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

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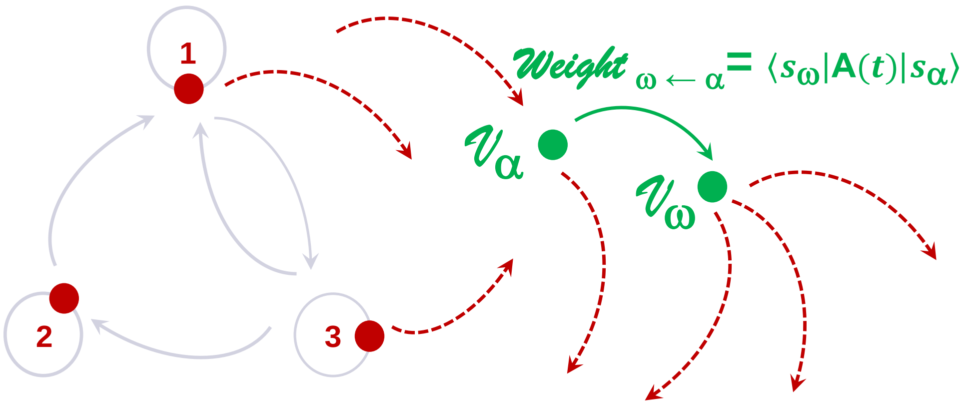

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General context – The evolution operator U(t)

Dyson time-ordering operator

$$\mathbf{U(t',t) = OE[-i\,H(t',t)] = \mathit{T}\,exp\left(-i\int_{t}^{t'} H(\tau)d\tau\right)}$$

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

Magnus

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

Floquet

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

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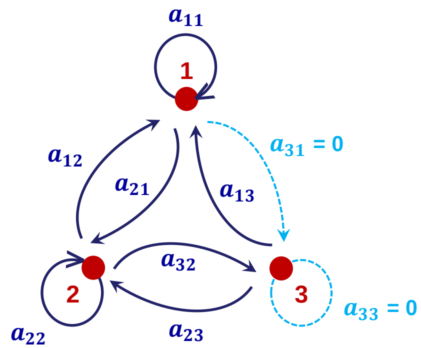
…

Outline

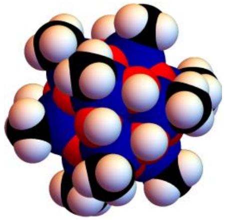
- Basic results of algebraic graph theory



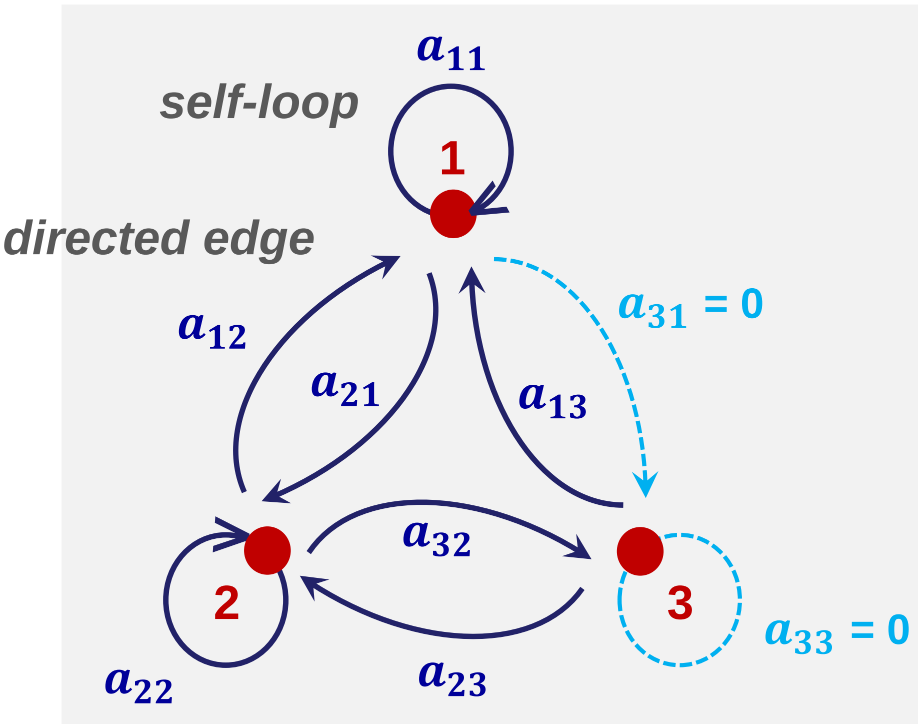
- Path-Sum applied to Ordered Exponential (OE)

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

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



$\mathcal{G}$ = ($\mathcal{V}$ertex set, $\mathcal{E}$dge set)

