A New Approach of Ordered Exponential in NMR: the Path-Sum

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General context – The evolution operator $U(t)$

$$U(t', t) = \text{OE}[-i H(t', t)] = T \exp(-i \int_t^{t'} H(\tau) d\tau)$$

$$U(\tau_c) = \exp \left( -i \tau_c \sum_{n=0}^{\infty} H^{(n)} \right)$$

**Dyson time-ordering operator**

**Magnus**

$$\vec{H} = (0) H - \frac{1}{2} \sum_{n \neq 0} \frac{(-n) \hat{H}, (n) \hat{H}}{n \omega_m} + \frac{1}{2} \sum_{n \neq 0} \frac{[(n) \hat{H}, (0) \hat{H}], (-n) \hat{H}}{(n \omega_m)^2}$$

**Floquet**

$$+ \frac{1}{3} \sum_{k, n \neq 0} \frac{[(n) \hat{H}, \hat{H}, (-n-k) \hat{H}]}{kn \omega_m^2} + \cdots$$

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E.S. Mananga, *Solid State NMR*, 2013


...
Outline

■ Basic results of algebraic graph theory

■ Path-Sum applied to Ordered Exponential (OE)

\[ \text{OE}[A](t',t) = \begin{pmatrix} \int_t^{t'} G_{K2,11}(t',\tau)d\tau & \text{OE}_{12}(t',t) \\ \text{OE}_{21}(t',t) & \int_t^{t'} G_{K2,22}(t',\tau)d\tau \end{pmatrix} \]

■ Applications:

► Circularly polarized excitation

► Linearly polarized excitation, Bloch-Siegert (BS) effect

► N spins: homonuclear dipolar Hamiltonian, \( H_D \)
Basic results of algebraic graph theory

\[ G = (V\text{ertex set}, E\text{dge set}) \]

**Adjacency finite matrix** \( A_G \)

\[
A_G = \begin{pmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    0 & a_{32} & 0
\end{pmatrix}
\]

entry: *weight* on a *directed edge*

ex.: **walk** \( \mathcal{W}_{1 \leftarrow 2} \) (from \( V_2 \) to \( V_1 \)) of **length** 4
Basic results of algebraic graph theory

**the powers** of the Adjacency matrix $A_G$ on a graph $G$ generate

**ALL weighted WALKS** $\mathcal{W}$ on $G$

$$A_G^2 = \begin{pmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    0 & a_{32} & 0
\end{pmatrix}^2 = \begin{pmatrix}
    \vdots & \vdots & \vdots
\end{pmatrix}
$$

W of length 2 from $V_2$ to $V_1$ ($1 \rightarrow 2$)

$$\Sigma = a_{11}a_{12} + a_{12}a_{22} + a_{13}a_{32}$$

N. Biggs, in: *Algebraic Graph Theory* (1993)
Basic results of algebraic graph theory

The powers of the adjacency matrix $A_G$ on a graph $G$ generate all weighted walks $W$ on $G$.

$$A_G = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ 0 & a_{32} & 0 \end{pmatrix}$$

2

Each element of $A_G^2$ is given by the sum of the weighted $W$ of length 2 from $v_2$ to $v_1$ (1 $\rightarrow$ 2)

$$a_{11} \times a_{12} + a_{12} \times a_{22} + a_{13} \times a_{32}$$

$\Sigma = a_{11}a_{12} + a_{12}a_{22} + a_{13}a_{32}$

N. Biggs, in: *Algebraic Graph Theory* (1993)
Path-Sum

◊ **simple path** $\mathcal{P}$ (self avoiding walk): $\mathcal{W}$ whose $V$ are all **distinct**

◊ **simple cycle** $\mathcal{C}$ (self avoiding polygon): $\mathcal{W}$ whose **endpoints** are **identical** and **intermediate** $V$ are all **distinct** and different from the endpoints

« **Fundamental Theorem of Arithmetic** » on $\mathcal{G}$  
(P.-L. Giscard, 2012)

