Towards Simulating Chemical Open System Quantum Dynamics on a quantum computer

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Why should we think of Chemical Dynamics as Quantum Open System Dynamics?
Electronic energy/charge/coherence transfer and decoherence

Fenna–Matthews–Olson complex (green sulfur bacteria)

Carotenoid-Porphyrin-C$_{60}$ triad in THF

\[
\begin{align*}
C - P - C_{60} & \quad \downarrow h\nu \\
C - P^* - C_{60} & \\
C - P^* - C_{60}^* & \quad \downarrow \\
C^+ - P - C_{60}^- & 
\end{align*}
\]

Bacterial photosynthetic reaction center

Organic photovoltaics
Example: Diabatic electronic states of a two-chromophore systems

\[ |CT1\rangle = |3\rangle \]

\[ |CT2\rangle = |4\rangle \]

\[ |EX1\rangle = |1\rangle \]

\[ |EX2\rangle = |2\rangle \]
Electronic Spectroscopy (including nonlinear and time resolved) probes coherences.

The populations of the excitonic and charge transfer states are dynamically coupled to the coherences, and dynamical pathways can involve coherence-to-population, population-to-coherence and coherence-to-coherence transfer in addition to population-to-population transfer (as well as coherence relaxation or dephasing when coupled to an environment).
The overall system Hamiltonian includes coupling to nuclear and sometimes also photonic DOF. The Hamiltonian is expressed as:

\[ \hat{H} = \sum_{j=1}^{N_{el}} H_j \left( \hat{R}, \hat{P} \right) |j\rangle \langle j| + \sum_{j,k=1}^{N_{el}} V_{jk} \left( \hat{R} \right) |j\rangle \langle k| \]

- **Nuclear/photonic DOF**
- **Coupling between electronic states**
- **Diabatic electronic states**
- **Electronic-state specific nuclear/photonic Hamiltonian**
Example: Frenkel exciton Hamiltonian (local excitation basis)

\[
\hat{H} = \sum_{j=1}^{N_e} \varepsilon_j^0 + \sum_{\alpha=1}^{N_{j'}} \frac{1}{2} \omega_{j\alpha}^2 \left( \hat{P}_{j\alpha}^2 + \left[ \hat{Q}_{j\alpha} + d_{j\alpha} \right]^2 \right) + \sum_{j' \neq j}^{N_{e}} \frac{1}{2} \omega_{j'\alpha}^2 \hat{P}_{j'\alpha}^2
\]

Uncoupled singly-excited state:

\[
|\varepsilon_j^0\rangle = |0_1\rangle \otimes |0_2\rangle \otimes \ldots \otimes |0_j\rangle \otimes \ldots \otimes |0_{N_e-1}\rangle \otimes |0_{N_e}\rangle
\]

\[
\begin{array}{c}
\bullet \\
\bullet \\
\ldots \\
\bullet \\
\bullet \\
\end{array}
\]

Chromophore 1 Chromophore 2 Chromophore j Chromophore N_{e-1} Chromophore N_e

Graph:

\[
\lambda = \frac{1}{2} \omega^2 d^2
\]

1st excited state

\[
\varepsilon + \frac{1}{2} \omega^2 (R - d)^2
\]

ground state

\[
R = 0 \quad R = -d
\]
Three inter-related grand challenges

✧ The electronic-structure challenge.

✧ The quantum dynamics challenge.

