t} = -\sum_{kmpq} \int_0^t \overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(\tau)\,\hat{\hat{Q}}^{\mathrm{D}}_{km}\hat{\hat{Q}}^{\mathrm{D}\dagger}_{pq}\sigma(\tau)}\,d\tau$$

(to facilitate subsequent treatment, one copy of the Hermitian $\hat{\hat{L}}^{\mathrm{D}}_1$ superoperator has been pasted in a conjugated form).

We need to introduce further assumptions at this point. Firstly, we shall assume that, because the perturbation Liouvillian is weak, the spin system dynamics is uncorrelated with the noise present in $\hat{\hat{L}}_1(t)$. This would allow us to take ensemble averages separately for the Liouvillian and the state vector:

$$\overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(\tau)\,\hat{\hat{Q}}^{\mathrm{D}}_{km}\hat{\hat{Q}}^{\mathrm{D}\dagger}_{pq}\sigma(\tau)} = \overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(\tau)}\,\hat{\hat{Q}}^{\mathrm{D}}_{km}\hat{\hat{Q}}^{\mathrm{D}\dagger}_{pq}\,\overline{\sigma(\tau)}$$

(the rotational basis operators $\hat{\hat{Q}}_{km}$ are static and do not change upon averaging). It is convenient to introduce a separate symbol for the rotational correlation functions (which, in the general anisotropic tumbling case can be different for different values of the *k,m,p,q* indices):

$$G_{kmpq}(t,\tau) = \overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(t+\tau)}$$

The second significant assumption is that the noise in the system is stationary, and therefore the correlation functions only depend on the time separation τ between the functions to be correlated, and not the absolute time t, therefore:

$$G_{kmpq}(\tau) = \overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(t+\tau)} = \overline{\mathfrak{D}^{(2)}_{km}(0)\,\mathfrak{D}^{(2)*}_{pq}(\tau)}$$

The third assumption (and this is where the perturbation theory is finally applied) is that these functions decay so fast on the time scale of the overall spin system evolution, that the latter barely happens and it is permissible to take the state vector out of the integral:

$$\frac{\partial \overline{\hat{\sigma}(t)}}{\partial t} = -\sum_{kmpq} \int_0^t G_{kmpq}(\tau)\,\hat{\hat{Q}}^{\mathrm{D}}_{km}\hat{\hat{Q}}^{\mathrm{D}\dagger}_{pq}\,d\tau\,\overline{\hat{\sigma}(t)}$$

Because the implicit update schemes are known to be more stable, we take $\hat{\sigma}(t)$ out of the integral, rather than $\hat{\sigma}(0)$ – this may be the reason why Redfield theory also works where it is not supposed to, but nobody knows for sure. We shall also drop the bars on the state vector for convenience. Another consequence of the fast correlation function decay assumption is that the upper limit of the integral may be extended to infinity:

$$\frac{\partial \hat{\sigma}(t)}{\partial t} = -\sum_{kmpq} \int_0^\infty \overline{\mathfrak{D}^{(2)}_{km}(t)\,\mathfrak{D}^{(2)*}_{pq}(\tau)}\,\hat{\hat{Q}}^{\mathrm{D}}_{km}\hat{\hat{Q}}^{\mathrm{D}\dagger}_{pq}\,d\tau\,\hat{\sigma}(t)$$

After returning to the Schrödinger representation, we get:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i\hat{\hat{L}}_0\hat{\rho}(t) - \sum_{kmpq} \int_0^\infty G_{kmpq}(\tau)\,\hat{\hat{Q}}_{km}\,e^{i\hat{\hat{L}}_0\tau}\,\hat{\hat{Q}}^{\dagger}_{pq}\,e^{-i\hat{\hat{L}}_0\tau}\,d\tau\,\hat{\rho}(t),$$

which now has the familiar two-term form:

$$\frac{\partial\hat{\rho}(t)}{\partial t}=-i\hat{\hat{L}}_0\hat{\rho}(t)+\hat{\hat{R}}\hat{\rho}(t)$$

and in which the *relaxation superoperator* governing the evolution under the stochastic processes taking place in the system has the following form:

$$\hat{\hat{R}}=-\sum_{kmpq}\int_0^\infty G_{kmpq}(\tau)\hat{\hat{Q}}_{km}e^{i\hat{\hat{L}}_0\tau}\hat{\hat{Q}}_{pq}^\dagger e^{-i\hat{\hat{L}}_0\tau}d\tau$$

The derivation above can be repeated in Hilbert space (exercise) to yield:

$$\frac{\partial\hat{\rho}(t)}{\partial t}=-\mathrm{i}[\hat{H}_0,\hat{\rho}(t)]-\sum_{kmpq}\int_0^\infty G_{kmpq}(\tau)[\hat{Q}_{km},[e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{pq}^\dagger e^{-\mathrm{i}\hat{H}_0\tau},\hat{\rho}(t)]]d\tau$$

$$\frac{\partial\hat{\rho}(t)}{\partial t}=-\mathrm{i}[\hat{H}_0,\hat{\rho}(t)]+\hat{\hat{R}}\hat{\rho}(t)$$

$$\hat{\hat{R}}=-\sum_{kmpq}\int_0^\infty G_{kmpq}(\tau)[\hat{Q}_{km},[e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{pq}^\dagger e^{-\mathrm{i}\hat{H}_0\tau},\cdot]]d\tau$$

The brave souls are advised to prove (as an exercise) that the two expressions for the relaxation superoperator are, in fact, equal.

Lecture 19: perturbative relaxation theories

Rotational factorization of real-life Hamiltonians

The primary source of stochastic interaction modulation that is responsible for spin relaxation in magnetic resonance systems is molecular rotation. We have seen in the SO(3) group lecture that irreducible spherical tensor operators of a given rank only transform amongst themselves under any rotation:

$$\hat{\hat{R}}(\alpha,\beta,\gamma)\hat{T}_m^{(l)}=\sum_{m'=-l}^{l}\hat{T}_{m'}^{(l)}\mathfrak{D}_{m',m}^{(l)}(\alpha,\beta,\gamma)$$

All major interactions in magnetic resonance are described by linear combinations of second-rank ISTs and therefore it is reasonable to expect (and we had already used this in the previous lecture) that the general transformation rule for the Hamiltonian under overall molecular rotation is

$$\hat{\hat{R}}(\alpha,\beta,\gamma)\hat{H}=\hat{H}_{\text{iso}}+\sum_{m=-2}^{2}\sum_{k=-2}^{2}\mathfrak{D}_{km}^{(2)}(\alpha,\beta,\gamma)\hat{Q}_{km}$$

where $\hat{Q}_{km}$ (called *rotational basis operators*) are linear combinations of irreducible spherical tensors corresponding to the interactions within the spin system. We will now derive the expressions for them in the case where the spin system has multiple spin interactions that have arbitrary orientations in the molecular frame. The advantage that they offer is that no matter how large and complicated the spin system may be, there are always just 25 rotational basis operators, and overall molecular rotations are always described by the simple equation above.

