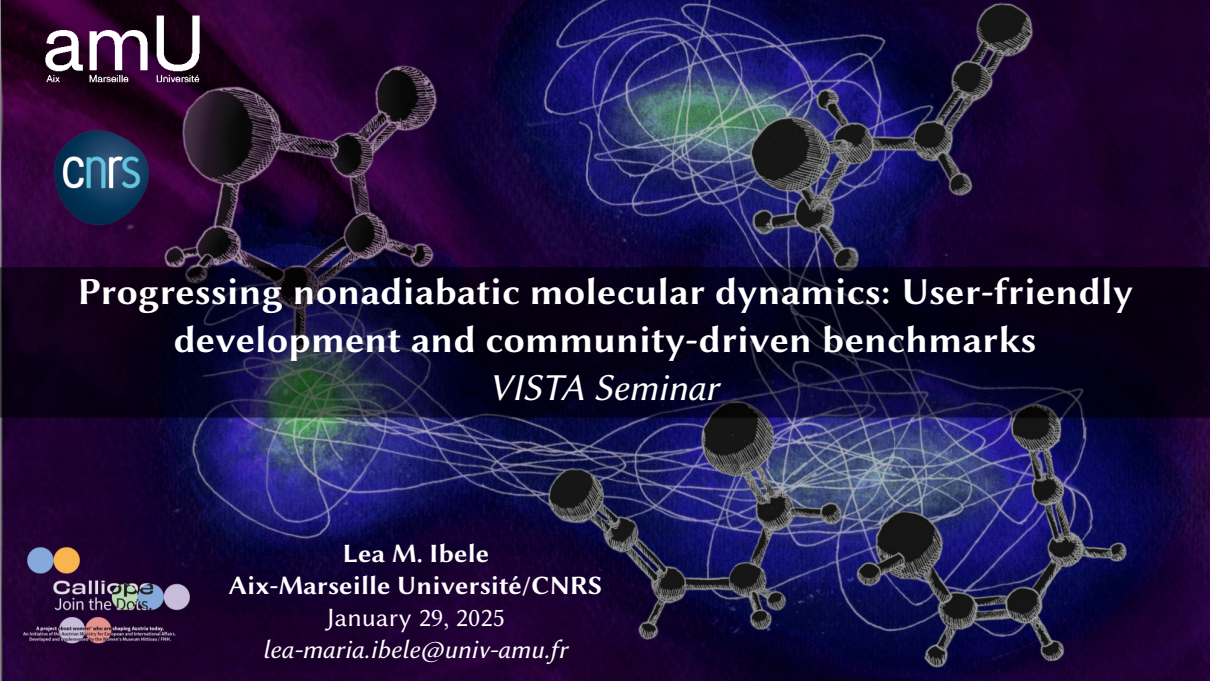


Progressing nonadiabatic molecular dynamics: User-friendly development and community-driven benchmarks

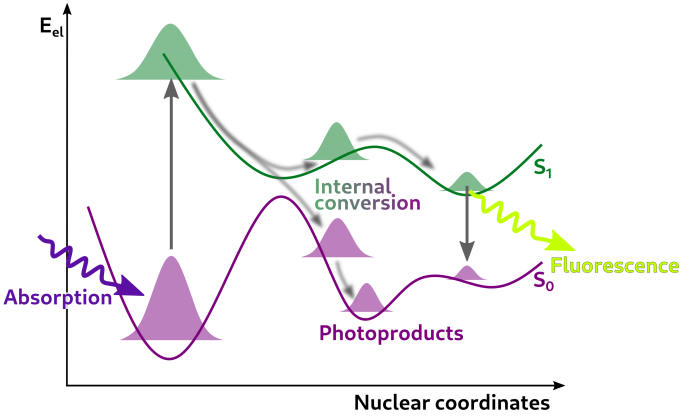
VISTA Seminar

Lea M. Ibele
Aix-Marseille Université/CNRS

January 29, 2025

lea-maria.ibele@univ-amu.fr

Photochemistry



Molecule is in its ground state

Absorbs a photon

Gets excited to e.g. S_1: creation of a *wavepacket*

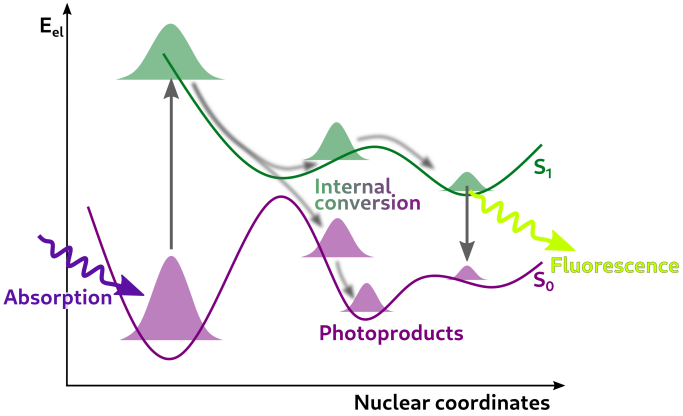
Evolution in S_1

Regions of high nonadiabaticity: wavepacket splits

Out-of-equilibrium dynamics

Very long timescales: radiative deactivation

Simulating Photochemistry



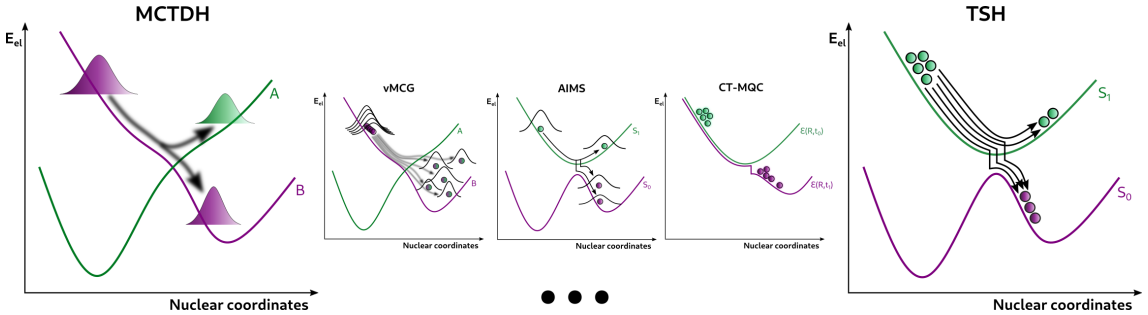
Challenge for theoretical chemistry:
Solving TDSE for molecules:

$$i\frac{\partial}{\partial t}\Psi(\boldsymbol{r},\boldsymbol{R},t) = \hat{H}(\boldsymbol{r},\boldsymbol{R})\Psi(\boldsymbol{r},\boldsymbol{R},t)$$

$$\hat{H}(\boldsymbol{r},\boldsymbol{R}) = \hat{T}_{\mathrm{n}}(\boldsymbol{R}) + \hat{H}_{\mathrm{BO}}(\boldsymbol{r},\boldsymbol{R})$$

- Electrons and nuclei coupled!
- **Beyond Born-Oppenheimer approximation**
- Accurate electronic structure
- **Nuclear dynamics**

Nonadiabatic Molecular Dynamics



Wavepacket propagation
Nuclear Quantum Effects
Analytical potentials

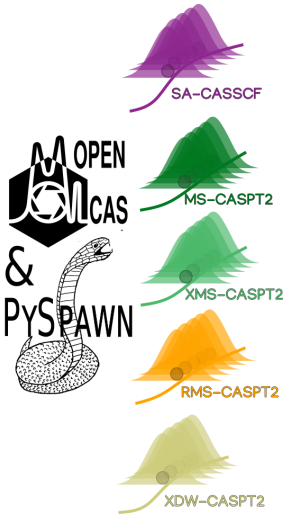
Classical trajectories
Mixed quantum-classical dynamics
Highly efficient dynamics

What limits the usability of different NAMD approaches?

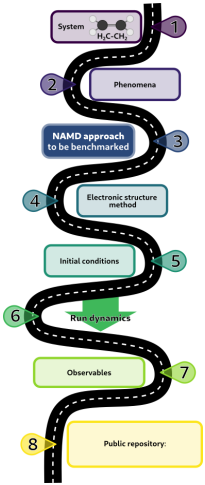
Nonadiabatic Molecular Dynamics – The User's Perspective

Two important questions:

Which software can I use?



Which method is the best for my problem?

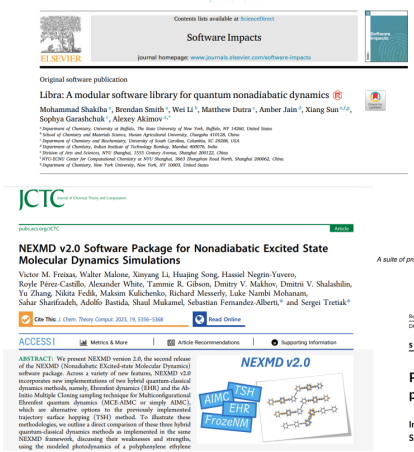


Freely Available/Open-Source NAMD Software

Desired Qualities:

- Different interfaces
- Efficient implementation
- User-friendly
- Up-to-date documentation
- Open-source/free

Many different surface hopping codes that fullfill all these criteria!


Contents lists available at ScienceDirect

Software Impacts

journal homepage: www.journals.elsevier.com/software-impacts

Original software publication

Libra: A modular software library for quantum nonadiabatic dynamics

Mohammad Shakiba [1], Brendan Smith [1], Wei Li [1], Matthew Dutra [1], Amber Jain [1], Xiang Sun [1,2,*], Sophya Garashchuk [1], Alexey Akimov [1,*]

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[2] School of Chemistry and Materials Science, Hunan Agricultural University, Changsha 410128, China
[3] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA
[4] Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India
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[7] Department of Chemistry, New York University, New York, NY 10003, United States

JCTC Journal of Chemical Theory and Computation

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NEXMD v2.0 Software Package for Nonadiabatic Excited State Molecular Dynamics Simulations

Victor M. Freixas, Walter Malone, Xinyang Li, Huajing Song, Hassiel Negrin-Yuvero, Royle Pérez-Castillo, Alexander White, Tammie R. Gibson, Dmitry V. Makhov, Dmitrii V. Shalashilin, Yu Zhang, Nikita Fedik, Maksim Kulichenko, Richard Messerly, Luke Nambi Mohanam, Sahar Sharifzadeh, Adolfo Bastida, Shaul Mukamel, Sebastian Fernandez-Alberti,* and Sergei Tretiak*

Cite This: J. Chem. Theory Comput. 2023, 19, 5156−5168 Read Online

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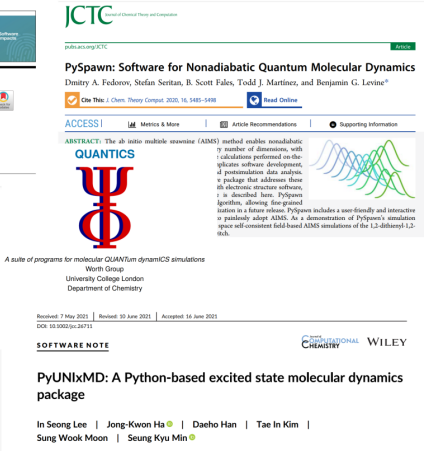
ABSTRACT: We present NEXMD version 2.0, the second release of the NEXMD (Nonadiabatic EXcited-state Molecular Dynamics) software package. Across a variety of new features, NEXMD v2.0 incorporates new implementations of two hybrid quantum-classical dynamics methods, namely, Ehrenfest dynamics (EHR) and the Ab-Initio Multiple Cloning-sampling technique for Multiconfigurational Ehrenfest quantum dynamics (MCE-AIMC or simply AIMC), which are alternative options to the previously implemented trajectory surface hopping (TSH) method. To illustrate these methodologies, we outline a direct comparison of these three hybrid quantum-classical dynamics methods as implemented in the same NEXMD framework, discussing their weaknesses and strengths, using the modeled photodynamics of a polyphenylene ethylene