✧ The connection with experiment challenge
Closed quantum system approach

Overall molecular system dynamics (all nuclear and electronic DOF)

\[
\frac{d}{dt} \hat{\rho}(t) = -\frac{i}{\hbar} \left[ \hat{H}, \hat{\rho}(t) \right] = -\frac{i}{\hbar} L \hat{\rho}(t)
\]

\[
\hat{\rho}(t) = e^{-i\hat{H}t/\hbar} \hat{\rho}(0) e^{i\hat{H}t/\hbar} = e^{-iLt/\hbar} \hat{\rho}(0)
\]

Calculate the electronic observable of interest:

- Electronic populations: \( \text{Tr} \left( \hat{\rho}(0) \langle j | \hat{\rho}(t) | j \rangle \otimes \hat{1}_n \right) \)
- Electronic coherences: \( \text{Tr} \left( \hat{\rho}(0) \langle j | \hat{\rho}(t) | k \rangle \otimes \hat{1}_n \right) \)

Open quantum system approach

Start out with the quantity of interest:

\[
\hat{\sigma}(t) = Tr_n \left[ e^{-i\hat{H}t/\hbar} \hat{\rho}(0) e^{i\hat{H}t/\hbar} \right]
\]

- Electronic populations: \( \sigma_{jj}(t) = \langle j | \hat{\sigma}(t) | j \rangle \)
- Electronic coherences: \( \sigma_{jk}(t) = \langle j | \hat{\sigma}(t) | k \rangle \)

Can we find \( \sigma_{jj}(t) \) and \( \sigma_{jk}(t) \) without having to first know the entire \( \hat{\rho}(t) \)?

What is the minimum we need to know about the overall system in order to simulate the dynamics of subset of electronic reduced density matrix elements of interest?

How to accurately and cost-effectively calculate it in complex molecular systems?
What is the equation of motion for \( \{\sigma_{jj}(t), \sigma_{jk}(t)\} \)?

*Quantum Master Equations (QMEs)*
Not all QMEs were created equal!

Lindbald QMEs

😊 Guaranteed to satisfy semigroup properties (including complete positivity).
😊 Ease of use.
😊 Not based on explicit overall system Hamiltonian.
😊 Relaxation mechanism assumed, as opposed to derived.
😊 Relaxation coefficients as adjustable parameters.
😊 Markovian.

Weak-coupling QMEs (Redfield, modified Redfield, NIBA, etc.)

😊 Derived for an explicit overall system Hamiltonian.
😊 Analytical for harmonic baths.
😊 Explicit expressions for relaxation coefficients.
😊 Perturbative.
😊 Often Markovian or time-local.
😊 Moderate ease of use.

Generalized QME (GQME)

😊 Derived for an explicit overall system Hamiltonian.
😊 Formally exact equation of motion for the quantity of interest (non-perturbative).
😊 Non-Markovian or time-non-local.
😊 Explicit expression for memory kernel.
😊 Projection flexibility.
😊 Work-intensive.
Chemical Dynamics via the GQME approach
Projection operators and the Nakajima-Zwanzig equation

\( P \) is a projector operator iff \( P^2 = P \)  \( \boxed{Q = 1 - P} \)  \( P + Q = 1 \); \( PQ = 0 \)

Liouville equation for overall system (assumed closed):
\[
\frac{d}{dt} \hat{\rho}(t) = -\frac{i}{\hbar} \mathcal{L}(\hat{\rho}(t))
\]

\[
\Rightarrow \quad \frac{d}{dt} \left( P \hat{\rho}(t) \right) = -\frac{i}{\hbar} \mathcal{P}(P \hat{\rho}(t)) - \frac{i}{\hbar} \mathcal{P}(Q \hat{\rho}(t))
\]

\[
\Rightarrow \quad \frac{d}{dt} \left( Q \hat{\rho}(t) \right) = -\frac{i}{\hbar} \mathcal{Q}(P \hat{\rho}(t)) - \frac{i}{\hbar} \mathcal{Q}(Q \hat{\rho}(t))
\]

\[
\Rightarrow \quad \hat{\rho}(t) = \exp \left( -\frac{i}{\hbar} \mathcal{Q} \mathcal{L} t \right) \hat{\rho}(0) - \frac{i}{\hbar} \int_0^t d\tau \exp \left[ -\frac{i}{\hbar} \mathcal{Q} \mathcal{L} \tau \right] \mathcal{Q} \left( P \hat{\rho}(t - \tau) \right)
\]