► $\mathcal{W}$ factor **uniquely** into **prime** elements, *i.e.* **simple paths** and **simple cycles**

► if $\mathcal{G}$ is **finite** the number of primes is **finite**

► resummation of all $\mathcal{W}$ involves a **finite** number of operations: **sum on simple paths** and **continuous fraction of simple cycles** with vertex removal
Power series of $A_g$

ex.: $\exp[A_g] = \sum_{k=0}^{\infty} \frac{1}{n!} A_g^k$

$$(A_g)^k = \left( \cdots (A_g)^{\omega \alpha} \cdots \right)$$

To keep in mind:

Each element of $A_g^k$ is given by the sum of the weighted $\mathcal{W}$ of length $k$ (standard $\times \times$ operation)
Power series of $A_\varphi$

ex.: $\exp[A_\varphi] = \sum_{k=0}^{\infty} \frac{1}{n!} A_\varphi^k$

$F(A_\varphi)_{\omega\alpha} = \sum_{k=0}^{\infty} c_k \sum \mathcal{W}_{\varphi, \alpha\omega; k} a_{\omega h_k} \ldots \times a_{h_3 h_2} \times a_{h_2 \alpha}$

power series of $A_\varphi$ all weighted walks $\mathcal{W}$ from $\mathcal{V}_\alpha$ to $\mathcal{V}_\omega$ of length $k$
Power series of $A_{\mathcal{G}}$

ex.: $\exp[A_{\mathcal{G}}] = \sum_{k=0}^{\infty} \frac{1}{n!} A_{\mathcal{G}}^k$

Path-Sum

\[ F(A_{\mathcal{G}})_{\omega \alpha} = \sum_{k=0}^{\infty} c_k \sum \omega_{\mathcal{G}, \alpha \omega; k} a_{\omega h_k} \ldots \times a_{h_3 h_2} \times a_{h_2 \alpha} \]

power series of $A_{\mathcal{G}}$ all weighted walks $\mathcal{W}$ from $\mathcal{V}_\alpha$ to $\mathcal{V}_\omega$ of length $k$

« Fundamental Theorem of Arithmetic » on $\mathcal{G}$ (P.-L. Giscard, 2012)

- $\mathcal{W}$ factor uniquely into prime elements, i.e. simple paths and simple cycles
- if $\mathcal{G}$ is finite the number of primes is finite
- resummation of all $\mathcal{W}$ involves a finite number of operations: sum on simple paths and continuous fraction of simple cycles with vertex removal
Power series of $A_G$

**Example:** $\exp[A_G] = \sum_{k=0}^{\infty} \frac{1}{k!} A_G^k$

$$F(A_G)_{\omega \alpha} = \sum_{k=0}^{\infty} c_k \sum \mathcal{W}_{G, \alpha \omega; k} a_{\omega h_k} \times a_{h_3 h_2} \times a_{h_2 \alpha}$$

**Path-Sum**

$$F(A_G)_{\omega \alpha} = \sum_{P \in \mathcal{P}_{G, \alpha \omega; l}} f(a_{\omega \omega}) \times a_{\omega \mu_1} \times f(a_{\mu_2 \mu_2}) a_{\mu_2 \alpha} \times f(a_{\alpha \alpha})$$

- Sum on the **finite** set of *simple paths* $\mathcal{P}$ of length $l$
- Sum over the **finite** set of *simple cycles* $\mathcal{C}$
- (continued fraction of **finite** breadth)
Ordered exponential (OE) (P.-L. Giscard, 2015)

\[
A_\varphi(t) = \begin{pmatrix}
\langle s_\omega | A(t) | s_\alpha \rangle \\
\vdots \\
\langle s_\omega | A(t) | s_\alpha \rangle
\end{pmatrix}
\]

\[
OE[A_\varphi](t',t) = \langle s_\omega | OE[A_\varphi](t',t) | s_\alpha \rangle
\]

\[
\sum \text{ALL weighted walks } \omega \leftarrow \alpha \text{ on } A_\varphi
\]

but using \( \star \) product

\[
(f \star g) = \int_t^{t'} f(t',\tau)g(\tau,t)\,d\tau
\]

instead of \( \times \)