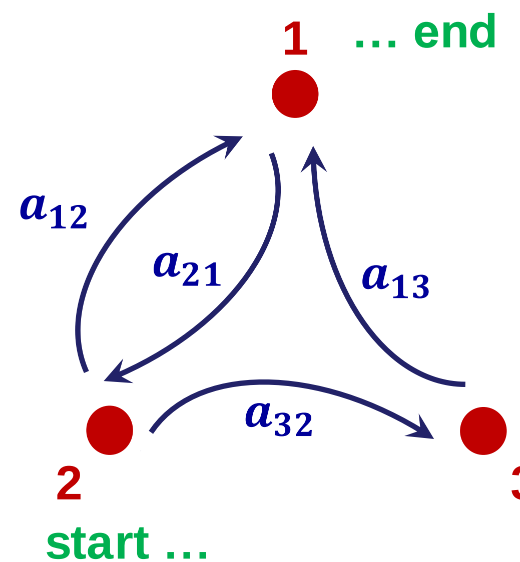


Adjacency *finite* matrix $\mathbf{A}_{\mathcal{G}}$

$$\mathbf{A}_{\mathcal{G}} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ 0 & a_{32} & 0 \end{pmatrix}$$

⬇

entry: *weight* on a ***directed edge***



ex.: ***walk*** $\mathcal{W}_{1\leftarrow 2}$ (from $\mathcal{V}_2$ **to** $\mathcal{V}_1$) of ***length* 4**

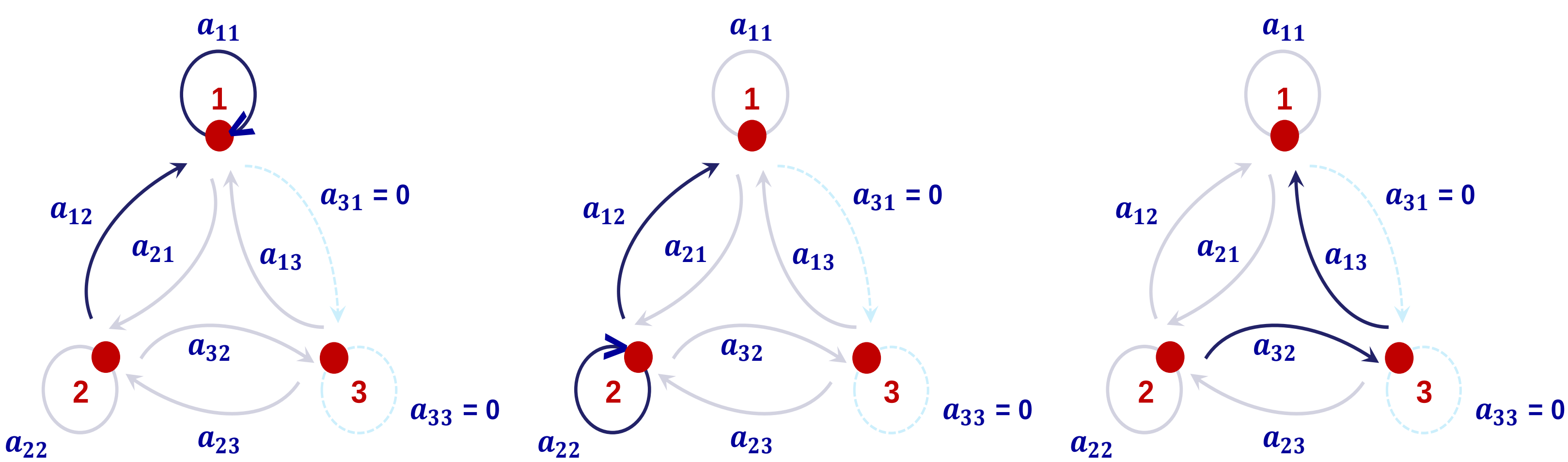
Basic results of algebraic graph theory

the *powers* of the Adjacency matrix $\mathbf{A}_{\mathcal{G}}$ on a graph $\mathcal{G}$ generate ALL *weighted* WALKS $\mathcal{W}$ on $\mathcal{G}$

$$\mathbf{A}_{\mathcal{G}}^{2} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ 0 & a_{32} & 0 \end{pmatrix}^{2} = \begin{pmatrix} \vdots & \blacksquare & \vdots \\ & \ddots & \\ & \cdots & \end{pmatrix}$$

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

$\mathcal{W}$ of ***length* 2** from v_2 to v_1 (**1** ← **2**)