\[
\Rightarrow \quad \frac{d}{dt} \left( P \hat{\rho}(t) \right) = -\frac{i}{\hbar} \mathcal{P} \mathcal{P}(P \hat{\rho}(t)) - \frac{1}{\hbar^2} \int_0^t d\tau \mathcal{P} \mathcal{L} \mathcal{P} \exp \left[ -\frac{i}{\hbar} \mathcal{Q} \mathcal{L} \tau \right] \mathcal{Q} \left( P \hat{\rho}(t - \tau) \right) - \frac{i}{\hbar} \mathcal{P} \mathcal{L} \mathcal{P} \exp \left[ -\frac{i}{\hbar} \mathcal{Q} \mathcal{L} t \right] \left( Q \hat{\rho}(0) \right)
\]

Dynamics induced by projected \( \mathcal{L} \)

Time-local

Dynamics induced by memory of state between \((0,t)\)

Time-nonlocal (Non-Markovian)

Dynamics induced by memory of initial preparation of overall system at time \( t=0 \)

Non-Markovian
Different projection operators and reduced-dimensionality GQMEs

\[
P_{\text{full}} \hat{A} = \sum_{\alpha, \alpha' = 1}^{N_x} P_{\alpha \alpha'} \hat{A} = \hat{\rho}_{\text{ref}} \otimes \text{Tr}_n(\hat{A})
\]

\[
P_{\text{full}} \left( \begin{array}{cc} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{array} \right) = \hat{\rho}_{\text{ref}} \otimes \left( \begin{array}{cc} \text{Tr}_n(\hat{\rho}_{11}) |1\rangle \langle 1| & \text{Tr}_n(\hat{\rho}_{21}) |1\rangle \langle 2| \\ \text{Tr}_n(\hat{\rho}_{12}) |2\rangle \langle 1| & \text{Tr}_n(\hat{\rho}_{22}) |2\rangle \langle 2| \end{array} \right)
\]

\[
P_{\text{pop}} \hat{A} = \sum_{\alpha = 1}^{N_x} P_{\alpha \alpha} \hat{A} = \sum_{\alpha = 1}^{N_x} \text{Tr} \left( |\alpha\rangle \langle \alpha| \otimes \hat{I}_n \right) \hat{A} \hat{\rho}_{\text{ref}} \otimes |\alpha\rangle \langle \alpha|
\]

\[
P_{\text{pop}} \left( \begin{array}{cc} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{array} \right) = \hat{\rho}_{\text{ref}} \otimes \left( \begin{array}{cc} \text{Tr}_n(\hat{\rho}_{11}) |1\rangle \langle 1| & 0 \\ 0 & \text{Tr}_n(\hat{\rho}_{22}) |2\rangle \langle 2| \end{array} \right)
\]

\[
P_{\text{coh}} \hat{A} = \sum_{\alpha \neq \alpha'} P_{\alpha \alpha'} \hat{A} = \sum_{\alpha \neq \alpha'} \text{Tr} \left( |\alpha\rangle \langle \alpha'| \otimes \hat{I}_n \right) \hat{A} \hat{\rho}_{\text{ref}} \otimes |\alpha\rangle \langle \alpha'|
\]

\[
P_{\text{coh}} \left( \begin{array}{cc} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{array} \right) = \hat{\rho}_{\text{ref}} \otimes \left( \begin{array}{cc} 0 & \text{Tr}_n(\hat{\rho}_{21}) |1\rangle \langle 2| \\ \text{Tr}_n(\hat{\rho}_{12}) |2\rangle \langle 1| & 0 \end{array} \right)
\]

\[
P_{\alpha \alpha} \hat{A} = \text{Tr} \left( |\alpha\rangle \langle \alpha| \otimes \hat{I}_n \right) \hat{A} \hat{\rho}_{\text{ref}} \otimes |\alpha\rangle \langle \alpha|
\]