Path-Sum
An example: 2 × 2 matrix

\[
A(t) = \begin{pmatrix} a_{11}(t) & a_{12}(t) \\ a_{21}(t) & a_{22}(t) \end{pmatrix}
\]

\[
OE[A](t', t) = \begin{pmatrix} \int_t^{t'} G_{K_2,11}(t', \tau) d\tau & OE_{12}(t', t) \\ OE_{21}(t', t) & \int_t^{t'} G_{K_2,22}(t', \tau) d\tau \end{pmatrix}
\]

Path-Sum

entry → solving an equation with **analytical tools**

finite number of operations → **unconditional convergence**

**non perturbative** formulation of OE

**scalability**
Fundamental Theorem of Arithmetic » on $\mathcal{G}$  
(P.-L. Giscard, 2012)

- $\mathcal{G}$ factor uniquely into prime elements, i.e. simple paths and simple cycles
- if $\mathcal{G}$ is finite the number of primes is finite
- resummation of all $\mathcal{G}$ involves a finite number of operations: sum on simple paths and continuous fraction of simple cycles with vertex removal

\[
A(t) = \begin{pmatrix} a_{11}(t) & a_{12}(t) \\ a_{21}(t) & a_{22}(t) \end{pmatrix}
\]

\[
\mathcal{G} = \begin{array}{c}
\bullet \\
1 \\
\rightarrow \\
\rightarrow \\
\bullet \\
2
\end{array}
\]

\[
\text{Path-Sum}
\]

\[
\text{OE}[A](t',t) = \begin{pmatrix}
\int_t^{t'} G_{K2,11}(t',\tau) d\tau & OE_{12}(t',t) \\
OE_{21}(t',t) & \int_t^{t'} G_{K2,22}(t',\tau) d\tau
\end{pmatrix}
\]

An example: $2 \times 2$ matrix
An example: 2 × 2 matrix

\[(f \star g) = \int_t^{t'} f(t', \tau)g(\tau, t)d\tau\]

\[
[1 - (\ast \ast \ast \cdots)]^{-1} = \sum_{n \geq 0} (\ast \ast \ast \cdots)^n
\]

Neumann series (analytical)
linear Volterra (2nd kind) (numerical)
An example: $2 \times 2$ matrix

$$(f \star g) = \int_t^{t'} f(t', \tau) g(\tau, t) d\tau$$

$$[1_* - (\ast \ast \ast \ldots)]^{-1} = \sum_{n \geq 0} (\ast \ast \ast \ldots)^n$$

Neumann series (analytical)
linear Volterra (2\textsuperscript{nd} kind) (numerical)

$$\text{OE}[A](t', t) = \left( \begin{array}{c} \int_t^{t'} G_{K_2,11}(t', \tau) d\tau \\ \text{OE}_{21}(t', t) \\ \int_t^{t'} G_{K_2,22}(t', \tau) d\tau \end{array} \right)$$

**sum on simple cycles**

$$G_{K_2,11} = \left[ 1_* - a_{11} - a_{12} \star G_{K_2\setminus \{1\}, 22} \star a_{21} \right]^{-1}$$

$$G_{K_2\setminus \{1\}, 22} = \left[ 1_* - a_{22} \right]^{-1}$$

**sum on simple paths**

$$\text{OE}_{12}(t', t) = \int_t^{t'} G_{K_2\setminus \{2\}, 11} \star a_{12} \star G_{K_2,22}(t', \tau) d\tau$$

► END of the continued fraction !
► finite sum on $\mathcal{C}$

► END!
► finite sum on simple $\mathcal{P}$
Summary (partial)

- ... take a **finite** matrix $A_{\mathcal{G}}(t)$ associated to $\mathcal{G}$ (Hermitian or not, periodic or not...)

