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CyberTraining: Modeling Quantum Dynamics of Excited States in Materials in the Era of Machine Learning, 2026

Alexey Akimov

University at Buffalo, SUNY

July 9, 2026

https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2026/

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Part 1: Libra Overview

Libra as a workhorse of our developments and applied studies

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- Modular, open-source methodology “discovery”/prototyping library for nonadiabatic and quantum dynamics (NAQD)
- Yet a software for practical simulation of NAQD in large atomistic systems

Akimov *JCC,* **2016**, 37, 1626

Shakiba, M.; Smith, B.; Li, W.; Dutra, M.; Jain, A.; Sun, X.; Garashchuk, S.; Akimov, A.V. "Libra: A modular software library for quantum nonadiabatic dynamics" *Software Impacts* **2022**, 14, 100445

https://github.com/Quantum-Dynamics-Hub/libra-code

Examples& Tutorials: **https://github.com/compchem-cybertraining**

Libra’s vision

- **Versatility:** encompass a comprehensive set of available methodologies
- **Community-centric:** be the platform for various methods developed by the community; we work with various groups to make their methods available to broader community
- **Modularity:** easy-to-use methodology building blocks, methodology development
- **User-friendliness & Open-source:** easy experience, without limitations
- **Facilitate “methodology development”:** Pythonic implementation and modular approach help create and test new workflows and methods
- **Practical:** not only “toy” models, but can handle systems with thousands of atoms

Versatile: Methods and Algorithms

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Latest Release Libra v5.12.0.

DOI 10.5281/zenodo.19162602

Akimov, A. V. "Fundamentals of Trajectory-Based Methods for Nonadiabatic Dynamics" Editor(s): Manuel Yáñez, Russell J. Boyd, *Comprehensive Computational Chemistry (First Edition), Elsevier* **2024** Pages 235-272, ISBN 9780128232569, link **Book Chapter in Book: "Comprehensive Computational Chemistry"**

Nonadiabatic dynamics:

- Exact: finite-difference, DVR (Colbert-Miller), SOFT
- TD-SE and Liouville equation
- Initialization and TD-SE integration: in adiabatic and diabatic rep
- Surface hopping and SH/SE populations: in adiabatic and diabatic rep
- Ehrenfest, FGR, HEOM, QTAG, ETSH/ETSH-3
- TSH methods: FSSH, GFSH, MSSH, BCE, FSSH-2, FSSH-3, MASH, QTSH, AFSSH, MFSD, etc.)
- Exact Factorization (XF) methods: SHXF, XFMF, MQCXF
- Decoherence (mSDM, EDC, ID-A, ID-F, DISH, DISH_rev2023, BCSH, Shenvi-Subotnik-Yang correction, Zhu correction for QCLE)
- Decoherence times: user-defined, Schwartz, Subotnik, XF, dephasing-informed correction, etc.
- Integrators: LD, NAC-based, rotation-based
- NAC-free methods: LZ, ZN, BLLZ workflow
- State tracking: LD, min-cost, stochastic tracking, F-tracking
- Phase corrections: time-overlap or NAC-based
- Couplings at the KS and TD-DFT levels
- Other: removal of molecular translation/rotation, ML-based methods, TC-NBRA

Models Database: Tully, Holstein, spin-Boson, Eckart barriers, SSY, Henon-Heiles, etc.

Interfaces: CP2K, MOPAC, OpenMolcas, Quantum Espresso, eQE, DFTB+, GAMESS, ErgoSCF, Psi4, …

Versatile: Model Hamiltonians

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Model Hamiltonians:

- Tully models I, II, III, generalized — Tully, J. C. *JCP* **1990**, *93*, 1061–1071
- Parandekar-Tully — Parandekar, P. V.; Tully, J. C. *JCP* **2005**, *122*, 094102; Parandekar, P. V.; Tully, J. C. *JCTC* **2006**, *2*, 229–235.
- Dual Rosen-Zener-Demkov
- Dual Landau-Zener-Stuckelberg — Sci. Rep. 6, 24198 (2016); J. Xu and L. Wang JCP 150, 164101 (2019)
- Renner-Teller
- Dumbbell geometry (Subotnik)
- Double arch geometry (Subotnik) — J. E. Subotnik and N. Shenvi JCP 134, 024105 (2011); J. Xu and L. Wang JCP 150, 164101 (2019)
- Shenvi-Subotnik-Yang — Shenvi, N.; Subotnik, J.; Yang, W. JCP 2011, 135, 024101
- Linear Vibronic Coupling (LVC) — Izmaylov, A. F.; Mendive-Tapia, D.; Bearpark, M. J.; Robb, M. A.; Tully, J. C.; Frisch, M. J. JCP, 2011, 135, 234106; Sun, X.; Geva, E. JCP **2016**, 144, 244105

- Generalized LVC (e.g. spin-boson) — Runeson, J. E., Manolopoulos, D. E. *JCP* **2023**, 159, 094115; Tempelaar, R., Reichman, D. R. *JCP* **2018**, 148, 102309; Wang, L., Prezhdo, O. V. *JPCL* **2014**, 5, 713–719; Jain, A., Alguire, E.; Subotnik, J. E. *JCTC* **2016**, 12, 5256–5268; Bondarenko, A. S., Tempelaar, R. *JCP* **2023**, 158, 054117; Mannouch, J. R., Richardson, J. O. *JCP* **2023**, 158, 104111

- Morse models — Corondao, E. A.; Xing, J.; Miller, W. H. Chem. Phys. Lett. 2001, 349, 521-529
- Holstein (many versions) — e.g. Qiu, J.; Bai, X.; Wang, L. *JPCL* **2018**, 9, 4319-4325;
- Henon-Heiles — Sim, E.; Makri, N. *JCP* **1995**, 102, 5616-5625
- Esch-Levine (linear crossings) — Esch, M. P.; Levine, B. G. *JCP* **2020**, 153, 114104;
- Ferretti — Ferretti, A.; Granucci, G.; Lami, A.; Persico, M.; Villani, G. *JCP* **1996**, 104, 5517–5527
- Granucci-Persico (2 models) — Granucci, G., Persico, M. *JCP* **2007**, 126, 134114; Granucci, G., Persico, M.; Zoccante, A. *JCP* **2010**, 133, 134111
- 1D and 2D Eckart barrier (Martens) — L. Wang, C.C. Martens, Y. Zheng, *JCP* **2012**, 137, 34113;
- and more…

Modular and User-friendly: C++/Python Interoperability

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Replace: Fully Pythonic

NumPy

PyTorch

C++ layer

Eigen 3

libint Public

boost C++ LIBRARIES

Call by C++

Translate code

Python layer

User-Customized & Library Python functions

libra_py

Prototype and Test (Discover)

Use in C++ codes

Use in Python codes

Documented: Training Resources

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The first one – Winter 2022:

Libra Winter School on Excited States and Non
Materials 2022

Libra Workshop and Summer School on Excited States and Nonadiabatic Dynamics 2024

https://compchem-cybertraining.github.io/Libra_Winter_School_2022/

https://compchem-cybertraining.github.io/Libra_Summer_School_2024/

Join Slack: https://join.slack.com/t/quantumdynamicshub/shared_invite/zt-mjbhjssx-GGhsbYHxeBMvhmumK_j7LA

The second one – Summer 2024:

Comutational Chemistry CyberTraining

https://github.com/compchem-cybertraining

Learning Libra: The dedicated set of tutorials: https://github.com/compchem-cybertraining/Tutorials_Libra

This CyberTraining Summer School!

