Reduced-order modeling techniques in Computational chemistry

Department of Mathematics

Penn State University

Xli@math.psu.edu

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Outline

- Dynamics models in computational chemistry
  - Classical molecular dynamics (MD)
  - Quantum electron dynamics (QED)
- Mori-Zwanzig projection for MD
  - Rational approximations of the memory
  - Consistency with the fluctuation-dissipation relation
  - Subspace projections
- Reduced Liouville von Neumann equation for QED
  - Projection for the density-operator
  - Long-range interactions

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Collaborators

Weiqi Chu (Umass)

Huan Lei (MSU)

Lina Ma (Trinity College)

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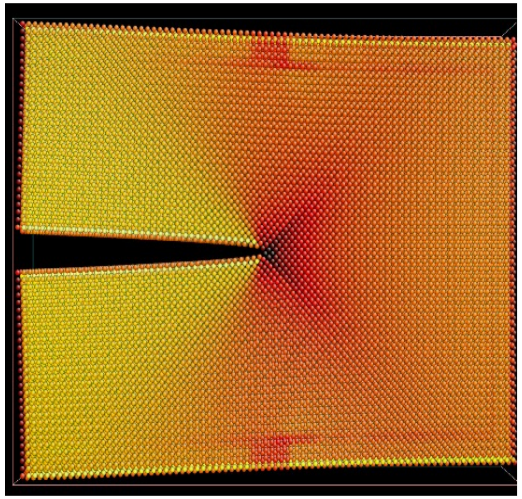
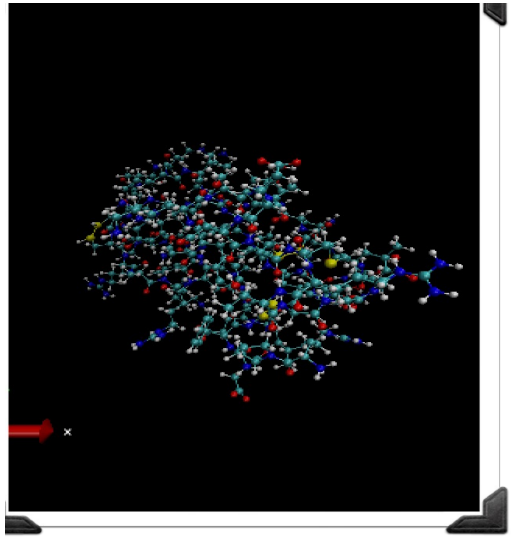
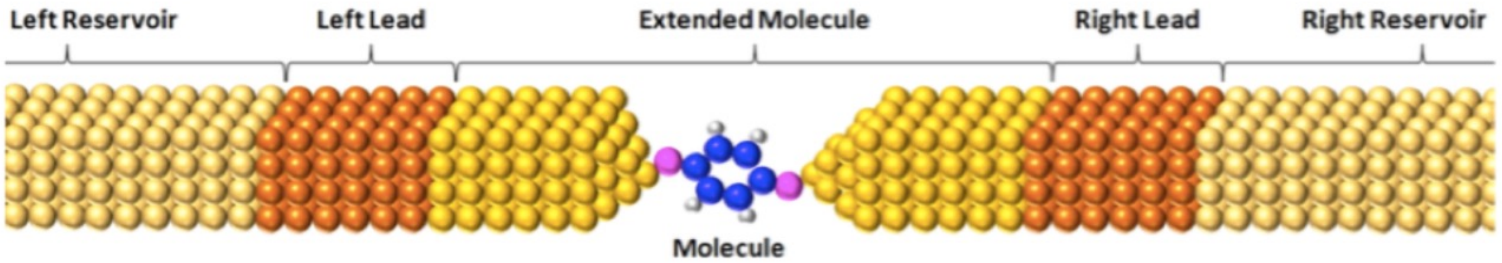
Models based on first principles

- Models with molecules/atoms/electrons
- Simple mathematical models.
- Overwhelming number of degrees of freedom
- Strong interactions.
- Fast inherent time scale ($10^{-18} - 10^{-15} s$)







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Dynamics models

Molecular dynamics

$$\begin{cases} \dot{x}_i = v_i, & x(0) = x_0, \\ m_i \dot{v}_i = f_i(x) = -\dfrac{\partial V(x)}{\partial x_i}, & v(0) = v_0. \end{cases}$$

- $x = (x_1, x_2, \cdots, x_N) \in \mathbb{R}^{3N}$
- v$= (v_1, v_2, \cdots, v_N) \in \mathbb{R}^{3N}$
- $V(x) = \sum_{i,j} \Phi(x_i, x_j) + \sum_{i,j,k} W(x_i, x_j, x_k)$
- Bond stretching/angles,Coulomb, Lennard-Jones
- $x_0, v_0 \sim \rho(x_0, v_0)$.

Driven Electron Dynamics

$$\partial_t \rho(t) = -i[H[n(t), t], \rho(t)]$$

- $\rho, H \in \mathbb{C}^{N \times N}$ and $n = \mathrm{diag}(\rho)$
- Hermitian property $\rho = \rho^*, H = H^*$
- Hamiltonian from TDDFT
- $H = -\frac{1}{2}\nabla^2 + V_{\text{nuclei}} + V_H[n(t)] + V_{XC}[n(t)] + U_{ext}(t)$
- Hartree : $V_H[n](x) = \int_\Omega \frac{n(x')}{|x - x'|} dx'$
- Exchange-correlation: $V_{XC}[n]$

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Part I. Coarse-graining molecular dynamics

Ma, Lina, Xiantao Li, and Chun Liu. "The derivation and approximation of coarse-grained dynamics from Langevin dynamics." ***The Journal of chemical physics*** 145.20 (2016).

Lei, Huan, Nathan A. Baker, and Xiantao Li. "Data-driven parameterization of the generalized Langevin equation." ***Proceedings of the National Academy of Sciences*** 113.50 (2016): 14183-14188.

Ma, Lina, Xiantao Li, and Chun Liu. "Coarse-graining Langevin dynamics using reduced-order techniques." ***Journal of Computational Physics*** 380 (2019): 170-190.

Chu, Weiqi, and Xiantao Li. "The Mori–Zwanzig formalism for the derivation of a fluctuating heat conduction model from molecular dynamics." ***Communications in Mathematical Sciences*** 17.2 (2019).

Chu, Weiqi, and Xiantao Li. "Nonlinear constitutive models for nano-scale heat conduction." ***Multiscale Modeling & Simulation*** 19.1 (2021): 533-549.

