

A gentle introduction to MCTDH

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- 1 Nuclear Quantum Dynamics
 - The Standard method
 - The Time-Dependent Hartree method
- 2 The Multiconfiguration Time-Dependent Hartree method
 - EOMs
 - Relaxation and block-improved relaxation
- 3 Potential energy surface representations
 - Tensor decomposition algorithms
- 4 Code structure and example applications

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Nuclear Quantum Dynamics

What

The subfield of Theoretical Chemistry in which both the **electrons** and the **nuclei** of a molecular system are treated in a **quantum-mechanical** manner.

Nuclear Quantum Dynamics

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The subfield of Theoretical Chemistry in which both the **electrons** and the **nuclei** of a molecular system are treated in a **quantum-mechanical** manner.

When

- Spectroscopy (e.g. IR transitions)
- Quantum tunneling
- Vibronic coupling
- ZPE determination

Nuclear Quantum Dynamics

Find the numerical solution of the TDSE truncating the Hilbert space to a finite dimension (Galerkin's method):

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (1)$$

Given a parametric representation of the WF (Ψ), the optimal solution can be found using the Dirac-Frenkel Variational Principle (DF-VP):

$$\langle \delta \Psi | \hat{H} - i \frac{\partial}{\partial t} | \Psi \rangle = 0 \quad (2)$$

The Standard method

Most direct representation of the WF:

$$\Psi(q_i, \dots, q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \dots j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa) \quad (3)$$

After plugging this WF into the DF-VP, and performing the corresponding algebra we obtain the following EOMs:

$$\begin{aligned} i\dot{\mathbf{C}}_L &= \sum_J \langle \varphi_L | \hat{H} | \varphi_J \rangle C_J \\ \mathbf{C}(t) &= e^{-iHt} \mathbf{C}(0) \end{aligned} \quad (4)$$

where we have introduced the composite indexes $J = (j_1, \dots, j_f)$.

The Time-Dependent Hartree method

If we now consider time-dependent single-particle functions (SPFs):

$$\Psi(q_1, \dots, q_f, t) = A(t) \prod_{\kappa=1}^f \underbrace{\sum_{\mu=1}^{N_{\kappa}} c_{\mu}^{(\kappa, j_{\kappa})}(t) \cdot \chi_{\mu}^{(\kappa)}(q_{\kappa})}_{\varphi_{\kappa}(q_{\kappa}, t)} \quad (5)$$

and use the DF-VP with arbitrary real constraints $g_{\kappa} = i \langle \varphi_{\kappa}(t) | \dot{\varphi}_{\kappa}(t) \rangle$, we get the EOMs:

$$\begin{aligned} A(t) &= A(0) \cdot e^{-i \int_0^t E(t') dt'} \\ i \dot{\varphi}_{\kappa} &= (\mathcal{H}^{(\kappa)} - E) \varphi_{\kappa} \end{aligned} \quad (6)$$

with $\mathcal{H}^{(\kappa)} = \langle \Phi^{(\kappa)} | H | \Phi^{(\kappa)} \rangle$.

Limitations of SM and TDH

Standard method

Its application is largely limited due to the **curse of dimensionality**. Only systems up to four atoms (6D) can be addressed in practice.

Time-Dependent Hartree

A better approach, but physically inaccurate. The **nuclear correlation** is harder to retrieve than the electronic correlation due to the nuclei's larger mass. The character of the nuclear WF is inherently **multiconfigurational**.

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Ansätze comparison

Standard Method (CI)

$$\Psi(q_i, \dots, q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \dots j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa) \quad (7)$$

Ansätze comparison

Standard Method (CI)

$$\Psi(q_i, \dots, q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \dots j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa) \quad (7)$$

Time-Dependent Hartree (HM)

$$\Psi(q_1, \dots, q_f, t) = A(t) \prod_{\kappa=1}^f \varphi_{\kappa}^{(\kappa)}(q_\kappa, t) \quad (8)$$

Ansätze comparison

Standard Method (CI)

$$\Psi(q_i, \dots, q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \dots j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa) \quad (7)$$

Time-Dependent Hartree (HM)

$$\Psi(q_1, \dots, q_f, t) = A(t) \prod_{\kappa=1}^f \varphi_{\kappa}^{(\kappa)}(q_\kappa, t) \quad (8)$$

Multiconfiguration Time-Dependent Hartree (MCSCF)

$$\Psi(q_1, \dots, q_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1, \dots, j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) \quad (9)$$