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

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

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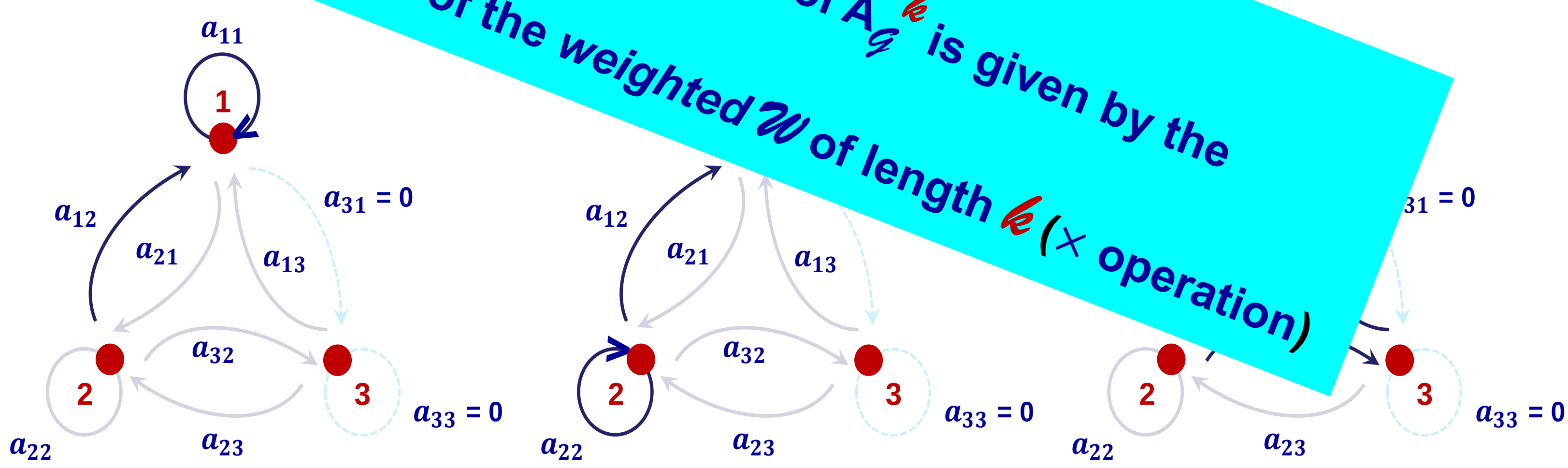
$$\mathbf{A}_{\mathcal{G}}^{2} = \begin{pmatrix} a_{11} & a_{12} & \cdots \\ a_{21} & a_{22} & \cdots \\ 0 & a_{3\cdots} & \cdots \end{pmatrix}$$

to keep in mind:
each element of $\mathbf{A}_{\mathcal{G}}^{k}$ is given by the sum of the weighted $\mathcal{W}$ of length k (× operation)



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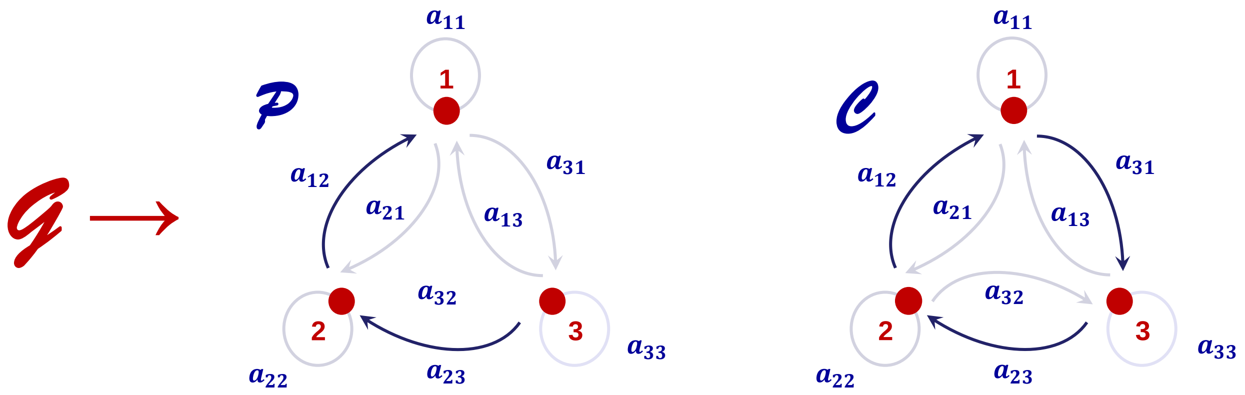
Path-Sum

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

◊ ***simple cycle*** $\mathcal{C}$ (self avoiding polygon): $\mathcal{W}$ whose **endpoints** are **identical** and **intermediate** $\mathcal{V}$ 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 $A_{\mathcal{G}}$

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

$$(A_{\mathcal{G}})^{k} = \begin{pmatrix} & \cdots & \\ \vdots & (A_{\mathcal{G}})^{k}_{\omega\alpha} & \vdots \\ & \cdots & \end{pmatrix}$$

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

power series of $\mathbf{A}_{\mathcal{G}}$

all *weighted* walks $\mathcal{W}$ **from** $\mathcal{V}_{\alpha}$ to $\mathcal{V}_{\omega}$ of length k