Lei, Huan, and Xiantao Li. "Petrov–Galerkin methods for the construction of non-Markovian dynamics preserving nonlocal statistics." ***The Journal of Chemical Physics*** 154.18 (2021)

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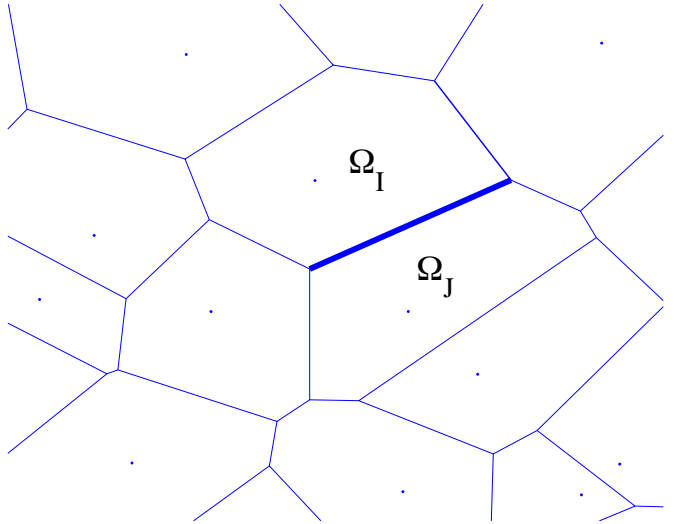
Perspective from Koopman

I. Mezic 2013; E Kaiser, JN Kutz, SL Brunton 2021.

- Dynamical system: $(x_0, v_0) \to \big(x(t), v(t)\big)$.
- Coarse-grain variables $a(x(t), v(t))$
  - The center of mass of residues (protein dynamics)
  - Local displacement and velocity (solid materials)
  - Local energy (nano-scale heat conduction)
- Trajectory-wise view: $A(x_0, v_0, t) = a(x(t), v(t))$
- Liouville operator: $L = v_0 \partial_{x_0} + \frac{1}{m} f(x_0) \partial_{v_0}$
- Variational equation: $\partial_t A = LA$.
- In Stat. Mech. This is directly expressed as $\dot{a}(t) = La(t)$.
- The nonlinear ODEs are expressed as linear PDEs.



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Mori-Zwanzig projection

(Nakajima 1958, Mori 1965, Zwanzig 1973, Chorin 1998, Li-E 2007)

Define a projection P onto space spanned by b,

$$P \cdot := \langle \cdot, b \rangle \langle b, b \rangle^{-1} b.$$

where $\langle g(t), b \rangle_{ij} = \int g_i(x_0, v_0, t) b_j(x_0, v_0, 0) \rho(x_0, v_0) dx_0 dv_0$.

Dyson's formula: $e^{t(A+B)} = \int_0^t e^{(t-s)(A+B)} A e^{sB} ds + e^{tB}$.

Dynamics of $a(t)$: $\dot{a}(t) = e^{tL} La = e^{tL} PLa + e^{tL} QLa$

$$\dot{a}(t) = e^{tL} PLa + \int_0^t e^{tL} PL e^{(t-s)QL} QLa \, ds + e^{tQL} QLa.$$

MZ Equations $\dot{a}(t) = \Omega b(t) + \int_0^t \theta(t-s) b(s) d + R(t),$

where $\Omega = \langle La, b \rangle \langle b, b \rangle^{-1}, R(t) = e^{tQL} QLa, \theta(s) = \langle L e^{sQL} QLa, b \rangle \langle b, b \rangle^{-1}$.

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Markovian embedding

MZ Equations $\dot{a}(t) = \Omega b(t) + \int_0^t \theta(t-s)b(s)ds + R(t)$ (Generalized Langevin)

Laplace transform of the kernel function $\hat{\theta}(\lambda) = \int_0^{+\infty} \theta(t)e^{-t/\lambda}dt$

Rational approximation $N_{k,k}(\lambda) = \left(I - \lambda B_1 - \cdots - \lambda^k B_k\right)^{-1}\left(A_0 + \lambda A_1 + \cdots + \lambda^k A_k\right) \approx \hat{\theta}(\lambda)$

- ❑ Zeroth order approximation:
  - $\dot{a}(t) = (\Omega + \Gamma)b(t) + F(t)$
- ❑ First order approximation:
  - $\dot{a}(t) = \Omega b(t) + z(t)$
  - $\dot{z}(t) = Ab(t) + Bz(t) + F(t)$
- ❑ Higher order approximation:

$$\begin{cases} \dot{a} = \Omega b + e^{\mathrm{T}} z \\ \dot{z} = Ab + Bz \end{cases}$$

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How to determine the coefficients?

- Statistical inference (Kalman filter, Fricks et al 2009, Harlim and Li 2015, Chorin and Lu, 2015, LSTM?)
- Integral equation

$$\langle \dot{a}(t), b(0) \rangle = \Omega \langle b(t), b(0) \rangle - \theta \star \langle a(t), b(0) \rangle$$

- Moment matching

$$\Theta(\lambda) = \int_0^{+\infty} \theta(t) e^{-t/\lambda} dt = M_1 \lambda + M_2 \lambda^2 + \cdots$$

- Pade-Hermite approximation

$$R_{k,k} = [I - \lambda B_1 - \cdots - \lambda^k B_k]^{-1} [\lambda A_1 + \cdots + \lambda^k A_k]$$

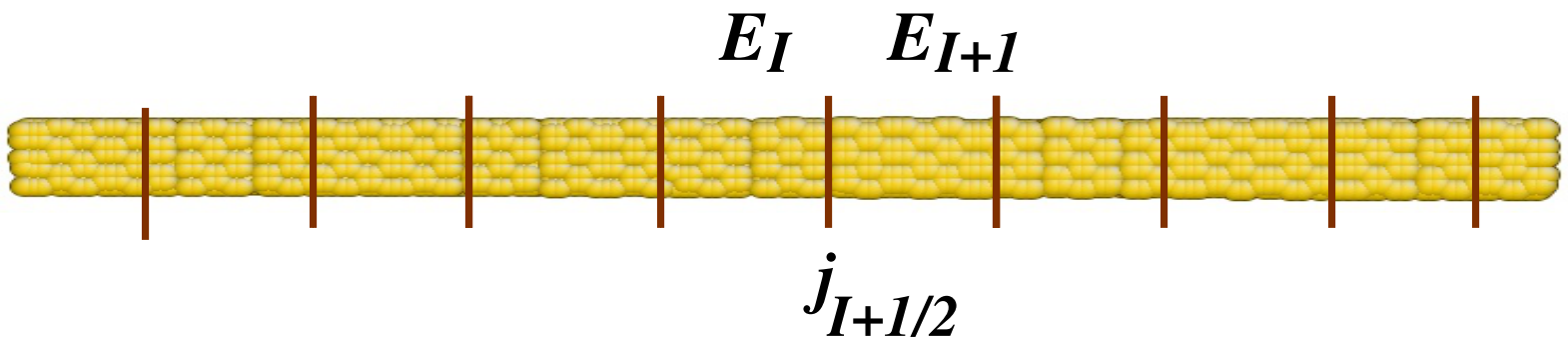
- **Short–time statistics**
  - $R_{k,k}(0) = \Theta(0)$
  - $R'_{k,k}(0) = \Theta'(0)$
  - $R''_{k,k}(0) = \Theta''(0)$