NEXMD v2.0

AIMC TSH EHR FrozeNM


JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

PySpawn: Software for Nonadiabatic Quantum Molecular Dynamics

Dmitry A. Fedorov, Stefan Seritan, B. Scott Fales, Todd J. Martínez, and Benjamin G. Levine*

Cite This: J. Chem. Theory Comput. 2020, 16, 5485−5498 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The ab initio multiple spawning (AIMS) method enables nonadiabatic dynamics by a number of dimensions, with [illegible] calculations performed on-the-fly. This [illegible] duplicates software development, and [illegible] postsimulation data analysis. We present a package that addresses these difficulties [illegible] electronic structure software, and [illegible] is described here. PySpawn [illegible] algorithm, allowing fine-grained parallelization in a future release. PySpawn includes a user-friendly and interactive [illegible] to painlessly adopt AIMS. As a demonstration of PySpawn's simulation [illegible] space self-consistent field-based AIMS simulations of the 1,2-dithienyl-1,2-[illegible]-tech.

QUANTICS

A suite of programs for molecular QUANTum dynamICS simulations

Worth Group
University College London
Department of Chemistry

Received: 7 May 2021 | Revised: 10 June 2021 | Accepted: 16 June 2021

DOI: 10.1002/jcc.26711

SOFTWARE NOTE

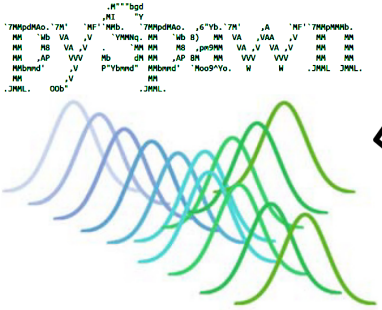
INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY WILEY

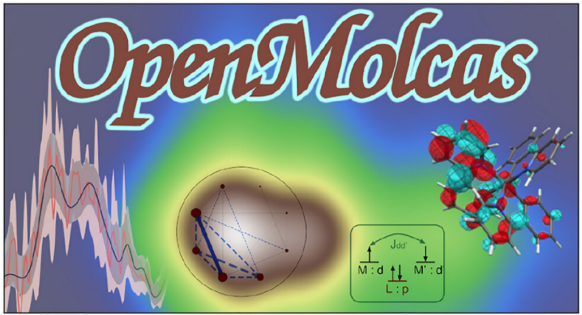
PyUNIxMD: A Python-based excited state molecular dynamics package

In Seong Lee | Jong-Kwon Ha* | Daeho Han | Tae In Kim | Sung Wook Moon | Seung Kyu Min*

PySpawn / OpenMolcas

Combining highly accurate nonadiabatic dynamics with highly accurate electronic structure





Fedorov et al., *JCTC* (**2020**), 16, 9, 5485

Li Manni et al., *JCTC* (**2023**), 19, 20, 6933

Davide Avagliano

Ben Levine

Arshad Mehmood

JCTC Journal of Chemical Theory and Computation

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Ab Initio Multiple Spawning Nonadiabatic Dynamics with Different CASPT2 Flavors: A Fully Open-Source PySpawn/OpenMolcas Interface

Lea M. Ibele,* Arshad Memhood, Benjamin G. Levine, and Davide Avagliano*

Gaussian Based Methods

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_J \Phi_J(\boldsymbol{r}; \boldsymbol{R}) \chi_J(\boldsymbol{R}, t)$$

$$\chi_J(\boldsymbol{R}, t) = \sum_k^{N_{\mathrm{TBF}}} C_k^{(J)}(t) \tilde{\chi}_k^J(\overline{\boldsymbol{R}}_k^{(J)}(t), \overline{\boldsymbol{P}}_k^{(J)}(t), \boldsymbol{\alpha})$$

Insert this in the TDSE, project onto an adiabatic state → evolution equations for coefficients

$$i\frac{\mathrm{d}\mathbf{C}^I}{\mathrm{d}t} = -i(\mathbf{S}^{-1})_{II}\left[(\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II})\mathbf{C}^I + \sum_{J\neq I}\mathbf{H}_{IJ}\mathbf{C}^J\right]$$

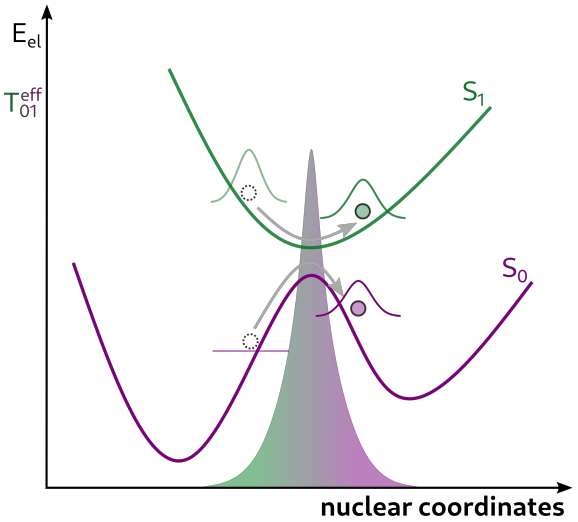
How to evolve the Gaussians?

