Theory of Solid State NMR: from Dyson, Magnus, Feynman to *Path-Sum*

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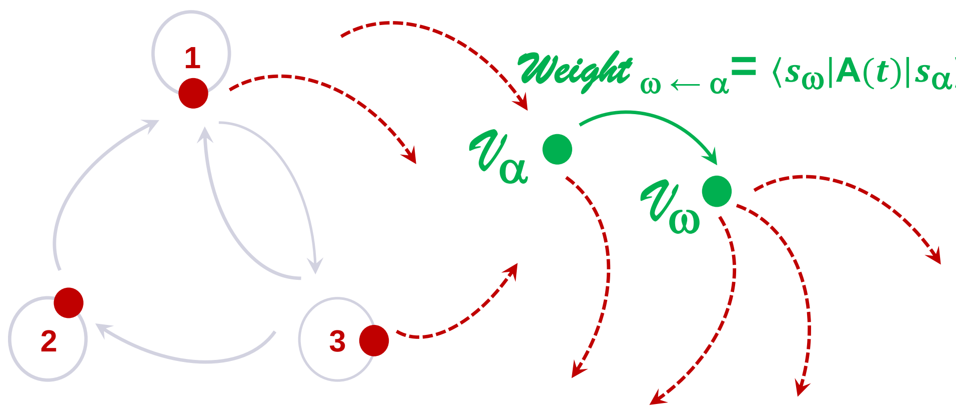

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General context

► **consider the *mathematical* problem of coupled LDE with non-constant coefficients a(t'), b(t')…**

$$\mathsf{A}(t')\mathsf{U}(t',t) = \frac{d}{dt'}\mathsf{U}(t',t), \quad \mathsf{U}(t,t) = \mathsf{Id},$$

N (finite)

$$\mathsf{A}(t') = \begin{pmatrix} a(t') & b(t') & \ldots \\ c(t') & \ldots & \ldots \\ \ldots & \ldots & \ldots \end{pmatrix} \text{ N}$$

bounded (over [*t* , *t'*])

Dyson time-ordering operator (1952)

$$\mathsf{U}(t',t) = \mathcal{T}\exp\left(\int_t^{t'} \mathsf{A}(\tau)\,d\tau\right)$$

Floquet (1883) (if A *periodic*)

Magnus (1954)