Learning Libra AND theory AND other packages: CyberTraining workshops

- 2023: https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2023/
- https://github.com/compchem-cybertraining/Cyber_Training_Workshop2023_course_proj
- 2022: https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2022/
- 2021: https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2021/

Excited States and Nonadiabatic Dynamics CyberTraining Workshop 2023

Community

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Mohammad Shakiba

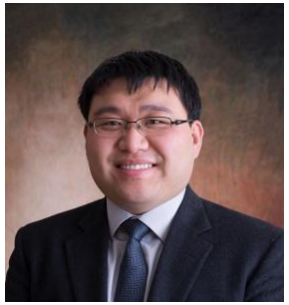
Brendan Smith

Daeho Han

Sophya Garashchuk

Amber Jain

Xiang Sun



Thomas Niehaus

- Taras Khvorost
- Leonardo Araujo
- Joseph Kelly
- Victor Suarez
- Xuecheng Shao
- Wenhui Mi

- Matthew Dutra
- Alva Dillon
- Miguel Recio Poo
- Qingxin Zhang
- Kevin Walsh
- Kosuke Sato

- Ekadashi Pradhan
- Dhara Trivedi
- Wei Li
- Story Temen
- Rebecca Gieseking
- Michele Pavanello

- Michele Dupuis
- Lili Rassouli
- Xuyan Ma
- Kosar Yasin
- more coming…

Published March 22, 2026 | Version v5.12.0

Libra

Akimov, Alexey V.[1]; Shakiba, Mohammad[1]; Han, Daeho[1]; Smith, Brendan[1]; Dutra, Matthew[2]; Sato, Kosuke[3]; Suarez, Victor[4]; Temen, Story[1]; Wang, Yuchen[5]; Li, Wei[6]; Khvorost, Taras[7]; Yasin, Kosar[1]; Sun, Xiang[8]; Balducci, Simone[9]; Zhang, Qingxin[1]; Niehaus, Thomas[10]; Stippell, Elizabeth[11]; Gerasimov, Igor S.[12]; Amber, Jain[13]

- Several new collaborations are ongoing
- Open for more …

Some metrics

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Zenodo statistics

2K VIEWS

211 DOWNLOADS

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Versions

Version v5.9.0 10.5281/zenodo.15438381	May 16, 2025
Version v5.8.1 10.5281/zenodo.14043087	Nov 6, 2024
Version v5.8.0 10.5281/zenodo.13239484	Aug 6, 2024
Version v5.7.1 10.5281/zenodo.11640243	Jun 13, 2024
Version v5.7.0 10.5281/zenodo.11221400	May 20, 2024

View all 17 versions

GitHub statistics

Readme
GPL-3.0, GPL-3.0 licenses found
Code of conduct
Activity
Custom properties
48 stars
11 watching
43 forks
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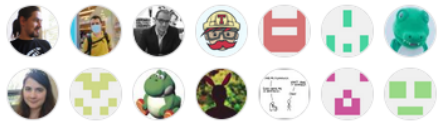
Libra v5.8.0: F-tracking and sim... Latest
13 hours ago

+ 14 releases

Packages

No packages published
Publish your first package

Contributors 14



Releases usually accompany our publications (if new methodologies are developed or assessed)

2 weeks ago
alexvakimov
v5.8.0
14a99c7
Compare

Libra v5.8.0: F-tracking and simplified NAC phase correction Latest

The main changes

- The new F-tracking and simplified NAC phase correction are added and tested (the main reason for this release)

May 20
alexvakimov
v5.7.0
58cfd6e
Compare

Libra v5.7.0

The major additions

- the new FSSH-3 methodology is implemented
- the FSSH-2 of Araujo et al. is implemented (with slight changes compared to the published version, but likely this is what was intended)
- added Jasper-Truhlar criterion of velocity reversal on frustrated hops

Mar 15
alexvakimov
v5.6.0
334d449
Compare

v5.6.0

Final version of the XF-based methods (SHXF, MQCXF, and MFXF), coming along with the manuscript submission.

Major implementation was done already in the previous implementations. The present version ensures the consistency of some underlying transformation.

Nov 26, 2023
alexvakimov
v5.5.0
ac57c3e
Compare

Libra with TC-NBRA, MASH, FSSH2, revDISH, revised TSH and Ehrenfest, phase-corrected exact calculations

1. Structural changes and paradigm changes

Community Use: Some papers that use Libra

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RETURN TO ISSUE | < PREV | **LETTER** | NEXT >

Charge Carrier Dynamics at the Interface of 2D Metal–Organic Frameworks and Hybrid Perovskites for Solar Energy Harvesting

Robert Stanton and Dhara J. Trivedi*

Cite this: *Nano Lett.* 2023, 23, 24, 11932−11939
Publication Date: December 15, 2023
https://doi-org.gate.lib.buffalo.edu/10.1021/acs.nanolett.3c04054
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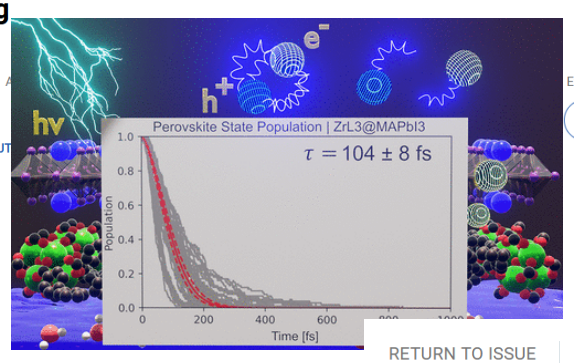
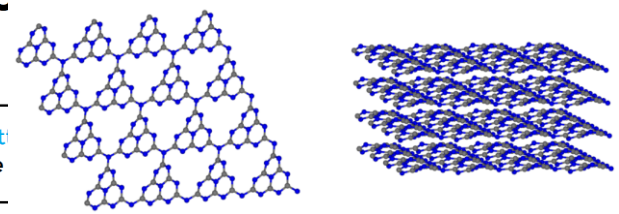


Ab initio quantum dynamics of charge carriers in graphitic carbon nitride nanosheets



Cite as: J. Chem. Phys. **153**, 054701 (2020); ht
Submitted: 13 April 2020 • Accepted: 11 June

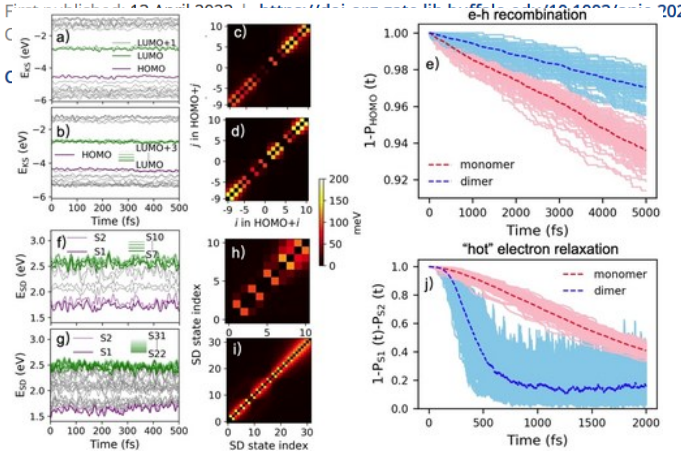
Sraddha Agrawal, Wei Lin, Oleg V. Prezhdo, et al.

Angewandte International Edition Chemie | GDCh | A Journal of the German Chemical Society

Research Article | Full Access

Insight into the Molecular Mechanism for Enhanced Longevity of Supramolecular Vesicular Photocatalysts

Dr. Yannan Liu, Dr. Fulu Zheng, Haojie Dai, Chuanshuang Chen, Yajing Chen, Dr. Haolin Wu, Prof. Chunyang Yu, Prof. Yiyong Mai, Prof. Thomas Frauenheim, Prof. Yongfeng Zhou



RETURN TO ISSUE | < PREV | **A: NEW TOOLS AND MET...** | NEXT >

Convergence of Time-Derivative Nonadiabatic Couplings in Plane-Wave DFT Calculations

Alva D. Dillon and Rebecca L. M. Gieseking*

Cite this: *J. Phys. Chem. A* 2023, 127, 45, 9612−9620
Publication Date: November 4, 2023
https://doi-org.gate.lib.buffalo.edu/10.1021/acs.jpca.3c04858
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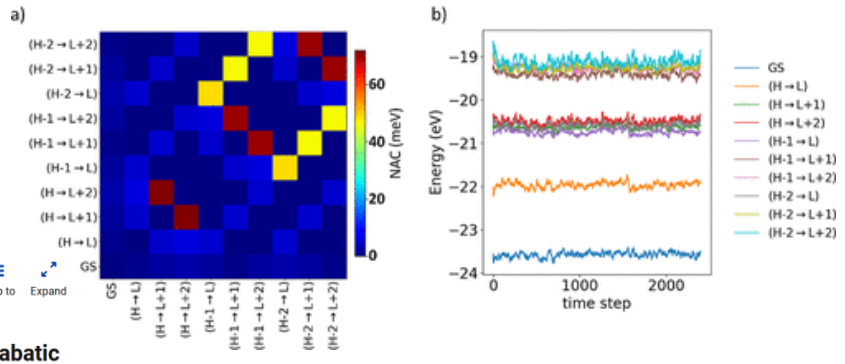