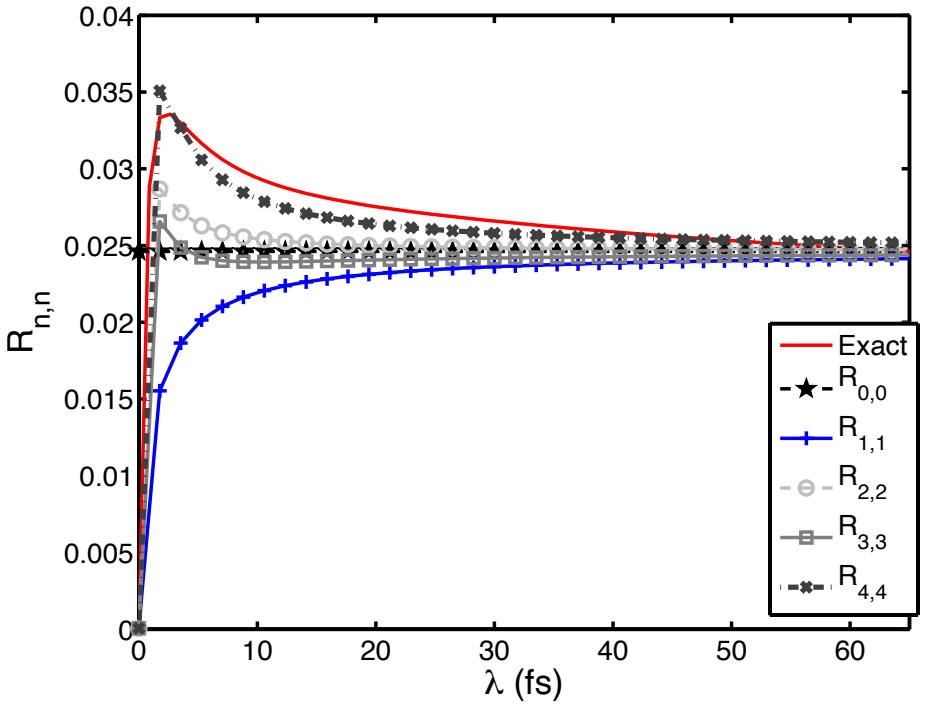
- **Long-time statistics**

$$\lim_{\lambda \to \infty} R_{k,k}(\lambda) = \lim_{\lambda \to \infty} \Theta(\lambda)$$

These conditions involve the statistics of $a(t)$ & $b(t)$

Results from rational interpolation (Chu-Li, 2021)





Testing the rational approx

- Cabon nano-tube;
- Tersoff potential;
- 3D atomistic model
- 1D partition
- 6^{th} order symplectic integrator to generate data
- Time correlation of the heat flux

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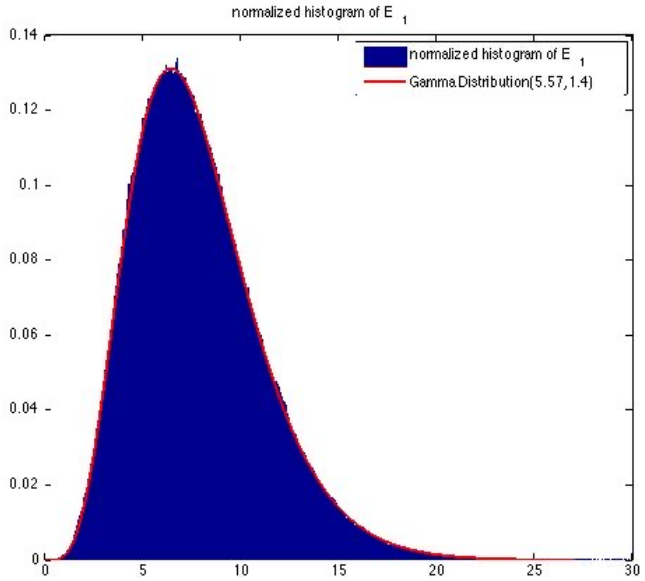
Marginal density

- $a(t)$ can be considered as part of (x(t),v(t)). $p(a) = \int p(x,v)\delta(a(x,v) - a)dxdv$
- The PDF of the observations $a(t)$ can be obtained from data
  - Local momentum: Gaussian
  - Reaction coordinates: Usually not Gaussian
  - Local energy: often follows a Gamma distribution
- If $b \propto a \Rightarrow$ reduced SDEs: linear drift term
- If the noise is additive $\Rightarrow a \sim N(\mu, \Sigma)$.

Theorem (Chu & Li, 2019, CMS). There exists an SDE system with linear drift and *multiplicative* noise, such that the stationary density is a Gamma distribution.



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Projection to potential of mean force (PMF)

- Given data at equilibrium, write $\rho_{eq}(a) = \Xi_0^{-1}\, exp\big(-S(a)\big)\,.$

Define $b = -\dfrac{\delta S(a)}{\delta a}$ –– potential of mean force (PMF)

Theorem *(Chu & Li, MMS. 2021)* $\rho_{eq}(a)$ is guaranteed to be the stationary density of the Fokker–Planck equations in the reduced models with additive noise.

Zeroth order approximation

$$\dot{a}(t) = -\Gamma \frac{\delta S(a)}{\delta a} + \sigma\xi(t)$$

$$\sigma\sigma^T = \Gamma + \Gamma^T$$

$$\rho_{eq}(a) = \frac{1}{\Xi_0}\exp[-S(a)]$$

First order approximation

$$\dot{a}(t) = z$$

$$\dot{z}(t) = -A\frac{\delta S(a)}{\delta a} + Bz + \sigma\xi(t)$$

$$\sigma\sigma^T = BA + AB^T$$

$$\rho_{eq}(a,z) = \frac{1}{\Xi_1}\exp\left[-S(a) - \frac{1}{2}z^T A^{-1} z\right]$$

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Imposing consistent noise in general

- The generalized Langevin: $\dot{a} = \Omega a - \int_0^t \theta(t-s)a(s)ds + R(t)$
- The fluctuation-dissipation theorem (FDT): $E[R(t)R(t')^T] = k_B T\theta(t-t').$
- The moment matching condition provides the coefficients of the extended stochastic models

$$\begin{cases} \partial_t a = \Omega a - e^{\mathrm{T}} z \\ \partial_t z = Aa + Bz + \sigma\xi \end{cases}$$

- The is a Markovian embedding of the generalized Langevin dynamics
- Lyapunov equation

$$BA + AB^T + \sigma\sigma^T = 0.$$

- It is consistent with the **fluctuation dissipation theorem (FDT)**: When $z(t)$ is substituted into the first equation, one obtains a GLE with the FDT exactly satisfied.

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Galerkin projection – a fast-slow model

Langevin dynamics

$$\dot{x} = v$$
$$\dot{v} = f(x) - \Gamma v + \zeta(t) \qquad \mathrm{E}[\zeta(t)\zeta(t')^T] = 2k_B T\Gamma\delta(t-t').$$

Partitioned Langevin: (Sweet et al JCP 2008)

- $Y = span\{\phi_1, \phi_2, \cdots, \phi_m\}$. (subspace based on RTB modes)
- $x = \phi q + \xi, v = \phi p + \eta, \xi\ and\ \eta \in Y^{\perp}$. ($q\ and\ p$: low modes)
- Effective dynamics

$$\dot{q} = p$$
$$\dot{p} = \phi^T F(\phi q) - Aq - \Gamma_{11} p - \int_0^t \theta(t-s)p(s)ds + f(t)$$
$$\mathrm{E}[f(t)f(t')^T] = 2k_B T\theta(t-t') + 2k_B T\Gamma_{11}\delta(t-t')$$

- We can apply the rational interpolation (moment matching) method.
- *Can we apply Galerkin projection*?

