Fresh insights onto diffusion-controlled reactions via Dirichlet-to-Neumann operators

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Mathematical aspects of the physics with non-self-adjoint operators (July 10-15, 2022, Banff, Canada)

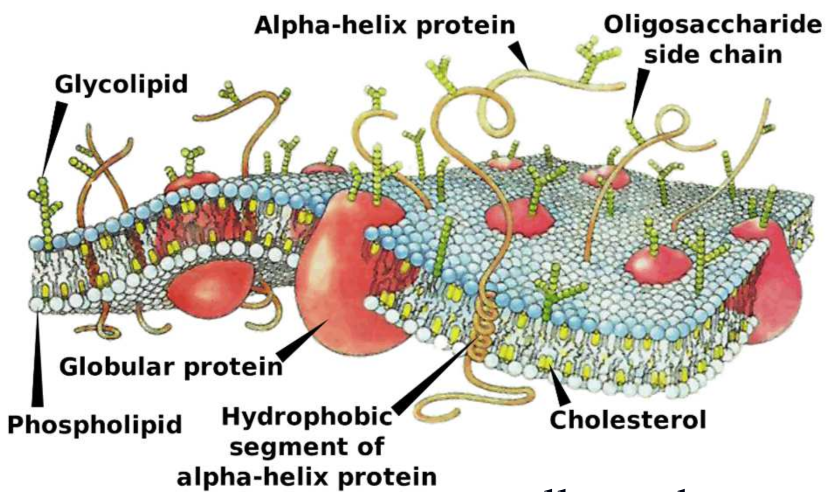
Outline of the talk

- Physical motivation
- Probabilistic description
- Spectral description
- Open problems
- Perspectives

DG, Phys. Rev. Lett. 125, 078102 (2020)
DG, J. Phys. A: Math. Theor. 55, 045203 (2022)