For the traceless part of a bilinear interaction between spins L and S:

$$\hat{T}_0^{(2)}(L,S)=+\sqrt{\frac{2}{3}}\left(\hat{L}_Z\hat{S}_Z-\frac{1}{4}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)\right)$$

$$\hat{T}_{-1}^{(2)}(L,S)=+\frac{1}{2}\left(\hat{L}_Z\hat{S}_-+\hat{L}_-\hat{S}_Z\right),\qquad \hat{T}_1^{(2)}(L,S)=-\frac{1}{2}\left(\hat{L}_Z\hat{S}_++\hat{L}_+\hat{S}_Z\right)$$

$$\hat{T}_{-2}^{(2)}(L,S)=+\frac{1}{2}\hat{L}_-\hat{S}_-,\qquad \hat{T}_2^{(2)}(L,S)=+\frac{1}{2}\hat{L}_+\hat{S}_+$$

($\hat{\vec{L}}$ to be replaced with $\vec{B}$ in the case of Zeeman interaction and with $\hat{\vec{S}}$ in the case of quadratic interactions, such as quadrupolar or ZFS). These have been derived when we were dealing with the SO(3) group. It is easy to prove (exercise) that for a traceless interaction tensor $\mathbf{A}$ with eigenvalues $\{a_{\text{XX}},a_{\text{YY}},a_{\text{ZZ}}\}$, written in its eigenframe:

$$\hat{\vec{L}}\cdot\mathbf{A}\cdot\hat{\vec{S}}=a_{\text{XX}}\hat{L}_{\text{X}}\hat{S}_{\text{X}}+a_{\text{YY}}\hat{L}_{\text{Y}}\hat{S}_{\text{Y}}+a_{\text{ZZ}}\hat{L}_{\text{Z}}\hat{S}_{\text{Z}}=$$
$$\frac{2a_{\text{ZZ}}-(a_{\text{XX}}+a_{\text{YY}})}{\sqrt{6}}\hat{T}_0^{(2)}(L,S)+\frac{a_{\text{XX}}-a_{\text{YY}}}{2}\hat{T}_{-2}^{(2)}(L,S)+\frac{a_{\text{XX}}-a_{\text{YY}}}{2}\hat{T}_2^{(2)}(L,S)$$

Irreducible spherical tensors form the basis of irreducible representations of the rotation group and therefore have very regular rotation properties:

$$\hat{\hat{R}}(\alpha,\beta,\gamma)\hat{T}_k^{(l)} = \sum_{m=-l}^{l} \hat{T}_m^{(l)} \mathfrak{D}_{mk}^{(l)}(\alpha,\beta,\gamma),$$

where $\hat{\hat{R}}$ denotes a rotation (which for our purposes is a superoperator) and $\mathfrak{D}_{m,k}^{(l)}$ are Wigner functions, accepting any rotation specification (Euler angles, quaternions *etc*) as an argument. For a multi-spin system in a rigid molecule, with the stochastic molecular rotation $\hat{\hat{R}}_{\mathrm{mol}}(t)$ applied on top of static internal rotation $\hat{\hat{R}}_{\mathrm{int}}$ for each interaction, we therefore have:

$$\hat{H} = \hat{H}_{\mathrm{iso}} + \hat{\hat{R}}_{\mathrm{mol}} \begin{pmatrix} \sum_{L} \hat{\hat{R}}_{\mathrm{int}}^{L} \left[\frac{Rh_L}{2}\left(\hat{T}_2^{(2)}(B,L) + \hat{T}_{-2}^{(2)}(B,L)\right) + \frac{Ax_L}{\sqrt{6}} \hat{T}_0^{(2)}(B,L) \right] + \\ \sum_{L,S} \hat{\hat{R}}_{\mathrm{int}}^{LS} \left[\frac{Rh_{LS}}{2}\left(\hat{T}_2^{(2)}(L,S) + \hat{T}_{-2}^{(2)}(L,S)\right) + \frac{Ax_{LS}}{\sqrt{6}} \hat{T}_0^{(2)}(L,S) \right] + \\ \sum_{S} \hat{\hat{R}}_{\mathrm{int}}^{SS} \left[\frac{Rh_{SS}}{2}\left(\hat{T}_2^{(2)}(S,S) + \hat{T}_{-2}^{(2)}(S,S)\right) + \frac{Ax_{SS}}{\sqrt{6}} \hat{T}_0^{(2)}(S,S) \right] \end{pmatrix},$$

where $\hat{H}_{\mathrm{iso}}$ is the isotropic part of the Hamiltonian, axiality and rhombicity parameters for each interaction tensor are defined as:

$$Ax = 2a_{\mathrm{ZZ}} - \left(a_{\mathrm{XX}} + a_{\mathrm{YY}}\right) \qquad Rh = a_{\mathrm{XX}} - a_{\mathrm{YY}},$$

and the three terms in brackets correspond to linear, bilinear and quadratic couplings within the spin system. After we apply the internal rotations, we get:

$$\hat{H} = \hat{H}_{\mathrm{iso}} + \hat{\hat{R}}_{\mathrm{mol}} \sum_{L} \sum_{m=-2}^{2} \hat{T}_m^{(2)}(B,L)\Phi_m(L) + \hat{\hat{R}}_{\mathrm{mol}} \sum_{LS} \sum_{m=-2}^{2} \hat{T}_m^{(2)}(L,S)\Phi_m(L,S) + \hat{\hat{R}}_{\mathrm{mol}} \sum_{S} \sum_{m=-2}^{2} \hat{T}_m^{(2)}(S,S)\Phi_m(S)$$

where the interaction amplitudes and orientations in the molecular frame have been collected into static internal orientation functions:

$$\Phi_m(L) = \frac{Rh_L}{2}\left(\mathfrak{D}_{m,-2}^{(2)}(L) + \mathfrak{D}_{m,2}^{(2)}(L)\right) + \frac{Ax_L}{\sqrt{6}} \mathfrak{D}_{m,0}^{(2)}(L)$$
$$\Phi_m(L,S) = \frac{Rh_{LS}}{2}\left(\mathfrak{D}_{m,-2}^{(2)}(L,S) + \mathfrak{D}_{m,2}^{(2)}(L,S)\right) + \frac{Ax_{LS}}{\sqrt{6}} \mathfrak{D}_{m,0}^{(2)}(L,S)$$
$$\Phi_m(S) = \frac{Rh_{SS}}{2}\left(\mathfrak{D}_{m,-2}^{(2)}(S) + \mathfrak{D}_{m,2}^{(2)}(S)\right) + \frac{Ax_{SS}}{\sqrt{6}} \mathfrak{D}_{m,0}^{(2)}(S)$$

Finally, after we apply the overall molecular rotation, we obtain

$$\hat{H} = \hat{H}_{\mathrm{iso}} + \sum_{m=-2}^{2} \sum_{k=-2}^{2} \mathfrak{D}_{km}^{(2)} \hat{Q}_{km}$$

where all information about the amplitudes and internal orientations of all interactions has been packaged into 25 operators:

$$\hat{Q}_{km} = \sum_{L} \Phi_m(L)\hat{T}_k^{(2)}(B,L) + \sum_{LS} \Phi_m(L,S)\hat{T}_k^{(2)}(L,S) + \sum_{S} \Phi_m(S)\hat{T}_k^{(2)}(S,S)$$

Correlation functions – isotropic rotational diffusion

The other part of the relaxation theory treatment that we have so far left unevaluated is the correlation function, defined (under the stationary noise assumption) as

$$G_{kmpq}(\tau)=\overline{\mathfrak{D}_{km}^{(2)}(t)\mathfrak{D}_{pq}^{(2)*}(t+\tau)}=\overline{\mathfrak{D}_{km}^{(2)}(0)\mathfrak{D}_{pq}^{(2)*}(\tau)}$$

The ensemble average can be recast in terms of probabilities of encountering systems in a particular orientation within the ensemble:

$$G_{kmpq}(\tau)=\overline{\mathfrak{D}_{km}^{(2)}(0)\mathfrak{D}_{pq}^{(2)*}(\tau)}=\iint \mathfrak{D}_{km}^{(2)}(\Omega_0)\mathfrak{D}_{pq}^{(2)*}(\Omega)P(\Omega_0)P(\Omega,\tau\,|\,\Omega_0,0)\,d\Omega_0 d\Omega$$

where $P(\Omega_0)$ is the probability density of the initial orientations and $P(\Omega,\tau\,|\,\Omega_0,0)$ is the probability density of a molecule having an orientation Ω at time τ, having had an orientation Ω_0 at time zero.