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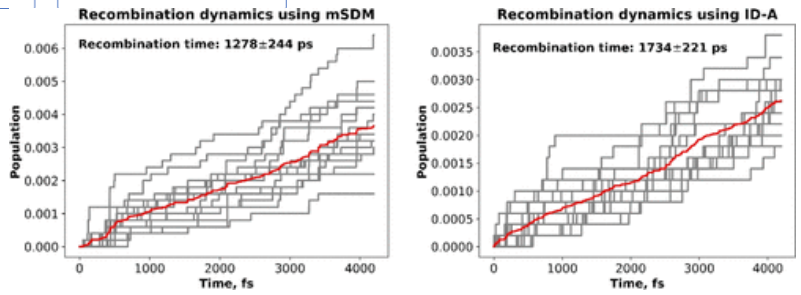
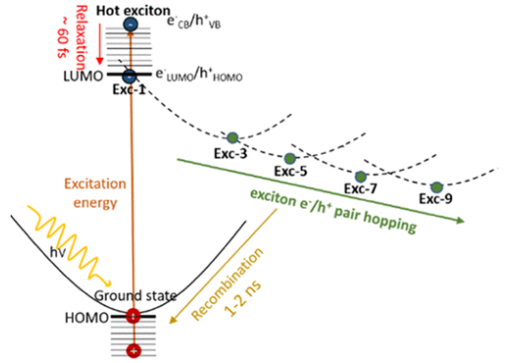
C: ENERGY CONVERSION AND STORAGE | August 9, 2024

Excitons in Hematite Fe_2O_3: Short-Time Dynamics from TD-DFT and Non-Adiabatic Dynamics Theories

Lili Rassouli, Mohammad Shakiba, Alexey V. Akimov, Xuyan Ma, and Michel Dupuis*

Open PDF | Supporting Information (1)





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Part 2: Libra Developments and Applications

Libra History

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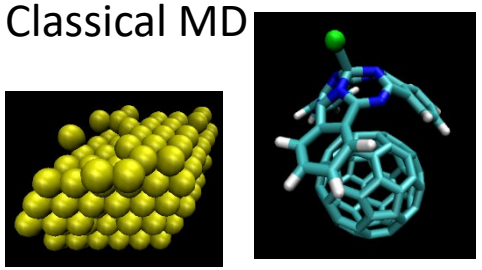
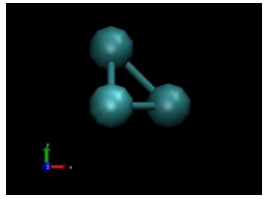
2007-2011 (LCCCS)

Classical MD



Rigid body MD

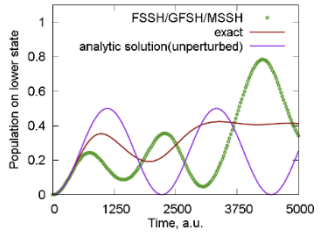


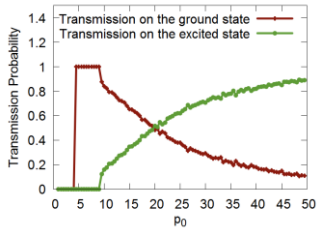
- Simplectic integrators for classical DOFs
- Thermostats
- Barostats
- Force fields
- ANN
- Chemical object representation

2011-2015 (Pyxaid)

Akimov, Prezhdo, *JCTC*, **2013**, 9, 4959.
Akimov, Prezhdo, *JCTC*, **2014**, 10, 789

Ehrenfest & TSH



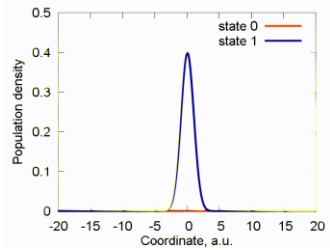


- Simplectic integrators for TDSE
- TSH, Ehrenfest, stand-alone scripts
- Decoherence methods
- Model problems
- Added HF and EHT to LCCCS
- Interface with VASP, then QE

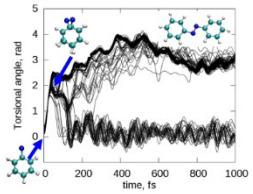
2015/2016 (Libra)

Akimov *JCC*, **2016**, 37, 1626

DVR



Back-reaction



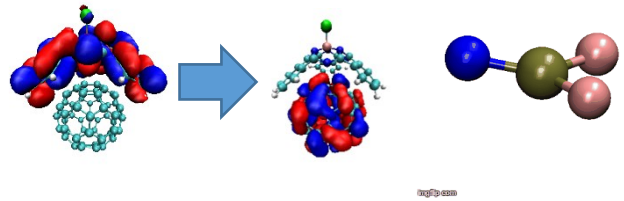
- Modularization and revision
- DVR methods
- Semiempirical Hamiltonians
- Molecular integrals
- Decoherence methods, TSH

2018 (Pyxaid2, Libra-X)

Libra-X (with Drs. Ryoji Asahi, Kosuke Sato, Ekadashi Pradhan)

Sato, Pradhan, Asahi, Akimov *PCCP* **2018,** 20, 25275
Pradhan, Sato, Akimov *J. Phys.: Condens. Matter*, **2018**, 30, 484002

- Interfaces with GAMESS, QE
- Added back-reaction for QE
- More modularization



Pyxaid2 (with Prof. Wei Li)

Li, Zhou, Prezhdo, Akimov *ACS Energy Lett*, **2018**, 3, 2159

- SOC, multiple k-points, etc.

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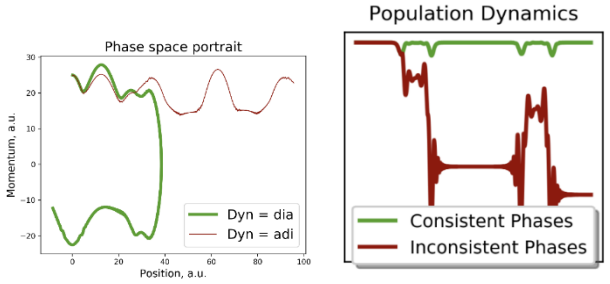
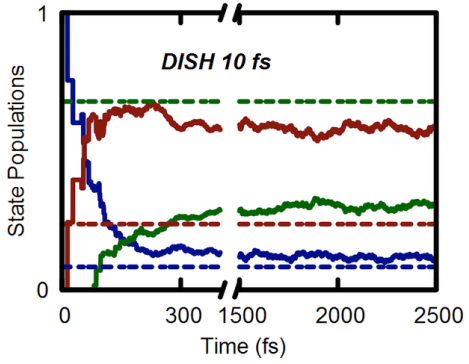
Phase correction for NACs

Akimov *JPCL* **2018** 9, 6096-6102



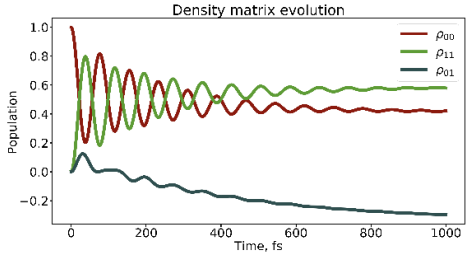
Bastida's Boltzmann-corrected Ehrenfest, mSDM

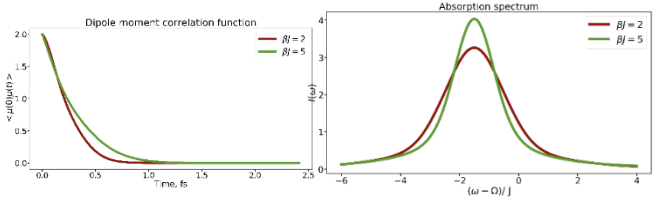
Smith; Akimov *JCP* **2019**, 151, 124107



HEOM

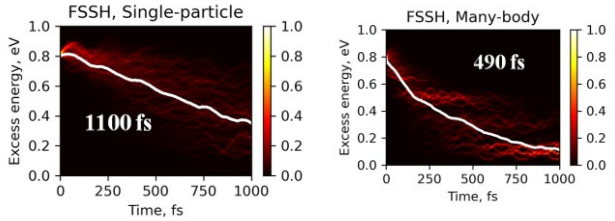
Temen, Jain, Akimov *Int. J. Quant. Chem.*, **2020**, 120, e26373