https://pmc.polytechnique.fr/pagesperso/dg/publi/publi_e.htm

Various phenomena on surfaces



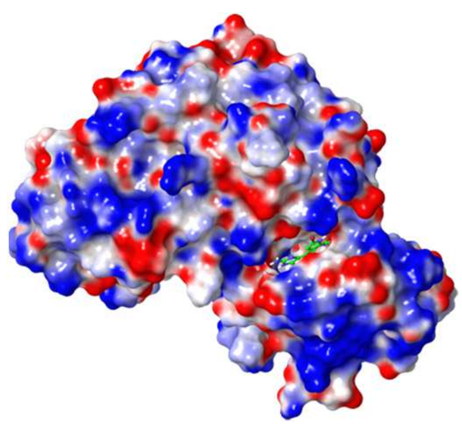
cell membrane

Heterogeneous catalysis

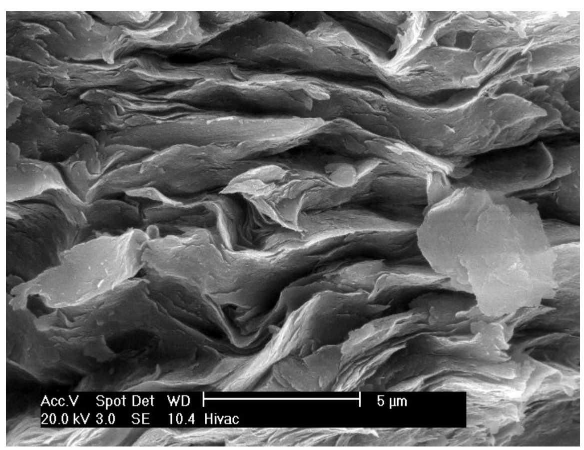
Biochemical processes

Permeation and filtering

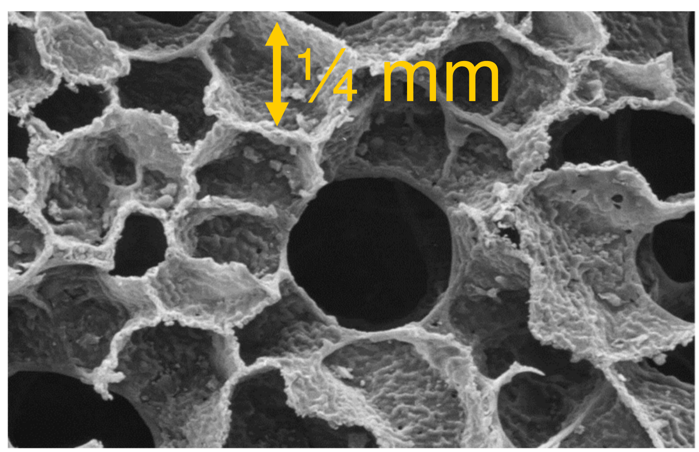
Surface relaxation in NMR



protein surface

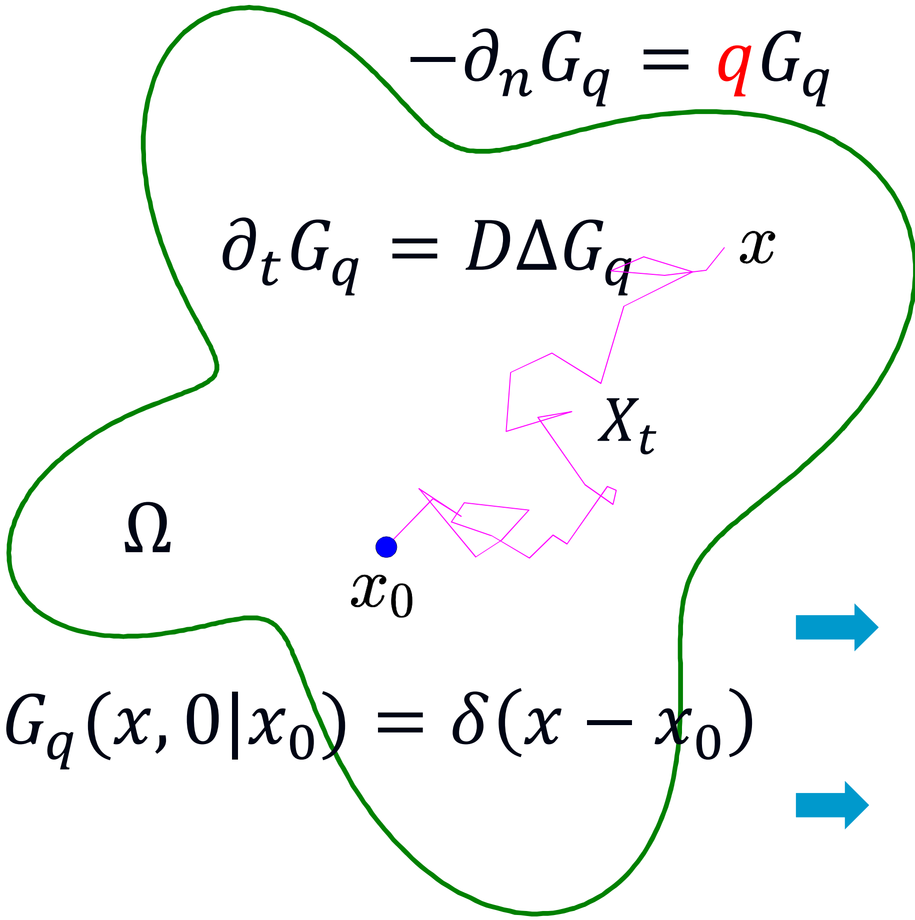


shales



human alveolar surface

Various phenomena on surfaces



$G_q(x, t|x_0)$

Reactivity $q = \kappa / D$

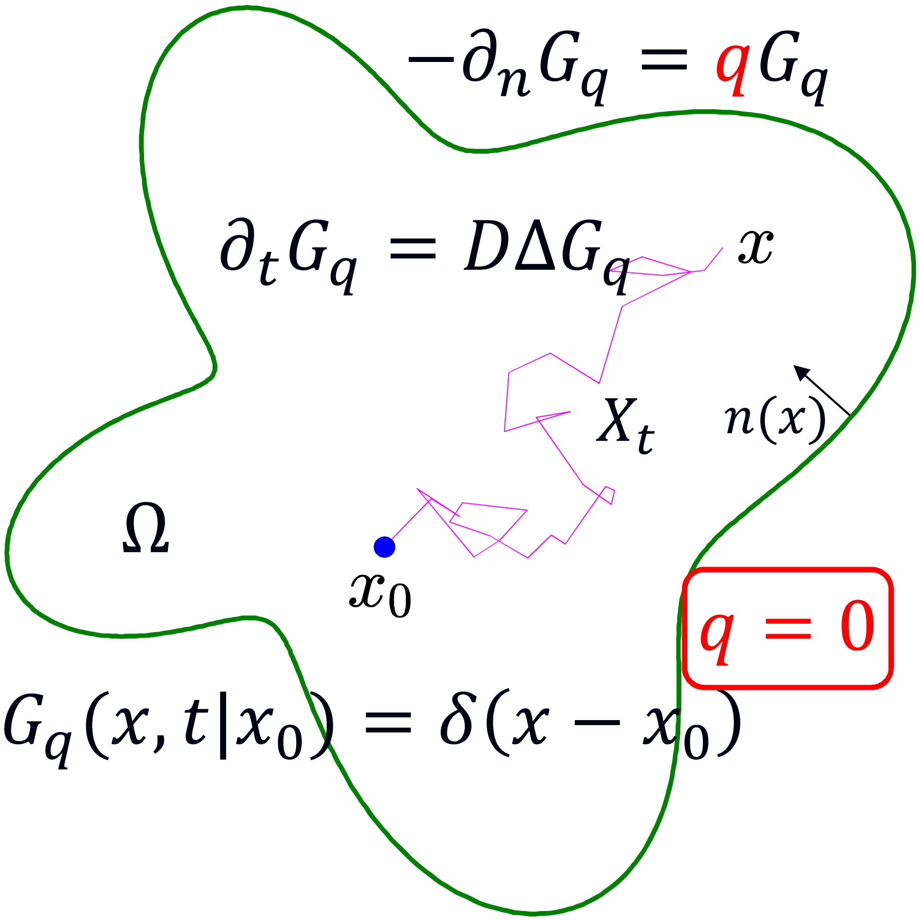
- $q = 0$ fully inert
- $q = \infty$ perfectly reactive
- $q > 0$ partially reactive

Disadvantages

- Propagator G_q depends implicitly on q through the boundary condition