We will assume in this section that the molecules in our sample are approximately spherical particles undergoing isotropic rotational diffusion. That means that the initial probability distribution $P(\Omega_0)$ is isotropic, meaning that $P(\Omega_0)=1/4\pi$, and so the integral simplifies to:

$$G_{kmpq}(\tau)=\frac{1}{4\pi}\iint \mathfrak{D}_{km}^{(2)}(\Omega_0)\mathfrak{D}_{pq}^{(2)*}(\Omega)P(\Omega,\tau\,|\,\Omega_0,0)\,d\Omega_0 d\Omega$$

The probability density $P(\Omega,\tau\,|\,\Omega_0,0)$, known to chemists as fractional concentration, conforms to the isotropic diffusion equation:

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-D\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)P(\Omega,t\,|\,\Omega_0,0)$$

where D is the diffusion constant. In spherical coordinates (which are more appropriate for our case), this transforms into:

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-D\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2}\right)P(\Omega,t\,|\,\Omega_0,0)$$

and if the diffusion takes place on the surface of a unit sphere, the radial part vanishes:

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-D\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)P(\Omega,t\,|\,\Omega_0,0)$$

The operator in brackets is $\hat{L}^2$ – the Casimir operator of SO(3). We have seen a few lectures ago that the eigenfunctions of $\hat{L}^2$ are spherical harmonics, and therefore the general solution for the equation above has the form:

$$P(\Omega,t\,|\,\Omega_0,0)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}A_{lm}(t\,|\,\Omega_0,0)Y_{lm}(\Omega)$$

If we substitute this solution back into the diffusion equation, we get the expression for the time-dependent coefficients $A_{lm}(t\,|\,\Omega_0,0)$:

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{\partial}{\partial t}A_{lm}\left(t\,|\,\Omega_0,0\right)Y_{lm}\left(\Omega\right)=-D\sum_{l=0}^{\infty}\sum_{m=-l}^{l}l\left(l+1\right)A_{lm}\left(t\,|\,\Omega_0,0\right)Y_{lm}\left(\Omega\right)$$

$$\frac{\partial}{\partial t}A_{lm}\left(t\,|\,\Omega_0,0\right)=-Dl\left(l+1\right)A_{lm}\left(t\,|\,\Omega_0,0\right)$$

$$A_{lm}\left(t\,|\,\Omega_0,0\right)=e^{-Dl(l+1)t}A_{lm}\left(0\right)$$

The general solution therefore acquires the form:

$$P\left(\Omega,t\,|\,\Omega_0,0\right)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}C_{lm}Y_{lm}\left(\Omega\right)e^{-Dl(l+1)t}$$

where C_{lm} are the coefficients determined by the initial condition. The initial condition is known (all systems pointing at Ω_0 at time zero, and therefore

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}C_{lm}Y_{lm}\left(\Omega\right)=\delta\left(\Omega-\Omega_0\right)\qquad\Rightarrow\qquad C_{lm}=Y_{lm}^{*}\left(\Omega_0\right)$$

meaning that

$$P\left(\Omega,t\,|\,\Omega_0,0\right)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}Y_{lm}^{*}\left(\Omega_0\right)Y_{lm}\left(\Omega\right)e^{-Dl(l+1)t}$$

We can now return to the definition of the correlation function and compute the integral:

$$\begin{aligned}
&G_{abcd}\left(\tau\right)=\frac{1}{4\pi}\iint\mathfrak{D}_{ab}^{(2)}\left(\Omega_0\right)\mathfrak{D}_{cd}^{(2)*}\left(\Omega\right)P\left(\Omega,\tau\,|\,\Omega_0,0\right)d\Omega_0 d\Omega=\\
&\frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}e^{-Dl(l+1)\tau}\iint\mathfrak{D}_{ab}^{(2)}\left(\Omega_0\right)\mathfrak{D}_{cd}^{(2)*}\left(\Omega\right)Y_{lm}^{*}\left(\Omega_0\right)Y_{lm}\left(\Omega\right)d\Omega_0 d\Omega=\\
&\frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}e^{-Dl(l+1)\tau}\left(\int\mathfrak{D}_{ab}^{(2)}\left(\Omega_0\right)Y_{lm}^{*}\left(\Omega_0\right)d\Omega_0\right)\left(\int\mathfrak{D}_{cd}^{(2)*}\left(\Omega\right)Y_{lm}\left(\Omega\right)d\Omega\right)=\\
&\frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}e^{-Dl(l+1)\tau}\left(\int\mathfrak{D}_{ab}^{(2)}\left(\Omega_0\right)\mathfrak{D}_{0m}^{(l)*}\left(\Omega_0\right)d\Omega_0\right)\left(\int\mathfrak{D}_{cd}^{(2)*}\left(\Omega\right)\mathfrak{D}_{0m}^{(l)}\left(\Omega\right)d\Omega\right)=\\
&\frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\delta_{l,2}\delta_{a,0}\delta_{b,m}\delta_{d,m}e^{-Dl(l+1)\tau}=\frac{1}{4\pi}\delta_{a,0}\delta_{c,0}\delta_{b,d}e^{-6D\tau}
\end{aligned}$$

And the final expression for the correlation function in the case of the isotropic rotational diffusion is:

$$G_{kmpq}\left(\tau\right)=\frac{1}{4\pi}\delta_{k0}\delta_{p0}\delta_{mq}e^{-\tau/\tau_{\mathrm{C}}}\qquad\tau_{\mathrm{C}}=\frac{1}{6D}=\frac{4\pi\eta r^3}{3kT}$$

The equation for the *correlation time* τ_{C} (the characteristic decay time of the correlation function) is known as the *Stokes-Einstein equation*.