MCTDH origins and distribution

MCTDH was originally developed by Meyer and coworkers from the University of Heidelberg, in the early nineties:

THE MULTI-CONFIGURATIONAL TIME-DEPENDENT HARTREE APPROACH

H.-D. MEYER, U. MANTHE and L.S. CEDERBAUM

Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, D-6900 Heidelberg, Federal Republic of Germany

Received 11 October 1989

There are currently three major implementations of the algorithm:



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The MCTDH EOMs

The MCTDH ansatz has a very flexible Sum-of-Products (SOP) form:

$$\Psi(q_1, \dots, q_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1, \dots, j_f}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) \quad (10)$$

with time dependent SPFs

$$\varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) = \sum_{\mu=1}^{N_\kappa} c_\mu^{(\kappa, j_\kappa)}(t) \cdot \chi_\mu^{(\kappa)}(q_\kappa) \quad (11)$$

The $\chi_\mu^{(\kappa)}(q_\kappa)$ are typically DVR functions.

The MCTDH EOMs

The *ansatz* WF is determined up to a multiplicative constant. To derive the EOMs arbitrary constraint operators ($\hat{g}^{(\kappa)}$) are introduced:

$$i \langle \varphi_l^{(\kappa)} | \dot{\varphi}_j^{(\kappa)} \rangle = \langle \varphi_l^{(\kappa)} | \hat{g}^{(\kappa)} | \varphi_l^{(\kappa)} \rangle \quad (12)$$

Using once again the DF-VP we get (for $\hat{g}^{(\kappa)} \equiv 0$):

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

$$i \dot{\varphi}_j^{(\kappa)} = (1 - \hat{P}^{(\kappa)}) \sum_{k,l=1}^{n_\kappa} (\rho^{(\kappa)-1})_{jk} \langle \hat{H} \rangle_{kl}^{(\kappa)} \varphi_l^{(\kappa)} \quad (13)$$

The MCTDH EOMs

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

$$i\dot{\varphi}_j^{(\kappa)} = (1 - \hat{\rho}^{(\kappa)}) \sum_{k,l=1}^{n_\kappa} (\rho^{(\kappa)-1})_{jk} \langle \hat{H} \rangle_{kl}^{(\kappa)} \varphi_l^{(\kappa)} \quad (14)$$

$$\Phi_J = \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)} \quad (15)$$

$$\rho_{kl}^{(\kappa)} = \langle \Psi_k^{(\kappa)} | \Psi_l^{(\kappa)} \rangle = \sum_{J^\kappa} A_{j_k^\kappa}^* A_{j_l^\kappa} \quad \langle \hat{H} \rangle_{kl}^{(\kappa)} = \langle \Psi_k^{(\kappa)} | \hat{H} | \Psi_l^{(\kappa)} \rangle \quad (16)$$

$$\hat{\rho}^{(\kappa)} = \sum_{j=1}^{n_\kappa} |\varphi_j^{(\kappa)}\rangle \langle \varphi_j^{(\kappa)}| \quad (17)$$

MCTDH integration scheme

The MCTDH-EOMs solution is expensive due to the large amount of multidimensional integrals to solve. Since the **mean fields** are not strongly oscillating we can consider (CMF integration):

$$\begin{aligned}
 i\dot{A}_J &= \sum_L \bar{\mathcal{K}}_{JL} A_J \\
 i\dot{\varphi}_j^{(1)} &= (1 - \hat{P}^{(1)}) \{ \hat{h}^{(1)} \varphi_j^{(1)} + \sum_{k,l=1}^{n_1} (\rho^{(1)})_{jk}^{-1} \langle \bar{H}_R \rangle_{kl}^{(1)} \varphi_l^{(1)} \} \\
 &\vdots \\
 i\dot{\varphi}_j^{(f)} &= (1 - \hat{P}^{(f)}) \{ \hat{h}^{(f)} \varphi_j^{(f)} + \sum_{k,l=1}^{n_f} (\rho^{(f)})_{jk}^{-1} \langle \bar{H}_R \rangle_{kl}^{(f)} \varphi_l^{(f)} \}
 \end{aligned} \tag{18}$$

Mode combination

Nothing prevents us from grouping physical coordinates into logical particles:

$$Q_\kappa \equiv (q_{\kappa,1}, q_{\kappa,1}, \dots, q_{\kappa,d})$$

$$\varphi_j^{(\kappa)}(Q_\kappa, t) = \varphi_j^{(\kappa)}(q_{\kappa,1}, q_{\kappa,1}, \dots, q_{\kappa,d}, t) \quad (19)$$