perturbative treatment

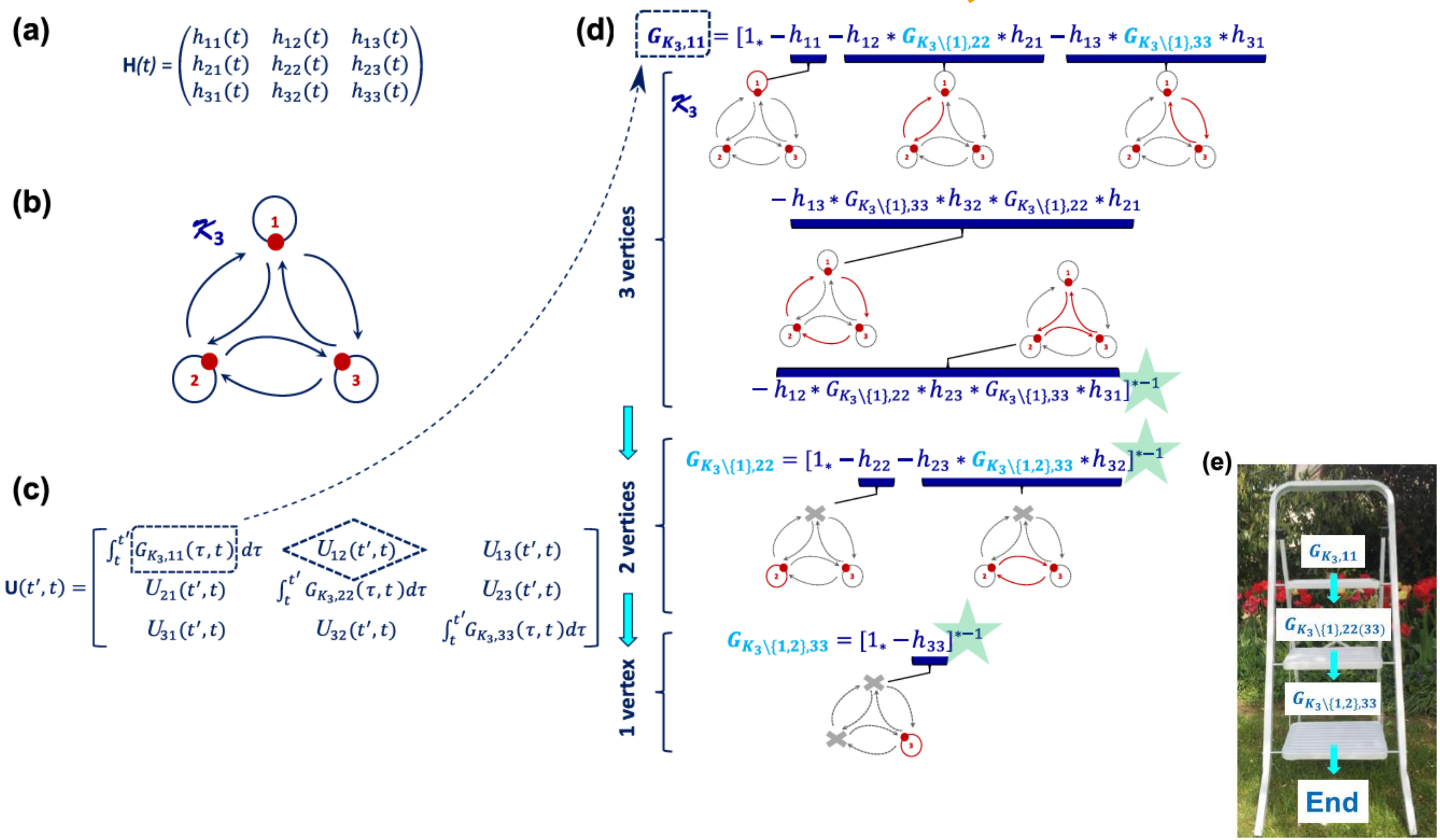
convergence (?)

The Path-Sum approach (P.-L. Giscard, 2015)

► Descending Ladder Principle (DLP)