\[
P_{\alpha \alpha} \left( \begin{array}{cc} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{array} \right) = \hat{\rho}_{\text{ref}} \otimes \left( \begin{array}{cc} \text{Tr}_n(\hat{\rho}_{11}) |1\rangle \langle 1| & 0 \\ 0 & 0 \end{array} \right)
\]

\[
P_{\alpha' \alpha'} \hat{A} = \text{Tr} \left( |\alpha\rangle \langle \alpha'| \otimes \hat{I}_n \right) \hat{A} \hat{\rho}_{\text{ref}} \otimes |\alpha\rangle \langle \alpha'|
\]

\[
P_{\alpha' \alpha'} \left( \begin{array}{cc} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{array} \right) = \hat{\rho}_{\text{ref}} \otimes \left( \begin{array}{cc} 0 & \text{Tr}_n(\hat{\rho}_{21}) |1\rangle \langle 2| \\ 0 & 0 \end{array} \right)
\]

In fact, one can project onto ANY subset of the reduced electronic density matrix elements!
Example #1: A GQME for the full electronic density matrix (full-GQME)

Projection operator: \( \mathbf{P}_{\text{full}} \hat{A} = \hat{\rho}_n(0) \otimes \text{Tr}_n\left(\hat{A}\right) \)

The reduced electronic density operator: \( \hat{\sigma}(t) = \text{Tr}_n\left(\hat{\rho}(t)\right) \)

Conveniently vanishes for the choice of unentangled initial state and projection operator

\[
\frac{d}{dt} \hat{\sigma}(t) = -\frac{i}{\hbar} \langle \mathbf{L} \rangle \hat{\sigma}(t) - \int_0^t d\tau \mathbf{K}_{\text{full}}(\tau) \hat{\sigma}(t - \tau) + \mathbf{I}_{\text{full}}(t)
\]

The memory kernel super-operator

\[
\mathbf{K}_{\text{full}}(\tau) = \frac{1}{\hbar^2} \text{Tr}_n \left\{ \text{Le}^{-i \frac{Q_{\text{full}} L}{\hbar} \tau} \mathbf{Q}_{\text{full}} \mathbf{L} \hat{\rho}_N(0) \right\}
\]

The inhomogeneous term

\[
\mathbf{I}_{\text{full}}(\tau) = -\frac{1}{\hbar} \text{Tr}_n \left\{ \text{Le}^{-i \frac{Q_{\text{full}} L}{\hbar} \tau} \mathbf{Q}_{\text{full}} \hat{\rho}_N(0) \right\}
\]
\[
\frac{d}{dt} \hat{\sigma}(t) = -\frac{i}{\hbar} \langle L \rangle \hat{\sigma}(t) - \int_0^t d\tau K^{\text{full}}(\tau) \hat{\sigma}(t-\tau)
\]

* This GQME is the EXACT equation of motion for the electronic reduced density operator \( \hat{\sigma}(t) \) [the electronic quantity of interest].

* \( K^{\text{full}}(\tau) \) represents the minimum input on the nuclear DOF required in order to account for their effect on the electronic DOF.

* \( K^{\text{full}}(\tau) \) is a superoperator represented by an \( N_e^2 \times N_e^2 \) matrix.

* In complex molecular systems, \( K^{\text{full}}(\tau) \) typically decays to zero within a finite life-time thereby minimizing errors and/or cost that may arise at longer times.
Calculating the exact memory kernel from projection-free inputs

Memory kernel (projection-dependent output)

\[ K^{\text{full}}(\tau) = i \dot{F}(\tau) - \frac{1}{\hbar} F(\tau) \langle L \rangle + i \int_0^\tau d\tau' F(\tau - \tau') K^{\text{full}}(\tau') \]

Volterra integral equation (iterative algorithm)

\[ K^{\text{full}}(\tau), F(\tau), \langle L \rangle \]

are \( N_e^2 \times N_e^2 \) matrices where \( N_e \) is the number of electronic states.