Under these conditions, the MCTDH *ansatz* will take the form:

$$\Psi(Q_1, \dots, Q_p, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_p=1}^{n_p} A_{j_1, \dots, j_p}(t) \prod_{\kappa=1}^p \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \quad (20)$$

$$\varphi_j^{(\kappa)}(Q_\kappa, t) = \sum_{i_1 \dots i_d} c_{i_1 \dots i_d}^{(\kappa, j)}(t) \prod_{\nu=1}^d \chi^{(\kappa, \nu)}(q_{\kappa, \nu})$$

Multilayer MCTDH (3-layer case)

We can propagate the multidimensional SPFs with MCTDH itself!

$$\Psi(q_1, q_2, q_3, t) = \sum_{j_{12}=1}^{n_{12}} \sum_{j_3=1}^{n_3} A_{j_{12}j_3}(t) \varphi_{j_{12}}^{(12)}(q_1, q_2, t) \varphi_{j_3}^{(3)}(q_3, t) \quad (21)$$

where we have introduced:

$$\varphi_{j_{12}}^{(12)}(q_1, q_2, t) = \sum_{k_1=1}^{n_1} \sum_{k_2=1}^{n_2} B_{k_1, k_2}^{(12, j_{12})} \prod_{\mu=1}^2 \xi_{k_\mu}^{(\mu)}(q_\mu, t) \quad (22)$$

and:

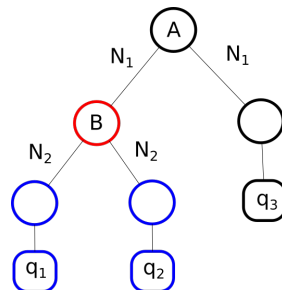
$$\xi_{k_\mu}^{(\mu)}(q_\mu, t) = \sum_{i_\mu=1}^{N_\mu} c_{i_\mu}^{(\mu, k_\mu)} \chi_{i_\mu}^{(\mu)}(q_\mu) \quad (23)$$

Multilayer MCTDH (3-layer case)

$$\Psi(q_1, q_2, q_3, t) = \sum_{j_{12}=1}^{n_{12}} \sum_{j_3=1}^{n_3} A_{j_{12}j_3}(t) \varphi_{j_{12}}^{(12)}(q_1, q_2, t) \varphi_{j_3}^{(3)}(q_3, t)$$

$$\varphi_{j_{12}}^{(12)}(q_1, q_2, t) = \sum_{k_1=1}^{n_1} \sum_{k_2=1}^{n_2} B_{k_1, k_2}^{(12, j_{12})} \prod_{\mu=1}^2 \xi_{k_\mu}^{(\mu)}(q_\mu, t)$$

$$\xi_{k_\mu}^{(\mu)}(q_\mu, t) = \sum_{i_\mu=1}^{N_\mu} c_{i_\mu}^{(\mu, k_\mu)} \chi_{i_\mu}^{(\mu)}(q_\mu)$$



Obtaining vibrational orbitals

MCTDH can be also used to solve the TISE. The GS distribution of the system can be obtained by propagation in negative imaginary time $\tau = -it$:

$$\dot{\Psi} = -\hat{H}\Psi \quad (24)$$

The new algorithm can be derived by applying the time-independent variational principle with Lagrange multipliers:

$$\delta\{\langle\Psi|\hat{H}|\Psi\rangle - E(\sum_J A_J^* A_J - 1) - \sum_{\kappa=1}^f \sum_{j,l=1}^{n_{\kappa}} \epsilon_{jl}^{(\kappa)} [\langle\varphi_j^{(\kappa)}|\varphi_l^{(\kappa)}\rangle - \delta_{jl}]\} = 0 \quad (25)$$

Obtaining vibrational orbitals

Taking the variations with respect to the complex conjugate of both the A-vector and the SPFs independently we get:

$$\sum_K H_{JK} A_K = E A_J$$

$$\frac{\partial \varphi_j^{(\kappa)}}{\partial \tau} = -(1 - \hat{P}^{(\kappa)}) \sum_{k,l} (\rho^{(\kappa)-1})_{jk} \langle \hat{H} \rangle_{kl}^{(\kappa)} \varphi_l^{(\kappa)} = 0 \quad (26)$$

The second of these equations implies that we can obtain the updated SPFs simply by relaxation. The A-vector in the first equation can be obtained by Davidson diagonalization algorithm.