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

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



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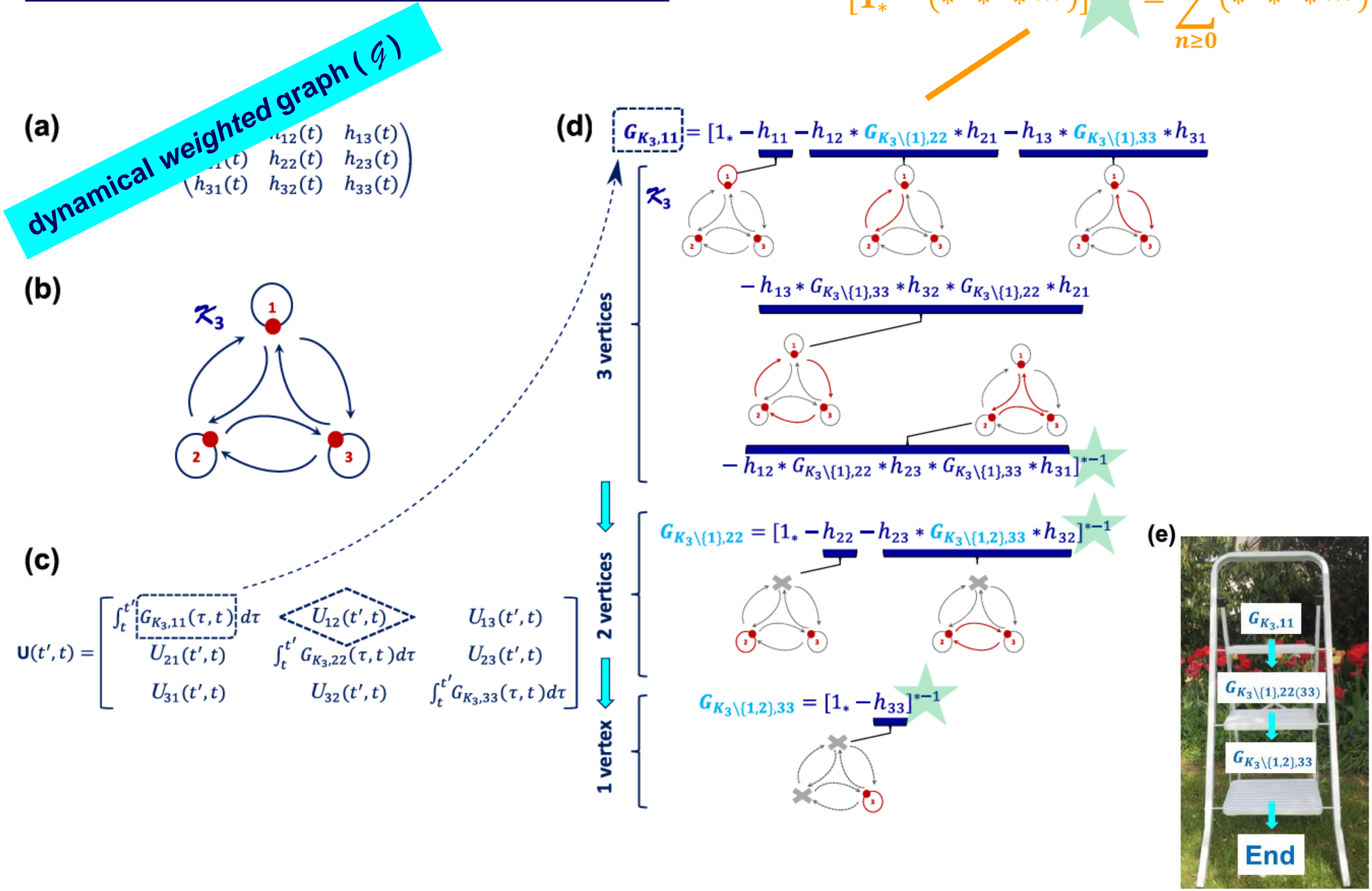

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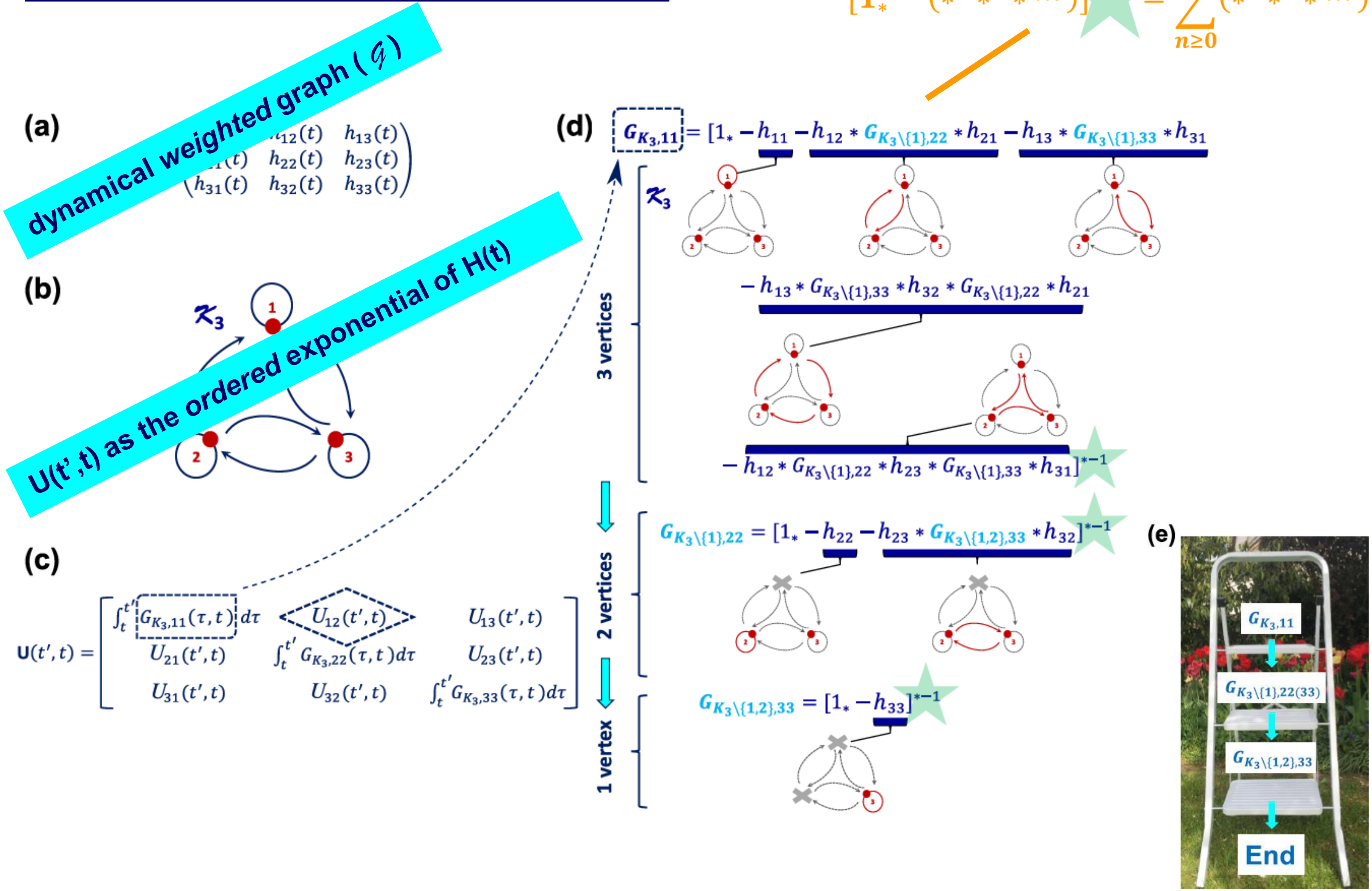