The generalized quantum Master equation (GQME):

\[
\frac{d}{dt} \hat{\sigma}(t) = -\frac{i}{\hbar} \langle L \rangle \hat{\sigma}(t) - \int_0^t d\tau K^{\text{full}}(\tau) \hat{\sigma}(t - \tau)
\]

Solved via Runge Kutta 4th-order algorithm

\[
\langle L \rangle = Tr_N \left( L \hat{\rho}_N(0) \right) ; \quad K^{\text{full}}(\tau) = \frac{1}{\hbar^2} Tr_N \left\{ L \exp \left[ -\frac{i}{\hbar} Q^{\text{full}} L \tau \right] Q^{\text{full}} L \hat{\rho}_N(0) \right\}
\]

The projection free input, $\textbf{F}(\tau)$, corresponds to the minimum we need to know about the overall system in order to simulate electronic dynamics!

The matrix elements of $\textbf{F}(\tau)$ are given by overall system two-time correlation functions.

$$
\begin{align*}
\left[ \textbf{F}(\tau) \right]_{jk,nn} = \frac{1}{\hbar} Tr \left\{ |k\rangle \langle j| e^{-\Delta \tau/\hbar} \hat{\rho}_N(0) |m\rangle \langle n| \right\} = + \frac{1}{\hbar} \sum_{k' \neq j} Tr \left\{ \hat{\rho}_N(0) |m\rangle \langle n| e^{i\hat{H}_\tau/\hbar} \hat{V}_{jk'} |k'\rangle \langle k| e^{-i\hat{H}_\tau/\hbar} \right\} \\
- \frac{1}{\hbar} \sum_{j' \neq k} Tr \left\{ \hat{\rho}_N(0) |m\rangle \langle n| e^{i\hat{H}_\tau/\hbar} \hat{V}_{j'k} |j'\rangle \langle j| e^{-i\hat{H}_\tau/\hbar} \right\}
\end{align*}
$$

$\textbf{F}(\tau)$ can be calculated via either exact (MCTDH, HOEM, QUAPI, TFD-TT) or approximate methods (Ehrenfest, LSC, SQC, FSSH, MQCL, etc.). Note that those methods tend to lose accuracy and/or feasibility with increasing time, so restricting their use to calculating the short lived $\textbf{K}(\tau)$ can be more cost-effective and/or accurate than direct use.
Example #2: A population-only GQME

\[ \mathbf{P}_{pop}^{\hat{A}} = \sum_{j=1}^{N_e} \mathbf{P}^{jj} \hat{A} \]

\[ \frac{d}{dt} \sigma_{jj}(t) = \sum_{k=1}^{N_e} \int_0^t d\tau K_{jj,kk}^{\text{pop}}(\tau) \sigma_{kk}(t-\tau) \]

\[ N_e \times N_e \text{ memory kernel: } K_{jj,kk}^{\text{pop}}(\tau) = \frac{1}{\hbar^2} \text{Tr} \left\{ \hat{\rho}_N(0) \right\} \]

Volterra integral equation for \( K_{jj,kk}^{\text{pop}}(\tau) \):

\[ K_{jj,kk}^{\text{pop}}(\tau) = i \hat{F}_{jj,kk}(\tau) + i \sum_{l=1}^{N_e} \int_0^\tau d\tau' F_{jj,ll}(\tau-\tau') K_{ll,kk}^{\text{pop}}(\tau') \]

- An exact equation of motion for \( \{\sigma_{11}(t), \ldots, \sigma_{N_eN_e}(t)\} \).

- The \( N_e \times N_e \) matrix \( \{K_{jj,kk}^{\text{pop}}(\tau)\} \) represents the minimum input required for calculating \( \{\sigma_{11}(t), \ldots, \sigma_{N_eN_e}(t)\} \).