1. Using the TDSE/DFVP → *variational multiconfigurational Gaussian (vMCG)*
2. Using mixed quantum/classical dynamics → *multiconfigurational Ehrenfest (MCE)*
3. Using classical dynamcis → *full and ab initio multiple spawning (FMS/AIMS)*

Full Multiple Spawning

FMS main principles:

- Nuclear wavefunction expanded in a set of Gaussians
- TDSE is replaced by the evolution equations of the complex coefficients
- FMS uses *frozen Gaussians*: $\boldsymbol{\alpha}_k^{(J)}(t) \rightarrow \boldsymbol{\alpha}$
- The Gaussians evolve as *classical trajectories*: $\overline{\boldsymbol{R}}_k^{(J)}(t)$ and $\overline{\boldsymbol{P}}_k^{(J)}(t)$ evolve according to Newton's equations
- FMS introduces a *spawning algorithm*, the number of TBFs adapts over time: $N_{\mathrm{TBF}} \rightarrow N_{\mathrm{TBF}}(t)$



Full Multiple Spawning

$$i\dot{\mathbf{C}}^I = -i(\mathbf{S}^{-1})_{II}\left[(\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II})\mathbf{C}^I + \sum_{J\neq I}\mathbf{H}_{IJ}\mathbf{C}^J\right]$$

with the nuclear overlap matrices, $(\mathbf{S}_{II})_{kl}$ and $\left(\dot{\mathbf{S}}_{II}\right)_{kl}$
The Hamiltonian matrix has different couplings between TBFs on the same and on different electronic states:

$$H^{II}_{kl} = \langle\tilde{\chi}^I_k|\,\hat{T}_\mathrm{n}\,|\tilde{\chi}^I_l\rangle_{\boldsymbol{R}} + \langle\tilde{\chi}^I_k|\,\epsilon^{(I)}_\mathrm{BO}\,|\tilde{\chi}^I_l\rangle_{\boldsymbol{R}} - \langle\tilde{\chi}^I_k|\sum_\nu \frac{1}{2M_\nu}\boldsymbol{D}_{II,\nu}(\boldsymbol{R})\,|\tilde{\chi}^I_l\rangle_{\boldsymbol{R}}$$

$$H^{IJ}_{kl} = -\langle\tilde{\chi}^I_k|\sum_\nu \frac{1}{M_\nu}\boldsymbol{d}_{IJ,\nu}(\boldsymbol{R})\nabla_\nu\,|\tilde{\chi}^J_l\rangle_{\boldsymbol{R}} - \langle\tilde{\chi}^I_k|\sum_\nu \frac{1}{2M_\nu}\boldsymbol{D}_{IJ,\nu}(\boldsymbol{R})\,|\tilde{\chi}^J_l\rangle_{\boldsymbol{R}}$$

Ab Initio Multiple Spawning

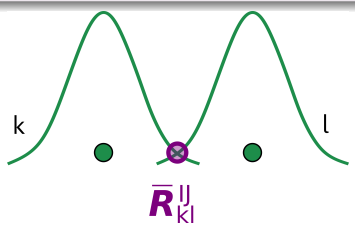
- FMS *in principle* exact; for simulation of molecules approximations necessary:
- → *Ab initio multiple spawning (AIMS)*:
- Neclect all second order couplings (DBOC and 2nd order NAC)

Saddle point approximation (SPA0)

$$H_{kl}^{IJ} = \langle \tilde{\chi}_k^J | \, \hat{T}_n \, | \tilde{\chi}_l^I \rangle_{\boldsymbol{R}} \, \delta_{IJ} \; + \; \underbrace{\langle \tilde{\chi}_k^J | \, \epsilon_{\mathrm{BO}}^{(I)} \, | \tilde{\chi}_l^I \rangle_{\boldsymbol{R}} \, \delta_{IJ}}_{\text{integral over all nuclear coordinates}}$$

Taylor expansion of order zero around centroid position of Gaussians ($\bar{\boldsymbol{R}}_{kl}^{IJ}$):

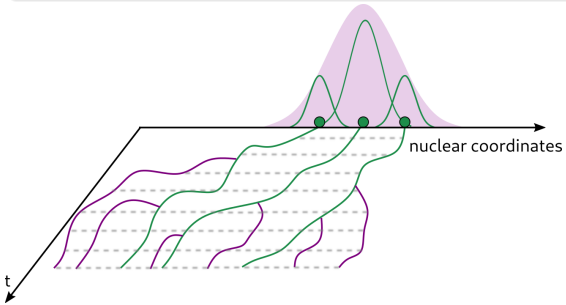
$$\langle \tilde{\chi}_k^J | \, \theta^{IJ} \, | \tilde{\chi}_l^I \rangle_{\boldsymbol{R}} \approx \theta^{IJ}(\bar{\boldsymbol{R}}_{kl}^{IJ}) \, \langle \tilde{\chi}_k^J | \tilde{\chi}_l^I \rangle_{\boldsymbol{R}}$$