- each entry of $A_{\mathcal{G}}^k$ is given is given by a **finite** number of operations by using Path-Sum (with $\times$ product)

- each entry of $OE[A_{\mathcal{G}}](t',t)$ is given is given by a **finite** number of operations by using Path-Sum (with $\ast$ product and $[1_{\ast} - (\ast \ast \ast \cdots )]^{-1}$)
... take a finite matrix $A_G(t)$ associated to $G$ (Hermitian or not, periodic or not...)

► each entry of $A_G^k$ is given is given by a finite number of operations by using Path-Sum (with $\times$ product)

► each entry of $OE[A_G](t',t)$ is given is given by a finite number of operations by using Path-Sum (with $\ast -$ product and $[1_\ast - (\ast \ast \ast \ast \ast \cdots)]^{-1}$)

- the matrix nature of the problem is fully replaced when working on entries

- or, one can keep it partially… → PARTITIONS (scalability)

- the convergence of the Neumann series (analytical) is superexponential

- a convenient (numerical) approach: linear Volterra equations (2nd kind)
Outline

■ Basic results of algebraic graph theory

■ Path-Sum applied to the ordered exponential (OE)

■ Applications:
  ► Circularly polarized excitation
  ► Linearly polarized excitation, Bloch-Siegert (BS) effect
  ► N spins homonuclear dipolar Hamiltonian, $H_D$
Applications – Circularly polarized excitation (test model)

\[ H(t) = \left( \frac{\omega_0}{2} \beta e^{-i\omega t}, \beta e^{i\omega t} - \frac{\omega_0}{2} \right), [H(t'), H(t)] \neq 0 \]

\[ H(t) = \frac{1}{2} \omega_0 \sigma_z + \beta [\sigma_x \cos(\omega t) + \sigma_y \sin(\omega t)] \]

Path-Sum

\[ G_{K2,11}(t) = (1 - \frac{\omega_0}{2i} + i\beta^2) \left( e^{-i\Delta(t'-t)} - 1 \right) \]

Neumann series

\[ OE[-iH](t)_{11} = 1 + \sum_{n=0}^{\infty} \frac{(-it \beta^2/\Delta)^{n+1}}{(n+1)!} \sum_{k=0}^{n+1} \binom{n+1}{k} (\frac{\Delta \omega_0}{2\beta^2} - 1)^k \]

\[ _2F_1 \left( -k, -k+n+1; -n-1; \frac{\Delta^2}{\Delta \omega_0 - \beta^2} \right) \]

Gauss hypergeometric

\[ U(t) = \exp \left( -\frac{1}{2} i\omega t \sigma_z \right) \exp \left( -it \left( \frac{1}{2} (\omega_0 - \omega) \sigma_z + \beta \sigma_x \right) \right) \]
Applications – Linearly polarized excitation, Bloch-Siegert (BS) effect

\[ H(t) = \frac{1}{2} \omega_0 \sigma_z + 2\beta \sigma_x \cos(\omega t) \]

\[ \begin{pmatrix} \frac{\omega_0}{2} & 2\beta \cos(\omega t) \\ 2\beta \cos(\omega t) & -\frac{\omega_0}{2} \end{pmatrix} \]

\( \omega = \omega_0 \) or \( \omega \neq \omega_0 \)

P(t) transition probability

\[ \beta / \omega = 1/10 \]
\[ \beta / \omega = 3/2 \]
\[ \beta / \omega = 10 \]

► analytical expression with few orders of the Neumann series

P.L. Giscard, C. Bonhomme, *to be submitted*
Applications – N spin systems, homonuclear dipolar Hamiltonian, $H_D$

t = 0

pure state

$H_1$

$H_2$

$H_3$

$H_4 \ldots H_{42}$

analytical expression

Coll.: F. Ribot, France

$(CH_3)_{12}(OH)_6Sn_{12}$

42 protons
« rigid » CH$_3$

MAS 10 kHz
rotor period 0.1 ms

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Applications – N spin systems, homonuclear dipolar Hamiltonian, $H_D$

$t = 0$

pure state

$H_1 \quad H_2 \quad H_3 \quad H_4 \ldots H_{42}$

$\text{analytical expression}$

Coll.: F. Ribot, France

$(\text{CH}_3)_{12}(\text{OH})_6\text{Sn}_{12}$

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Conclusions and acknowledgments

Path-Sum

► a new approach
► analytical expression for U(t)
► unconditional convergence
► non perturbative formulation
► scalable to large spin systems
► other theory/applications to come...