Lecture 20: perturbative relaxation theories

Correlation functions – anisotropic rotational diffusion

The rotational diffusion of a spherical molecule could be described by a single scalar – the diffusion constant (see the previous lecture):

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-D\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)P(\Omega,t\,|\,\Omega_0,0)$$

For a non-spherical particle the diffusion constant becomes a positive-definite tensor:

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-\begin{pmatrix}\frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\end{pmatrix}^{\mathrm{T}}\mathbf{D}\begin{pmatrix}\frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\end{pmatrix}P(\Omega,t\,|\,\Omega_0,0)=$$

$$\frac{\partial}{\partial t}P(\Omega,t\,|\,\Omega_0,0)=-\sum_{\substack{i,j=\\x,y,z}}D_{ij}\frac{\partial^2}{\partial r_i\partial r_j}P(\Omega,t\,|\,\Omega_0,0)$$

While slightly more complicated, this equation is still separable:

$$P(\Omega,t)=P_{\mathrm{r}}(\Omega)P_{\mathrm{t}}(t)\qquad\Rightarrow\qquad\begin{cases}\left[\sum_{\substack{i,j=\\x,y,z}}D_{ij}\frac{\partial^2}{\partial r_i\partial r_j}\right]P_{\mathrm{r}}(\Omega)=\lambda P_{\mathrm{r}}(\Omega)\\ \frac{\partial}{\partial t}P_{\mathrm{t}}(t)=-\lambda P_{\mathrm{t}}(t)\end{cases}$$

where λ are the eigenvalues of the differential operator in square brackets. The general solutions to the two equations have the form:

$$P_{\mathrm{r}}(\Omega)=\sum_k C_k\Psi_k(\Omega)\qquad P_{\mathrm{t}}^{(k)}(t)=P_{\mathrm{t}}^{(k)}(0)e^{-\lambda_k t}$$

$$\left[\sum_{\substack{i,j=\\x,y,z}}D_{ij}\frac{\partial^2}{\partial r_i\partial r_j}\right]\Psi_k(\Omega)=\lambda_k\Psi_k(\Omega)$$

and therefore the general solution is:

$$P(\Omega,t)=\sum_k C_k\Psi_k(\Omega)e^{-\lambda_k t}$$

The expressions for the eigenfunctions $\Psi_k(\Omega)$ are, in general, unknown. The only thing that we know about them is that they form a complete orthonormal set of functions of Euler angles Ω. Taking into account the initial condition, we get:

$$\left(\sum_k C_k\Psi_k(\Omega)e^{-\lambda_k t}\right)_{t=0}=\delta(\Omega-\Omega_0)\qquad\Rightarrow\qquad C_k=\Psi_k^*(\Omega_0)$$

$$P(\Omega,t\,|\,\Omega_0,0)=\sum_k\Psi_k^*(\Omega_0)\Psi_k(\Omega)e^{-\lambda_k t}$$

After plugging this back into the expression for the ensemble correlation function (see the previous lecture), we get:

$$G_{kmpq}\left(\tau\right)=\frac{1}{8\pi^2}\sum_n e^{-\lambda_n t}\iint \mathfrak{D}^{(2)}_{km}\left(\Omega_0\right)\mathfrak{D}^{(2)*}_{pq}\left(\Omega\right)\Psi^*_n\left(\Omega_0\right)\Psi_n\left(\Omega\right)d\Omega_0 d\Omega=$$

$$\frac{1}{8\pi^2}\sum_n e^{-\lambda_n\tau}\left[\int \mathfrak{D}^{(2)*}_{km}\left(\Omega_0\right)\Psi_n\left(\Omega_0\right)d\Omega_0\right]^*\left[\int \mathfrak{D}^{(2)*}_{pq}\left(\Omega\right)\Psi_n\left(\Omega\right)d\Omega\right]$$

While the closed-form expressions for $\Psi_n\left(\Omega\right)$ functions do not exist, their integrals with Wigner functions yield simple analytical expressions in terms of the elements of the $\mathbf{D}$ matrix:

$$G_{kmpq}\left(\tau\right)=\frac{\delta_{kp}}{5}\sum_{n=-2}^{2}a^*_{nm}a_{np}e^{-\lambda_n\tau}$$

n	-2	-1	0	1	2
λ_n	$6D_{\text{iso}}-2\Delta$	$3D_{\text{Y}}+3D_{\text{iso}}$	$3D_{\text{Z}}+3D_{\text{iso}}$	$3D_{\text{X}}+3D_{\text{iso}}$	$6D_{\text{iso}}+2\Delta$

$$a_{nm}=\begin{array}{c|ccccc} & 2 & 1 & 0 & -1 & -2 \\ \hline 2 & \frac{u}{N\sqrt{2}} & 0 & \frac{w}{N} & 0 & \frac{u}{N\sqrt{2}} \\ 1 & 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} \\ -1 & 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 \\ -2 & -\frac{u}{N\sqrt{2}} & 0 & \frac{w}{N} & 0 & -\frac{u}{N\sqrt{2}} \end{array}$$

$$\Delta=\sqrt{\left(D_{\text{Z}}-D_{\text{X}}\right)\left(D_{\text{Z}}-D_{\text{Y}}\right)+\left(D_{\text{Y}}-D_{\text{X}}\right)^2}\qquad D_{\text{iso}}=\frac{1}{3}\left(D_{\text{X}}+D_{\text{Y}}+D_{\text{Z}}\right)$$

$$w=2D_{\text{Z}}-\left(D_{\text{X}}+D_{\text{Y}}\right)+2\Delta\qquad u=\sqrt{3}\left(D_{\text{X}}-D_{\text{Y}}\right)$$

$$N=2\sqrt{w\Delta}\qquad D_{\text{X}}<D_{\text{Y}}<D_{\text{Z}}$$

The original literature on the subject is full of errors – this partially explains the reluctance with which the anisotropic rotational diffusion expressions are used at present.

Spectral density functions

Let us look at a specific element of the relaxation superoperator in Hilbert space in a representation where the static Hamiltonian is diagonal (this is a significant assumption – it is not always feasible, for purely numerical reasons, to diagonalize a Hamiltonian):

$$\left\langle\hat{\rho}_a\middle|\hat{\hat{R}}_{ab}\middle|\hat{\rho}_b\right\rangle=\sum_{kmpq}\int_0^\infty G_{kmpq}\left(\tau\right)\mathrm{Tr}\left(\hat{\rho}_a^\dagger[\hat{Q}_{k,m},[e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}^\dagger_{p,q}e^{-\mathrm{i}\hat{H}_0\tau},\hat{\rho}_b]]\right)d\tau$$

Using the cyclic permutation rule, we can reorder the commutators under the trace:

$$\mathrm{Tr}\left(\hat{\rho}_a^\dagger[\hat{Q}_{k,m},[e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{p,q}^\dagger e^{-\mathrm{i}\hat{H}_0\tau},\hat{\rho}_b]]\right)=\mathrm{Tr}\left(e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{p,q}^\dagger e^{-\mathrm{i}\hat{H}_0\tau}[\hat{\rho}_a,[\hat{\rho}_b^\dagger,\hat{Q}_{k,m}]]\right)=$$

$$\mathrm{Tr}\left(e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{p,q}^\dagger e^{-\mathrm{i}\hat{H}_0\tau}\hat{P}_{k,m}^{(a,b)}\right),\qquad \hat{P}_{k,m}^{(a,b)}=[\hat{\rho}_a,[\hat{\rho}_b^\dagger,\hat{Q}_{k,m}]]$$