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

Path-Sum

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power series of $A_{\mathcal{G}}$

all *weighted* walks $\mathcal{W}$ **from** $\mathcal{V}_\alpha$ to $\mathcal{V}_\omega$ of length k

Path-Sum

$$F(A_{\mathcal{G}})_{\omega\alpha} = \sum_{\mathcal{P}_{\mathcal{G},\alpha\omega;\ell}} f(a_{\omega\omega}) \times a_{\omega\mu_\ell} \cdots f(a_{\mu_2\mu_2}) a_{\mu_2\alpha} \times f(a_{\alpha\alpha})$$

edge weight

effective $\mathcal{V}$ weight

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***)

$$\mathbf{OE}[\mathbf{A}_{\mathcal{G}}](t',t) = \begin{pmatrix} \cdots \\ \langle s_\omega | \mathbf{OE}[\mathbf{A}_{\mathcal{G}}](t',t) | s_\alpha \rangle \\ \cdots \end{pmatrix}$$

$$\mathbf{A}_{\mathcal{G}}(t) = \begin{pmatrix} \cdots \\ \langle s_\omega | \mathbf{A}(t) | s_\alpha \rangle \\ \cdots \end{pmatrix}$$

Σ **ALL *weighted* walks $\omega \leftarrow \alpha$ on $\mathbf{A}_{\mathcal{G}}$**

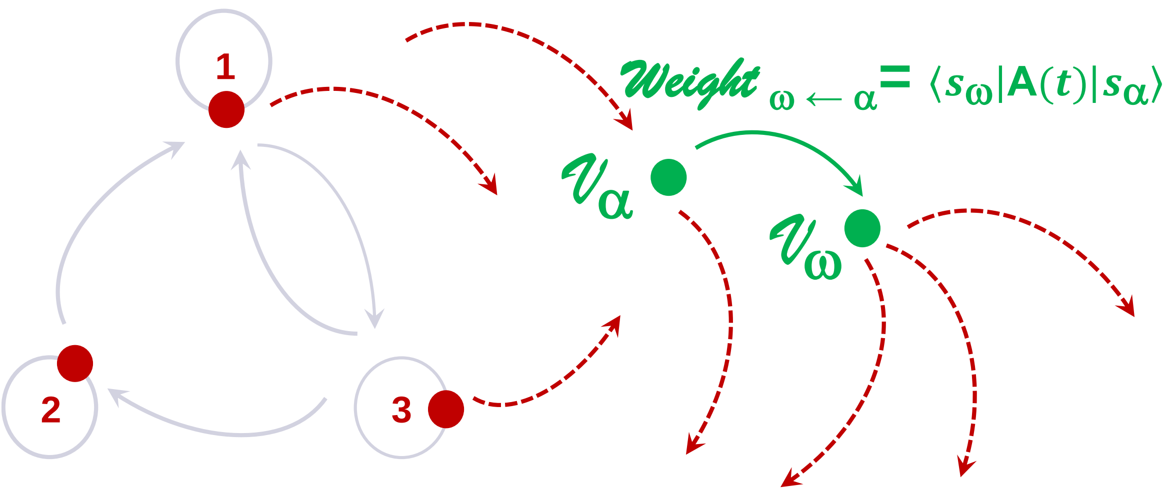
but using $*$–product

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

instead of $\times$

Path-Sum

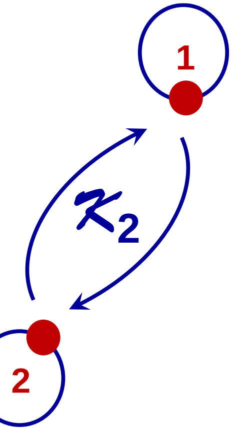
$\mathbf{A}_{\mathcal{G}}$



An example: 2 × 2 matrix

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

$\mathcal{G} =$



Path-Sum

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

- ► ***entry*** → solving an equation with ***analytical tools***
- ► ***finite*** number of operations → ***unconditional convergence***
- ► ***non perturbative*** formulation of OE
- ► ***scalability***

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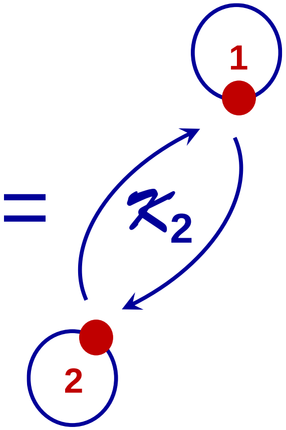

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$a_{ij}(t)$

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

$$[\mathbf{1}_* - (* \quad * \quad * \cdots)]^{*-1} = \sum_{n\geq 0} (* \quad * \quad * \cdots)^{*n}$$

Neumann series (analytical)

linear Volterra (2nd kind) (numerical)