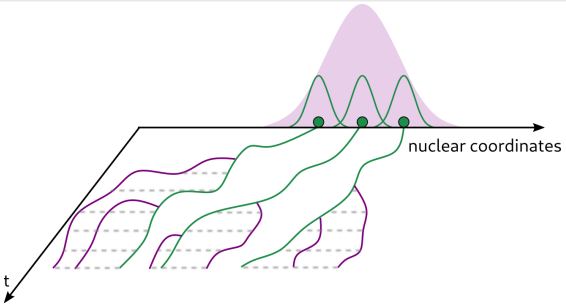


Ab Initio Multiple Spawning

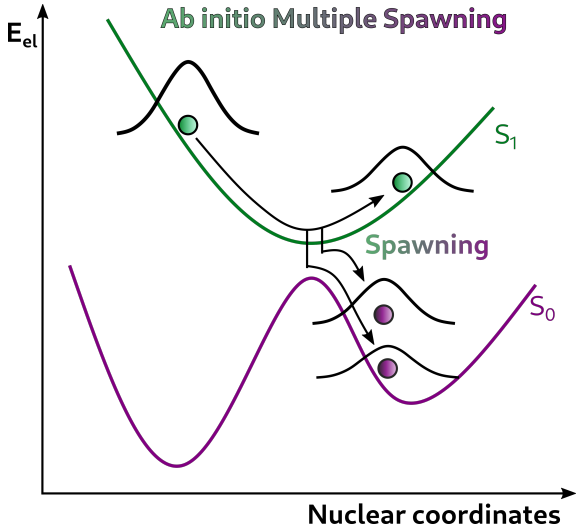
Independent first generation approximation (IFGA)

Initial nuclear wave packet usually spreads rapidly in phase space
→ initially coupled TBFs will uncouple rapidly
→ approximate that parent TBFs are uncoupled from the beginning.





Summary Ab Initio Multiple Spawning

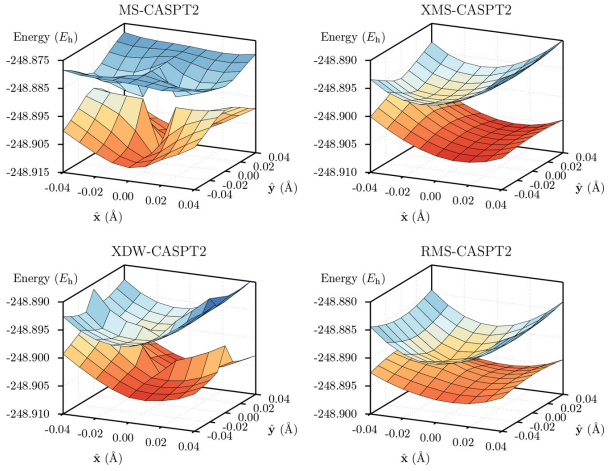


- Nuclear wavefunction expressed in basis of *Gaussian trajectory basis functions (TBFs)*
- TBFs propagated classically, but are fully coupled
- Spawning allows to adapt the size of the basis in regions of high nonadiabaticity
- Full Multiple Spawning (FMS) *in principle* exact
- Ab Initio Multiple Spawning (AIMS) for molecules approximates couplings:
  - Saddle Point Approximation of order zero (SPA0)
  - Independent First Generation Approximation (IFGA)

Martínez et al., *JPC* (**1996**), 100, 7884;
Martínez et al., *ACP* (**2002**), 121, 439-513

Flavours Of CASPT2

CASPT2 widely regarded as the most accurate electronic structure method for NAMD



Li Manni et al., *JCTC* (**2023**), 19, 20, 6933

MS-CASPT2 highly accurate FC energies, nonsmoothness of PES when states are close and mixed

XMS-CASPT2 considers full Fock operator, fixes nonsmoothness but energies get worse

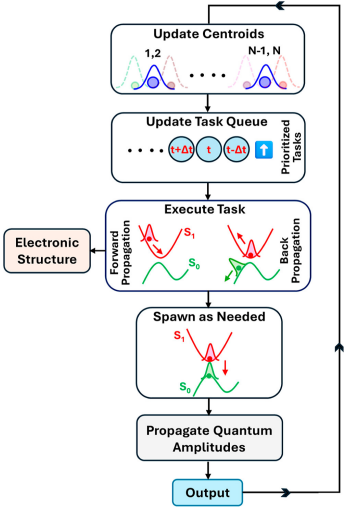
XDW-CASPT2 best of both worlds, interpolates between MS and XMS depending of separation of states

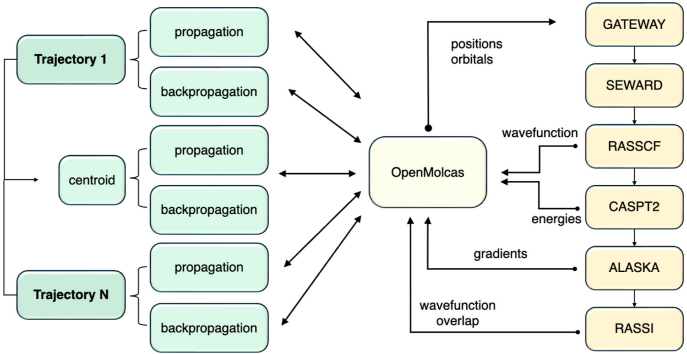
RMS-CASPT2 does not mix states of different irreps, parameter free.

Efficient analytical gradients in OpenMolcas

Nishimoto, *JCP* (**2021**), 154, 194103
Nishimoto et al., *JCTC* (**2022**), 18, 4269

Interface PySpawn / OpenMolcas





Ibele et al., *JCTC* (**2024**), 20, 18, 8140

PySpawn: A User-Friendly AIMS Code

https://github.com/blevine37/pySpawn17.git

Input `start.py`

```
# finite wigner temperature
wigner_temp = 0

# random number seed
seed=12345

# Velocity Verlet classical propagator
clas_prop = "vv"

# adapative 2nd-order Runge-Kutta quantum propagator
qm_prop = "fulldiag"

# adiabtic NPI quantum Hamiltonian
qm_ham = "adiabatic"

# use OpenMolcas CASSCF or CASPT2 to compute potentials
potential = "molcas_cas"

# initial time
t0 = 0.0

# time step
ts = 5.0

# final simulation time
tfinal = 1000.00

# number of dimensions
numdims = natoms*3

# number of electronic states
numstates = 2
```

