A *gentle* introduction to MCTDH

With emphasis in potential representations

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November 5, 2020

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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.

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When

- Spectroscopy (e.g. IR transitions)
- Quantum tunneling
- Strong vibronic coupling
- Accurate ZPE determination

Nuclear Quantum Dynamics

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

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \tag{1}$$

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

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

The Standard method

Simplest representation of the WF:

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

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

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

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

A slightly more clever *ansatz*:

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

$$\Psi(q_1, \ldots, q_f, t) = A(t) \prod_{\kappa=1}^{f} \varphi_\kappa(q_\kappa, t) \tag{5}$$

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:

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

Main limitations

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** harder to retrieve than the electronic correlation. The character of the nuclear WF in inherently **multiconfigurational**.

Ansätze comparison

Standard Method (CI)

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

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Multiconfiguration Time-Dependent Hartree (MCSCF)

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

Bibliography

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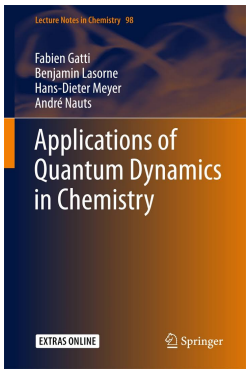

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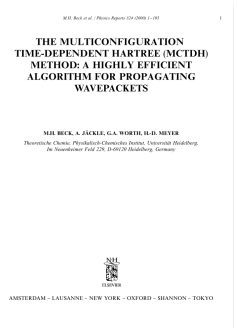

Thanks for your attention!

Questions?