- Bulk dynamics/geometry are tightly coupled to surface reactions in G_q

Smoluchowski, Z. Phys. Chem. 92U, 129 (1917)
Collins & Kimball, J. Coll. Sci. 4, 425 (1949)
Redner, *A Guide to First Passage Processes* (2001)

Encounter-based approach



$$-\partial_n G_q = q G_q$$

$$\partial_t G_q = D \Delta G_q$$

$$q = 0$$

$$G_q(x,t|x_0) = \delta(x - x_0)$$

Langevin (Skorokhod) equation

$$dX_t = \sqrt{2D}\, dW_t + n(X_t)\, d\ell_t$$

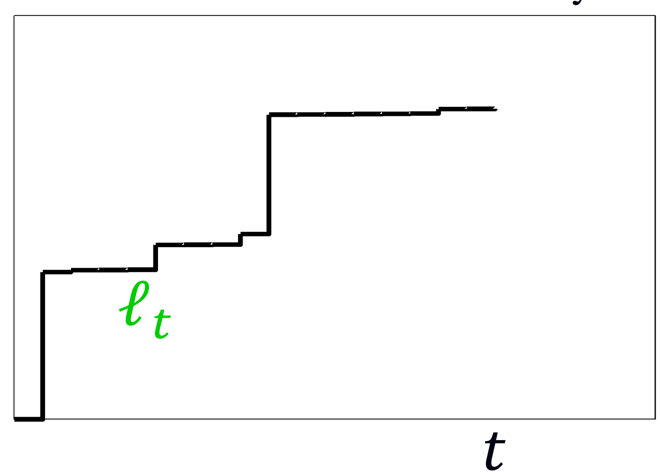
random displacements in the bulk

reflections on the boundary

boundary local time

$$\ell_t = \lim_{a\to 0} \frac{D}{a} \int_0^t I_{\partial\Omega_a}(X_s)\, ds$$

residence time in a thin surface layer



One equation determines (X_t, ℓ_t)

Full propagator: $P(x, \ell, t|x_0)$

DG, PRL 125, 078102 (2020)

