

The Multiconfiguration Time-Dependent Hartree (MCTDH) Method and its Multi-Layer (ML-MCTDH) Extension

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- 1 Multiconfiguration time-dependent Hartree, MCTDH
- 2 Multi-Layer MCTDH
- 3 MCTDH and ML-MCTDH viewed as tensor decomposition methods
- 4 Compact representations of the PES
- 5 Highlights and Conclusions

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The *ansatz* for the MCTDH wavefunction reads

$$\begin{aligned}\Psi(q_1, \dots, q_f, t) &= \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1, \dots, j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) \\ &= \sum_J A_J \Phi_J\end{aligned}$$

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Single-particle functions:

$$\varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) = \sum_{l=1}^{N_\kappa} c_{j_\kappa l}^{(\kappa)}(t) \chi_l^{(\kappa)}(q_\kappa)$$

MCTDH equations of motion:

$$i\dot{A}_J = \sum_L \langle \Phi_J | \hat{H} | \Phi_L \rangle A_L$$

$$i\dot{\varphi}_j^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \sum_{k,l} \rho_{j,k}^{(\kappa)-1} \langle \hat{H} \rangle_{k,l}^{(\kappa)} \varphi_l^{(\kappa)}$$

Time-independent Schrödinger equation

Applying a variational principle leads to an eigenvalue problem for the coefficients

$$\sum_L \langle \Phi_J | \hat{H} | \Phi_L \rangle A_L = E A_J$$

and a relaxation procedure for the single-particle functions

$$\frac{\partial}{\partial \tau} \varphi_j^{(\kappa)} := - \left(1 - P^{(\kappa)} \right) \sum_{k,l=1}^{n_\kappa} \left(\rho^{(\kappa)} \right)_{jk}^{-1} \langle \hat{\mathbf{H}} \rangle_{kl}^{(\kappa)} \varphi_l^{(\kappa)} \rightarrow 0.$$

- Equations must be fulfilled simultaneously
- Start with a guess wavefunction
- Solve iteratively until self-consistency ("Improved relaxation")

MCTDH with Mode Combination

$$\underbrace{(q_1, q_2)}_{Q_1}, \underbrace{(q_3, q_4, q_5)}_{Q_2}, \underbrace{(q_6)}_{Q_3}, \dots, \underbrace{(q_{f-1}, q_f)}_{Q_p}$$

MCTDH with Mode Combination

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MCTDH wavefunction

$$\begin{aligned} \Psi(q_1, \dots, q_f, t) &\equiv \Psi(Q_1, \dots, Q_p, t) \\ &= \sum_{j_1}^{n_1} \dots \sum_{j_p}^{n_p} A_{j_1, \dots, j_p}(t) \prod_{\kappa=1}^p \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \end{aligned}$$

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Single-particle functions:

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \sum_{l_1=1}^{N_{1,\kappa}} \cdots \sum_{l_d=1}^{N_{d,\kappa}} c_{j_\kappa l_1 \dots l_d}^{(\kappa)}(t) \chi_{l_1}^{(\kappa)}(q_{1,\kappa}) \cdots \chi_{l_d}^{(\kappa)}(q_{d,\kappa})$$

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Exponential Scaling:

$$\text{Standard} : N^f, \quad \text{MCTDH} : n^f, \quad \text{combined} : (\tilde{n}^{1/d})^f$$

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- Mode-combination has proved to be very helpful
- But mode-combination orders larger than 3 or 4 make the propagation of the SPFs infeasible
- Use MCTDH to propagate the SPFs of an underlying MCTDH calculation

H. Wang and M. Thoss J.Chem.Phys. **119** (2003), 1289.

U. Manthe J.Chem.Phys. **128** (2008), 164116.

O. Vendrell and H.-D. Meyer J.Chem.Phys. **134** (2011), 044135.

ML-MCTDH expansion of wavefunction

$$\Psi(Q_1^1, \dots, Q_p^1) = \sum_{j_1=1}^{n_1^1} \cdots \sum_{j_p=1}^{n_p^1} A_{1;j_1, \dots, j_p}^1 \prod_{\kappa_1=1}^p \varphi_{j_{\kappa_1}}^{(1; \kappa_1)}(Q_{\kappa_1}^1)$$