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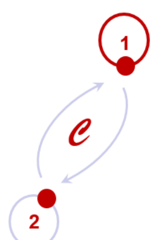
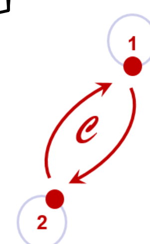
$a_{ij}(t)$

sum on *simple cycles*

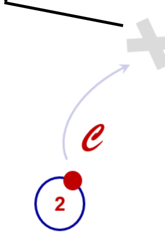
$$G_{K_2,11} = [1_* - a_{11} - a_{12} * G_{K_2\backslash\{1\},22} * a_{21}]^{*-1}$$

$\mathcal{K}_2$



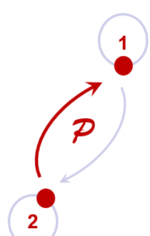


$$G_{K_2\backslash\{1\},22} = [1_* - a_{22}]^{*-1}$$



$$OE_{12}(t',t) = \int_t^{t'} G_{K_2\backslash\{2\},11} * a_{12} * G_{K_2,22}(t',\tau)d\tau$$

sum on *simple paths*



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

Summary (partial)

► **…** take a ***finite*** matrix $\mathbf{A}_{\mathcal{G}}\mathbf{(t)}$ associated to $\mathcal{G}$ (Hermitian or not, periodic or not…)

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

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

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

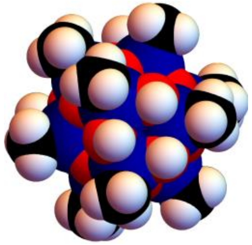
- the ***matrix*** nature of the problem is ***fully replaced*** when working on ***entries***
- or, one can keep it partially… → **PARTITIONS** (***scalability***) ←
- the ***convergence*** of the **Neumann** series (***analytical***) is ***superexponential***
- a convenient (***numerical***) approach: 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)

$$\mathbf{H}(t) = \begin{pmatrix} \frac{\omega_0}{2} & \beta e^{-i\omega t} \\ \beta e^{i\omega t} & -\frac{\omega_0}{2} \end{pmatrix}, [\mathbf{H}(t'), \mathbf{H}(t)] \neq 0$$

$$\mathbf{H}(t) = \frac{1}{2}\omega_0 \boldsymbol{\sigma}_\mathbf{z} + \beta[\boldsymbol{\sigma}_\mathbf{x}\cos(\omega t) + \boldsymbol{\sigma}_\mathbf{y}\sin(\omega t)]$$

$$[\mathbf{1}_* - (* \quad * \quad * \cdots)]^{*-1}$$

Path-Sum

$$G_{K_2,11}(t) = \left(1_* - \frac{\omega_0}{2i} + \frac{i\beta^2}{\Delta}\left(e^{-i\Delta(t'-t)} - 1\right)\right)^{*-1}$$

OE entry

Neumann series

$$OE[-i\mathbf{H}](t)_{11} = 1 + \sum_{n=0}^{\infty} \frac{(-it\,\beta^2/\Delta)^{n+1}}{(n+1)!} \sum_{k=0}^{n+1} \binom{n+1}{k} \left(\frac{\Delta\omega_0}{2\beta^2} - 1\right)^k {}_2F_1\left(-k, -k+n+1; -n-1; \frac{\Delta^2}{\frac{\Delta\omega_0}{2} - \beta^2}\right)$$

Gauss hypergeometric

$$OE[-i\mathbf{H}](t)$$

$$\begin{pmatrix} e^{-\frac{1}{2}it\left(\Delta+\frac{\omega_0}{2}\right)}\left(\cos(\alpha t/2) + \frac{i}{\alpha}\left(\Delta - \frac{\omega_0}{2}\right)\sin(\alpha t/2)\right) & -\frac{2i\beta}{\alpha}e^{-\frac{1}{2}it\left(\Delta+\frac{\omega_0}{2}\right)}\sin(\alpha t/2) \\ -\frac{2i\beta}{\alpha}e^{\frac{1}{2}it\left(\Delta+\frac{\omega_0}{2}\right)}\sin(\alpha t/2) & e^{\frac{1}{2}it\left(\Delta+\frac{\omega_0}{2}\right)}\left(\cos(\alpha t/2) - \frac{i}{\alpha}\left(\Delta - \frac{\omega_0}{2}\right)\sin(\alpha t/2)\right) \end{pmatrix}$$

$$\mathbf{U}(t) = \exp\left(-\frac{1}{2}i\omega t\boldsymbol{\sigma}_\mathbf{z}\right)\exp(-it\left(\frac{1}{2}(\omega_0 - \omega)\boldsymbol{\sigma}_\mathbf{z} + \beta\boldsymbol{\sigma}_\mathbf{x}\right))$$