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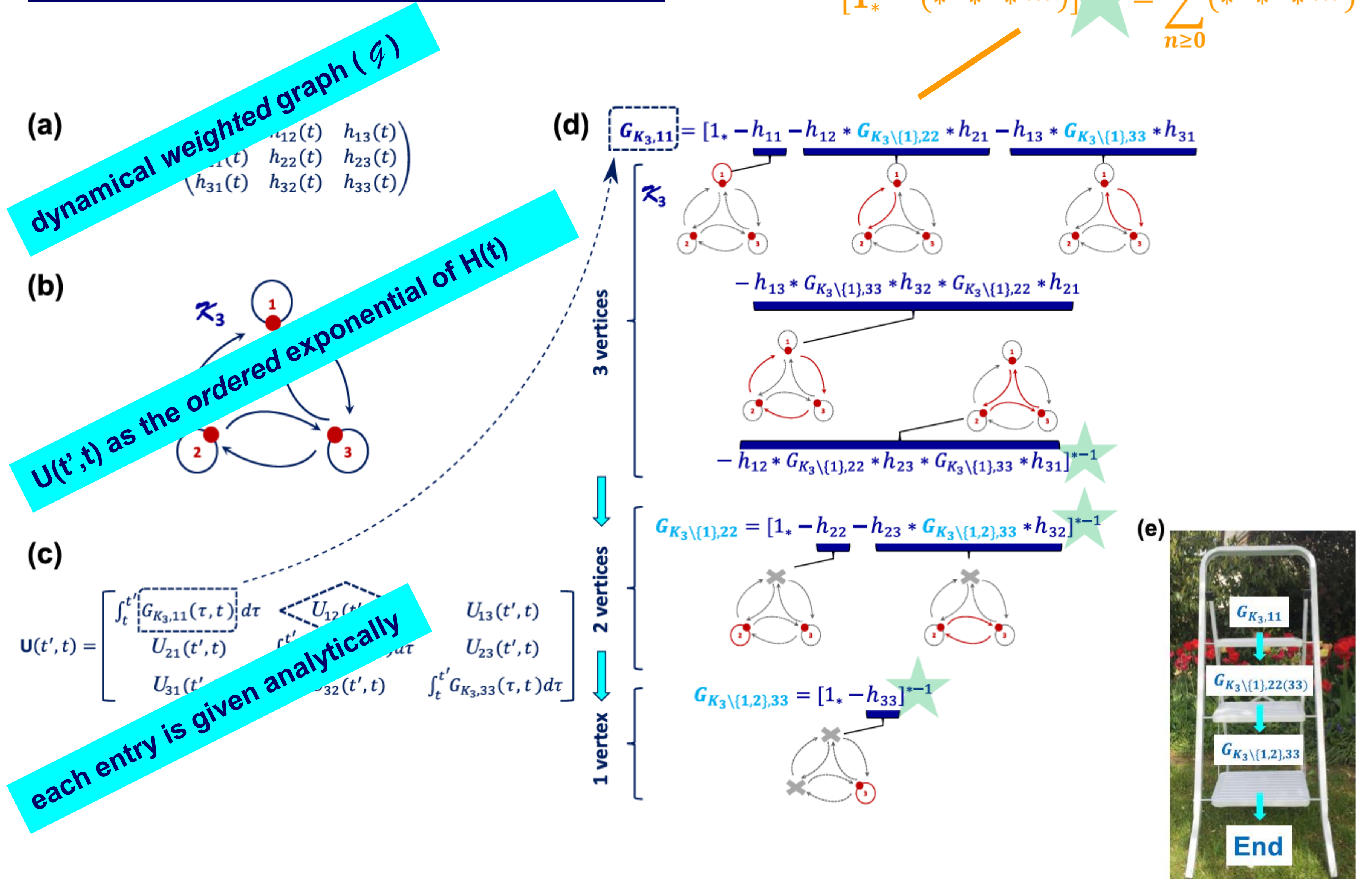