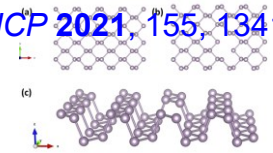
Many-body (TD-DFT) NA-MD

Smith, B.; Shakiba, M.; AVA *JCTC* **2021**, 17, 678
Smith, B.; Shakiba, M.; AVA *JPCL* **2021**, 12, 2444



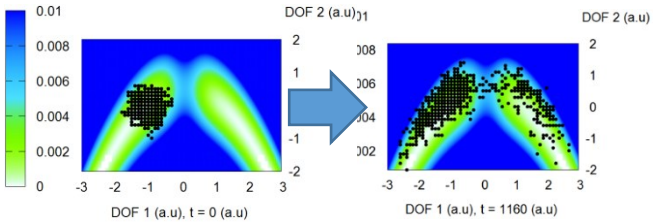
Revised DISH, new workflows

Akimov *JCP* **2021**, 155, 134106



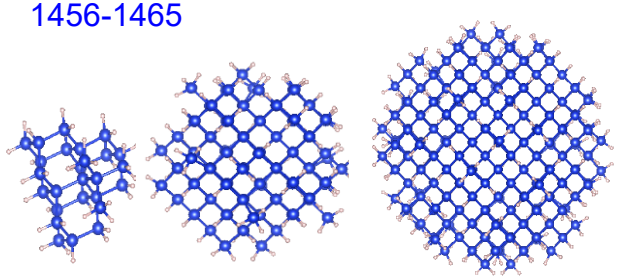
Entangled trajectories

Smith, Akimov *JCP* **2018**, 148, 144106

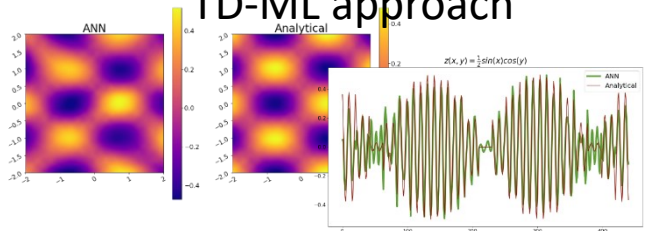


Belyaev-Lebedev LZ method

Smith, B.; Akimov, A. V *JPCL* **2020**, 11, 1456-1465



Machine Learning revised. TD-ML approach



Akimov *JPCL* **2021**, 12, 12119

2018 **2019** **2020** **2021**

Libra History

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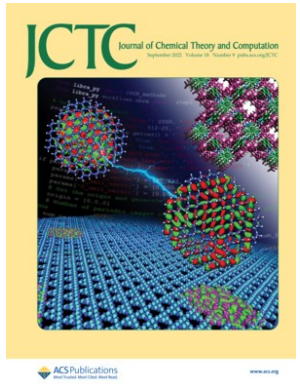
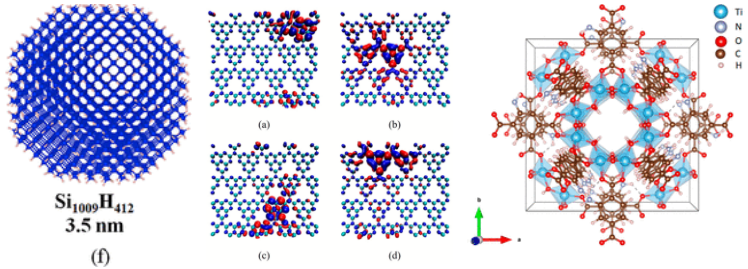
NA-MD with xTB – applications to large systems
Also: effect of spin-adaptation

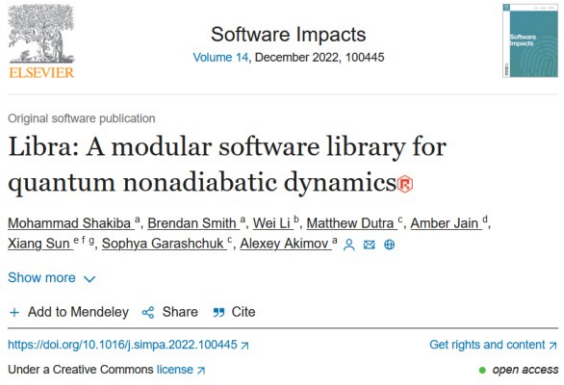
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157





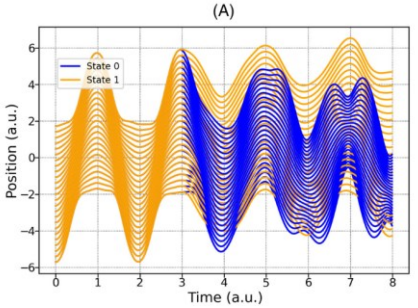
Shakiba, M.; Smith, B.; Li, W.; Dutra, M.; Jain, A.; Sun, X.; Garashchuk, S.; Akimov, A.V. *Software Impacts* **2022** 14, 100445

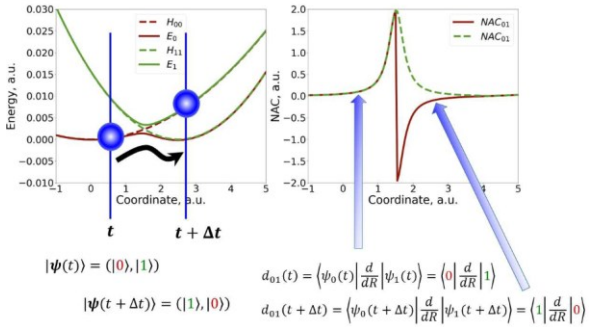
https://codeocean.com/capsule/4727375/tree/v1



Generalized Local-Diabatization approach is adopted. New integrators. Liouville's formalism

Shakiba, M.; Akimov, A.V. *TCA* **2023** 142, 68



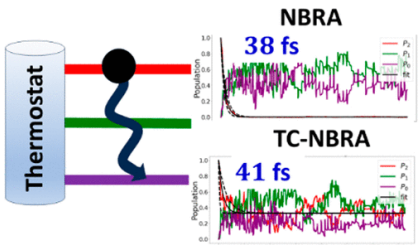


QTAG added

Dutra, M.; Garshchuk, S.; Akimov, A. *IJQC* **2023.** 123, e27078

TC-NBRA workflow

Akimov, A.V. *JPCL* **2023** 14, 11673



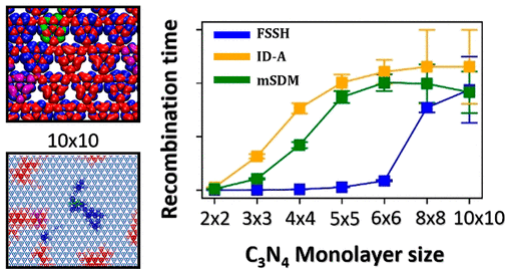
Hop $i \to j$: $e_{kin}^{tr} \to e_{kin}^{tr} + E_{i(t+\Delta t)} - E_{j(t+\Delta t)}$

Thermostat: $e_{kin} \to e_{kin} \exp(-2\xi_1 \Delta t)$

NAC renormalize: $NAC_{eff}^{tr} \to NAC_{ref}^{tr} \sqrt{e_{kin}^{tr}/e_{kin}^{ref}}$

NA-MD with xTB: dependence of rates on carrier concentration

Shakiba, M.; Akimov, A.V. *JPCC* **2023** 127, 9083



2022 **2023**

Libra History

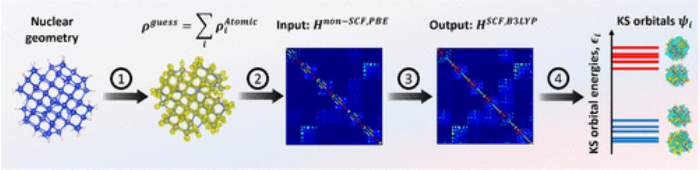
University at Buffalo
The State University of New York