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The importance of the SOP form

The multidimensional integrals arising from the MCTDH-EOMs are the bottleneck of the propagation. To address this issue, we impose SOP form to **all quantities**:

$$\begin{aligned}\hat{O} &= \sum_{\alpha=1}^S c_{\alpha} \prod_{\kappa=1}^f \hat{o}_{\alpha}^{(\kappa)} \\ \langle \Phi_J | \hat{O} | \Phi_L \rangle &= \sum_{\alpha=1}^S c_{\alpha} \prod_{\kappa=1}^f \langle \varphi_{j_{\kappa}}^{(\kappa)} | \hat{o}_{\alpha}^{(\kappa)} | \varphi_{l_{\kappa}}^{(\kappa)} \rangle\end{aligned}\tag{27}$$

- KEO already in the desired form (TANA and TNUM software)
- PES might be challenging to transform

Transforming the PES

Usually the PES needs to be refitted (**tensor decomposed**) before using it. The POTFIT algorithm is an elegant way of achieving this in **Tucker form**:

$$V_{i_1, \dots, i_f} = V(q_{i_1}^{(1)}, \dots, q_{i_f}^{(f)})$$

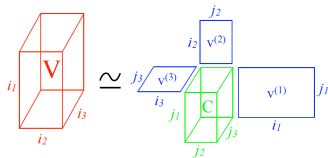
$$V_{i_1, \dots, i_f} = \sum_{j_1=1}^{m_1} \cdots \sum_{j_f=1}^{m_f} C_{j_1 \dots j_f} \prod_{\kappa=1}^f u_{i_\kappa j_\kappa}^{(\kappa)} \quad (28)$$

with the core tensor coefficients given by the overlap with the potential:

$$C_{j_1 \dots j_f} = \sum_{i_1 \dots i_f} V_{i_1 \dots i_f} u_{i_1 j_1}^{(1)} \cdots u_{i_f j_f}^{(f)} \quad (29)$$

The Tucker form

The tucker decomposition of a 3D tensor can be represented graphically as¹



which can be contrasted with the algebraic and tensor forms:

$$V_{i_1, \dots, i_f} = \sum_{j_1=1}^{m_1} \cdots \sum_{j_f=1}^{m_f} C_{j_1 \cdots j_f} \prod_{\kappa=1}^f u_{i_\kappa j_\kappa}^{(\kappa)} \quad (30)$$

$$\mathcal{V} = \mathcal{C} \times_1 \mathbf{U}_1 \cdots \times_n \mathbf{U}_n$$

¹Panadés-Barrueta R., and Peláez D. JCP (in review)

Tensor decomposition algorithms

There is a number of tensor decomposition algorithms currently in use (e.g. POTFIT, MGPF, MCPF, MLPF), however, they are all limited by the size of the grids. The **SOP-FBR** method was developed as an alternative to the former:

$$V(q_1, \dots, q_f) = \sum_{j_1=1}^{m_1} \cdots \sum_{j_f=1}^{m_f} C_{j_1 \dots j_f} \prod_{\kappa=1}^f \Phi_{j_\kappa}^{(\kappa)}(q_\kappa) \quad (31)$$

$$\Phi_{j_\kappa}(q_\kappa) = \sum_{\nu_\kappa=1}^{t_\kappa} B_{\nu_\kappa j_\kappa}^{(\kappa)} T_{\nu_\kappa}(q_\kappa)$$

This is a fully analytical SOP form, differentiable *ad infinitum*, and that can be directly interfaced with MCTDH.

The POTFIT and HOOI algorithms

Algorithm 1: POTFIT

Result: $\mathcal{C}, U_1, \dots, U_n$

 Input: \mathcal{V} ;

for $k \leftarrow 1$ **to** n **do**

 $U_k \leftarrow \text{EVD}(V_{(k)}^\dagger \cdot V_{(k)})$
end
 $\mathcal{C} \leftarrow \mathcal{V} \times_1 U_1^{-1} \dots \times_n U_n^{-1}$

Algorithm 2: HOSVD HOOI

Result: $\mathcal{C}, U_1, \dots, U_n$

 Input: \mathcal{V} ;

repeat

 for $k \leftarrow 1$ **to** n **do**

 $\mathcal{Y} \leftarrow \mathcal{V} \times_1 U_1^{-1} \dots \times_{k-1} U_{k-1}^{-1} \times_{k+1}$