The trace of a product of four matrices can be computed explicitly in the indexed notation:

$$\mathrm{Tr}\left(e^{\mathrm{i}\hat{H}_0\tau}\hat{Q}_{p,q}^\dagger e^{-\mathrm{i}\hat{H}_0\tau}\hat{P}_{k,m}^{(a,b)}\right)=\sum_{irsj}\left[e^{\mathrm{i}\hat{H}_0\tau}\right]_{ir}\left[\hat{Q}_{p,q}^\dagger\right]_{rs}\left[e^{-\mathrm{i}\hat{H}_0\tau}\right]_{sj}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}=$$

$$=\sum_{ij}e^{\mathrm{i}\omega_i\tau}\left[\hat{Q}_{p,q}^\dagger\right]_{ij}e^{-\mathrm{i}\omega_j\tau}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}=\sum_{ij}e^{\mathrm{i}\left(\omega_i-\omega_j\right)\tau}\left[\hat{Q}_{p,q}^\dagger\right]_{ij}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}=\sum_{ij}e^{\mathrm{i}\omega_{ij}\tau}\left[\hat{Q}_{p,q}^\dagger\right]_{ij}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}$$

and the integral becomes a collection of Fourier transforms:

$$\left\langle\hat{\rho}_a\middle|\hat{\hat{R}}_{ab}\middle|\hat{\rho}_b\right\rangle=-\sum_{ijkmpq}\left[\hat{Q}_{p,q}^\dagger\right]_{ij}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}\int_0^\infty G_{kmpq}\left(\tau\right)e^{\mathrm{i}\omega_{ij}\tau}d\tau=-\sum_{ijkmpq}\left[\hat{Q}_{p,q}^\dagger\right]_{ij}\left[\hat{P}_{k,m}^{(a,b)}\right]_{ji}J_{kmpq}\left(\omega_{ij}\right)$$

$$J_{kmpq}\left(\omega_{ij}\right)=\int_0^\infty G_{kmpq}\left(\tau\right)e^{\mathrm{i}\omega_{ij}\tau}d\tau$$

The Fourier transform of the correlation function is called the *spectral density function*. It has a physical meaning of energy density of the stochastic perturbation at a given frequency. In the isotropic tumbling approximation we have:

$$J\left(\omega\right)=\int_0^\infty e^{-\tau/\tau_\mathrm{C}}e^{\mathrm{i}\omega_{ij}\tau}d\tau=\frac{1}{1/\tau_\mathrm{C}+i\omega}=\frac{\tau_\mathrm{C}}{1+\omega^2\tau_\mathrm{C}^2}-\frac{i\omega\tau_\mathrm{C}^2}{1+\omega^2\tau_\mathrm{C}^2}$$

The real part of this function is a Lorentzian curve. It determines the relaxation rate (it would acquire a minus when it appears in the Liouville – von Neumann equation). The (usually much smaller) imaginary part contributes to the frequency part of the LvN equation and for that reason is known as *dynamic frequency shift*. The DFS is usually ignored in practical simulations.

Spectral densities in non-rigid molecules: the Lipari-Szabo model

Analytical simplicity is a rare virtue in relaxation theory, and it is probably the only virtue of the Lipari-Szabo restricted local motion model. We can observe that, in a spherical molecule where the overall rotational diffusion is independent from the restricted local diffusion of a particular group, the correlation function can be factored as

$$G\left(\tau\right)=G_\mathrm{global}\left(\tau\right)G_\mathrm{local}\left(\tau\right)$$

Lipari-Szabo approximation assumes that both functions are exponential and the resulting spectral density function therefore is:

$$J\left(\omega\right)=\frac{S^2\tau_\mathrm{C}}{1+\omega^2\tau_\mathrm{C}^2}+\frac{\left(1-S^2\right)\tau}{1+\omega^2\tau^2},\qquad \tau=\left(\frac{1}{\tau_\mathrm{C}}+\frac{1}{\tau_\mathrm{int}}\right)^{-1}$$

where S^2 is called *order parameter*. It can be interpreted as a fraction of the full body angle that is spanned by the restriction cone of the internal motion. This form for the spectral density function is widely used in protein NMR spectroscopy.

Lecture 21: generalized cumulant expansion

GCE method is a generalization and rectification of BRW theory – it explicitly considers terms of all orders in the perturbation expansion and avoids the convoluted handwaving (coarse-graining of time, fast correlation function decay, lack of correlation between the system and the bath, *etc*) that is inherent in BRW theory. The core argument of this method is that, to be correct, the ensemble averaging must be performed on the exponential propagator applied to the initial state of the system, rather than the differential equation of motion. As all perturbative theories, GCE leads to meaningfully convergent results only for $\left\|\hat{H}_1(t)\right\|\tau_{\mathrm{C}} < 1$, but it is the most accurate of those theories.

Definitions

The *n-th moment* m_n of a real-valued distribution function $f(x)$ around the centre x_0 is defined as

$$m_n = \left\langle (x-x_0)^n \right\rangle = \int_{-\infty}^{\infty} (x-x_0)^n f(x)\,dx$$

The centre is often chosen so as to have $m_1 = \langle x - x_0 \rangle = 0$. In the context of spin dynamics, the distribution function $f(x)$ corresponds to the frequency-domain spectrum.

The *moment-generating function* $M_X(t)$ of a random variable X is

$$M_X(t) = \left\langle e^{Xt} \right\rangle$$

$$M_X(t) = \left\langle \sum_{n=0}^{\infty} \frac{X^n t^n}{n!} \right\rangle = \sum_{n=0}^{\infty} \frac{\left\langle X^n \right\rangle t^n}{n!} = \sum_{n=0}^{\infty} \frac{m_n t^n}{n!}$$

it has its name because the moments of the variable X are its derivatives, specifically:

$$m_n = \left(\frac{\partial^n}{\partial t^n} M_X(t) \right)_{t=0}$$

The *cumulant-generating function* $K_X(t)$ of a random variable X is the logarithm of the moment-generating function

$$K_X(t) = \ln\left(\left\langle e^{Xt} \right\rangle \right), \qquad \left\langle e^{Xt} \right\rangle = e^{K_X(t)}$$

The Taylor terms in the expansion of $K_X(t)$, or, equivalently, its derivatives with respect to time

$$K_X(t) = \sum_{n=1}^{\infty} \frac{\kappa_n t^n}{n!}, \qquad \kappa_n = \left(\frac{\partial^n}{\partial t^n} K_X(t) \right)_{t=0}$$

are called the *cumulants* κ_n of X.

Cumulant expansion method

The *cumulant expansion theorem* states that for a stochastic variable $x(t)$, which is a function of a continuous parameter t, we have:

$$\left\langle \exp\left(\int_a^b x(t)\,dt\right)\right\rangle = \exp\left(\sum_{n=1}^{\infty}\int_a^b dt_1\int_a^{t_1} dt_2\ldots\int_a^{t_{n-1}} dt_n \left\langle x(t_1)x(t_2)\ldots x(t_n)\right\rangle_{\mathrm{C}}\right)$$

in which the cumulant average $\langle . \rangle_{\mathrm{C}}$ is defined as:

$$\begin{aligned}
&\langle x_1\rangle_{\mathrm{C}} = \langle x_1\rangle \\
&\langle x_1x_2\rangle_{\mathrm{C}} = \langle x_1x_2\rangle - \langle x_1\rangle\langle x_2\rangle \\
&\langle x_1x_2x_3\rangle_{\mathrm{C}} = \langle x_1x_2x_3\rangle - \langle x_1\rangle\langle x_2x_3\rangle - \langle x_2\rangle\langle x_3x_1\rangle - \langle x_3\rangle\langle x_1x_2\rangle + 2\langle x_1\rangle\langle x_2\rangle\langle x_3\rangle
\end{aligned}$$

(further terms are tabulated in the literature).