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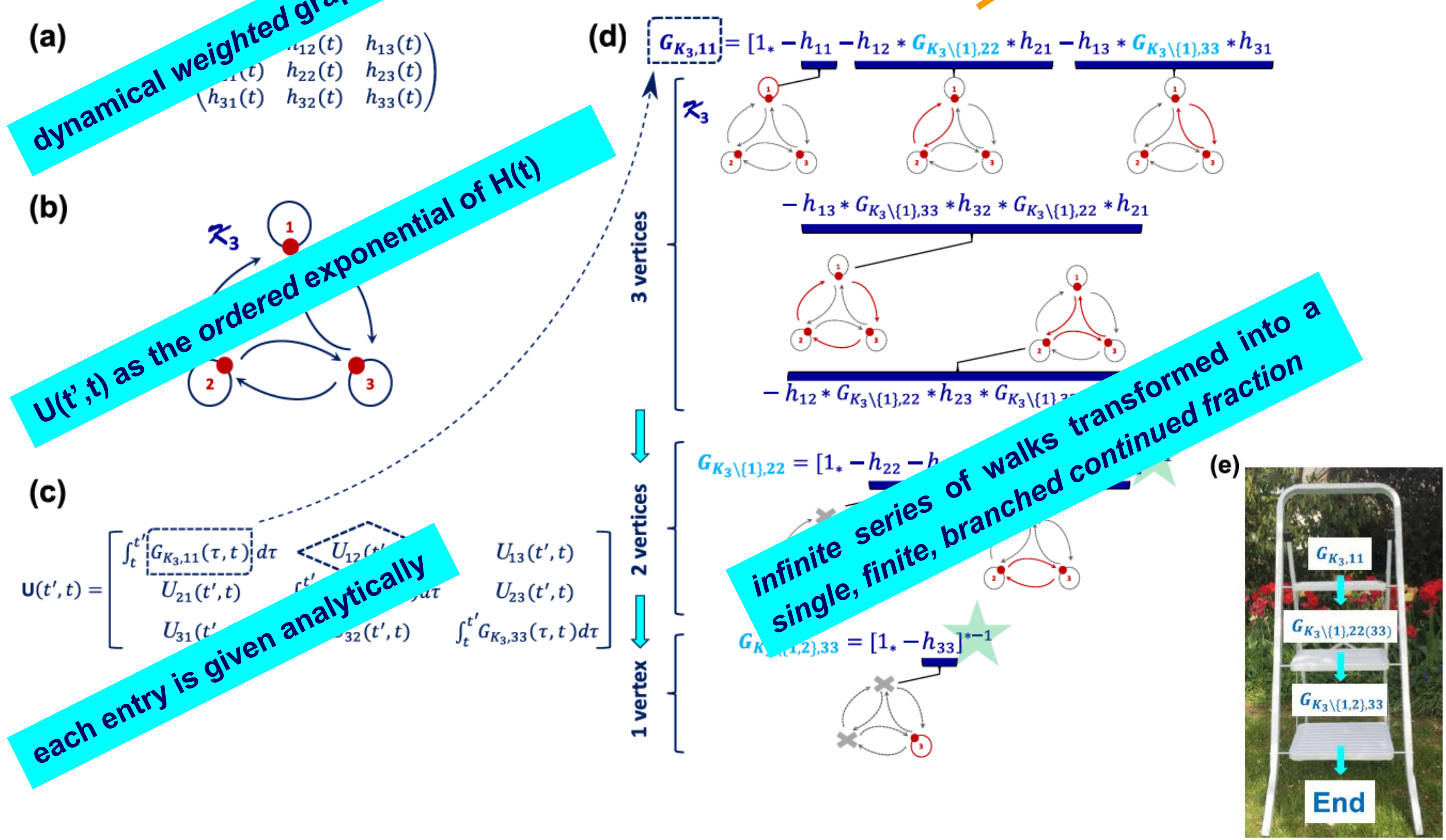