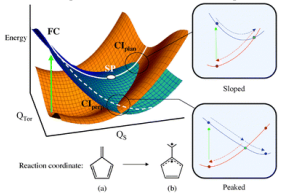
```
# OpenMolcas job options
molcas_options = {
    "method":       'caspt2',
    "pt2":          'xms',   #only used if caspt2 above
    "basis":        '6-31g*',
    "atoms":        atoms,
    "charge":       0,
    "spinmult":     1,
    "closed":       7,
    "nactel":       6,
    "actorb":       6,
    "inactive":     18,
    "ipea":     0.0,
    "imaginary":    0.2,
    "cassinglets":  numstates,
    "castargetmult": 1,
    "cas_energy_states": [0, 1],
    "cas_energy_mults": [1, 1],
    "python3" : ## ADD the path to python 3
    "project": 'fulvene_test'
    }
```

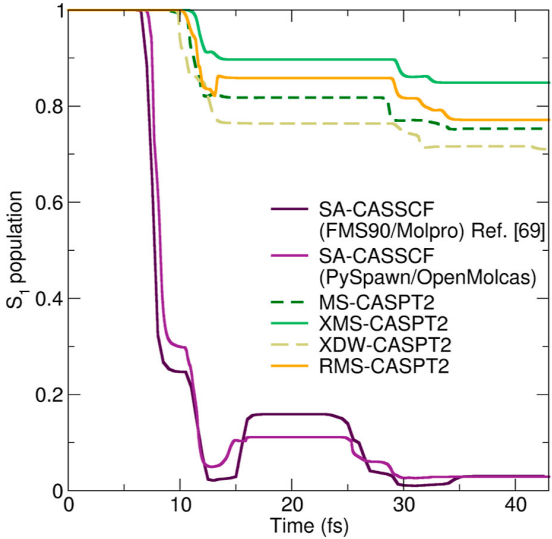
Analysis and results of dynamics: `analysis.py`

```
# this analysis script processes the sim.hdf5 file into various human-readable
# formats.  This script can be run while the simulation is in progress.
import copy
import pyspawn
import matplotlib.pyplot as plt
import numpy as np


def plot_total_pop(times):
    """ This plots the total electronic population on each
    electronic state (over all basis functions)"""

    g5 = plt.figure("Total Electronic Populations")
    for n_state in range(nstates):
        plt.plot(times, el_pop[:, n_state], color=colors[n_state],
                 label='S' + str(n_state))
    plt.xlabel('Time, au', fontsize=medium_size)
    plt.ylabel('Population', fontsize=medium_size)
#    plt.text(time['00'][-1] - 13, el_pop[-1, 0] - 0.1,
#             str(round(el_pop[-1, 0] * 100)) + "%", fontsize=medium_size)
    plt.title('Total Electronic Population', fontsize=large_size)
    plt.tick_params(axis='both', which='major', labelsize=small_size)
    plt.legend(fontsize=medium_size)
    plt.tight_layout()
    g5.savefig("Total_El_pop.png", dpi=300)


def plot_energies(keys, numstates, istates, colors,
                  linetypes, xlimits, ylimits):
```

Fulvene Dynamics

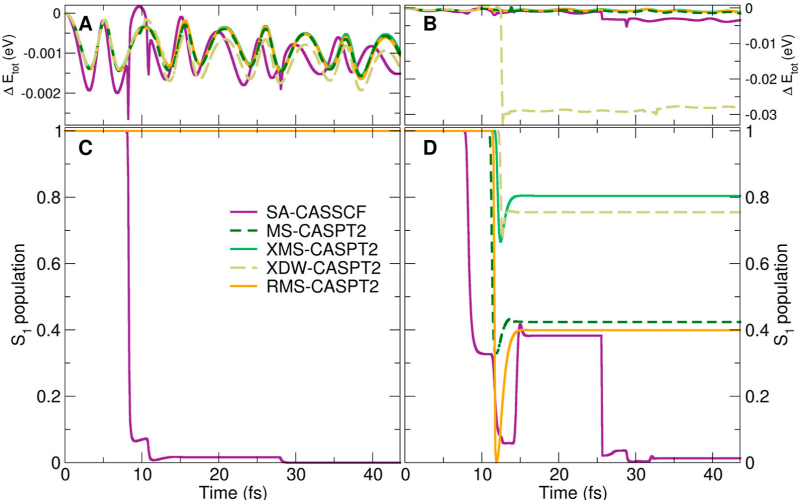
Testsystem: Fulvene
CAS(6,6)/6-31G*, 20 initial conditions
(Wigner sampled, $\boldsymbol{p} = 0$)
"Molecular Tully model III"
With CASSCF two accessible conical intersections: peaked and sloped



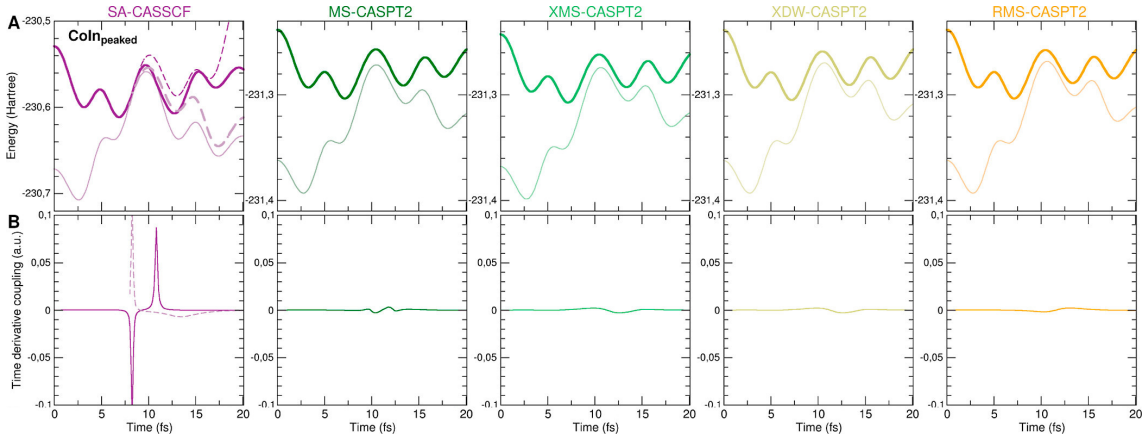


Mendive-Tapia et al., *PCCP* (**2010**), 12, 15725
Ibele and Curchod, *PCCP* (**2020**), 22, 15183