- \( \{K_{jj,kk}^{\text{pop}}(\tau)\} \) can be obtained from a subset of the same projection-free inputs!

Mulvihill and Geva JCP 156 044119-17 (2022)
Example #3: A scalar GQME for a single population

$$\mathbf{P}^{ij} \hat{A} = \text{Tr} \left[ \hat{j} \langle j | \hat{A} | j \rangle \hat{\rho}_n (0) \otimes | j \rangle \langle j | \right]$$

$$\frac{d}{dt} \sigma_{jj} (t) = - \int_0^t d\tau K^{jj} (\tau) \sigma_{jj} (t - \tau) + I^{jj} (t)$$

A scalar memory kernel:

$$K^{jj} (\tau) = \frac{1}{\hbar^2} \text{Tr} \left\{ \hat{j} \langle j | L e^{\frac{-i}{\hbar} Q^{\mu} L \tau} Q^{jj} L \hat{\rho}_n (0) | j \rangle \langle j | \right\}$$

A scalar inhomogeneous term:

$$I^{jj} (\tau) = -\frac{1}{\hbar} \text{Tr}_n \left\{ \hat{j} \langle j | L e^{\frac{-i}{\hbar} Q^{\mu} L \tau} Q^{jj} \hat{\rho}_n (0) | j \rangle \langle j | \right\}$$

A scalar Volterra integral equation for $K^{jj} (\tau)$

$$K^{jj} (\tau) = i\hat{F}^{jj} (\tau) + i \int_0^\tau d\tau' F^{jj} (\tau - \tau') K^{jj} (\tau')$$

A scalar Volterra integral equation for $I^{jj} (t)$

$$I^{jj} (t) = Z^{jj} (t) + i F^{jj} (t) \sigma_{jj} (0) + i \int_0^t d\tau F^{jj} (t - \tau) I^{jj} (\tau)$$

- An exact equation of motion for $\sigma_{jj} (t)$.
- Scalar $K^{jj} (t)$ and $I^{jj} (t)$ represent the minimum input required for calculating $\sigma_{jj} (t)$.
- $K^{jj} (t)$ and $I^{jj} (t)$ can be obtained from a subset of the same projection-free inputs!

Mulvihill and Geva JCP 156 044119-17 (2022) [see also Rabani et al.]
Quantum-mechanically exact memory kernels and inhomogeneous terms via TFT-TT
(see poster for more details)
Projection-free inputs

Memory kernels and inhomogeneous terms

GQME

Reduced dynamics of electronic populations and coherences

Exact fully quantum input method (TFD-TT)

Approximate semiclassical input method (LSC)
Why calculate quantum-mechanically exact memory kernels and inhomogeneous terms?

- The memory kernels and inhomogeneous terms in the case of quantum open systems serve a similar role to that of the Hamiltonian in the case of closed quantum systems.
- Benchmark for approximate memory kernels and inhomogeneous terms (perturbative or based on semiclassical PFIs).
- Simulating the quantum dynamics via a GQME can be more cost-effective than the direct use of the numerically-exact quantum dynamics method.
Projection free inputs (PFSs) for different reduced dimensionality GQMEs

<table>
<thead>
<tr>
<th>Full electronic density matrix PFIs</th>
<th>Populations-only PFIs</th>
<th>Single-population scalar PFIs</th>
</tr>
</thead>
</table>
| \[ F_{j,k}(\tau) \text{ Eq. (11)} \] \[
\begin{pmatrix}
F_{11,11}(\tau) & F_{11,12}(\tau) & F_{11,21}(\tau) & F_{11,22}(\tau) \\
F_{12,11}(\tau) & F_{12,12}(\tau) & F_{12,21}(\tau) & F_{12,22}(\tau) \\
F_{21,11}(\tau) & F_{21,12}(\tau) & F_{21,21}(\tau) & F_{21,22}(\tau) \\
F_{22,11}(\tau) & F_{22,12}(\tau) & F_{22,21}(\tau) & F_{22,22}(\tau)
\end{pmatrix}
\] | \[ F_{j,k}(\tau) \text{ Eq. (26)} \] \[
\begin{pmatrix}
F_{11,11}(\tau) & F_{11,22}(\tau) \\
F_{22,11}(\tau) & F_{22,22}(\tau)
\end{pmatrix}
\] | \[ F^{\parallel}(\tau) \text{ Eq. (18)} \text{ and } Z^{\parallel}(\tau) \text{ Eq. (20)} \] \[
\begin{pmatrix}
F^{11}(\tau) \\
F^{22}(\tau) \\
iZ^{22}(\tau)
\end{pmatrix}
\]
TFD-TT vs. LSCII for the Real Part of the Full Memory Kernels for Model 4