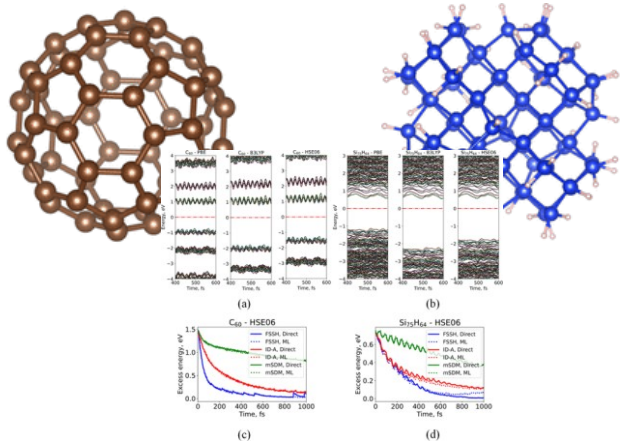
Theory of many methods available (and yet to be added) in Libra:

Akimov, A. V. "Fundamentals of Trajectory-Based Methods for Nonadiabatic Dynamics" Editor(s): Manuel Yáñez, Russell J. Boyd, *Comprehensive Computational Chemistry (First Edition), Elsevier* **2024** Pages 235-272, ISBN 9780128232569, link **Book Chapter in Book: "Comprehensive Computational Chemistry"**

ML for KS Hamiltonian mapping

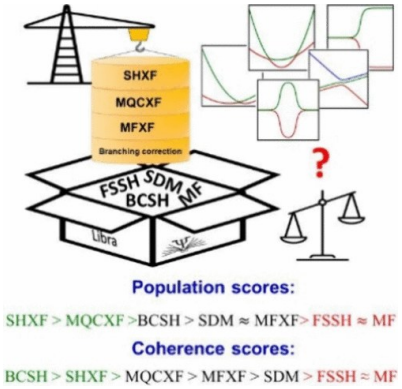
Shakiba, M.; Akimov, A.V. *JCTC* **2024** 20, 2992





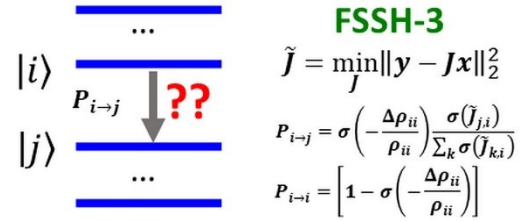
Exact factorization methods

Han, D.; Akimov, A.V. *JCTC* **2024** 20, 5022



FSSH3, FSSH2

Akimov, A. V. *Mol. Phys.* **2024** e2376893

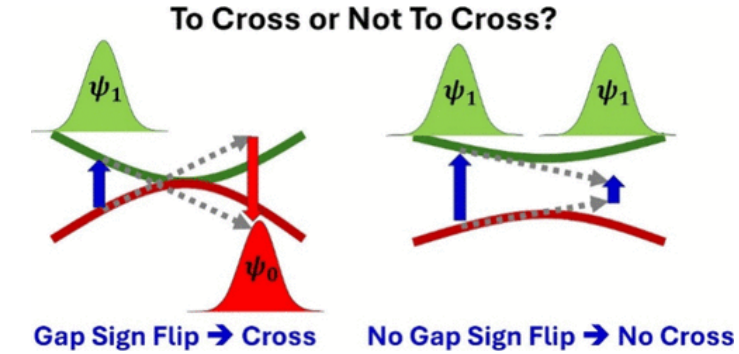


Force-based state tracking

Akimov, A.V. *JPCL* **2024** 15, 11944

Libra/eQE interface – application to crystalline pentacene; IDF, DISH_rev2023

Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *JPCM* **2024** 36, 385901



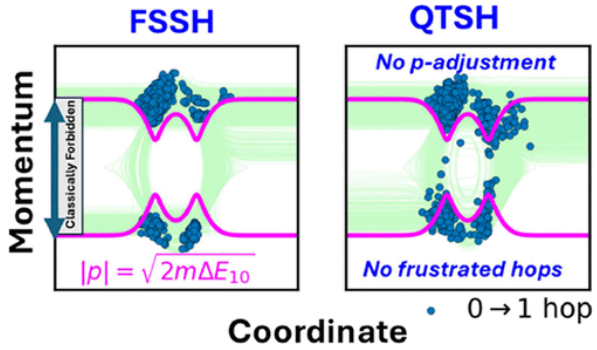
2024

Libra History

University at Buffalo
The State University of New York

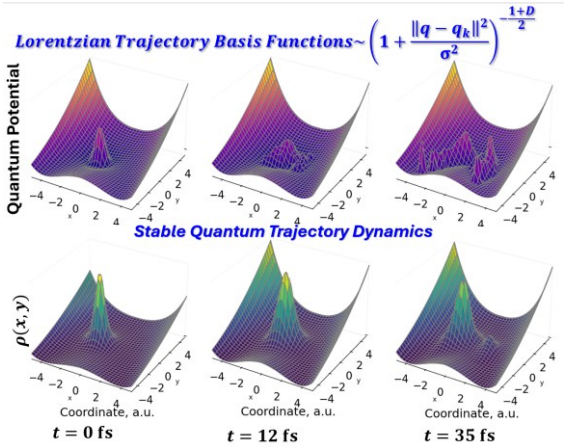
QTSH generalization to many states

Han, D.; Martens, C. C; Akimov, A. V. *JCTC* **2025**, 21, 6, 2839



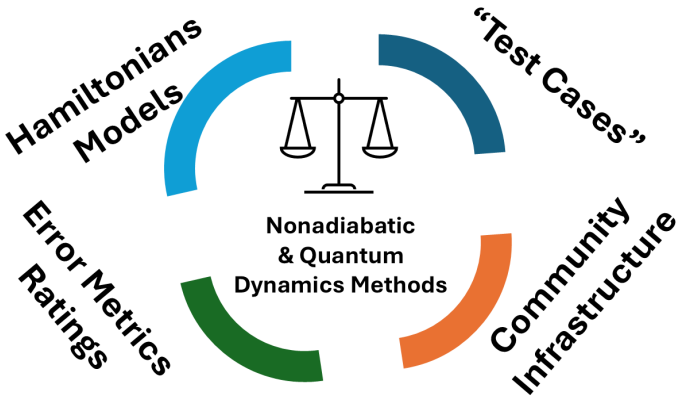
Lorentzian trajectory basis functions for Bohmian dynamics

Akimov, A. V. *JCP* **2025** 163, 171102



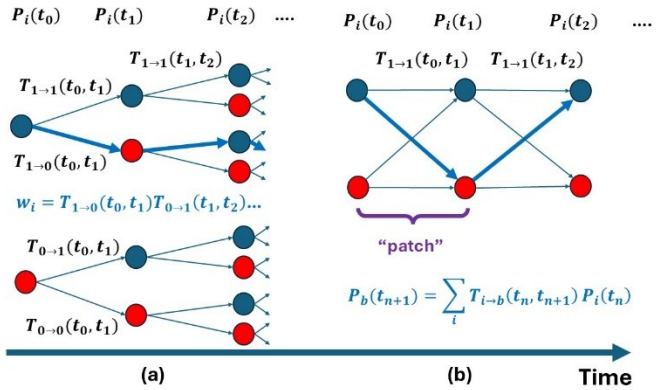
Perspective on NA-MD methods assessment/benchmarking

Akimov, A. V. *JCTC* **2025** 21, 11821



FISH: Decoherence and hop resummation in the NBRA workflow

Han, D.; Shakiba, M.; Akimov, A. V. *JPCL* **2025** 16, 7168



2025

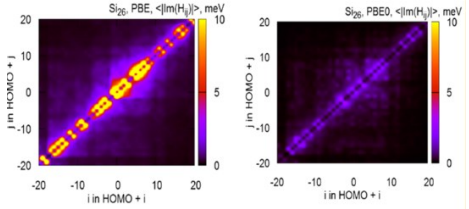
Libra in Materials Research: (0D)Quantum Dots and Molecules

University at Buffalo
The State University of New York

Bare and hydrogenated Si clusters

Lin, Y.; AVA *JPCA*. **2016**, 120, 9028

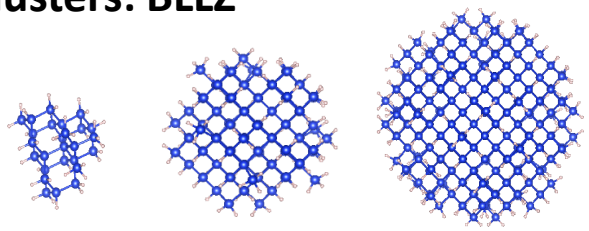
Nonadiabatic $\langle \psi_i | \frac{d}{dt} | \psi_j \rangle$ coupling