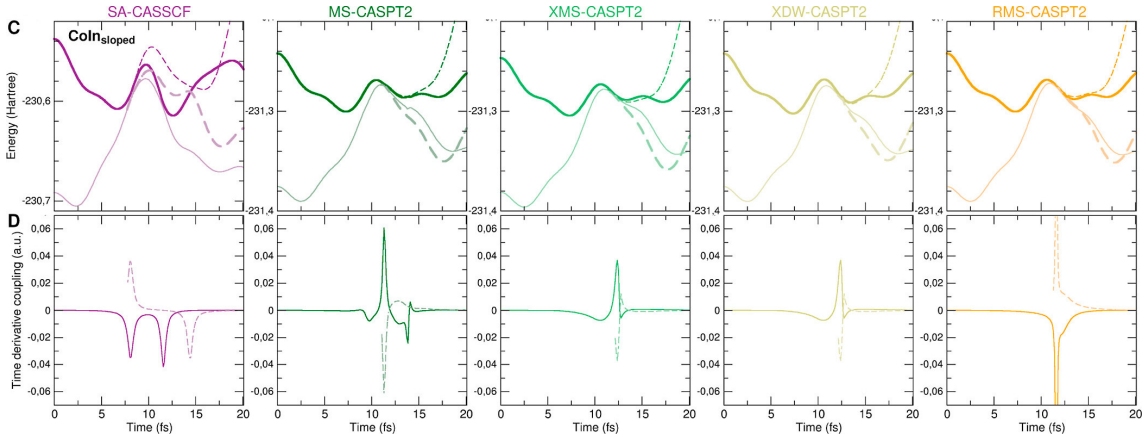
Fulvene Dynamics



Fulvene Dynamics



Fulvene Dynamics

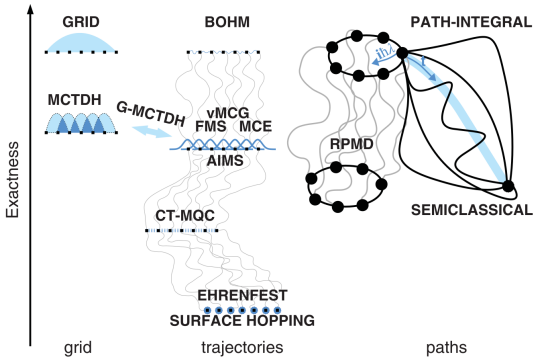


Future Developments

D. Avagliano, *in revision*

Benchmarks for NAMD

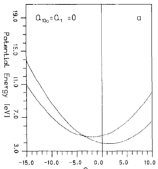
Which method is the best for my problem?

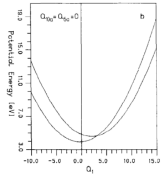


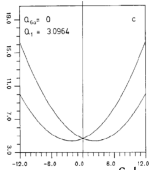
Not a clear hierarchy of nonadiabatic dynamics methods.

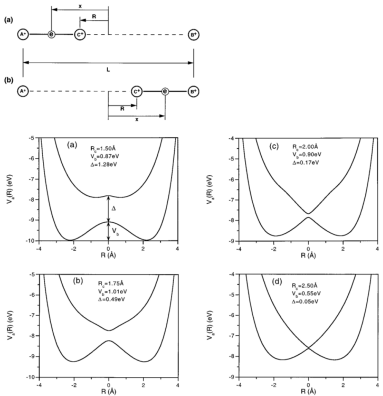
Gómez et al. (**2020**) *Motivation and Basic Concepts*. In *Quantum Chemistry and Dynamics of Excited States* (eds González and Lindh).

Existing Benchmarks - Low Dimensional Models



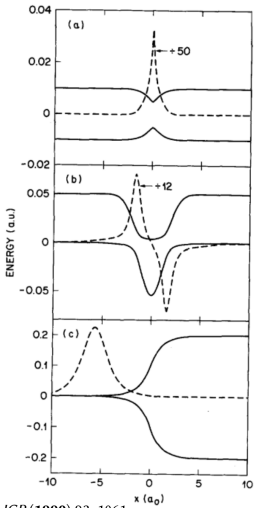




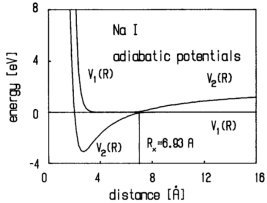


Shin and Metiu, *JCP* (**1995**) 102, 9285

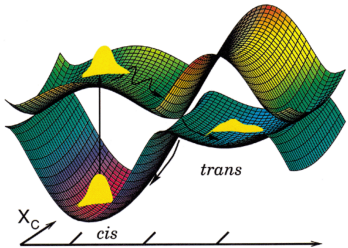
Schneider and Domcke, *CPL* (**1988**) 150, 235



Tully, *JCP* (**1990**) 93, 1061



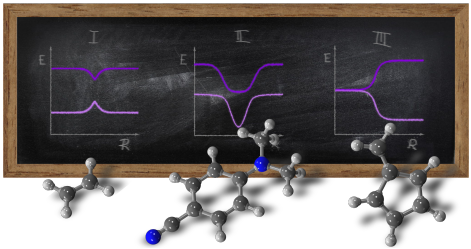
Engel and Metiu, *JCP* (**1989**) 90, 6116



Hahn and Stock, *JPCB* (**2000**) 104, 1146.