 $U_{k+1}^{-1} \dots \times_n U_n^{-1};$

 $U_k \leftarrow \text{SVD}(V_{(k)})$ SVD($\mathcal{Y}_{(k)}$)

 end

 $\mathcal{C} \leftarrow \mathcal{V} \times_1 U_1^{-1} \dots \times_n U_n^{-1}$
until $\|\mathcal{V}_{app} - \mathcal{V}\| < \epsilon;$

- $\text{EVD}(V_{(k)}^\dagger \cdot V_{(k)}) \equiv \text{SVD}(V_{(k)})$!
- POTFIT optimizes the factor matrices in a slightly different manner:

$$\tilde{v}_j^{(\kappa)} = v_j^{(\kappa)} + \sum_{l=n_\kappa+1}^{N_\kappa} \mu_{jl}^{(\kappa)} v_l^{(\kappa)}$$

The SOP-FBR algorithm

Function `sopfbr` (B, C):

```

 $I \leftarrow 0$ ;
for  $k \leftarrow 0$  to  $D$  do
  for  $j \leftarrow 0$  to  $M[k]$  do
    for  $i \leftarrow 0$  to  $G_{ab}[:, k]$  do
       $U_{ij}^{(k)} \leftarrow \text{chebyshev}(G_{ab}[i, k], B(I : I + T[k]));$ 
    end
     $I \leftarrow I + T[k];$ 
  end
end
 $E_{sop} \leftarrow C \times_1 U^{(1)} \dots \times_D U^{(D)};$ 
return  $E_{sop}$ 

```

Algorithm 3: SOP-FBR

Result: x_{opt}

Input: x_{guess} guess parameters, D dimensionality, M number of basis functions, T degree of Chebyshev series, N_g number of geometries, ϵ threshold ;

 $k \leftarrow 0$; $x_0 \leftarrow x_{guess}$; $G_{ab}, E_{ab} \leftarrow \text{geogen}(N_g)$;**Function** `target` (B, C):

```

   $E_{sop} \leftarrow \text{sopfbr}(B, C);$ 

```

```

   $\rho \leftarrow \|E_{ab} - E_{sop}\|_{L_2};$ 

```

return ρ **repeat**

```

   $B, C \leftarrow \text{split}(x_k, T \times M);$ 

```

```

   $B \leftarrow \text{BFGS}(\text{target}(B, \tilde{C}));$ 

```

```

   $\rho, C \leftarrow \text{Powell}(\text{target}(\tilde{B}, C));$ 

```

```

   $x_{k+1} \leftarrow \text{concatenate}(B, C);$ 

```

```



   $k \leftarrow k + 1;$ 

```

until $\rho < \epsilon \vee k < N$; $x_{opt} \leftarrow x_k$

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The Heidelberg implementation of MCTDH

The actual implementation is written mainly in `f(ortran)`, with some small  and  contributions. The program has a modular structure with a very intuitive and consistent input syntax. Some sections of a POTFIT input file:

```

RUN-SECTION
  name = h2o.pfit
end-run-section

OPERATOR-SECTION
  pes = pjt2{binding}
  vcut < 0.5
end-operator-section

PRIMITIVE-BASIS-SECTION
  r1    sin    34    1.0    3.475
  r2    sin    34    1.0    3.475
  theta Leg/R  50    0    all 0.5 3.2
end-primitive-basis-section
  
```

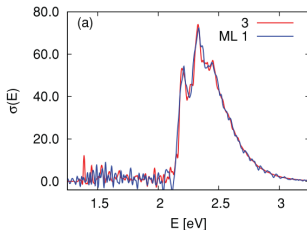
System declaration
The file extension only
suggests a POTFIT calculation

Define Hamiltonian

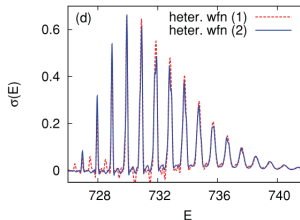
Define coordinates
and basis functions

Applications

Some interesting applications that showcase the power of MCTDH are ²:



(a) 24D



(b) 1458D

Figure: Power spectrum obtained with ML-MCTDH for (a) pyrazine (b) the Henon-Heiles Hamiltonian

²Vendrell, O., and Meyer, H.D., JCP 134.4 (2011): 044135.

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Thanks for your attention!

Questions?