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$$\varphi_m^{(1; \kappa_1)}(Q_{\kappa_1}^1) = \sum_{j_1=1}^{n_1^2} \cdots \sum_{j_{p_{\kappa_1}}=1}^{n_{p_{\kappa_1}}^2} A_{m; j_1, \dots, j_{p_{\kappa_1}}}^{2; \kappa_1} \prod_{\kappa_2=1}^{p_{\kappa_1}} \varphi_{j_{\kappa_2}}^{(2; \kappa_1, \kappa_2)}(Q_{\kappa_2}^{2; \kappa_1})$$

ML-MCTDH expansion of wavefunction

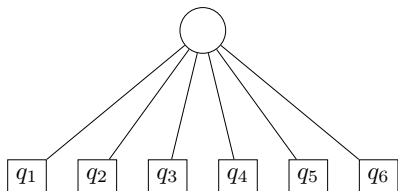
$$\Psi(Q_1^1, \dots, Q_p^1) = \sum_{j_1=1}^{n_1^1} \cdots \sum_{j_p=1}^{n_p^1} A_{1;j_1, \dots, j_p}^1 \prod_{\kappa_1=1}^p \varphi_{j_{\kappa_1}}^{(1; \kappa_1)}(Q_{\kappa_1}^1)$$

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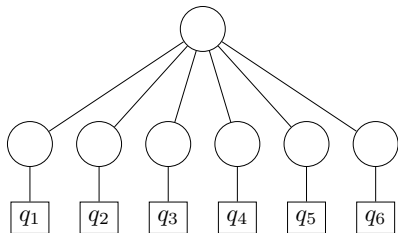
$$\varphi_m^{(2; \kappa_1, \kappa_2)}(\underbrace{Q_{\kappa_2}^{2; \kappa_1}}_{q_\alpha}) = \sum_{j=1}^{N_\alpha} A_{m;j}^{3; \kappa_1, \kappa_2} \chi_j^{(\alpha)}(q_\alpha)$$

$$Q_{\kappa_\ell}^{\ell; \kappa_1, \dots, \kappa_{\ell-1}} = \{Q_1^{\ell+1; \kappa_1, \dots, \kappa_\ell}, \dots, Q_{p_{\kappa_\ell}}^{\ell+1; \kappa_1, \dots, \kappa_\ell}\}$$