Proof: let us suppose that we have several random variables $\{X_1,\ldots X_N\}$. The joint moment and cumulant generating functions are going to be

$$M_X(t_1,\ldots t_N) = \left\langle \exp\left(\sum_{k=1}^{N} X_k t_k\right)\right\rangle = \left\langle \sum_{n=0}^{\infty}\frac{1}{n!}\left(\sum_{k=1}^{N} X_k t_k\right)^n\right\rangle =$$

$$= \sum_{r_1,\ldots r_N}\sum_{n=0}^{\infty}\left(\prod_{k=1}^{N}\frac{t_k^{r_k}}{r_k!}\right)\left\langle X_1^{r_1}\ldots X_N^{r_N}\right\rangle = \exp\left(\sum_{r_1,\ldots r_N}\sum_{n=0}^{\infty}\left(\prod_{k=1}^{N}\frac{t_k^{r_k}}{r_k!}\right)\left\langle X_1^{r_1}\ldots X_N^{r_N}\right\rangle_{\mathrm{C}}\right) = \exp\left(K_X(t_1,\ldots t_N)\right)$$

Equating the terms of the same order in t (exercise), we get the expressions for the cumulative averages in terms of plain averages. Taking the Riemann limit on the sum and moving to a stochastic variable $x(t)$ which is a function of a continuous parameter t, we get:

$$\left\langle \exp\left(\int_a^b x(t)\,dt\right)\right\rangle = \exp\left(\sum_{n=1}^{\infty}\frac{1}{n!}\int_a^b dt_1\int_a^b dt_2\ldots\int_a^b dt_n \left\langle x(t_1)x(t_2)\ldots x(t_n)\right\rangle_{\mathrm{C}}\right) =$$

$$= \exp\left(\sum_{n=1}^{\infty}\int_a^b dt_1\int_a^{t_1} dt_2\ldots\int_a^{t_{n-1}} dt_n \left\langle x(t_1)x(t_2)\ldots x(t_n)\right\rangle_{\mathrm{C}}\right)$$

this completes the proof.

To relate this theorem to perturbative relaxation theory, we note that we have seen in the TDPT section that the interaction representation of the Liouville – von Neumann equation

$$\frac{\partial\hat{\sigma}(t)}{\partial t} = -i\hat{\hat{L}}_1^{\mathrm{D}}(t)\hat{\sigma}(t)$$

may be formally integrated to yield

$$\hat{\sigma}(t) = \hat{\sigma}(0) + (-i)\int_0^t \hat{\hat{L}}_1^{\mathrm{D}}(t')\hat{\sigma}(t')\,dt'$$

in principle, this process may be continued indefinitely to eventually yield

$$\hat{\sigma}(t) = \hat{\sigma}(0) + \sum_{n=1}^{\infty}(-i)^n\int_0^t dt_1\int_0^{t_1} dt_2\ldots\int_0^{t_{n-1}} dt_n \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2)\ldots\hat{\hat{L}}_1^{\mathrm{D}}(t_n)\hat{\sigma}(0)$$

This defines the *time-ordered exponential* propagator that takes the system forward from 0 to t in the case where the Liouvillian is time-dependent:

$$\hat{\sigma}(t) = \exp_{\mathrm{O}}\left(-i\int_0^t \hat{\hat{L}}_1^{\mathrm{D}}(t')\,dt' \right)\hat{\sigma}(0)$$

$$\exp_{\mathrm{O}}\left(-i\int_0^t \hat{\hat{L}}_1^{\mathrm{D}}(t')\,dt' \right) = 1 + \sum_{n=1}^{\infty}(-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2)\ldots\hat{\hat{L}}_1^{\mathrm{D}}(t_n)$$

The time ordering is necessary because $\hat{\hat{L}}_1^{\mathrm{D}}(t)$ need not commute with itself at different times. The exponential propagator, however, is not very helpful if we are after the relaxation rates and other *properties* of the spin system, rather than brute-force numerical simulation. Therefore, a very important question is this context is whether we can find the logarithm of the ensemble average of this propagator, that is, a superoperator $\hat{\hat{K}}(t)$, such that

$$\left\langle \exp_{\mathrm{O}}\left(-i\int_0^t \hat{\hat{L}}_1^{\mathrm{D}}(t')\,dt' \right) \right\rangle = \exp_{\mathrm{O}}\left(\hat{\hat{K}}(t) \right)$$

If we can, then the differential equation governing the spin system evolution in the interaction representation becomes:

$$\frac{\partial \hat{\sigma}(t)}{\partial t} = \hat{\hat{K}}'(t)\hat{\sigma}(t)$$

and it may be analysed and solved in any standard way. It is reasonable to partition the superoperator $\hat{\hat{K}}(t)$ into terms of different order in $\hat{\hat{L}}_1^{\mathrm{D}}(t)$, so that:

$$\hat{\hat{K}}(t) = \sum_{n=0}^{\infty}\hat{\hat{K}}_n(t), \qquad \hat{\hat{K}}_n(t) \sim O\left[\left(\hat{\hat{L}}_1^{\mathrm{D}}(t) \right)^n \right]$$

Using the cumulant expansion theorem and assuming (without loss of generality) that $\left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t) \right\rangle = 0$, we obtain the following expressions for the *generalized cumulants* $\hat{\hat{K}}_n(t)$:

$$\hat{\hat{K}}_1 = 0$$

$$\hat{\hat{K}}_2 = (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2) \right\rangle$$

$$\hat{\hat{K}}_3 = (-i)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2)\hat{\hat{L}}_1^{\mathrm{D}}(t_3) \right\rangle$$

$$\hat{\hat{K}}_4 = (-i)^4 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \left(\begin{array}{l} \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2)\hat{\hat{L}}_1^{\mathrm{D}}(t_3)\hat{\hat{L}}_1^{\mathrm{D}}(t_4) \right\rangle - \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_2) \right\rangle \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_3)\hat{\hat{L}}_1^{\mathrm{D}}(t_4) \right\rangle - \\ \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_3) \right\rangle \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_2)\hat{\hat{L}}_1^{\mathrm{D}}(t_4) \right\rangle - \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_1)\hat{\hat{L}}_1^{\mathrm{D}}(t_4) \right\rangle \left\langle \hat{\hat{L}}_1^{\mathrm{D}}(t_2)\hat{\hat{L}}_1^{\mathrm{D}}(t_3) \right\rangle \end{array} \right)$$

and so the first term that is different from we could have obtained from a naive extension of BRW theory is $\hat{\hat{K}}_4$. The three extra terms serve to eliminate some divergences that BRW theory exhibits for large values of t. The simple connection from the GCE truncated at the second term to BRW theory is left as an exercise.