TFD-TT vs. LSCII for the Imag Part of the Full Memory Kernels for Model 4

TFD-TT vs. LSCII for the Real Part of the Reduced-Dimensionality Memory Kernels for Model 4

TFD-TT vs. LSCII for the Imag Part of the Reduced-Dimensionality Memory Kernels for Model 4

Model 4
Reduced-dimensionality GQMEs with quantum-mechanically exact TT-TFD-based projection-free inputs

<table>
<thead>
<tr>
<th>Model #</th>
<th>$\epsilon$</th>
<th>$\Gamma$</th>
<th>$\beta$</th>
<th>$\xi$</th>
<th>$\omega_c$</th>
<th>$\omega_{\text{max}}$</th>
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<td>2.5</td>
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</tbody>
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TFD-TT:
Borrelli & Gelin
Simulating open quantum system dynamics via the GQME on quantum computing devices

Yuchen Wang
Andrew Hu
Sabre Kais
Saurabh Shivpuje
Ningyi Lyu
Micheline Soley
Ellen Mulvihill
Victor Batista
Yudan Liu

(See poster for more details)
Closed system

\[ \frac{d}{dt} U(t) = -\frac{i}{\hbar} \mathcal{L} U(t) \]

\[ \hat{\sigma}(t) = U(t) \hat{\sigma}(0) \]

No dilation needed

Quantum circuit

Open system

EoM

\[ \frac{d}{dt} G(t) = -\frac{i}{\hbar} \mathcal{L}_n^0 G(t) - \int_0^t d\tau \mathcal{K}(\tau) G(t - \tau) \]

Propagator

\[ \hat{\sigma}(t) = G(t) \hat{\sigma}(0) \]

Dilation

\[ \tilde{\sigma}(t) = U_{\mathcal{G}}(t) \tilde{\sigma}(0) \]

Quantum circuit
Spin-boson model simulated by the GQME quantum algorithm as implemented on the QASM simulator.

<table>
<thead>
<tr>
<th>Model #</th>
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<th>$\beta$</th>
<th>$\xi$</th>
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<td>5.0$\Gamma^{-1}$</td>
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</tr>
<tr>
<td>4</td>
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<td>1.0</td>
<td>5.0$\Gamma^{-1}$</td>
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<td>2.5$\Gamma$</td>
</tr>
</tbody>
</table>
Spin-boson model simulated by the GQME quantum algorithm as implemented on the IBM quantum computers ibmq quito and ibmq lima.
The GQME formalism provide a rich general-purpose multi-scaling platform for formulating the exact dynamics of any quantity interest in terms of a minimal temporally and spatially compact memory kernel and inhomogeneous term, that can calculated from overall system two-time correlation functions (generally, as opposed to just in the linear response regime!).

The GQME approach appears to be very promising when it comes to simulating photo-induced electronic energy, charge and coherence dynamics in complex molecular systems and bridge the gap between theory and experiment.

Applications to molecular systems (need electronic-state-specific force fields and electronic couplings!).

Implementation with other input methods (approximate and exact).

Extension to non-electronic observables (nuclear, photonic and entangled).

Implementation on qudit quantum computing platforms.