Standard Method and MCTDH trees

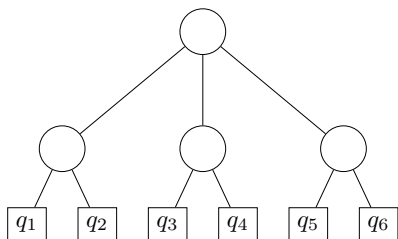


Standard
Method

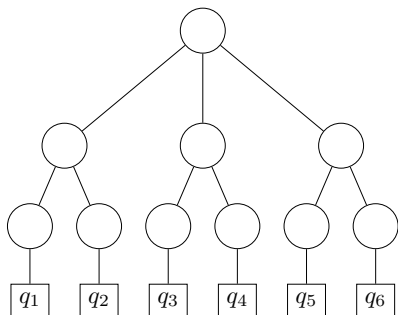


MCTDH

MCTDH and ML-MCTDH trees

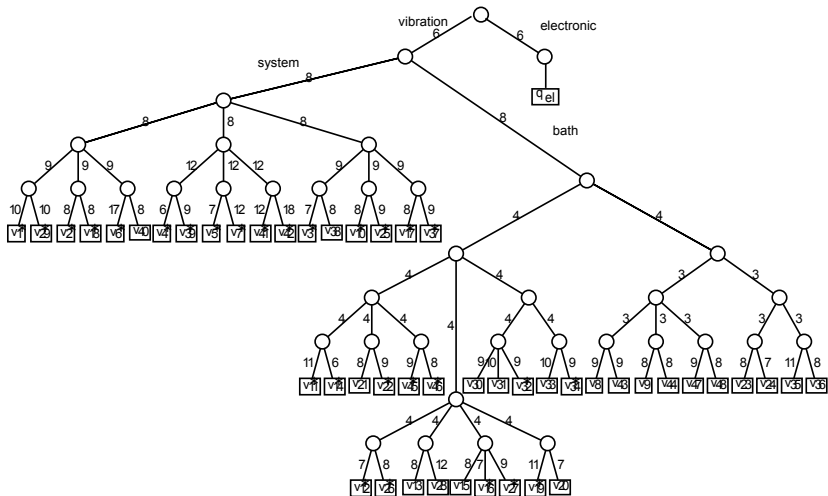


MCTDH
combined

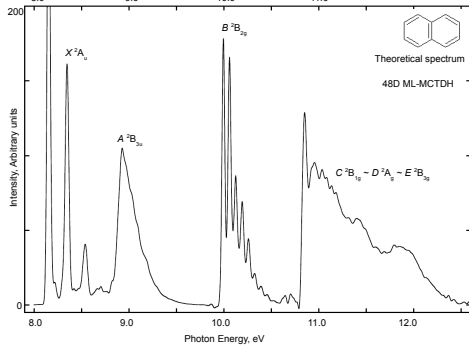
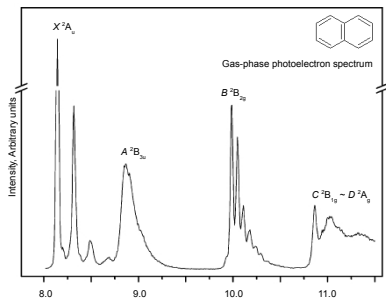


ML-MCTDH

ML-MCTDH tree for naphthalene (48D)



PE-spectrum of naphthalene (48D) Q. Meng



- Henon-Heiles: 6D, 18D, 1458D
- Pyrazine: 24D, 2E
- Difluorobenzene cation: 30D, 5E
- Naphtalene cation: 48D, 6E
- Anthracene cations: 66D, 6E
- Formaldehyde Oxide: 9D, 5E

Conclusions ML-MCTDH

- ML-MCTDH is capable to treat very large systems with hundreds of degrees of freedom.
- ML-MCTDH is very suitable for studying system/bath problems.
- ML-MCTDH is most useful when using model Hamiltonians. However, model Hamiltonians like the VC-Hamiltonian can be very helpful to investigate real chemical systems.
- ML-MCTDH is very fast in a low accuracy mode but may become costly if a high accuracy is asked for.

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Standard Method

$$\Psi(q_1, \dots, q_f) = \sum_{i_1}^{N_1} \cdots \sum_{i_f}^{N_f} \psi_{i_1, \dots, i_f} \chi_{i_1}^{(1)}(q_1) \cdots \chi_{i_f}^{(f)}(q_f)$$

Expansion of coefficients

Standard Method

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MCTDH

$$\Psi_{i_1, \dots, i_f} = \sum_{j_1, \dots, j_f} A_{j_1, \dots, j_f} c_{j_1, i_1}^{(1)} \cdots c_{j_f, i_f}^{(f)}$$

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MCTDH combined

$$\Psi_{i_1, \dots, i_f} = \sum_{j_1, \dots, j_p} A_{j_1, \dots, j_p} c_{j_1, i_1 \dots i_d}^{(1)} \cdots c_{j_p, i_{d+1} \dots i_f}^{(p)}$$

Expansion of coefficients

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MCTDH is a decomposition of the wave-function tensor into a (time-dependent) Tucker form!

Expansion of coefficients in ML-MCTDH form

ML-MCTDH (one extra layer)

$$\begin{aligned}\Psi_{i_1, \dots, i_f} = & \sum_{j_1, \dots, j_p} A_{j_1, \dots, j_p}^{(1)} \left(\sum_{k_1, \dots, k_{p_1}} A_{j_1, k_1, \dots, k_{p_1}}^{(2;1)} A_{k_1, i_1}^{(3;1,1)} \dots A_{k_{p_1}, i_{p_1}}^{(3;1, p_1)} \right) \times \dots \\ & \dots \times \left(\sum_{k_1, \dots, k_{p_{\kappa_1}}} A_{j_{\kappa_1}, k_1, \dots, k_{p_{\kappa_1}}}^{(2; \kappa_1)} A_{k_1, i_\alpha}^{(3; \kappa_1, 1)} \dots A_{k_{p_{\kappa_1}}, i_f}^{(3; \kappa_1, p_{\kappa_1})} \right) \times \dots \\ & \dots \times \left(\sum_{k_1, \dots, k_{p_p}} A_{j_p, k_1, \dots, k_{p_p}}^{(2; p)} A_{k_1, i_\alpha}^{(3; p, 1)} \dots A_{k_{p_p}, i_f}^{(3; p, p_p)} \right)\end{aligned}$$

Hierarchical Tucker format

CANDECOMP, CP

$$\Psi(q_1, \dots, q_f) = \sum_r a_r \varphi_r^{(1)}(q_1) \cdots \varphi_r^{(f)}(q_f)$$

$$\Psi_{i_1, \dots, i_f} = \sum_r a_r c_{r, i_1}^{(1)} \cdots c_{r, i_f}^{(f)}$$

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Tensor Train (TT) format. Similar to matrix product states.