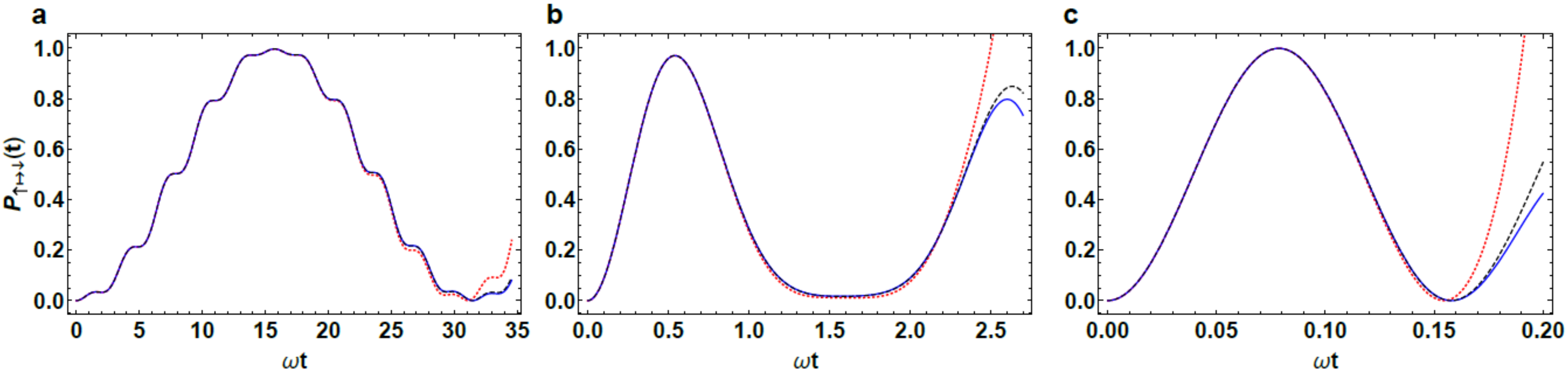
A test example (NMR, qubit physics…)

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

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

P(t) transition probability

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



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

► **Bloch-Siegert effect**

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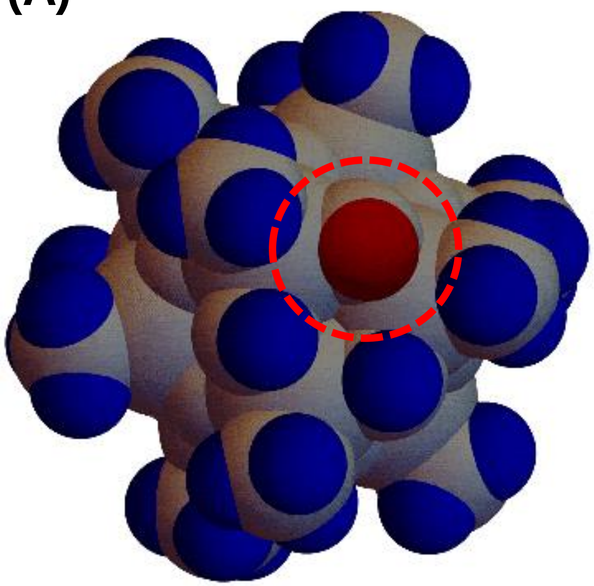
Scale invariance of Path-Sum

