Time-Dependent Density Matrix Renormalization Group for Electron-Vibration Coupled Problems

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Electron-vibration coupled problems

Organic molecules are flexible electron motion $\rightarrow$ nuclear motion

inter/intra-molecular vibrations

Decoherence and dissipation of electronic states

Electron-vibration coupling is key to light-emitting, charge/energy transfer/transport in organic optoelectronic materials and biological systems


1. approximate method is not universally applicable
2. quantum exponential wall for many-body wavefunction theory

<table>
<thead>
<tr>
<th>N</th>
<th>Memory</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.6 M</td>
</tr>
<tr>
<td>10</td>
<td>160 G</td>
</tr>
<tr>
<td>50</td>
<td>$10^{41}$ G</td>
</tr>
<tr>
<td>scaling</td>
<td>$\sim O(10^N)$</td>
</tr>
</tbody>
</table>

10 basis for 1 DoF
Density matrix renormalization group

The idea of RG:

- effective DoFs (states) with effective interaction


DMRG: truncation scheme based on reduced density matrix

\[ \rho_A = \text{Tr}_B(\rho) = \text{Tr}_B(|\Psi\rangle\langle\Psi|) = \sum_i w_i |i\rangle_A \langle i|_A \]

\[ \sum_i w_i = 1 \]


A subspace + B subspace

- \(|i\rangle\) : renormalized states
- \(w_i\) : weight of renormalized state
- Entanglement: von Neummann entropy

\[ S = \sum_i -w_i \log w_i \]

- The first M renormalized states form the best approximation in the 2-norm
Matrix product state (MPS)

\[ |\Psi\rangle = \sum_{\{\sigma\}} C_{\sigma_1\sigma_2...\sigma_N} |\sigma_1\sigma_2...\sigma_N\rangle \]

\[ = \sum_{\{a\},\{\sigma\}} A_{a_1}^{\sigma_1} A_{a_2}^{\sigma_2} ... A_{a_{N-1}}^{\sigma_N} |\sigma_1\sigma_2...\sigma_N\rangle \]

The size of a (bond dimension \(M_S\)) controls the accuracy

- Locality in physics
- Locality in math

The complexity of algorithm is polynomial

Matrix product operator (MPO)

\[
\hat{O} = \sum_{\{a\},\{\sigma\},\{\sigma'\}} W^{\sigma_1,\sigma'_1}_{a_1} W^{\sigma_2,\sigma'_2}_{a_1a_2} \cdots W^{\sigma_N,\sigma'_N}_{a_{N-1}} |\sigma_1 \sigma_2 \cdots \sigma_N\rangle \langle \sigma'_1 \sigma'_2 \cdots \sigma'_N|
\]


MPO takes advantage of the sparsity in operator, and the bond dimension \( M_O \) is much smaller than the number of operator terms.

\[
\hat{H}_{\text{Holstein}} = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{i \neq j} J_{ij} a_i^\dagger a_j + \sum_{i n} \frac{1}{2}(p_{in}^2 + \omega_{in}^2 x_{in}^2) + \sum_{i n} c_{in} a_i^\dagger a_i x_{in}
\]

The number of terms is \( O(N_{\text{mol}} N_{\text{vib}}) \), the full matrix representation is of size \( O(2^{N_{\text{mol}}} d^{N_{\text{mol}} N_{\text{vib}}}) \).

If written in MPO, \( M_O = 5 \) for 1D nearest neighbor hopping, otherwise \( O(N_{\text{mol}}) \).
Propagation and Compression (P&C)

\[ \Psi(t + dt) = \Psi(t) - i\hat{H}\Psi(t)dt \]

- \( M_O \)
- \( M_S \)
- \( M_O M_S \)
- \( M_S \)

\[ M_O \]
\[ M_S \]
\[ M_O M_S \]
\[ M_S \]

\[ \Phi \approx \hat{H}\Psi(t) \]

Time-dependent variational principle

\[ \langle \delta\Psi | i\frac{\partial}{\partial t} - \hat{H} |\Psi \rangle = 0 \]
\[ \frac{\partial|\Psi\rangle}{\partial t} = -i\hat{H}|\Psi\rangle \]

\[ \hat{P} = \sum_{i=1}^{N} \hat{P}[1:i-1] \otimes \hat{I}_i \otimes \hat{P}[i+1:N] - \sum_{i=1}^{N-1} \hat{P}[1:i] \otimes \hat{P}[i+1:N] \]

- energy conservation
- wavefunction norm conservation
- no large tensor decomposition


Temperature effect and density matrix evolution

Purify any density matrix to a wavefunction in an enlarged space $P \otimes Q, Q \equiv P$

$$\rho = \sum_{l} w_{l} |l\rangle_P \langle l |_P = \text{Tr}_Q |\Psi\rangle \langle \Psi|, |\Psi\rangle = \sum_{l} \sqrt{w_{l}} |l\rangle_P |l\rangle_Q$$