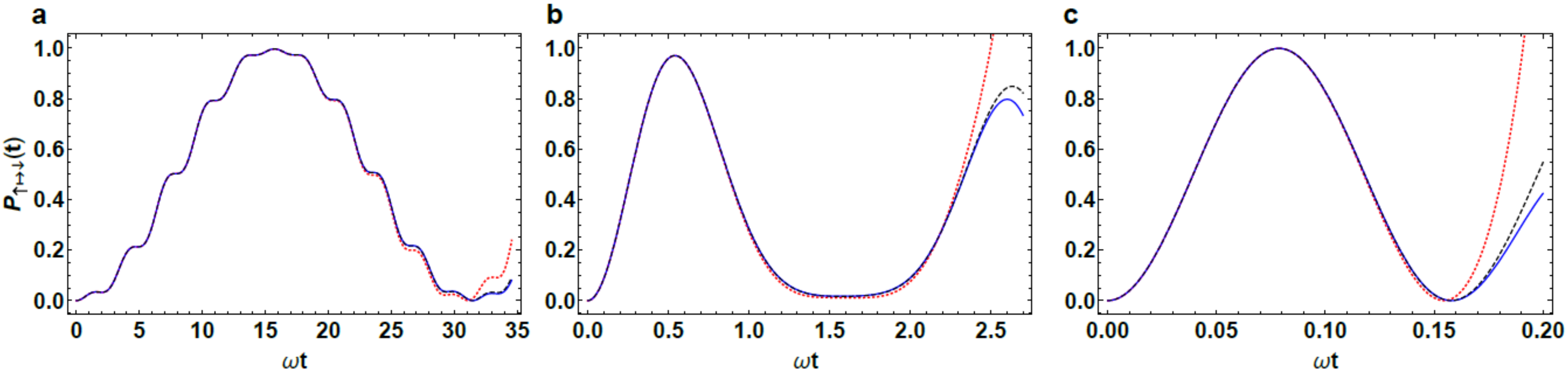
Applications – Linearly polarized excitation, Bloch-Siegert (BS) effect

$$\mathbf{H}(t) = \frac{1}{2}\omega_0 \boldsymbol{\sigma}_\mathbf{z} + 2\beta\, \boldsymbol{\sigma}_\mathbf{x} \cos(\omega t)$$

$$\mathbf{H}(t) = \begin{pmatrix} \frac{\omega_0}{2} & 2\beta\cos(\omega t) \\ 2\beta\cos(\omega t) & -\frac{\omega_0}{2} \end{pmatrix}$$

P(t) transition probability

$\boldsymbol{\omega = \omega_0 \text{ or } \omega \neq \omega_0}$



$\boldsymbol{\beta/\omega = 1/10}$ $\boldsymbol{\beta/\omega = 3/2}$ $\boldsymbol{\beta/\omega = 10}$

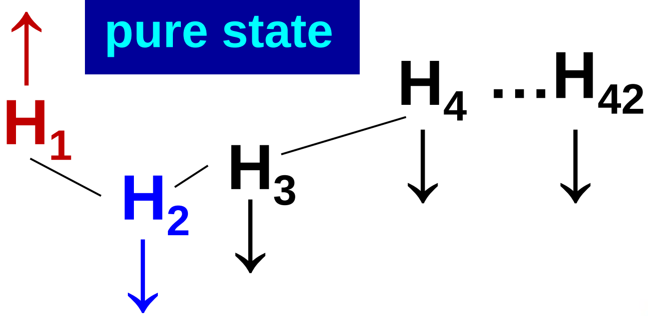
► **analytical** expression with **few orders** of the **Neumann series**

P.L. Giscard, C. Bonhomme, *to be submitted*

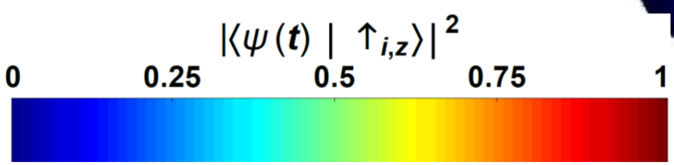
Applications – N spin systems, homonuclear dipolar Hamiltonian, H_D