Encounter-based approach

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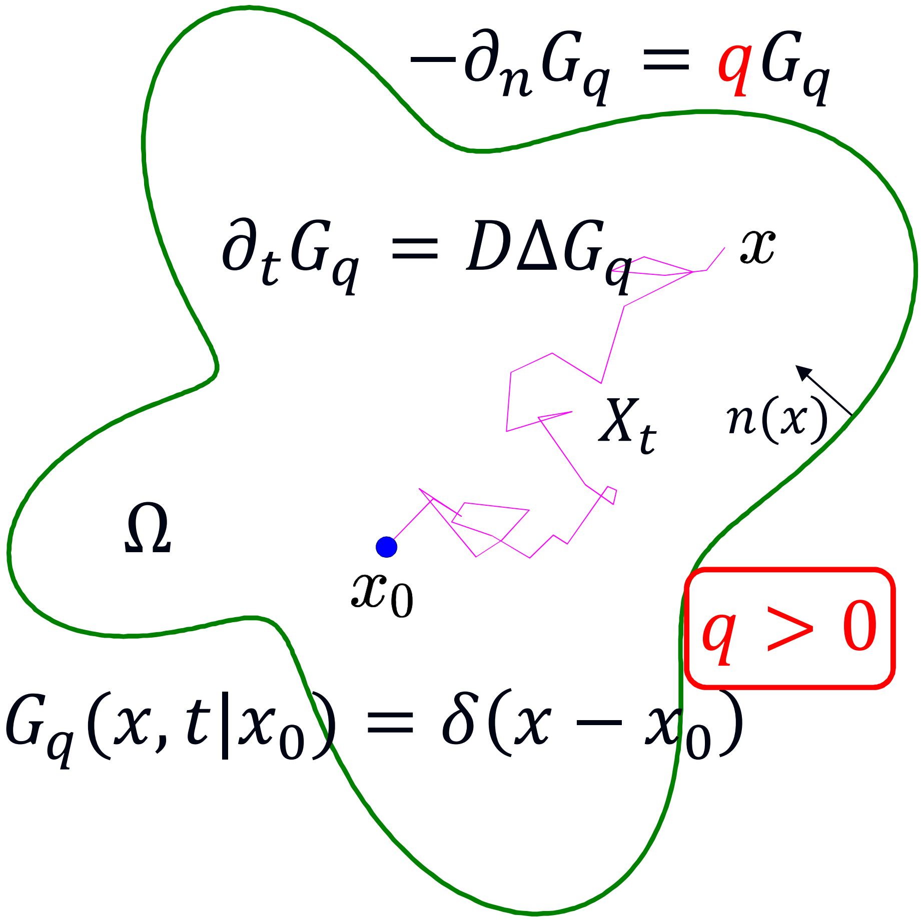
$$\partial_t G_q = D \Delta G_q$$