Pure DFT Hybrid DFT

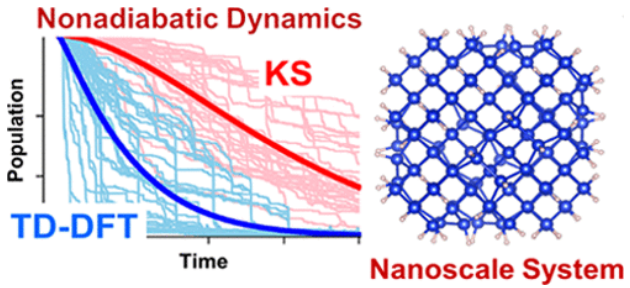
H- and F-terminated Si nanoclusters: BLLZ

Smith, B.; Akimov, A. V
JPCL **2020**, 11, 1456-1465



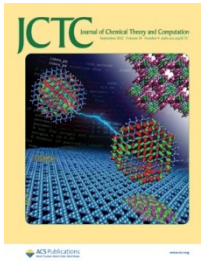
Si and CdSe nanoclusters: TD-DFT vs. KS

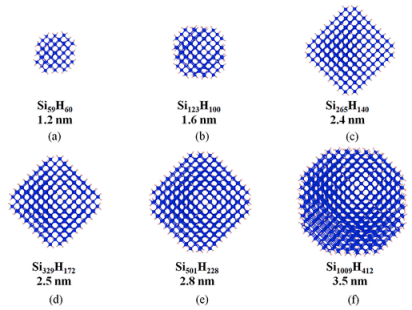
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157



Si nanoclusters: xTB approach

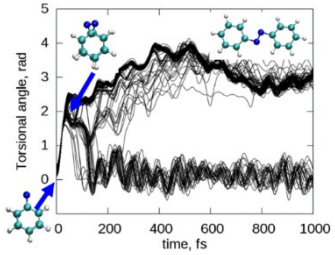
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V.
JCTC **2022** 18, 5157

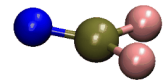




Azobenzene and HFCO: Delta-SCF approach

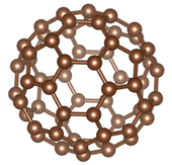
Pradhan et al. *JPCM*, **2018**, 30, 484002

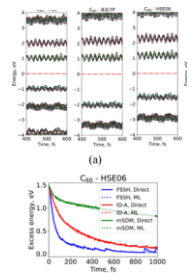


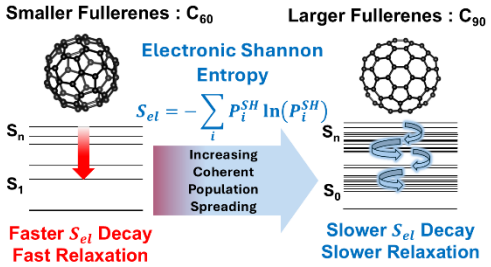


Si nanoclusters and C_{60}: ML KS Hamiltonian mapping

Shakiba, M.; Akimov, A.V. *JCTC* **2024** 20, 2992





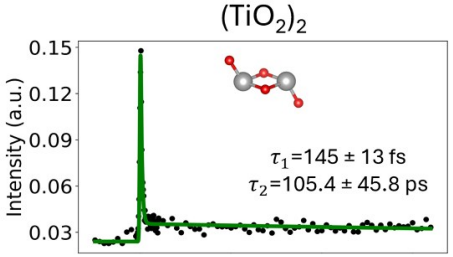


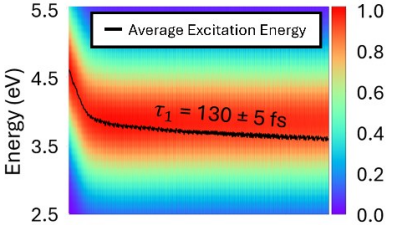
Excited state relaxation in Fullerenes

Yasin, K.; Shakiba, M.; Akimov, A. V.
JPCL **2026** 17, 2812

Atomically-precise metal oxide clusters

Recio-Poo, M.; Rotteger, C. H.; Illas, F.; Bromley, S. T.; Morales-García, A.; Sayres, S. G.; Akimov, A. V.
JACS **2025** 147, 40900



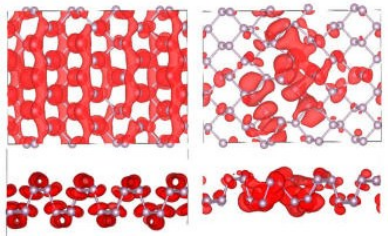


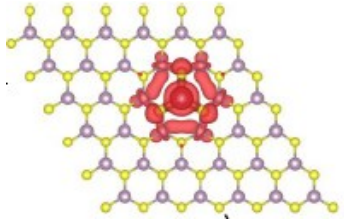
Libra in Materials Research: 2D materials and heterojunctions

University at Buffalo
The State University of New York

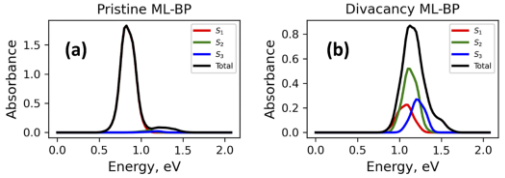
Black phosphorus monolayers (Phosphorene)

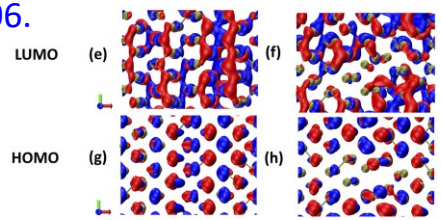
Long el al. *JPCL* **2016**, *7*, 653.



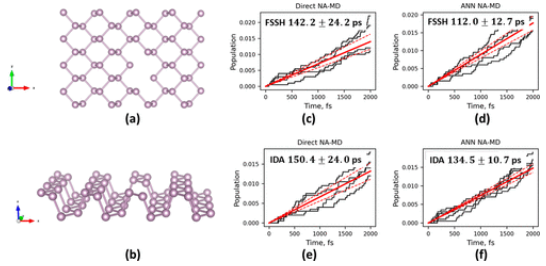


Akimov, A. V. *JCP* **2021**, *155*, 134106.

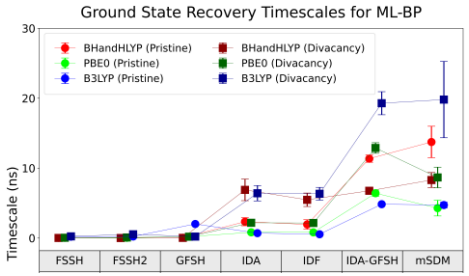




Akimov, A. V. *JPCL* **2021**, *12*, 12119–12128.

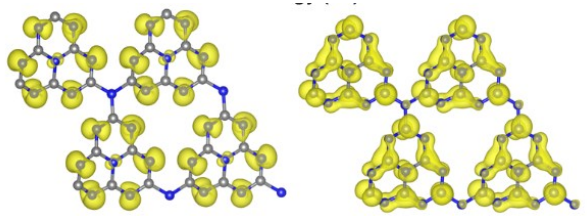


Zabihi, H.; Zhang, Q.; Khayati, G. R.; Irannejad, A.; Akimov, A. V. *JCTC* **2025** 21, 7991

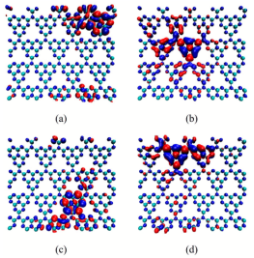


$g\text{-}C_3N_4$

Agrawal, S.; Lin, W.; Prezhdo, O. V.; Trivedi, D. J. *J. Chem. Phys.* **2020**, *153*, 054701.