Lecture 22: stochastic Liouville equation

General formalism

For each specific molecule in the ensemble, the Liouville – von Neumann equation is a stochastic differential equation defining the stochastic process $\hat{\rho}(t)$ in terms of the stochastic process $\hat{\hat{H}}_1(\Omega(t))$:

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -i\left(\hat{\hat{H}}_0 + \hat{\hat{H}}_1(\Omega(t))\right)\hat{\rho}(t)$$

where $\Omega(t)$ are the time-dependent parameters (coordinates, angles, *etc.*), for which some model is assumed (Markovian, Brownian, *etc.*). In this equation, the state vector $\hat{\rho}(t)$ records the dynamics of probabilities of the spin system being in a particular set of states. For a large ensemble of systems, we could extend this description to also describe the spatial aspect of the dynamics, that is, the probabilities of occupying a certain region in the physical as well as spin coordinate space. We would assume that the spatial probability density $p(\Omega,t)$ also evolves according to some deterministic law:

$$\frac{\partial p(\Omega,t)}{\partial t} = \hat{\Gamma}_\Omega p(\Omega,t), \qquad \hat{\Gamma}_\Omega p(\Omega,\infty) = 0$$

where $\hat{\Gamma}_\Omega$ is a static operator. It could, for example, be the diffusion equation, in which case:

$$\frac{\partial p(\Omega,t)}{\partial t} = -D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)p(\Omega,t), \qquad \Omega = (x,y,z)$$

We can then merge the space and the spin part by introducing the joint probability density $P(\Omega,\hat{\rho},t)$ of systems in a particular physical space point Ω (which is now a parameter that is independent from time) and spin space point $\hat{\rho}$ (which is similarly a time-independent variable specifying location in spin space). It would allow us to compute the ensemble-averaged density matrix:

$$\overline{\hat{\rho}(\Omega,t)} = \int \hat{\rho} P(\Omega,\hat{\rho},t)\,d\hat{\rho}$$

This, however, is a very high-dimensional integral – our only hope is to obtain the equation of motion for $\overline{\hat{\rho}(\Omega,t)}$ directly. Quite remarkably, this can be done (a lot of background reasoning is skipped here, see the original papers by Kubo and Freed):

$$\begin{aligned}\frac{\partial}{\partial t}\overline{\hat{\rho}(\Omega,t)} &= \int\left(\frac{\partial}{\partial t}P(\Omega,\hat{\rho},t)\right)\hat{\rho}\,d\hat{\rho} = \int\left(-i\hat{\hat{H}}(\Omega) + \hat{\Gamma}_\Omega\right)P(\Omega,\hat{\rho},t)\,\hat{\rho}\,d\hat{\rho} = \\ &= \left(-i\hat{\hat{H}}(\Omega) + \hat{\Gamma}_\Omega\right)\int P(\Omega,\hat{\rho},t)\,\hat{\rho}\,d\hat{\rho} = \left(-i\hat{\hat{H}}(\Omega) + \hat{\Gamma}_\Omega\right)\overline{\hat{\rho}(\Omega,t)}\end{aligned}$$

and so we get (after dropping the bars):

$$\frac{\partial}{\partial t}\hat{\rho}(\Omega,t) = -i\hat{\hat{H}}(\Omega)\hat{\rho}(\Omega,t) + \hat{\Gamma}_\Omega\hat{\rho}(\Omega,t) = -i[\hat{H}(\Omega),\hat{\rho}(\Omega,t)] + \hat{\Gamma}_\Omega\hat{\rho}(\Omega,t)$$

where $\hat{H}(\Omega,t)$ is the Hamiltonian written as a function of space coordinates Ω and $\hat{\Gamma}_\Omega$ is the operator from the equation describing the space dynamics of the system in those coordinates. Collectively this is known as the Stochastic Liouville Equation (SLE).

Consider now the expansion of the Hamiltonian in terms of algebraic functions $g_k(\Omega)$ of space variables (which we choose to be eigenfunctions of $\hat{\Gamma}_\Omega$) and static superoperators $\hat{\hat{h}}_k$:

$$\hat{\hat{H}}(\Omega)=\sum_k g_k(\Omega)\hat{\hat{h}}_k, \qquad \hat{\Gamma}_\Omega g_k(\Omega)=\gamma_k g_k(\Omega)$$

(in the case of isotropic rotational diffusion these would be Wigner functions and irreducible spherical tensor operators). The state vector admits a similar expansion, but with a time-dependent spin part:

$$\hat{\rho}(\Omega,t)=\sum_k g_k(\Omega)\hat{r}_k(t)$$

With this notation in place, the SLE can be re-written as:

$$\sum_n g_n(\Omega)\frac{\partial \hat{r}_n(t)}{\partial t}=-i\sum_{nk} g_n(\Omega)g_k(\Omega)\hat{\hat{h}}_n\hat{r}_k(t)+\sum_k \gamma_k g_k(\Omega)\hat{r}_k(t)$$

Because the functions $g_n(\Omega)$ are a complete set, they have the property of an algebra, that is

$$g_n(\Omega)g_k(\Omega)=\sum_m c_{nkm}g_m(\Omega), \qquad c_{nkm}=\int g_n(\Omega)g_k(\Omega)g_m^*(\Omega)d\Omega$$

where (as we hopefully remember) the coefficients c_{nkm} are called the structure coefficients. Using this property on our SLE, we get:

$$\sum_n g_n(\Omega)\frac{\partial \hat{r}_n(t)}{\partial t}=-i\sum_{nkm} c_{nkm}g_m(\Omega)\hat{\hat{h}}_n\hat{r}_k(t)+\sum_k \gamma_k g_k(\Omega)\hat{r}_k(t)$$

For this equation, we can take a scalar product with each of the $g_m(\Omega)$ functions in turn and get a system of equations for the expansion the state vector:

$${}_m\left\{\frac{\partial \hat{r}_m(t)}{\partial t}=-i\sum_{nk} c_{nkm}\hat{\hat{h}}_n\hat{r}_k(t)+\gamma_m\hat{r}_m(t)\right.$$

This is a system of linear equations that can be solved using standard techniques. The sums are, in principle, infinite, but in practice they can be truncated according to a user-specified accuracy tolerance (as we shall see later, the higher ranks decay faster). Note that the matrix dimensions involved in solving this system are considerably greater than in BRW theory – essentially the spin state space is crossed with the space state space, and the latter can be huge. SLE solutions are therefore only practical for the smallest spin systems.

SLE treatment of isotropic rotational diffusion

Below is a practical walkthrough done for the (by now) familiar case of isotropic rotational diffusion. We take the Hamiltonian (interaction representation with respect to all isotropic interactions) and the spatial dynamics operator from the earlier lectures (note the sum over ranks in $\hat{\rho}(\Omega,t)$):

$$\hat{H}(\Omega)=\sum_{km}\mathfrak{D}_{km}^{(2)}(\Omega)\hat{Q}_{km}, \qquad \hat{\Gamma}_\Omega=-D\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$\hat{\rho}(\Omega,t)=\sum_{lkm}\mathfrak{D}_{km}^{(l)}(\Omega)\hat{r}_{km}^{(l)}(t), \qquad \hat{\Gamma}_\Omega\mathfrak{D}_{km}^{(l)}(\Omega)=-Dl(l+1)\mathfrak{D}_{km}^{(l)}(\Omega)$$

With this notation in place, the SLE becomes:

$$\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\frac{\partial}{\partial t}\hat{r}^{(l)}_{km}(t)=-i\sum_{lkmpq}\mathfrak{D}^{(2)}_{km}(\Omega)\mathfrak{D}^{(l)}_{pq}(\Omega)\hat{\hat{Q}}_{km}\hat{r}^{(l)}_{pq}(t)-D\sum_{lkm}l(l+1)\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t)$$

$$\mathfrak{D}^{(2)}_{km}(\Omega)\mathfrak{D}^{(l)}_{pq}(\Omega)=\sum_{L=|l-2|}^{l+2}\sum_{MN}C^{L,M}_{2,k,l,p}C^{L,N}_{2,m,l,q}\mathfrak{D}^{(L)}_{MN}(\Omega)$$

where $C^{L,M}_{l,m,l',m'}$ are Clebsch-Gordan coefficients. After separating the ranks and projections of the Wigner functions, we get:

$$\left\{\frac{\partial}{\partial t}\hat{r}^{(L)}_{MN}(t)=-i\sum_{lkmpq}C^{L,M}_{2,k,l,p}C^{L,N}_{2,m,l,q}\hat{\hat{Q}}_{km}\hat{r}^{(l)}_{pq}(t)-DL(L+1)\hat{r}^{(L)}_{MN}(t)\right.\quad {}_{L,M,N}$$