TT can be viewed as a simplified, restricted form of the Hierarchical Tucker format (i.e. ML-MCTDH).

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Product representation of the Hamiltonian

The computation of the Hamiltonian matrix $\langle \Phi_J | \hat{H} | \Phi_L \rangle$ and the mean-fields $\langle \hat{\mathbf{H}} \rangle_{k,l}^{(\kappa)}$ requires the evaluation of multi-dimensional integrals. It is essential that these integrals are done fast.

To this end we require the Hamiltonian to be in product form

$$\hat{H} = \sum_{r=1}^s c_r \prod_{\kappa=1}^p \hat{h}_r^{(\kappa)}$$

where $\hat{h}_r^{(\kappa)}$ operates on the κ -th particle only.

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where $\hat{h}_r^{(\kappa)}$ operates on the κ -th particle only.

The multi-dimensional integrals can then be written as a sum of products of one- or low-dimensional integrals

$$\langle \Phi_J | \hat{H} | \Phi_L \rangle = \sum_{r=1}^s c_r \langle \varphi_{j_1}^{(1)} | \hat{h}_r^{(1)} | \varphi_{l_1}^{(1)} \rangle \dots \langle \varphi_{j_p}^{(p)} | \hat{h}_r^{(p)} | \varphi_{l_p}^{(p)} \rangle$$

The most direct way to the product form is an expansion in a product basis. Hence we approximate some given potential V by

$$V^{\text{app}}(Q_1, \dots, Q_p) = \sum_{j_1=1}^{m_1} \dots \sum_{j_p=1}^{m_p} C_{j_1 \dots j_p} v_{j_1}^{(1)}(Q_1) \dots v_{j_p}^{(p)}(Q_p)$$

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working with grids:

$$V_{i_1 \dots i_p}^{\text{app}} = \sum_{j_1=1}^{m_1} \dots \sum_{j_p=1}^{m_p} C_{j_1 \dots j_p} v_{i_1 j_1}^{(1)} \dots v_{i_p j_p}^{(p)}$$

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Tucker format!

The coefficients are given by overlap

$$C_{j_1 \dots j_p} = \sum_{i_1=1}^{N_1} \dots \sum_{i_p=1}^{N_p} v_{i_1 j_1}^{(1)} \dots v_{i_p j_p}^{(p)} V_{i_1 \dots i_p}$$

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More difficult is to find optimal single-particle potentials (SPPs). We define the SPPs as eigenvectors of the potential density matrices

$$\varrho_{kk'}^{(\kappa)} = \sum_I V_{i_1 \dots i_{\kappa-1} k i_{\kappa+1} \dots i_p} V_{i_1 \dots i_{\kappa-1} k' i_{\kappa+1} \dots i_p}$$

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POTFIT is feasible for at most 10^9 grid points (7 DOF, say).

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POTFIT (1996), HOSVD (2000).

MGPF

- Chose a fine (N_{κ}) and a coarse (n_{κ}) product grid. The coarse grid should be part of the fine grid.
- Perform a full (i.e. exact) POTFIT on the coarse grid.
- Interpolate the SPPs to the fine grid ($\tilde{\cdot}$ = fine-grid):

$$\tilde{\mathbf{v}}^{(\kappa)} = \tilde{\boldsymbol{\rho}}^{(\kappa)} \boldsymbol{\rho}^{(\kappa)^{-1}} \mathbf{v}^{(\kappa)}$$

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MCPF

- Perform all "integrations" over the grid by Monte Carlo.
- To be accurate, the determination of the coefficients requires now the inversion of a huge matrix.
- A Boltzmann weighting is easy to include.

Further size reduction, CANDECAMP and ML-Potfit

Potfit and its MG and MC variants express the potential tensor in a Tucker format. But MCTDH does not require this structure, a CANDECAMP is sufficient. As the latter can be more compact, we want to further decrease the size of the potential representation by reducing the Tucker format generated by MG- or MC-Potfit to a CANDECAMP. But how to do that?

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As there is ML-MCTDH, one may think of ML-POTFIT. This will lead to a more compact representation, but not to a faster evaluation, because MCTDH cannot make use of the hierarchical Tucker format structure.

However, ML-MCTDH can do!