t = 0

pure state



analytical expression

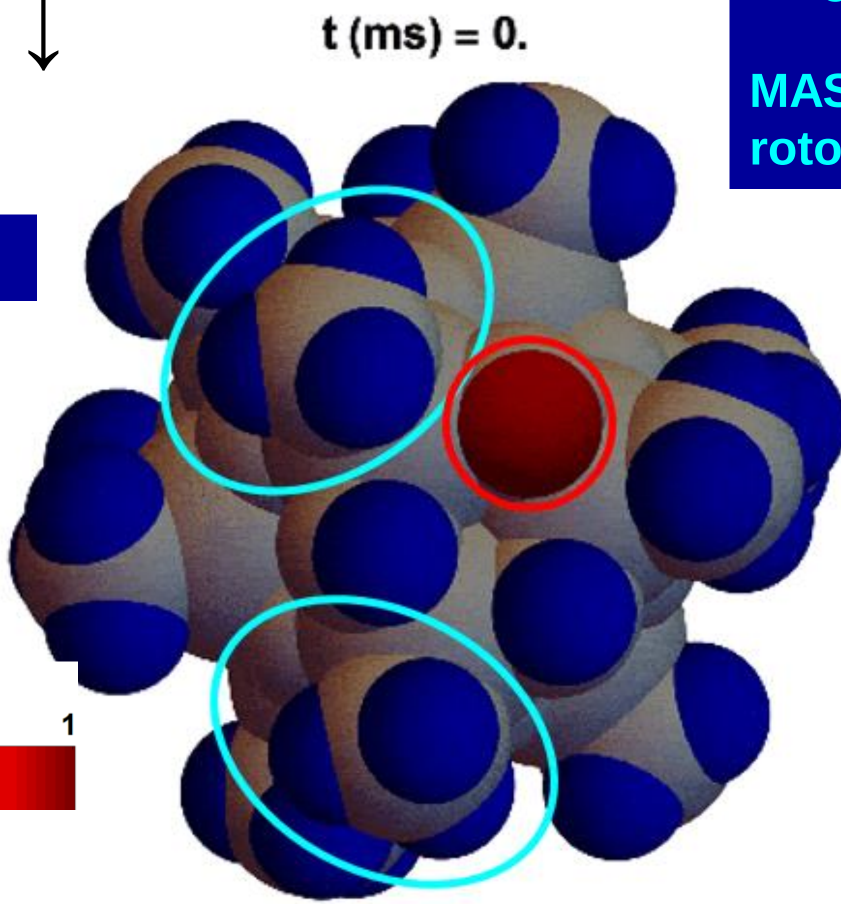


Coll.: F. Ribot, France

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

42 protons
« rigid » CH_3

MAS 10 kHz
rotor period 0.1 ms



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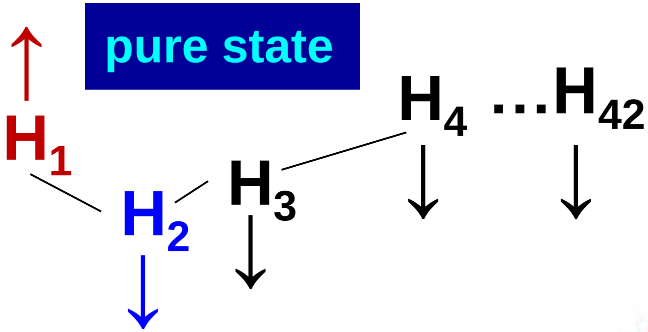