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Reduced-order formulation

(Feldmann-Freund 1995; Bai 2002, Gugercin-Antoulas 2004).

- High modes $y = (\xi, \eta)$; low modes: $u(t) = (q, p)$.
- Fast dynamics:

$$\dot{y} = Dy + Ru(t) + f_2(t)$$

- Slow dynamics: $\dot{q} = p, \dot{p} = \phi^T F(\phi q) - \Gamma_{11} p + Ly(t) + f_1(t)$

Theorem (Ma-Li-Liu JCP) The coupled dynamics is equivalent to the GLE.

Galerkin: $y \in span\{V_1, \cdots, V_n\}$, such that residual $\perp span\{W_1, \cdots, W_n\}$

Projected dynamics: $\dot{z} = \widehat{M}^{-1}\widehat{D}z + \widehat{M}^{-1}W^T Ru(t) + \hat{f}(t)$

The Galerkin project induces an approximation of $\theta(t)$ and $\zeta(t)$.

Theorem (Ma-Li-Liu JCP 2019) The reduced dynamics satisfies the FDT if $\widehat{M}\hat{Q}V^T L^T = W^T Q L^T$.

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Relation to the moment-matching

Moment matching

- $M_0 = \theta(0), M_1 = \theta'(0), \cdots, M_\infty = \int_0^{+\infty} \theta(t)dt.$

Approximate kernel

$$\Theta_n(s) = (s^n I - s^{n-1}B_0 - \cdots - B_{n-1})^{-1}(s^{n-1}C_0 + \cdots + C_{n-1})$$
$$\Theta_n(0) = M_\infty, \theta^{(\ell)}(0) = M_\ell.$$

Galerkin with Krylov subspace

- $V_1 = R, V_2 = DR, \cdots. W_1 = D^{-T}L^T, W_2 = L^T, W_3 = D^T L^T, \cdots$

Theorem (Ma-Li-Liu 2019) The reduced dynamics is equivalent to moment matching and it satisfies the FDT automatically $(n \leq 6)$.

Therefore, the Galerkin projection provides a systematic treatment of the noise.

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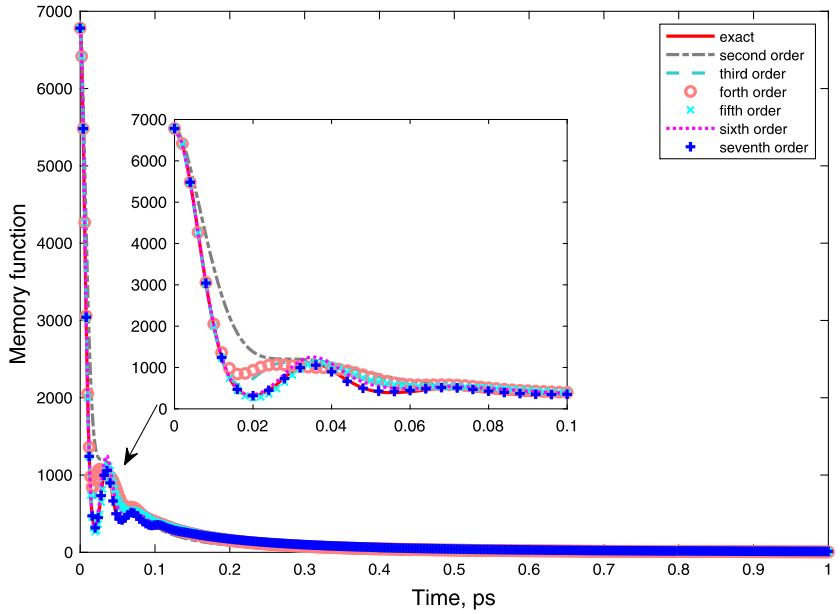
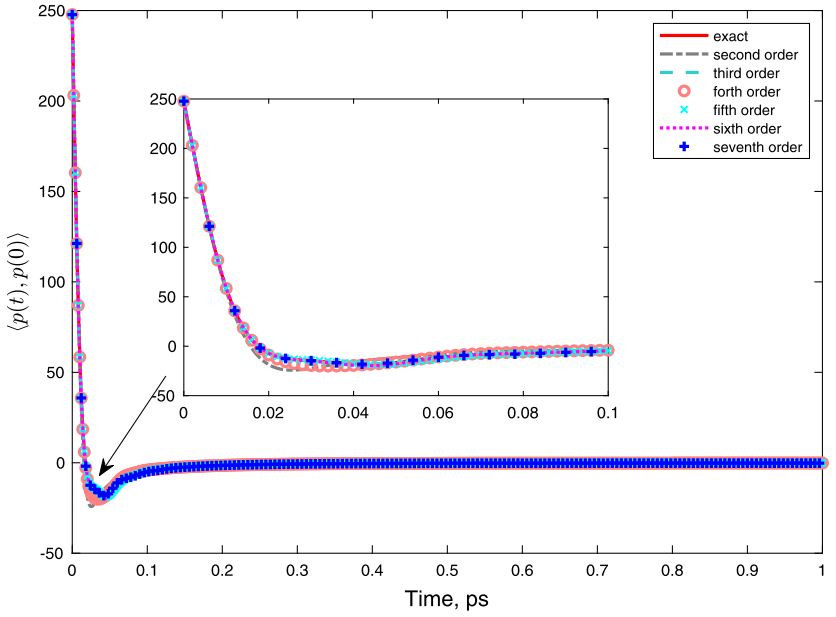
Numerical test on Chignolin





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Galerkin approach for ergodic dynamics

- Dynamics in the Koopman picture

  $\dot{a} = La$. L is a differential operator.

- Inner product: $(f, g) \coloneqq E_{\mu_{eq}}[fg]$ Type equation here.
- Projection: $V = [a(0), La(0), \cdots], W = [L^{-1}a(0), a(0), La(0)]$.

$$L^{-1}a(0) \approx \int_0^{+\infty} e^{t(-\epsilon I + L)} a(0) dt.$$

- First order approximation: $\mathrm{M}\dot{a} = Ka + \Sigma\zeta(t)$.
- K is related to the correlation length of $a(t)$.
- In general, the elements of M and K are statistics of $a(t)$.
- Nonlocal statistics can also be incorporated.

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Part II. Reduced-order modeling for electron dynamics

Chu, Weiqi, and Xiantao Li. "Reduced-order modeling approach for electron transport in molecular junctions." ***Journal of Chemical Theory and Computation*** 16.6 (2020): 3746-3756.

Chu, Weiqi, and Xiantao Li. "A projection-based reduced-order method for electron transport problems with long-range interactions." ***The Journal of Chemical Physics*** 155.11 (2021).