Thermo field dynamics

Thermal equilibrium density matrix at $\beta$

$$\rho_{\beta} = \frac{e^{-\beta H_P}}{Z_{\beta}}$$

$$|\Psi(\beta/2)\rangle = \sum_{k} \frac{e^{-\beta/2 \hat{H}_P}}{\sqrt{Z_{\beta}}} |k\rangle_P |k\rangle_Q$$

$$\langle \Psi(\beta/2) | \Psi(\beta/2) \rangle = 1$$

$$\beta = 0 \quad |\Psi(0)\rangle = \prod_{i} \sum_{\sigma_i} \frac{1}{\sqrt{d_i}} |\sigma_i\rangle_P |\sigma_i\rangle_Q$$

maximally entangled state, $M_0=1$

imaginary time SE:

$$-\frac{\partial}{\partial \tau} \Psi(\tau) = \hat{H}_P \Psi(\tau) \quad \tau = 0 \rightarrow \beta/2$$

normalization after each time-step

Spin-boson model with sub-Ohmic spectral density

\[ H = \epsilon \sigma_z + \Delta \sigma_x + \frac{1}{2} \sum_i \left( p_i^2 + \omega_i^2 q_i^2 \right) + \sigma_z \sum_i c_i q_i \]

sub-Ohmic spectral density

\[ \mathcal{J}(\omega) = \frac{\pi}{2} \alpha \omega^s \omega_c^{1-s} e^{-\omega/\omega_c} \]

\( \omega_c = 20, s = 0.5, \epsilon = 0, \Delta = 1, T = 0 \)

delocalization to localization phase transition

Computational cost with respect to the number of modes

Energy transfer in 7-site Fenna–Matthews–Olson complex

\[ H = \sum_m \varepsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_m a_m^\dagger a_n + \frac{1}{2} \sum_{mi} (p_{mi}^2 + \omega_{mi}^2 q_{mi}^2) + \sum_{mi} c_{mi} q_{mi} a_m^\dagger a_m \]

\[ d = 10, \quad N = 74 \times 7, \quad T = 77 \text{ K} \]

\[ \rho(0) = |1\rangle \otimes e^{-\beta \hat{H}_B} / Z_B(\beta) \]

Emission of DSB crystal

<table>
<thead>
<tr>
<th>N molecules</th>
<th>N modes</th>
<th>N phonons</th>
<th>dimension of Hilbert space</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-DMRG</td>
<td>18</td>
<td>14</td>
<td>18 × 10^{252}</td>
</tr>
<tr>
<td>1-particle</td>
<td>18</td>
<td>5</td>
<td>18432</td>
</tr>
<tr>
<td>2-particle</td>
<td>18</td>
<td>2</td>
<td>73728</td>
</tr>
</tbody>
</table>

\[
\sigma(\omega) \propto -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} C(t)e^{i\omega t} dt
\]

\[
C(t) = -i\theta(t) \langle [\hat{\mu}(t), \hat{\mu}] \rangle_{\text{gs,ex}}
\]

correlated initial state \[ \hat{H}|\psi\rangle = E|\psi\rangle \]

\[
\text{Exp: } 1.4 \text{ K} \quad \text{Wu, C.; Delong, M.; Vardeny, Z.; Ferraris, J.} \text{ Synth. Met.} \text{ 2003, 137, 939.}
\]

\[
\text{Ren, J.; Shuai, Z.; Kin-Lic Chan, G.} \text{ J. Chem. Theory Comput.} \text{ 2018, 14, 5027.}
\]

Anharmonic effect in molecular photophysics

\[ \hat{H}_{i/f} = \hat{T} + V_{i/f}(q) \]

\[ q_{i,m} = \sum_l J_{ml}q_{f,l} + \Delta q_{i,m} \]

**displacement, torsion, rotation**

weak nonadiabatic coupling regime (FGR is valid):

\[ \Psi_{i/f}(r, q) = \phi_{i/f}(r; q)X_{i/f}(q) \]

\[ k_{ic} = \int_{-\infty}^{\infty} e^{i\Delta E_{\text{ad}}t} C(t) \, dt \]

\[ \hat{H}_1 = -\sum_l F_{fi}^l(q) |\phi_l| \langle \phi_l | \frac{\partial}{\partial q_l} | \phi_f \rangle + \text{h.c.} \]

\[ C(t) = \langle \hat{H}_1(t)\hat{H}_1 \rangle_T = \text{Tr} \left( \frac{e^{-\beta \hat{H}_1}}{Z(\beta)} e^{i\hat{H}_1 dt} e^{-i\hat{H}_1 dt} \hat{H}_1 \right) \]

\[ F_{fi}^l(q) = \langle \phi_f | \frac{\partial}{\partial q_l} | \phi_i \rangle \]