If different $\hat{r}^{(L)}_{MN}(t)$ state vectors are concatenated vertically, this system of equations may be laid out into a single block matrix equation of the following general structure:

$$\frac{\partial}{\partial t}\begin{pmatrix}\hat{r}^{(0)}_{0,0}(t)\\ \hat{r}^{(1)}_{1,-1}(t)\\ \vdots\end{pmatrix}=-i\begin{pmatrix}\sum_{lkm}C^{0,0}_{2,k,l,0}C^{0,0}_{2,m,l,0}\hat{\hat{Q}}_{km} & \sum_{lkm}C^{0,0}_{2,k,l,1}C^{0,0}_{2,m,l,-1}\hat{\hat{Q}}_{km} & \cdots\\ \sum_{lkm}C^{1,1}_{2,k,l,0}C^{1,-1}_{2,m,l,0}\hat{\hat{Q}}_{km} & \sum_{lkm}C^{1,1}_{2,k,l,1}C^{1,-1}_{2,m,l,-1}\hat{\hat{Q}}_{km}+2Di & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}\hat{r}^{(0)}_{0,0}(t)\\ \hat{r}^{(1)}_{1,-1}(t)\\ \vdots\end{pmatrix}$$

with the initial condition that (for example) all systems are pointing in random directions and all systems start in the same state $\hat{\rho}_0$, the initial condition for the block matrix equation becomes

$$\hat{\rho}(\Omega,t)=\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t)=\hat{\rho}_0\quad\Rightarrow\quad\hat{r}^{(0)}_{0,0}(0)=\hat{\rho}_0,\ \hat{r}^{(l)}_{km}(0)=0$$

Examples

Analytical SLE solutions, even for simple systems, tend to be quite cumbersome. Consider a single spin with an axial secular Zeeman interaction, tumbling isotropically:

$$\hat{H}=\omega\hat{L}_Z+\frac{Ax}{\sqrt{6}}\hat{T}_{2,0}(L,B)\mathfrak{D}^{(2)}_{0,0}(\Omega),\qquad\hat{\Gamma}_\Omega=-D\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$\hat{\rho}(\Omega,t)=\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t),\qquad\hat{\Gamma}_\Omega\mathfrak{D}^{(l)}_{km}(\Omega)=-Dl(l+1)\mathfrak{D}^{(l)}_{km}(\Omega)$$

The SLE becomes:

$$\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\frac{\partial}{\partial t}\hat{r}^{(l)}_{km}(t)=$$

$$=-i\left(\omega\hat{\hat{L}}_Z+\frac{Ax}{\sqrt{6}}\hat{\hat{T}}_{2,0}\mathfrak{D}^{(2)}_{0,0}(\Omega)\right)\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t)-D\sum_{lkm}l(l+1)\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t)=$$

$$=-i\frac{Ax}{\sqrt{6}}\hat{\hat{T}}_{2,0}\sum_{lkm}\mathfrak{D}^{(l)}_{km}(\Omega)\mathfrak{D}^{(2)}_{0,0}(\Omega)\hat{r}^{(l)}_{km}(t)-\sum_{lkm}\left(Dl(l+1)+i\omega\hat{\hat{L}}_Z\right)\mathfrak{D}^{(l)}_{km}(\Omega)\hat{r}^{(l)}_{km}(t)$$

The product of Winger functions falls apart into several terms:

$$\mathfrak{D}^{(l)}_{km}\left(\Omega\right)\mathfrak{D}^{(2)}_{0,0}\left(\Omega\right)=\sum_{L=\left|l-2\right|}^{l+2}\sum_{M=-L}^{L}\sum_{N=-L}^{L}C^{L,M}_{l,k,2,0}C^{L,N}_{l,m,2,0}\mathfrak{D}^{(L)}_{MN}\left(\Omega\right)$$

After Winger function rank separation, and evaluation (with considerable effort, even in Mathematica) we get the following system of equations:

$$\begin{cases}\dfrac{\partial}{\partial t}\hat{r}^{(0)}_{0,0}\left(t\right)=-i\dfrac{Ax}{5\sqrt{6}}\hat{\hat{T}}_{2,0}\hat{r}^{(2)}_{0,0}\left(t\right)-i\omega\hat{\hat{L}}_{\mathrm{Z}}\hat{r}^{(0)}_{0,0}\left(t\right)\\ \dfrac{\partial}{\partial t}\hat{r}^{(2)}_{0,0}\left(t\right)=-i\dfrac{Ax}{\sqrt{6}}\hat{\hat{T}}_{2,0}\left(\hat{r}^{(0)}_{0,0}\left(t\right)+\dfrac{2}{7}\hat{r}^{(2)}_{0,0}\left(t\right)+\dfrac{2}{7}\hat{r}^{(4)}_{0,0}\left(t\right)\right)-\left(6D+i\omega\hat{\hat{L}}_{\mathrm{Z}}\right)\hat{r}^{(2)}_{0,0}\left(t\right)\\ \dfrac{\partial}{\partial t}\hat{r}^{(4)}_{0,0}\left(t\right)=-i\dfrac{Ax}{\sqrt{6}}\hat{\hat{T}}_{2,0}\left(\dfrac{18}{35}\hat{r}^{(2)}_{0,0}\left(t\right)+\dfrac{20}{77}\hat{r}^{(4)}_{0,0}\left(t\right)+\dfrac{45}{143}\hat{r}^{(6)}_{0,0}\left(t\right)\right)-\left(20D+i\omega\hat{\hat{L}}_{\mathrm{Z}}\right)\hat{r}^{(4)}_{0,0}\left(t\right)\\ \ldots\end{cases}$$

This is a block-tridiagonal system of differential equations. If we (very crudely) ignore terms of rank 4 and higher, we get the following closed differential equation:

$$\frac{\partial}{\partial t}\begin{pmatrix}\hat{r}^{(0)}_{0,0}\left(t\right)\\ \hat{r}^{(2)}_{0,0}\left(t\right)\end{pmatrix}=\begin{pmatrix}-i\omega\hat{\hat{L}}_{\mathrm{Z}} & -i\dfrac{Ax}{5\sqrt{6}}\hat{\hat{T}}_{2,0}\\ -i\dfrac{Ax}{\sqrt{6}}\hat{\hat{T}}_{2,0} & -i\dfrac{2Ax}{7\sqrt{6}}\hat{\hat{T}}_{2,0}-\left(6D+i\omega\hat{\hat{L}}_{\mathrm{Z}}\right)\end{pmatrix}\begin{pmatrix}\hat{r}^{(0)}_{0,0}\left(t\right)\\ \hat{r}^{(2)}_{0,0}\left(t\right)\end{pmatrix};\qquad \hat{r}^{(0)}_{0,0}\left(0\right)=\hat{\rho}_0,\ \hat{r}^{(2)}_{0,0}\left(0\right)=0$$

which may be solved using standard methods. For accurate practical calculations all L ranks up to ~ 15 may be required.