Wu, Xiaojie, and Xiantao Li. "Absorbing boundary conditions for the time-dependent Schrödinger-type equations in R 3." ***Physical Review E*** 101.1 (2020): 013304.

Li, Xiantao. "Absorbing boundary conditions for time-dependent Schrödinger equations: A density-matrix formulation." ***The Journal of chemical physics*** 150.11 (2019).

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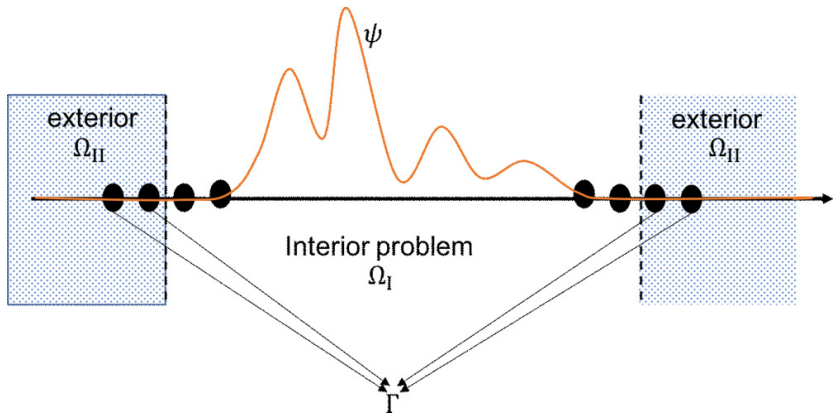
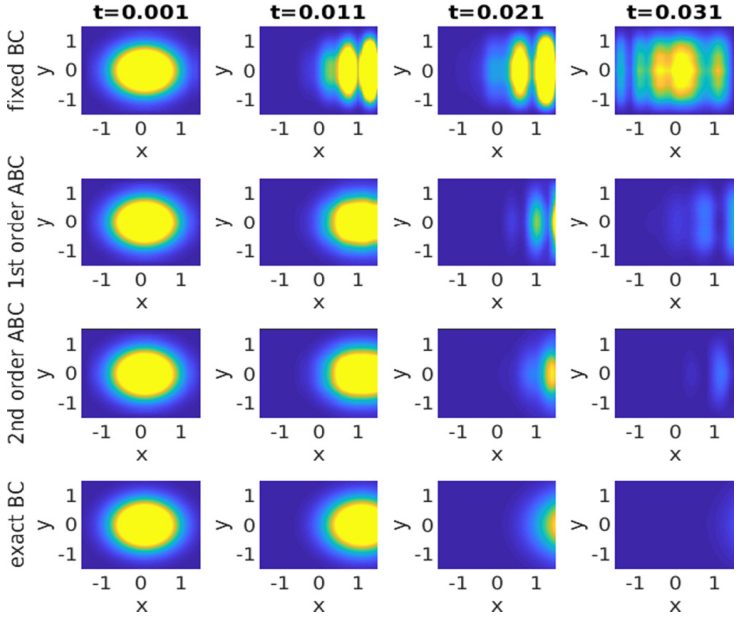
Absorbing boundary conditions

- Semi-discrete formulation: $\mathrm{i}\frac{d}{dt}\psi = H\psi.\ H = \begin{bmatrix} H_{I,I} & H_{I,E} \\ H_{E,I} & H_{E,E} \end{bmatrix}$. I: interior; E: exterior
- Exact time-dependent DtN: $\mathrm{i}\frac{d}{dt}\psi_I = H_{I,I}\psi_I - i\int_0^t \Gamma(t-\tau)\psi_I(\tau)d\tau.$
- Krylov subspace + Galerkin ⇒ Absorbing (transparent) boundary conditions





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Electron transport

- Electron transport in open quantum system
  - a quantum system that interacts with another quantum system (bath)
- How to avoid a large number of variables from the bath?
  - RoM--> find closed equations to describe the system with much fewer variables.
- Time-dependent Schrödinger equation: $\partial_t \hat{\psi}(t) = -i\hat{H}(t)\,\hat{\psi}(t)$
- Liouville-von Neumann (LvN) equation: $\partial_t \hat{\rho}(t) = -i\left(\hat{H}(t)\hat{\rho}(t) - \hat{\rho}(t)\hat{H}(t)\right)$
- Density matrix operator $\hat{\rho}(t) = \sum_j n_j \hat{\psi}(t)\hat{\psi}(t)^*$
- Real-space realization: $\rho(x, x', t) = \langle x|\hat{\rho}(t)|x'\rangle,\ H(x, x', t) = \left\langle x\middle|\hat{H}(t)\middle|x'\right\rangle$
- Charge density: $n(x, t) = \rho(x, x, t)$

Wave-function approach vs density-matrix approach

- WF: restrict the wave functions to the center region and formally eliminate the part of the wave functions in the bath) (Kurth et al. PRB, 2005). Similar to absorbing boundary conditions.
- **Issues:**

➢ The number of wave functions is proportional to the number of electrons.

➢ The wave functions are often extended.

➢ The initialization of the wave functions.

DM: restrict the density-matrix to the center region

Advantages:

➢ The dimension of the reduced density-matrix only depends on the size of the center region

➢ The initialization is straightforward. $\rho(0) \propto \mathrm{f}\left(-\frac{H}{k_B T}\right)$.

Potential issue: it can be a dense matrix. (Hope for local structure).

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Liouville von Neumann for the entire system

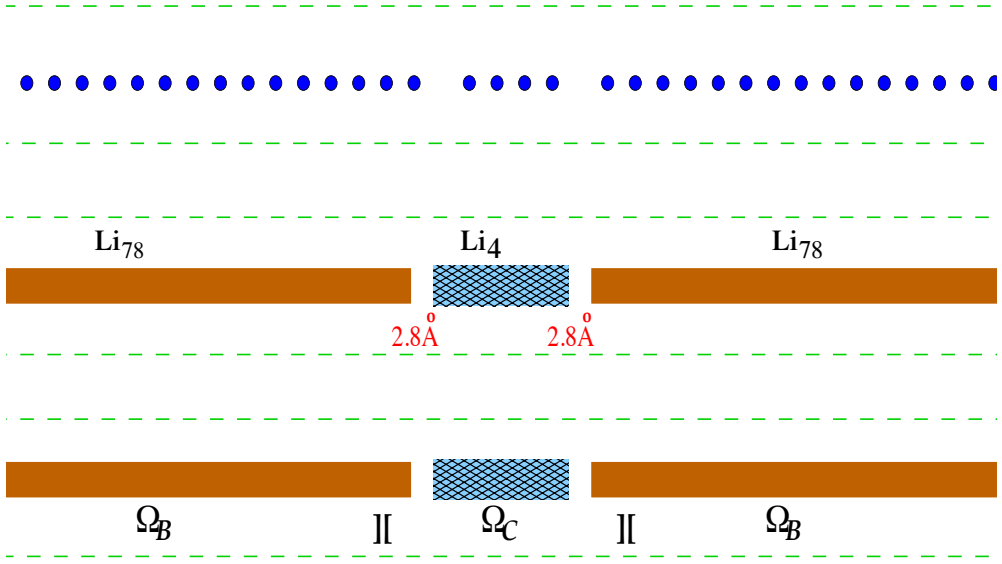
- Discretize x and use a matrix representation