Existing Benchmarks - Molecular Models

Molecular Tully models



Molecular model consisting of:
System, electronic structure, initial conditions
Problems:

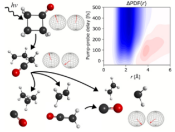
- Comparison based on adiabatic populations
- Trajectory oriented initial conditions
- Commercial electronic structure software

Ibele and Curchod, *PCCP* (**2020**), 22, 15183

Prediction Challenge: Cyclobutanone Photochemistry

Prediction Challenge: Cyclobutanone Photochemistry

The simulation of photochemical molecular dynamics has been a major challenge to theoretical chemistry because of the need to simultaneously describe quantum mechanical effects of both nuclei and electrons. Numerous advances have been made over the past decade and many would agree that excited state simulations have demonstrated their value in the interpretation of experiments. However, one can question whether these simulations have been unambiguously predictive. True predictive capabilities would pave the way to rational design of light-driven molecular systems, with revolutionary implications for renewable solar energy (directly to electricity or to fuels), bioimaging, optogenetics, and photochemical synthesis. Thankfully, new ultrafast diffraction experiments1 have come on-line which provide both spatio-temporal resolution on the atomic scale, i.e. molecular movies. This provides a novel opportunity — a double-blind test of the accuracy of excited state simulations.



Roadmap

cecam

MENU

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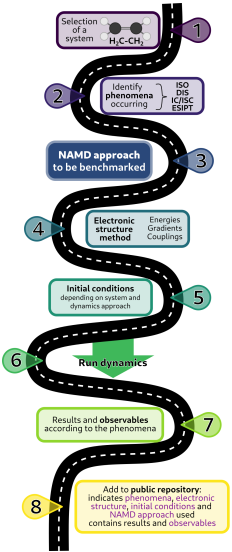
Flagship Workshop

Standardizing nonadiabatic dynamics: towards common benchmarks

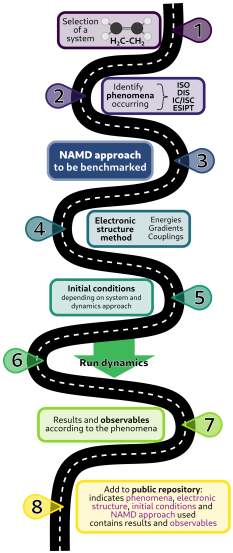
May 21, 2024 - May 24, 2024
Registration deadline: March 14, 2024
Location: CECAM-FR-MOSER
Hosting node: CECAM-FR-MOSER

Discussions around a workplan how to benchmark NAMD

Result: Roadmap

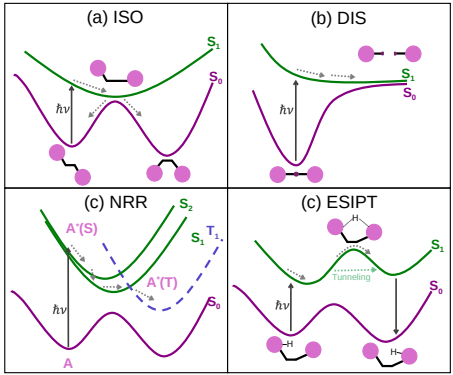


Roadmap



System selection:

Choose from common ***phenomena***



Electronic sturcture:

Fixed method, freely available software. Analytical potentials only if parametrized with exact same electronic sturcture

Initial Conditions:

Define the intial wavefunction and use appropriate sampling techniques for trajectory methods. Sudden excitation approximation.

Results and Observables:

Evaluate experimental observables. No representation-dependent quantities.

Benchmark by comparison:

Difficult to have a ground-truth. Experiment not always reliable as a reference.

Public repository

Roadmap

Preprint of the Roadmap expected in 2-3 weeks!

Main responsibles: Federica Agostini, Sandra Gómez, Lea Ibele, Antonio Prlj

Chapter contributions: Léon Cigrang, Basile Curchod, Rebecca Ingle, Aaron Kelly, Jonathan Mannouch

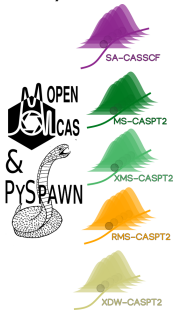
Contributions: Davide Accomasso, Alexander Alijah, Mario Barbatti, Wiem Chebbi, Nađa Došlić, Antonio Freibert, Leticia González, Giovanni Granucci, Federico Hernandez, Javier Hernández-Rodríguez, Amber Jain, Jiří Janoš, David Lauvergnat, Brieuc Le Dé, Yeha Lee, Seung Kyu Min, David Picconi, Eduarda Sangiogo Gil, Marin Sapunar, Peter Schürger, Patricia Vindel-Zandbergen, Graham Worth

Input, comments and contributions from the community highly desired!

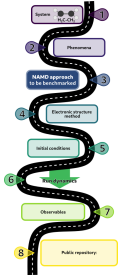
Summary

Advancing nonadiabatic dynamics can only be a community effort!

Reliable, freely available software



Molecular benchmarks



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cnrs

ICR Institut Chimie Radicalaire

Calliope Join the Dots.
A project about women who are shaping Austria today.
An initiative of the Austrian Ministry for European and International Affairs.
Developed and implemented by the Women's Museum Hittisau / FIMH.