► Path-Sum can be used in conjunction with all *state-space reduction* techniques

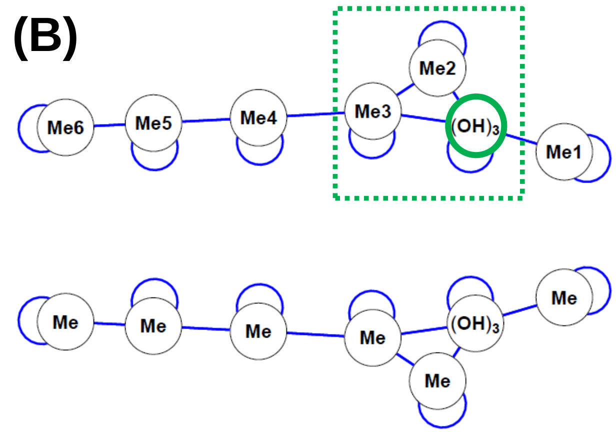
(A)



$(CH_3)_{12}(OH)_6Sn_{12}$
42 protons
MAS 10 kHz
pure state

PARTITIONS

(B)



$\mathcal{G}_t$

(C)

$$U_{(OH)_3} = 1 * \Big(\mathrm{Id}_* + i\mathrm{H}_{(OH)_3} + \mathrm{H}_{(OH)_3\mathrm{Me}_1} * \Gamma_1 * \mathrm{H}_{\mathrm{Me}_1(OH)_3} + \mathrm{H}_{(OH)_3\mathrm{Me}_2} * \Sigma_2 * \mathrm{H}_{\mathrm{Me}_2(OH)_3} + \mathrm{H}_{(OH)_3\mathrm{Me}_3} * \Sigma_3 * \mathrm{H}_{\mathrm{Me}_3(OH)_3} - i\,\mathrm{H}_{(OH)_3\mathrm{Me}_2} * \Gamma_2 * \mathrm{H}_{\mathrm{Me}_2\mathrm{Me}_3} * \Sigma_3 * \mathrm{H}_{\mathrm{Me}_3(OH)_3} - i\,\mathrm{H}_{(OH)_3\mathrm{Me}_3} * \Sigma_3 * \mathrm{H}_{\mathrm{Me}_3\mathrm{Me}_2} * \Sigma_2 * \mathrm{H}_{\mathrm{Me}_2(OH)_3} \Big)^{*-1},$$

$$\Sigma_2 = \frac{1}{\mathrm{Id}_* + i\mathrm{H}_{\mathrm{Me}_2} + \mathrm{H}_{\mathrm{Me}_2\mathrm{Me}_3} * \Sigma_3 * \mathrm{H}_{\mathrm{Me}_3\mathrm{Me}_2}},$$

$$\Sigma_3 = \frac{1}{\mathrm{Id}_* + i\mathrm{H}_{\mathrm{Me}_3} + \mathrm{H}_{\mathrm{Me}_3\mathrm{Me}_4} * \Sigma_4 * \mathrm{H}_{\mathrm{Me}_4\mathrm{Me}_3}},$$

$$\Sigma_4 = \frac{1}{\mathrm{Id}_* + i\mathrm{H}_{\mathrm{Me}_4} + \mathrm{H}_{\mathrm{Me}_4\mathrm{Me}_5} * \Sigma_5 * \mathrm{H}_{\mathrm{Me}_5\mathrm{Me}_4}},$$

$$\Sigma_5 = \frac{1}{\mathrm{Id}_* + i\mathrm{H}_{\mathrm{Me}_5} + \mathrm{H}_{\mathrm{Me}_5\mathrm{Me}_6} * \Gamma_6 * \mathrm{H}_{\mathrm{Me}_6\mathrm{Me}_5}},$$