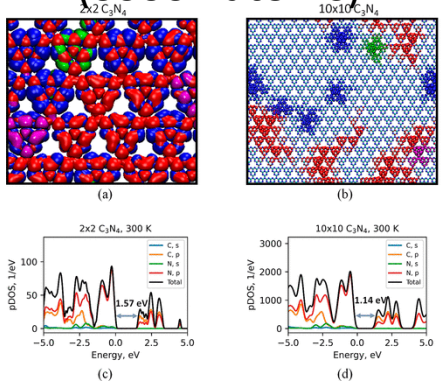


Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157

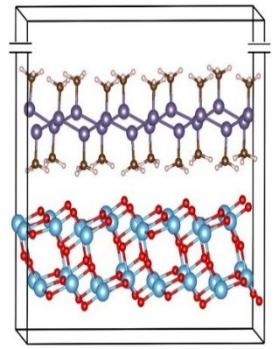


Shakiba, M.; Akimov, A.V. *JPCC* **2023** 127, 9083

(6000+ atoms)



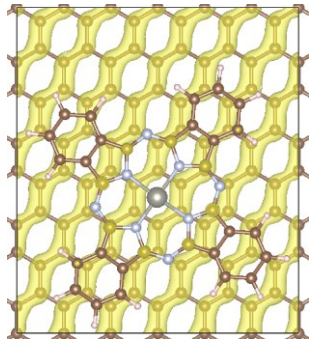
SiR/TiO_2 and GeR/TiO_2



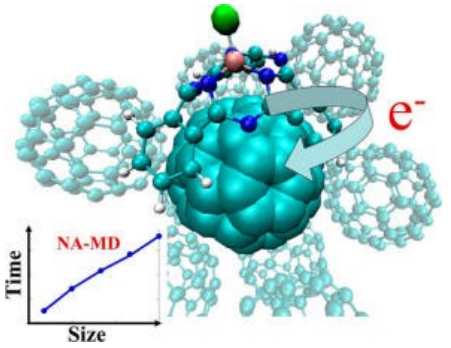
Nijamudheen, A.; AVA *JPCC*, **2017**, *121*, 6520

ZnPc/graphene

Mehdipour, H.; Smith, B.; Rezakhani, A. T.; Tafreshi, S. S.; de Leeuw, N. H.; Prezhdo, O. V.; Moshfegh, A. Z.; Akimov, A. V. *PCCP* **2019** 21, 23198-23208



$SubPc/C_{60}$



Akimov, A. V. *JCTC* **2016**, *12*, 5719–5736

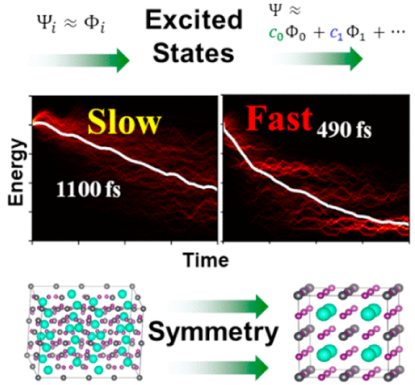
Sato et al. *PCCP*, **2018**, 20, 25275.

Libra in Materials Research: 3D-Periodic Solids

University at Buffalo
The State University of New York

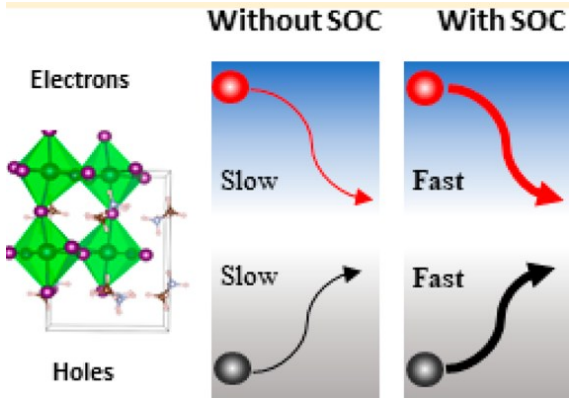
Lead halide perovskites: MB effects

Smith, B.; Shakiba, M.; AVA *JPCL* **2021**, 12, 2444



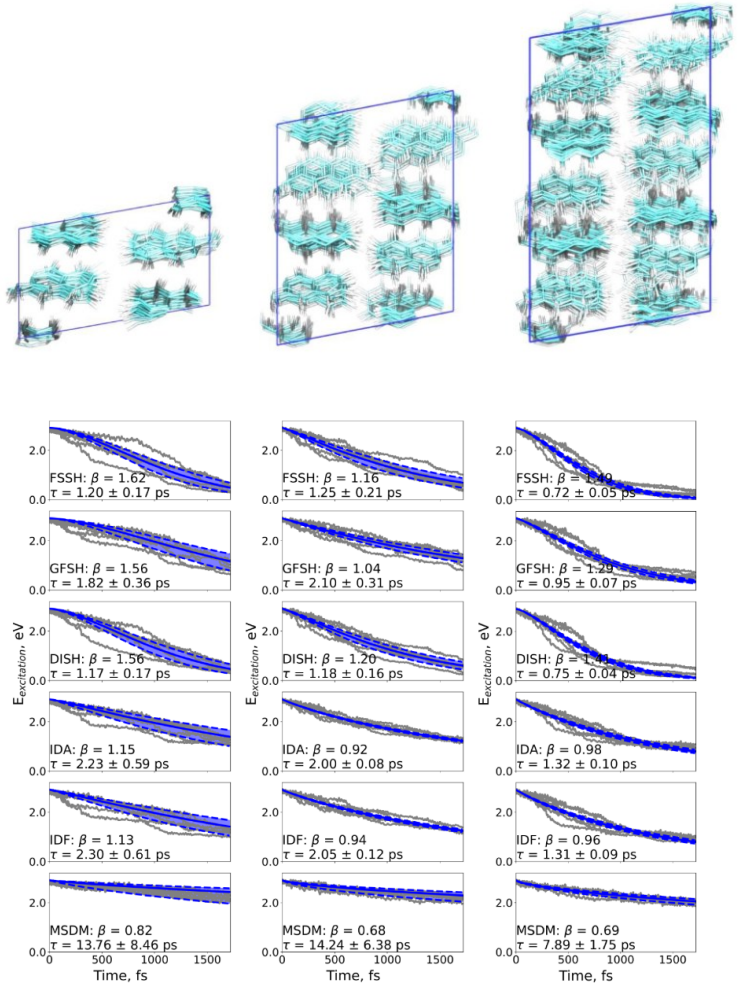
Lead halide perovskites: SOC effects

Li, W.; Zhou, L.; Prezhdo, O. V.; Akimov, A. V.
ACS Energy Lett. **2018**, *3*, 2159–2166.



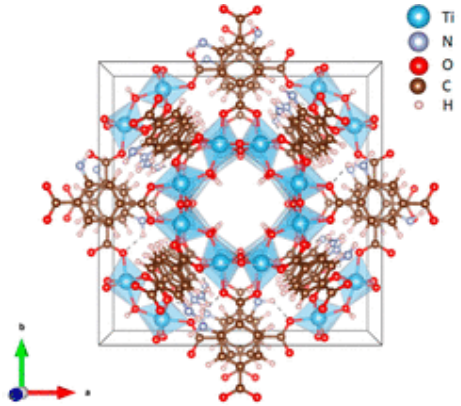
Crystalline pentacene

Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *JPCM* **2024**, 36, 385901



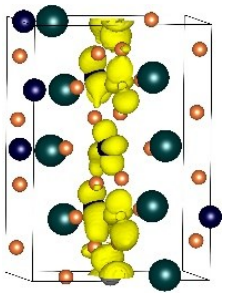
MOFs: With xTB

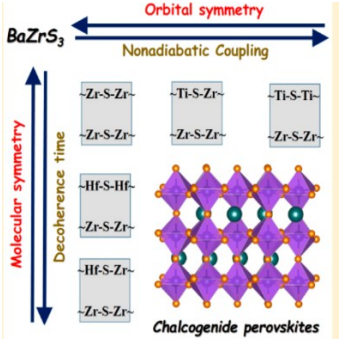
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V.
JCTC **2022** 18, 5157



BZTS perovskites

Nijamudheen, A.; AVA *JPCL* **2018**, *9*, 248





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Part 3: Theory of Nonadiabatic Molecular Dynamics and Trajectory Surface Hopping (TSH)

Born-Oppenheimer Approximation

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$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}}, t) = \hat{T}(\hat{\boldsymbol{R}}) + \hat{H}_{el}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}}, t) + \hat{V}_{nn}(\hat{\boldsymbol{R}}, t)$$

Includes el-el and el-nucl interactions

$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}})\Psi_n(\boldsymbol{r}, \boldsymbol{R}) = E_n\Psi_n(\boldsymbol{r}, \boldsymbol{R})$$

This is an **electron-nuclear (vibronic)** Hamiltonian

This is an **electron-nuclear (vibronic)** wavefunction

Born-Oppenheimer approximation: a general **time-scale separation** approximation = there are fast and slow degrees of freedom, in general. **Enables factorization** $\boldsymbol{X(fast, slow) \approx x(slow)y(fast; slow)}$
the adiabatic approximation applied to **electrons and nuclei**