N-mode representation (n-MR) theory

The first anti-Kasha emissive molecule  
$S_1 \rightarrow S_0$ internal conversion is very fast

- **1-mode, 2-mode, 3-mode... hierarchical expansion**

\[ V(q_1, q_2, \ldots, q_N) = V^{(0)}(q^{\text{ref}}) + \sum_i V^{(1)}(q_i; q_i^{\text{ref}}) \]
\[ + \sum_{i<j} V^{(2)}(q_i, q_j; q_i^{\text{ref}}) + \cdots \]

\[ V^{(1)}(q_i; q_i^{\text{ref}}) = V(q_i; q_i^{\text{ref}}) - V^{(0)}(q^{\text{ref}}) \]

\[ V^{(2)}(q_i, q_j; q_i^{\text{ref}}) = V(q_i, q_j; q_i^{\text{ref}}) - V^{(1)}(q_i; q_i^{\text{ref}}) \]

\[ -V^{(1)}(q_j; q_i^{\text{ref}}) - V^{(0)}(q^{\text{ref}}) \]


- **reorganization energy (check the quality of the PES) units: cm$^{-1}$**

<table>
<thead>
<tr>
<th></th>
<th>4-points method</th>
<th>harmonic</th>
<th>1-MR</th>
<th>2-MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$ surface</td>
<td>3481.9</td>
<td>3399.2</td>
<td>3421.4</td>
<td>3495.7</td>
</tr>
<tr>
<td>error</td>
<td>-82.7</td>
<td>-60.5</td>
<td>13.8</td>
<td></td>
</tr>
</tbody>
</table>

b3lyp/6-31g(d)
**$k_{ic}$ of azulene from $S_1$ to $S_0$**

<table>
<thead>
<tr>
<th>Method</th>
<th>$k_{ic} \times 10^{10}$ s$^{-1}$ at 0 K</th>
<th>$k_{ic} \times 10^{10}$ s$^{-1}$ at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HA 1-MR 2-MR</td>
<td>HA 1-MR 2-MR</td>
</tr>
<tr>
<td>TVCF</td>
<td>0.79 - -</td>
<td>1.00 - -</td>
</tr>
<tr>
<td>TD-DMRG</td>
<td>0.79 1.47 (186%) 3.56 (451%)</td>
<td>0.97 1.86 (192%) 4.53 (467%)</td>
</tr>
</tbody>
</table>

$t = 425$ fs, SHO basis = 20
100 cm$^{-1}$ Gaussian broadening

- 1-MR is 2 times the rate of HA
- 2-MR is 4 times the rate of HA

**HA: Thermal Vibration Correlation Function approach (TVCF) is analytically exact**

Final state resolved transition rate

\[ k = \int_{-\infty}^{\infty} \langle \psi_0 | \hat{H}_1(t) \hat{H}_1 | \psi_0 \rangle dt \]

\[ = \int_{-\infty}^{\infty} \text{Tr}(\hat{H}_1 | \psi_0 \rangle \langle \psi_0 | \hat{H}_1(t)) dt \]

\[ = \int_{-\infty}^{\infty} \sum_{\{\sigma\}} \langle \{\sigma\} | \rho(t) | \{\sigma\} \rangle dt \]

\[ = \sum_{\{\sigma\}} \int_{-\infty}^{\infty} \langle \{\sigma\} | \rho(t) | \{\sigma\} \rangle dt \]

\[ = \sum_{\{\sigma\}} k(\psi_0 \rightarrow \{\sigma\}) \]

If the primitive basis \{\sigma\} is the eigenbasis, the final state resolved rate corresponds to each configuration coefficient of the integral of \(\rho(t)\).

- HA: SHO (exact)
- 1-MR: VSCF modal (exact)
• High frequency C-H vibrations with ~0 Huang-Rhys factor are able to accept energy;
• the mean vibrational quantum number of the other modes decreases;

the FC factor is larger and the rate is faster.

Contribution of each final state

Monte Carlo sampling to get $5 \times 10^5$ configurations (in total $10^{48}$)

<table>
<thead>
<tr>
<th></th>
<th>PES</th>
<th>HA</th>
<th>1-MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of total rate</td>
<td>71.5%</td>
<td>70.8%</td>
<td></td>
</tr>
</tbody>
</table>

$\rho(\omega) = \sum_i k_i \delta(\omega - \omega_i)$

10 cm$^{-1}$ Gaussian broadening

The larger the energy gap, the more pronounced the anharmonic effect.

High-accurate, high-efficient TD-DMRG algorithm for high-dimensional quantum dynamics at both zero and finite temperature.

- system-bath model with harmonic bath and linear coupling
- molecular photophysical properties on anharmonic PES

https://github.com/shuaigroup/Renormalizer
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Thanks for your attention!