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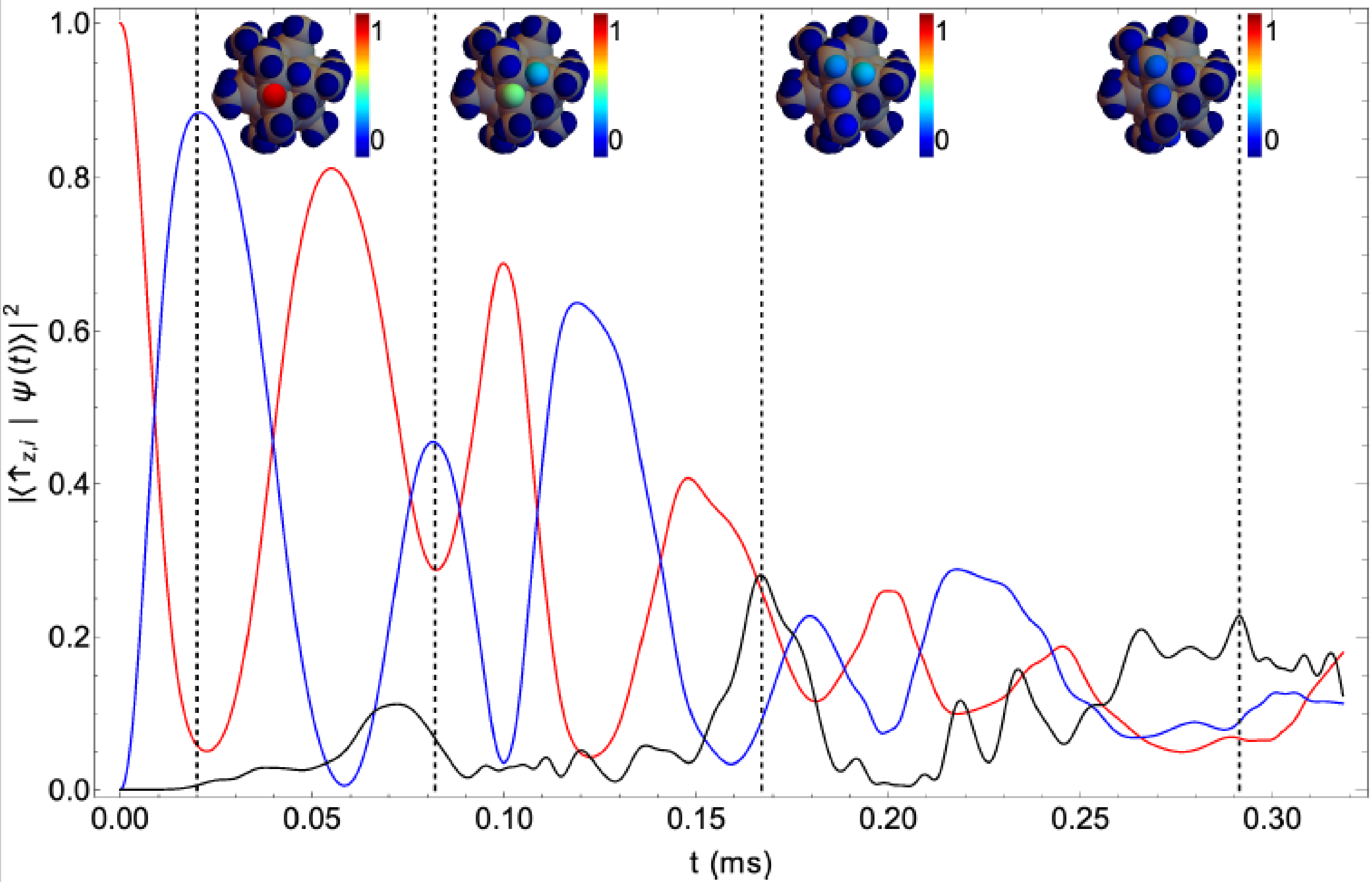
Scale invariance of Path-Sum



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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