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Ass. Pr. in Calais, France
Liouville laboratory
Algebraic Combinatorials
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Post doctoral position available in Paris: on NMR instrumentation & DNP
To go further – Path-Sum vs other methods

- **main goal** → get an *exact* form for $U(t)$

- **FLOQUET** | **ZASSENHAUS** | **MAGNUS** | **PATH-SUM**
  - **FER/TROTTER-SUZUKI**

- **usually:** ![Warning_icon] on $H(t)$ → choice in
  - **FLOQUET** | **ZASSENHAUS** | **MAGNUS**
  - **FER/TROTTER-SUZUKI**

- **PATH-SUM** is *exact* and PARTITIONS allow to *choose the dimension* of the working space from $H(t)$ to $U(t)$
To go further – Scale invariance

Take a partition of a spin system in a set of (smaller, independent) sub-systems

sub-system n°1

sub-system n°2

sub-system n°3

Magnus or Floquet or Fer or …

the exact evolution of the entire spin system as functions of the evolutions of the isolated sub-systems is given by Path-Sum

(though non contiguous blocks in H(t) matrix!)
To go further – WHY does Path-Sum work?

- the **EXACT** result is given by a **FINITE** number of terms
- the **matrix** nature of the problem is **fully replaced** when working on entries
- or, one can keep it partially… → **PARTITIONS**

- **hard** work → \([1_\star - (\star \star \star \cdots)]^{*1}\)

- hopefully: the **Neumann series** give the analytical solution at any order with unconditional convergence (not to be “found” … just apply a "recipe")

- the **convergence** of the Neumann series is **superexponential**

- a **convenient** numerical approach: linear **Volterra** equations (**2\(^{nd}\) kind**)

\[
D_x^2 u + \left[ \frac{\gamma}{x} + \frac{\delta}{x-1} + \frac{\epsilon}{x-a} \right] D_x u + \left[ \frac{\alpha \beta x - q}{x(x-1)(x-a)} \right] u = 0
\]

**ex.**: the best obtainable solution for the **general 2 × 2 matrix** (closed form for the **confluent Heun’s special functions**) (see Q. Xie, 2018)

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To go further – Exponential explosions

- **1st explosion**: related to the *size of $H(t)$* with *many-body* systems (Q nature)
- **2nd explosion**: related to the *time* needed to isolate the *primes* (G nature)

**Lanczos–Path-Sum (numerical)** *fixes* the 2nd explosion:

Idea behind: initial $H(t) \rightarrow$ time dependent *tridiagonal matrix*

**expectations**: to reach *excellent convergence* with the breadth of the continued fraction and why not?... "Circumvent" the 1st explosion

P.-L. Giscard *et al.*, 2019, *in preparation*
To go further – Complexity theory

► for finite $\mathcal{G}$ : the decomposition of $\mathcal{W}$ in primes (e.g. simple paths & cycles) for the $\square$ (nested) operation exists and is unique

► to determine the existence of a prime of length $L$ is NP-complete (no(?) algorithm with polynomial complexity)

► to count them is $\#P$-complete (the same but for counting problems)

► to count them for a fixed length $L$ is $\#W[1]$-complete (same as $\#P$-complete but with parameters, such as $L$, taken into account)

► BUT: for sparse $\mathcal{G}$ : counting becomes polynomial in the max degree of $\mathcal{G}$!

see: P. L. Giscard et al., Algorithmica, 2019
To go further – Mathematical conditions on $A(t)$ for Path-Sum to be valid

- fundamentally: $\mathcal{R} \text{esolvent}[A(t)] \star \text{product} = \frac{d}{dt} \text{OE}[A(t)] \rightarrow \text{Path-Sum}$