$$\partial_t \rho(t) = -i[H[n(t), t], \rho(t)]$$

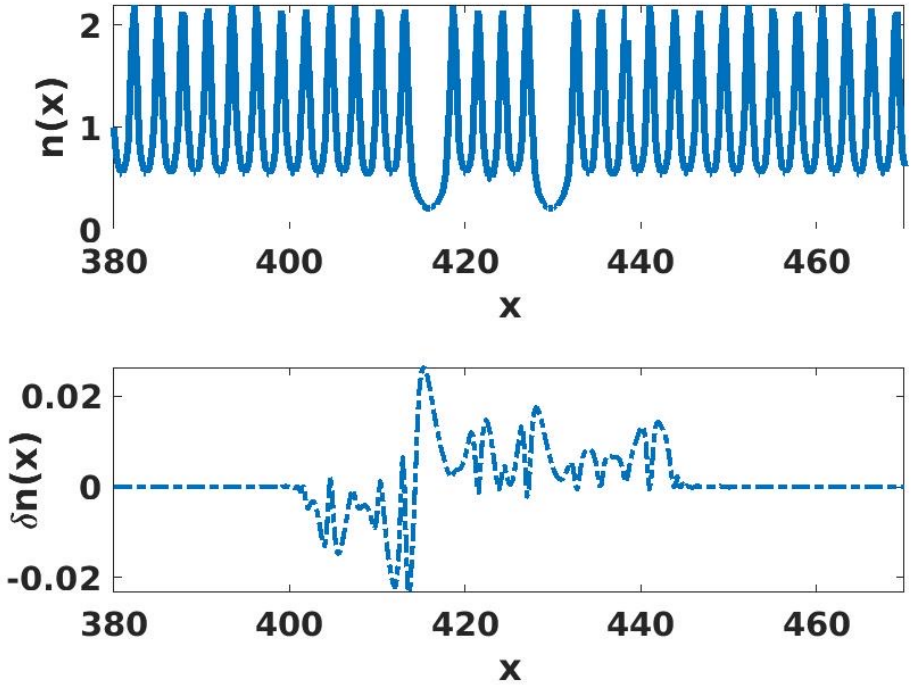
- Matrix representation: $\rho, H \in \mathbb{C}^{N \times N}$ and $n = \mathrm{diag}(\rho)$
- Transient (non-equilibrium) nature: external control $U_{ext}(t)$
- Coupling with the bath $\rho = \begin{bmatrix} \rho_S & \rho_{BS} \\ \rho_{SB} & \rho_B \end{bmatrix}$, $\dim\{\rho_B\} \gg \dim\{\rho_S\}$

Charge density observation

- Charge density n extends to the entire bath.
- The charge perturbation $\delta n = n - n_0$ is compact near the junction area.



A one-dimensional molecular junction that contains three Lithium chains



Charge density vs location

Perturbed dynamics (Linear response)

- Perturbed density matrix $\delta\rho(t) = \rho(t) - \rho_0$
- Linear response $\delta H(t) = H(t) - H_0,\ [H_0, \rho_0] = 0$
- Perturbed LvN equation after dropping higher order terms

$$\partial_t \delta\rho(t) = -i([H_0, \delta\rho(t)] + [\delta H(t), \rho_0] + \cancel{[\delta H(t), \delta\rho]})$$

- The bracket is generalized quantum commutator

$$[A, B] = A^* B - B^* A$$

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How does reduced-order modeling come in?

- LvN Equation:

$$i\frac{d}{dt}\begin{pmatrix} \delta\rho_{LL} & \delta\rho_{LC} & \delta\rho_{LR} \\ \delta\rho_{CL} & \delta\rho_{CC} & \delta\rho_{CR} \\ \delta\rho_{RL} & \delta\rho_{RC} & \delta\rho_{RR} \end{pmatrix} = \left[\begin{pmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{pmatrix}, \begin{pmatrix} \delta\rho_{LL} & \delta\rho_{LC} & \delta\rho_{LR} \\ \delta\rho_{CL} & \delta\rho_{CC} & \delta\rho_{CR} \\ \delta\rho_{RL} & \delta\rho_{RC} & \delta\rho_{RR} \end{pmatrix}\right] + \Theta.$$

- The equation in the left bath

$$i\partial_t\delta\rho_{LL} = [H_{LL}, \delta\rho_{LL}] + H_{LC}\delta\rho_{CL} - \delta\rho_{LC}H_{CL} = [H_{LL}, \delta\rho_{LL}] + [H_{LC}, \delta\rho_{CL}].$$

- Since the matrix H_{LC} is short ranged, the input can be regarded as **low dimensional**.
- The off-diagonal block:

$$i\partial_t\delta\rho_{LC} = H_{LL}\,\delta\rho_{LC} - \delta\rho_{LL}H_{LC} + H_{LC}\delta\rho_{CC} - \delta\rho_{LC}H_{CC} + \Theta_{LC}(t).$$

- In practice, we only need $\delta\rho_{LL}H_{LC}$, which is a **low-dimensional output.**
- **This is a reduced-order modeling problem.**

Projected LvN equation

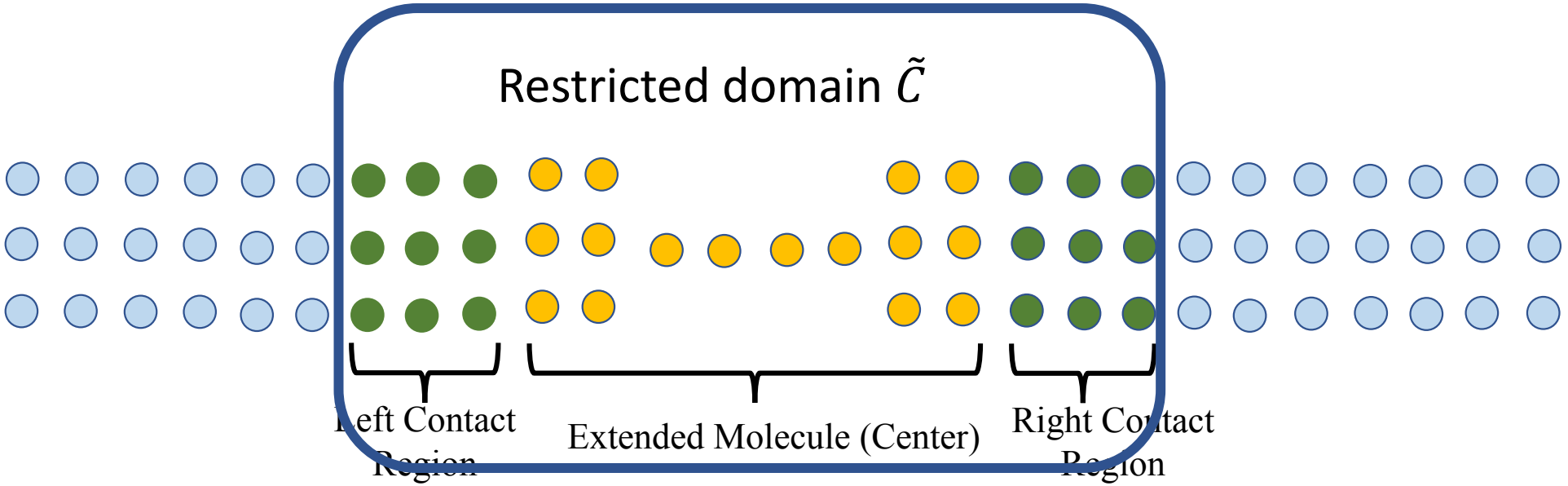
- Solution subspace and test subspace $V, W \in \mathbb{C}^{N \times n},\ N \gg n$
  - $\delta\rho(t) = VD(t)V^*,\ D = D^*$
  - $W^* \partial_t \delta\rho(t) W = W^*(-i([H_0, \delta\rho(t)] + [\delta H(t), \rho_0]))W$
- Reduced dynamics for $D \in \mathbb{C}^{n \times n}$