See: F. Otto, J.Chem.Phys. **140**, 014106 (2014)

High dimensional model representation, HDMR

Hierarchical representation of a multidimensional function

$$\tilde{V}(\mathbf{q}) = V^{(0)} + \sum_{\alpha=1}^f V_{\alpha}^{(1)}(q_{\alpha}) + \sum_{\alpha < \beta}^f V_{\alpha\beta}^{(2)}(q_{\alpha}, q_{\beta}) + \sum_{\alpha < \beta < \gamma}^f V_{\alpha\beta\gamma}^{(3)}(q_{\alpha}, q_{\beta}, q_{\gamma}) \cdots$$

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The component functions (clusters) are determined as:

$$V^{(0)} = V(\mathbf{a})$$

$$V_{\alpha}^{(1)}(q_{\alpha}) = V(q_{\alpha}; \mathbf{a}^{\alpha}) - V^{(0)}$$

$$V_{\alpha\beta}^{(2)}(q_{\alpha}, q_{\beta}) = V(q_{\alpha}, q_{\beta}; \mathbf{a}^{\alpha\beta}) - V_{\alpha}^{(1)}(q_{\alpha}) - V_{\beta}^{(1)}(q_{\beta}) - V^{(0)}$$

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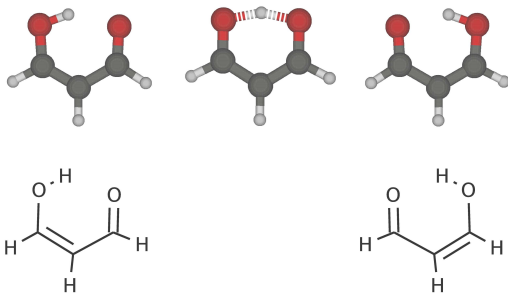
$$\begin{aligned} V^{(0)} &= V(\mathbf{a}) \\ V_{\alpha}^{(1)}(q_{\alpha}) &= V(q_{\alpha}; \mathbf{a}^{\alpha}) - V^{(0)} \\ V_{\alpha\beta}^{(2)}(q_{\alpha}, q_{\beta}) &= V(q_{\alpha}, q_{\beta}; \mathbf{a}^{\alpha\beta}) - V_{\alpha}^{(1)}(q_{\alpha}) - V_{\beta}^{(1)}(q_{\beta}) - V^{(0)} \end{aligned}$$

Unfortunately, the number of clusters increases strongly with order.

Possible improvements:

- Perform the cluster expansion in combined modes
- One may use more than one reference point
- One may use a reference path rather than a reference point

Tunneling splitting in malonaldehyde



9 Atoms, 21 degrees of freedom

J. Chem. Phys. **134** (2011), 234307

J. Chem. Phys. **141** (2014), 034116

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Highlights and Breakthroughs

- 1990, Very first MCTDH publication, Meyer, Manthe, Cederbaum
- 1999, pyrazine, 24D, 2E, Raab, Worth, Meyer, Cederbaum
- 2003, Dissipative quantum dynamics, 61D, Nest, Meyer
- 2005, Vibronic spectrum of $C_5H_4^+$, 21D 5E, Markmann *et al*
- 2007, IR spectrum of $H_5O_2^+$, (15D) Vendrell *et al*
- 2008, Tunneling dynamics of bosons, Zöllner *et al*
- 2009, Isotopologues of $H_5O_2^+$, (15D) Vendrell *et al*
- 2011, 2014, Tunnelling splittings in malonaldehyde, 21D, Schröder, Meyer
- 2013, Vibronic dynamics of naphthalene (48D,6E) and anthracene (66D,6E) cations, Meng, Meyer

Conclusions

MCTDH, realistic problems with 5 to 9 atoms

- Search for good coordinates.
- Deriving the KEO can be cumbersome, but it is a solved problem.
- Finding a compact representation for the PES is a major problem for molecules with 5 or more atoms.
The PES representation is often the source of largest errors.
Work on improving PES-representations is in progress.
- Finally, the MCTDH calculation as such may take a considerable amount of CPU-time, but MCTDH is stable and we can check its accuracy.

People, who made the Heidelberg MCTDH package

- Graham Worth, Birmingham (MCTDH, pyrazine)
- Fabien Gatti, Montpellier (Kinetic energy operators)
- Oriol Vendrell, Hamburg (ML-MCTDH, Zundel-cation)
- Michael Brill (Parallelization of MCTDH)
- Andreas Raab (Density operator propagation)
- Markus Schröder, Heidelberg (Malonaldehyde, MC-Potfit)
- Frank Otto, Hong Kong (ML-MCTDH, ML-Potfit)
- Daniel Pelaez-Ruiz, Lille (MG-Potfit, H_3O_2^-)
- Qingyong Meng, Dalian (ML calculations with VCH)

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Thank you!

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