- each entry of $A(t)$ must be bounded on $[0,t]$, a bounded interval of time

- if the entries are not bounded, Path-Sum still work … but perhaps the Neumann series will not converge

- continuity is not necessary

- if continuity: Volterra equations are much easier to handle

- $A(t)$ can be Hermitian or not, periodic or not … and entries can be: matrices, quaternions, octonions, division rings…
To go further – Mathematical conditions on A(t) for Path-Sum to be valid

► finite \( A(t) \): sufficient condition for finite breadth of the continued fraction

► NOT a necessary condition: ex. a finite number of simples cycles in an infinite matrix

► in some cases, Path-Sum can still be applied on infinite matrices: strong symmetry, e.g. invariance by translation (soluble non-linear Volterra equations)

In other words:

► infinity of cycles … but self-similar like in a fractal

► the corresponding continued fraction is of finite breadth
To go further – Taylor… or Neumann series?

▶ take one entry: \( f(t) = \text{OE}[A(t)]_{ij} \)

▶ **Taylor** series: expansion in \( t^n \) i.e. \( f(t) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} t^n \)

ex.: \( \frac{1}{1-t} = \sum_{n=0}^{\infty} t^n = 1 + t + t^2 + \cdots + t^n + \cdots \) with \( r = 1 \) (radius of CV)

▶ **Neumann** series: uses the \( \star \)–product, i.e. \( f(t) = \sum_{n=0}^{\infty} f^\star n \)

each order contains functions represented by infinite Taylor series

\( r = \infty \) (!) with **uniform** & **superexponential** CV
To go further – N spins starting with a pure state

- starting with a **pure state** with 1 up-spin (total: N, *any geometry*)

Path-sum contains all **N-order correlations**

\[ \text{if } \omega_{rot} = 0 \]

all terms of the Neumann series are **explicitly** known

\[ \text{if } \omega_{rot} \neq 0 \]

still **analytical** up to the CV of the series to the solution

- starting with a **pure state** with 4 or 5 up-spin is still tractable

(*i.e. no exponential explosion*)
To go further – Pure state vs partial polarization

- **Pure state:** if \( k \) up-spins over \( N \) and \( k \ll N \rightarrow \) space of states dim. \( \approx N^k \)
  (suppression of the exponential explosion)

- **Partial polarization:** a cut-off is needed \( \rightarrow \) if \( \frac{\text{int}_{i,j}}{\text{int}_V} \leq \frac{1}{\text{cut-off}} \) then \( \text{int}_{i,j} = 0 \)

  **cut-off:** « high » for chains but decreases for more « dense » spin systems

next target: to extend Path-Sum to mixed states via a decomposition on pure states
To go further – Path-Sum vs Floquet theory for Bloch-Siegert effect

P(t) transition probability

ω = ω₀ or ω ≠ ω₀

P.L. Giscard, C. Bonhomme, *to be submitted*
To go further – N spin chains and $H_D$

$t = 0$

$H_1$ → $H_2$ → $H_3$ → $H_4$ → $...$ → $H_{10}$ → $...$ → $H_{30}$ → $...$

$p$ure state \[ \omega_{rot} = 0 \]

$N = 10$

$N = 30$

P.L. Giscard, C. Bonhomme, *to be submitted*
To go further – Liouvillian space, Feynman paths and diagrams

extension of Path-Sum in the Liouvillian space is possible using the adjoint operator of $H(t)$

« With application to quantum mechanics, path integrals suffer most grievously from a serious defect. They do not permit a discussion of spin operators or other such operators in a simple and lucid way » (R.P. Feynman)

Path-sum can be used starting from the Lagrangian with action as weight on a given $\mathcal{W}$

Path-sum can be used starting from the Hamiltonian with energy as weight on a given $\mathcal{W}$

Feynman diagrams: $\mathcal{W}$ of $\mathcal{G}$ in the state space (but continuous)

Path-sum performs a formal re-summation of an infinite number of $\mathcal{W}$, i.e. Feynman diagrams!