$$\partial_t D(t) = -i[H_{\text{eff}}(t), D(t)] - i\Theta(t)$$

- Effective Hamiltonian $H_{\text{eff}} = (W^*V)^{-1} W^* H V$
- Driven term $\Theta(t) = (W^*V)^{-1} W^* [\delta H(t), \rho_0] W (V^*W)^{-1}$
- How do we pick subspaces V and W?
  - A domain decomposition-based strategy

Solution subspace

- Include contact region (green) into subspace domain
- Select solution subspace $V = [0_{\text{blue}}, ; I_{\text{green+yellow}}]$
- Coarse-grained variables $D = V^* \delta\rho V = \delta\rho_{\tilde{C}}$



Test subspaces

- Green's function $\mathrm{G}(z) = (zI - H)^{-1}$ is related to the density matrix

$$\rho = \frac{1}{2\pi i} \oint_{\mathbb{C}} \mathrm{G}(z) dz$$

- Advanced Green's function

$$G^A(\varepsilon) = \lim_{\mathrm{Im}(\varepsilon) \to 0_-} (\varepsilon I - H_0)^{-1}$$

- Test space $W = (\varepsilon I - H_0)^{-1} V, \varepsilon \in \mathbb{C}$
- We require $\mathrm{Im}(\varepsilon) < 0$ to maintain stability (Chu & Li 2020 JCTC)

Reduced dynamics

- With W and V ready, one can simplify terms in the driven LvN eq:

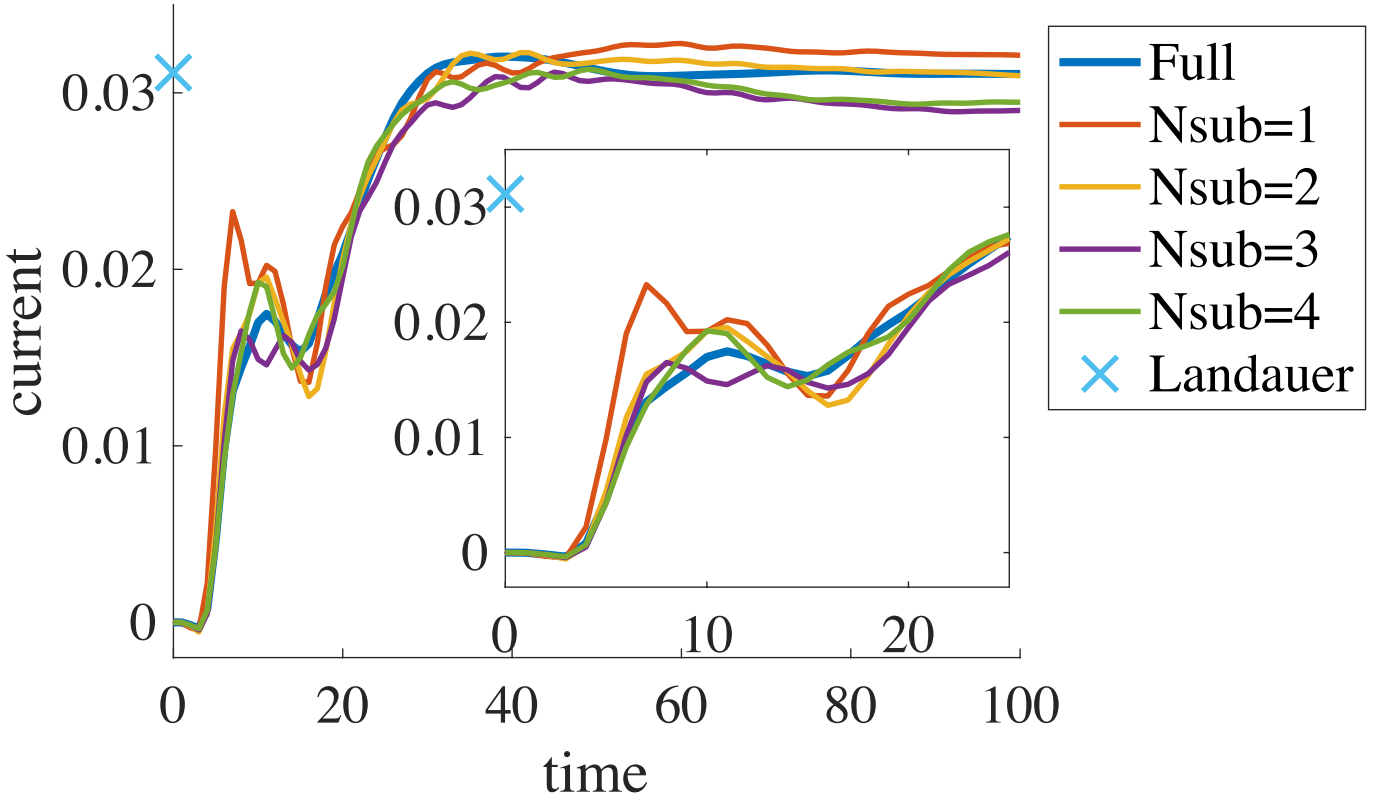
$$\partial_t D = -i[H_{\text{eff}}, D] - i\Theta$$

- A partition of H based on the domain decomposition $H = \begin{bmatrix} H_S & H_{BS} \\ H_{SB} & H_B \end{bmatrix}$
- Effective Hamiltonian $H_{\text{eff}} = H_S + \Sigma(\varepsilon)$
- Self-energy $\Sigma(\varepsilon) = H_{SB}(\varepsilon I - H_B)^{-1} H_{BS}$ reflects energy enters
- Non-homogenous term $\Theta = (\varepsilon^* I - H_{\text{eff}}) W^* [\delta H(t), \rho_0] W (\varepsilon\, I - H_{\text{eff}})$
- Σ, Θ can be computed fast using selective inversion (boundary element).