$$q > 0$$

$$G_q(x,t|x_0) = \delta(x - x_0)$$

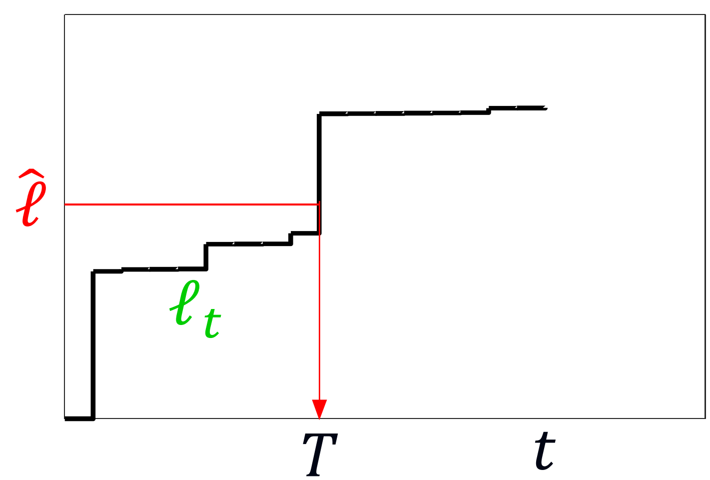
Langevin (Skorokhod) equation

$$dX_t = \sqrt{2D}\, dW_t + n(X_t) d\ell_t$$

random displacements in the bulk — reflections on the boundary

$$P\{\hat{\ell} > \ell\} = e^{-q\ell}$$

$$T = \inf\{t > 0 : \ell_t > \hat{\ell}\}$$



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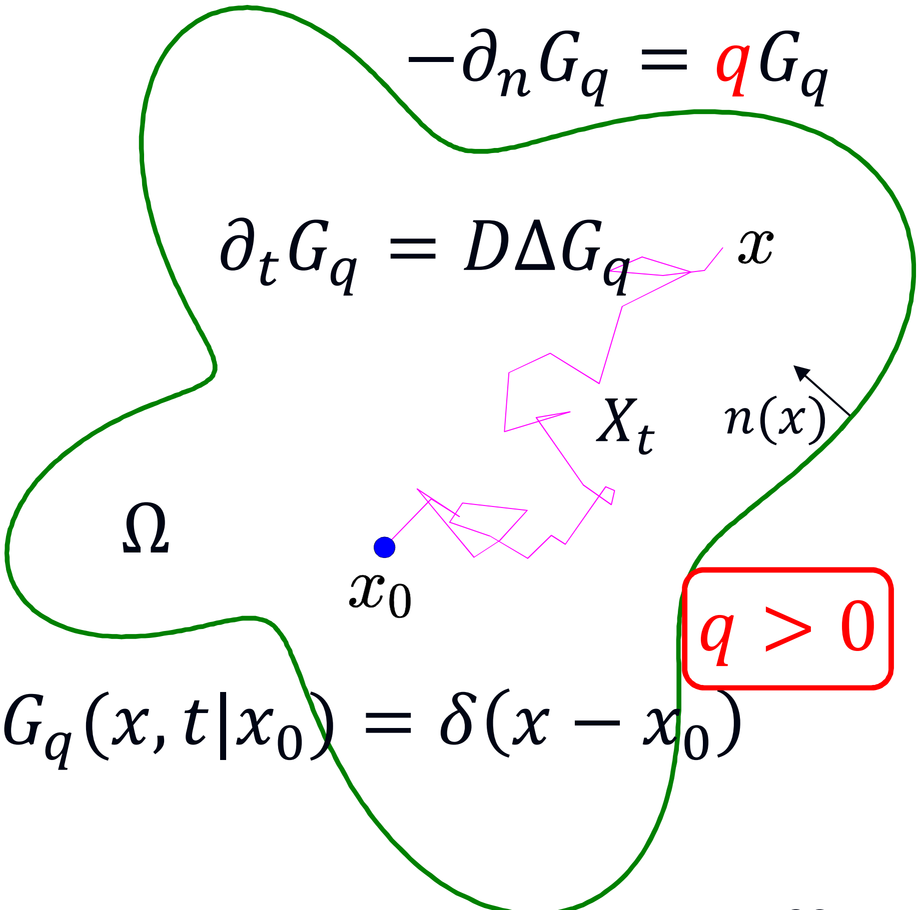
DG, PRL 125, 078102 (2020)

Encounter-based approach



$$-\partial_n G_q = q G_q$$

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random displacements in the bulk

reflections on the boundary

$$P\{\hat{\ell} > \ell\} = e^{-q\ell}$$

$$T = \inf\{t > 0 : \ell_t > \hat{\ell}\}$$

Reactivity *q* appears **explicitly**

$$G_q(x,t|x_0) = \int_0^\infty d\ell \;\; e^{-q\ell} \; P(x,\ell,t|x_0)$$

DG, PRL 125, 078102 (2020)

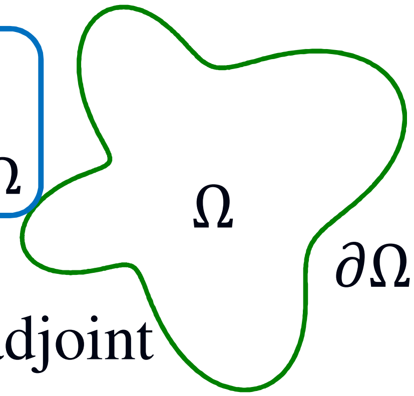
Spectral description

Dirichlet-to-Neumann operator

Let $\Omega \subset R^d$ with a bounded "smooth" boundary $\partial\Omega$, and $p \geq 0$

$$(-\Delta + p)w = 0 \quad \text{in } \Omega$$
$$w = f \quad \text{on } \partial\Omega$$

$$M_p: f \to g = \partial_n w \Big|_{\partial\Omega}$$



If the boundary is "smooth enough", then M_p is a self-adjoint pseudo-differential operator, $M_p: H^{\frac{1}{2}}(\partial\Omega) \to H^{-\frac{1}{2}}(\partial\Omega)$, with a discrete spectrum of eigenvalues $0 \leq \mu_0^{(p)} \leq \mu_1^{(p)} \leq \cdots \nearrow +\infty$ and eigenfunctions $\{v_k^{(p)}\}$ forming a complete basis of $L_2(\partial\Omega)$