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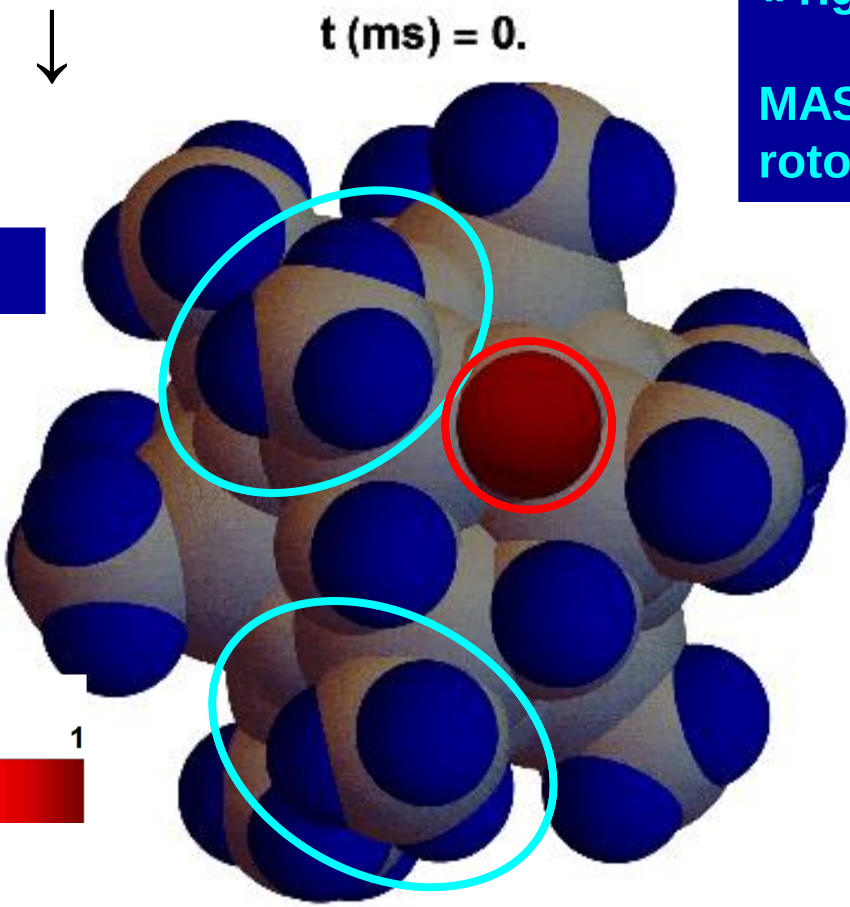
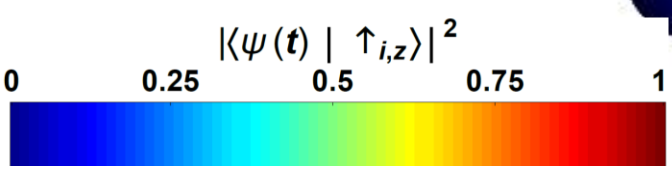
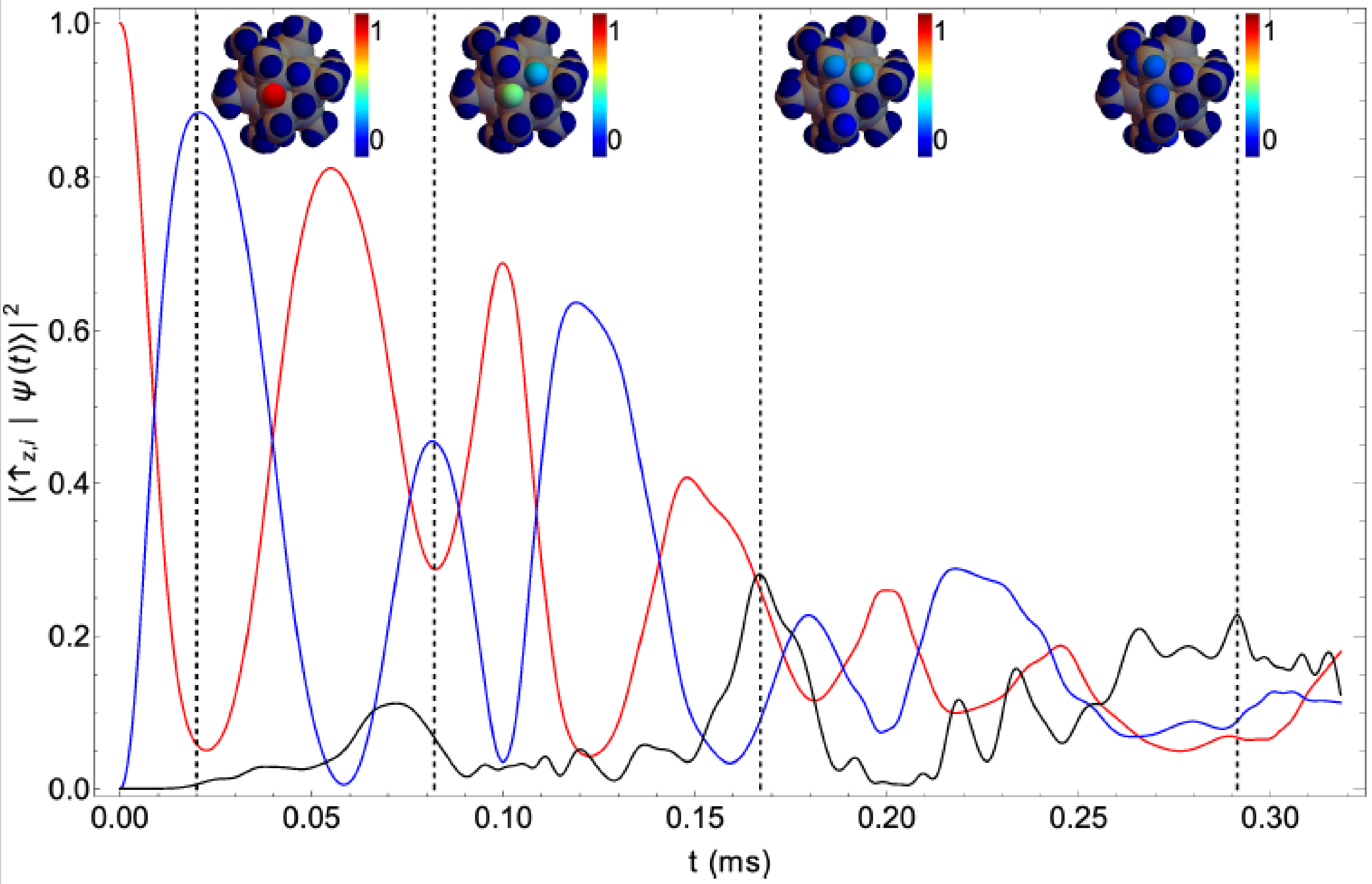
MAS 10 kHz
rotor period 0.1 ms





P.L. Giscard, C. Bonhomme, *to be submitted*

Applications – N spin systems, homonuclear dipolar Hamiltonian, H_D



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…

(very) warm thanks to P.-L. Giscard

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Algebraic Combinatorials

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Post doctoral position available in Paris: on NMR instrumentation & DNP