Observation of the electron current

- Simulation of a DC circuit: constant bias $U_L = -U_R = 0.1$ a. u.
- The electron current: $J(x_i) = -\mathrm{Im}(\rho(x_i, x_{i+1}) \,/\, \Delta x$

[Chu & Li, 2020, JCPC]

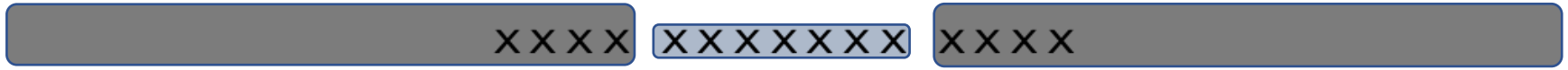


Coulomb interactions

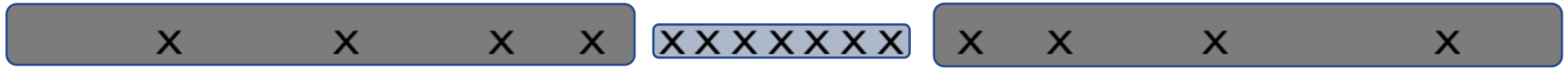
- Coulomb interactions play an important role in electron transport and other quantum observations, such as Coulomb blockade.
- Dependence on the electron density must be taken into consideration.
  - $H[n] = -\frac{1}{2}\nabla^2 + V_H[n] + V_{XC}[n] + V_{\text{nuclei}} + U_{ext}(t)$
  - $\delta H[n] = V_H[\delta n] + V_{XC}[n] - V_{XC}[n_0] + U_{ext}(t)$
  - n_0 is the charge density without the external potential
- The Coulomb force is a long-range force. Particles in the far end of bath have an influence on the system.
- Hartree potential: $V_H[n](x) = \int_\Omega \frac{n(x')}{|x-x'|} dx$

Multi-connected domain decomposition

- Uniform grids in contact regions (previous case) will not work
  - $\Omega_{\tilde{C}} = \Omega_C \cup \{x_n = x_R + na\} \cup \{x_n = x_L - na\}$



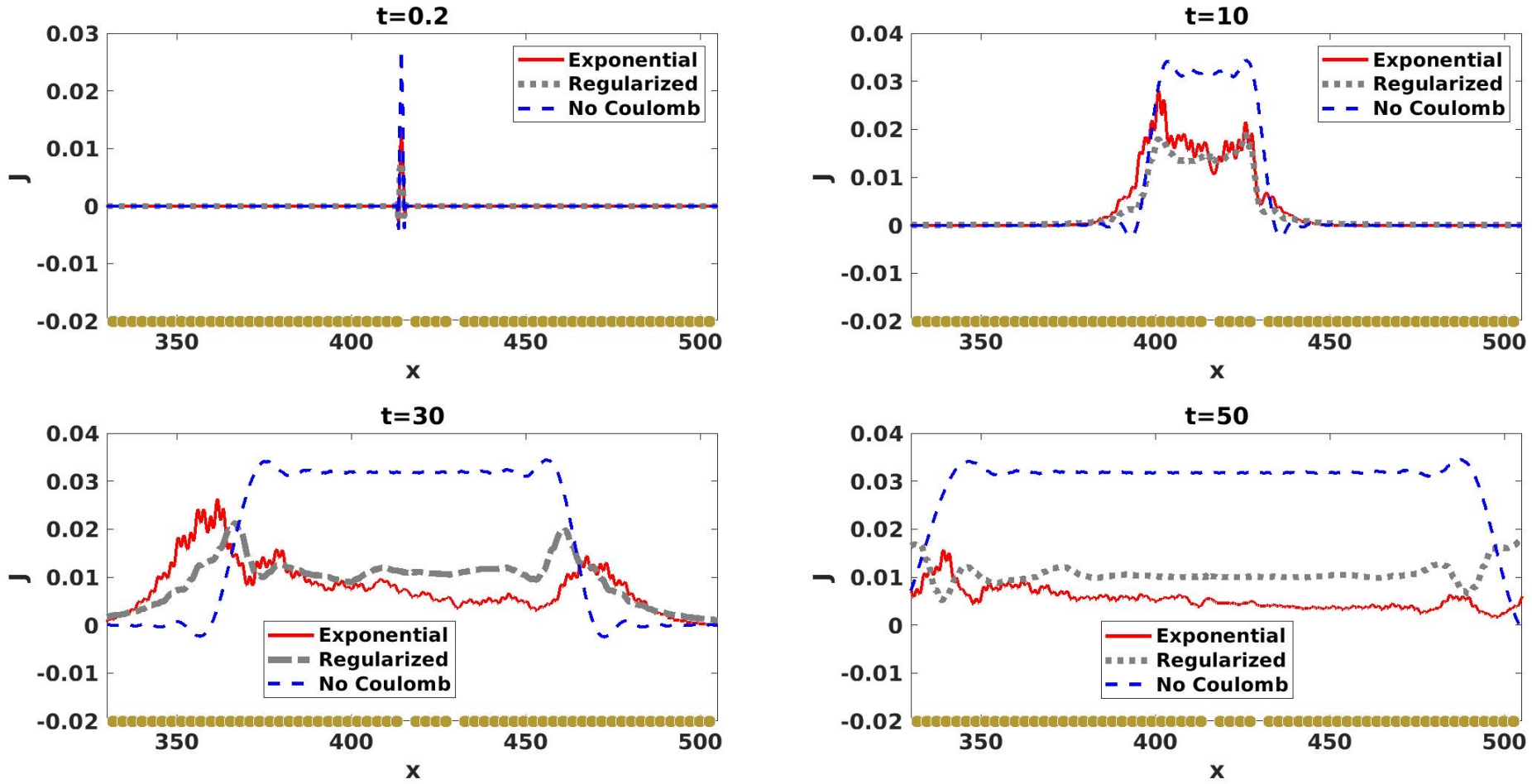
- Recover the global electron density using a spline interpolation with logarithmic grids
  - $\Omega_{\tilde{C}} = \Omega_C \cup \{x_R + a^n\} \cup \{x_L - a^n\}$



- Reconstruct the Hartree part using quadrature

$$V_H[n](x) = \int_\Omega \frac{n(x')}{|x - x'|} dx \approx \sum_{x_\alpha \in \Omega_{\tilde{C}}} w(x, x_\alpha) n(x_\alpha)$$

Observation of Coulomb blockade



[Chu & Li 2021, JCP]

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Summary

- Molecular dynamics
  - Generalized Langevin equation can be derived from a projection procedure
  - Appropriate projection so that the marginal density is easier to fit.
  - Moment matching for the kernel and the FDT
  - A Galerkin projection: more robust; automatically satisfies the FDT
  - Open issues: Stability; Accuracy; Adaptivity.
- Electron dynamics
  - Partition of the density matrix
  - Reduced-order modeling to efficiently mimic the effect of the bath
  - Subspace projection; Green's function.
  - Open issues: The subspace can only involve $H_{C,L}\left(zI - H_{L,L}\right)^{-1}H_{L,C}$. But not higher order inverse.