Let $V_k^{(p)}(x)$ be an extension of $v_k^{(p)}$ to Ω

$$(-\Delta + p)V_k^{(p)} = 0 \quad \text{in } \Omega$$
$$\partial_n V_k^{(p)} = \mu_k^{(p)} V_k^{(p)} \quad \text{on } \partial\Omega$$

the Steklov problem

Arendt & ter Elst, J. Diff. Eq. 251, 2100 (2011); Girouard & Polterovich, J. Spectr. Th. 7, 321 (2017)

Dirichlet-to-Neumann operator

Compute $P(x,\ell,t|x_0)$? $\tilde{P}(x,\ell,p|x_0) = \int_0^\infty dt\, e^{-pt}\, P(x,\ell,t|x_0)$

$$\tilde{P}(x,\ell,p|x_0) = \tilde{G}_\infty(x,p|x_0)\delta(\ell) + \frac{1}{D}\sum_{k=1}^{\infty} V_k^{(p)}(x_0)V_k^{(p)}(x)\, e^{-\mu_k^{(p)}\ell}$$

$$G_q(x,t|x_0) = \sum_{k=1}^{\infty} u_k^{(q)}(x_0)u_k^{(q)}(x)\, e^{-\lambda_k^{(q)}t}$$

$$-D\Delta u_k^{(q)} = \lambda_k^{(q)}u_k^{(q)} \quad \text{in } \Omega$$
$$-\partial_n u_k^{(q)} = q u_k^{(q)} \quad \text{on } \partial\Omega$$

$$\Delta_q \Rightarrow M_p$$

$$(-\Delta + p)V_k^{(p)} = 0 \quad \text{in } \Omega$$
$$\partial_n V_k^{(p)} = \mu_k^{(p)} V_k^{(p)} \quad \text{on } \partial\Omega$$

the Steklov problem

DG, JCP 151, 104108 (2019); DG PRL 125, 078102 (2020)

M_p **(Possibly) open problems**

- Small-p asymptotic behavior?
  Irregular boundary?
  $\mu_0^{(p)} = \frac{|\Omega|}{|\partial\Omega|} p^{\alpha} + O(p^2)$ (bounded)
  $\mu_0^{(p)} \simeq \frac{c_1}{c_2 - \ln p}$ (exterior of a disk)
  $\mu_0^{(p)} \to \mu_0^{(0)} > 0$ (exterior of a ball)

  Conjecture:
  $\mu_0^{(0)} > 0 \Leftrightarrow$ transient diffusion

- Large-p asymptotic behavior? $\mu_k^{(p)} \propto \sqrt{p}$

- Large-k asymptotic behavior (Weyl-type law)?

- Geometric structure of functions $V_k^{(p)}$?

- Extension to $p \in \mathbb{C}$? Non-self-adjoint operator!

$$\tilde{P}(x,\ell,p|x_0) = \tilde{G}_\infty(x,p|x_0)\delta(\ell) + \frac{1}{D}\sum_{k=1}^{\infty} V_k^{(p)}(x_0) V_k^{(p)}(x)\, e^{-\mu_k^{(p)}\ell}$$

DG, PRE 100, 062110 (2019); J. Phys. A 54, 015003 (2021); J. Phys. A 55, 045203 (2022)

M_p # (Possibly) open problems

- Small-p asymptotic behavior? Irregular boundary?
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- Geometric structure of functions $V_k^{(p)}$?
- Extension to $p \in \mathbb{C}$? Non-self-adjoint operator!
- Extension to p being a function? $\Delta \to$ Fokker-Planck operator

DG, PRE 100, 062110 (2019); J. Phys. A 54, 015003 (2021); J. Phys. A 55, 045203 (2022)

Perspectives

- Discovery of many unknown properties
- Extension to the non-self-adjoint case
- Spectral properties versus geometric structure
- Relations to probabilistic description
- Applications to diffusion-controlled reactions

Looking for collaborations!

https://pmc.polytechnique.fr/pagesperso/dg/publi/publi_e.htm