- Nuclei are heavier than electrons, so nuclei are seeing by electrons as static entities
- Electrons move in the field created by immobile nuclei and themselves
- $m_{nucl} \gg m_{elec}$, so treat nuclei classically, and electrons – quantum-mechanically

$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}})\Psi_n(\boldsymbol{r}, \boldsymbol{R}) = E_n\Psi_n(\boldsymbol{r}, \boldsymbol{R}) \quad \Rightarrow \quad \hat{H}(\hat{\boldsymbol{r}}; \boldsymbol{R}(t))\Psi_n(\boldsymbol{r}; \boldsymbol{R}) = E_n(\boldsymbol{R})\Psi_n(\boldsymbol{r}; \boldsymbol{R}(t))$$

BO approximation

Coordinates of nuclei are the dynamical variables
Energy - is a number

Coordinates of nuclei are parameters
Energy – is a function of these parameters: **potential energy surface**

Adiabatic Approximation. Adiabatic and Nonadiabatic Dynamics

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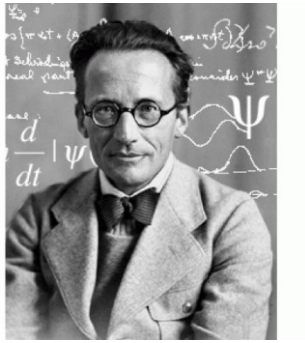
$$i\hbar \frac{\partial \Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_i(\mathbf{r};\mathbf{R}(t))$$

Except for in the exact factorization ansatz!



Adiabatic approximation: keep only one term

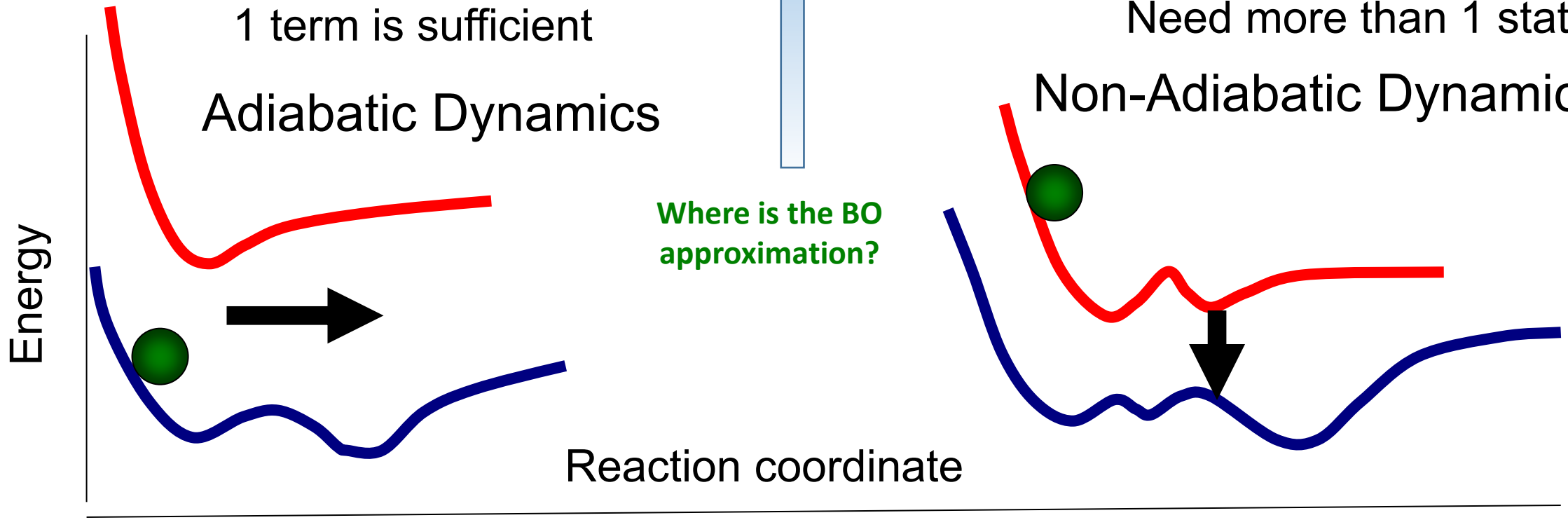
1 term is sufficient

Adiabatic Dynamics

Need more than 1 state

Non-Adiabatic Dynamics

Where is the BO approximation?



When NA dynamics is needed: Failure of the Born-Oppenheimer Approximation

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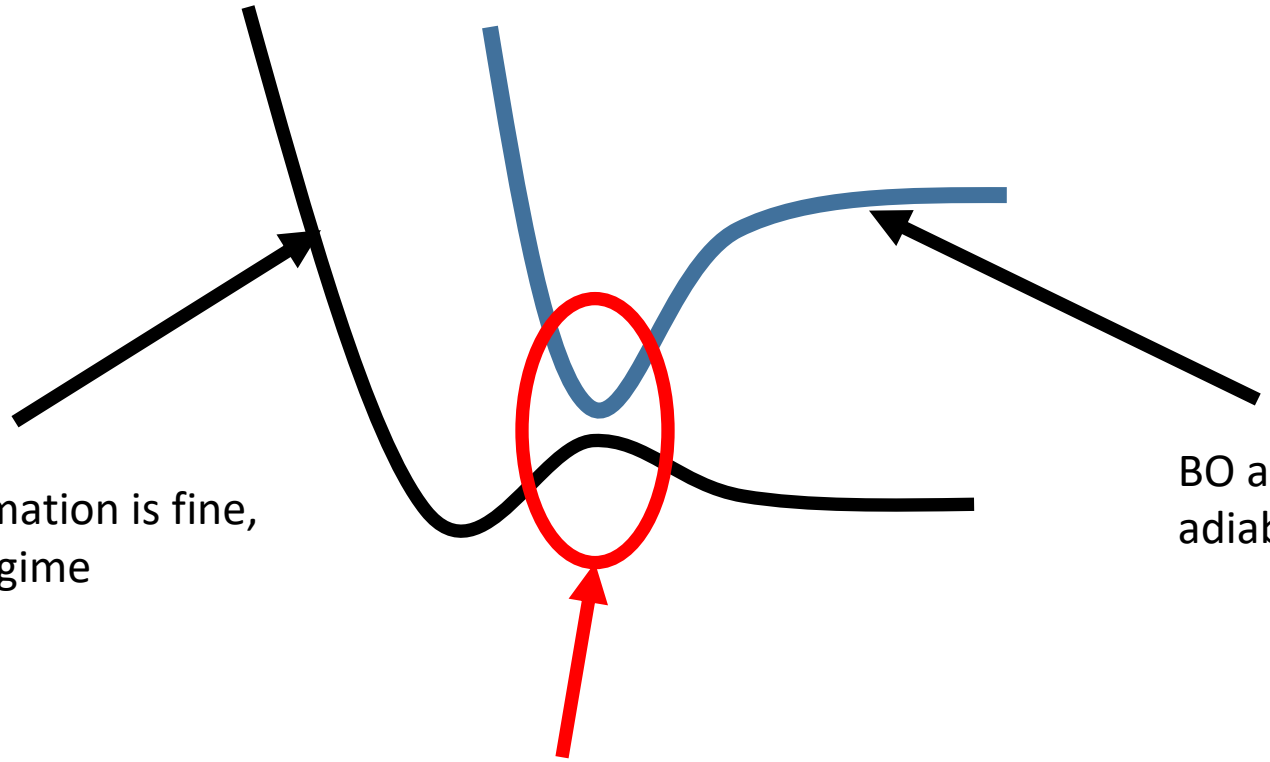
$$E_{kin} \gg |E_i - E_j|$$

$$v = \frac{p}{m}$$

- light atoms (e.g. H – quantum nuclear effects)
- high-energy (momentum) – e.g. colliding particles
- degeneracies of quantum states (bond-breaking, plasmas, metals)



BO approximation is fine, adiabatic regime

BO approximation is fine, adiabatic regime

BO approximation breaks down here, non-adiabatic regime

Terminology: Adiabatic and Diabatic States

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Adiabatic

- unique
- eigenstates of molecular Hamiltonian:
- not always chemically-intuitive

Adiabatic (Hamiltonian is diagonal):

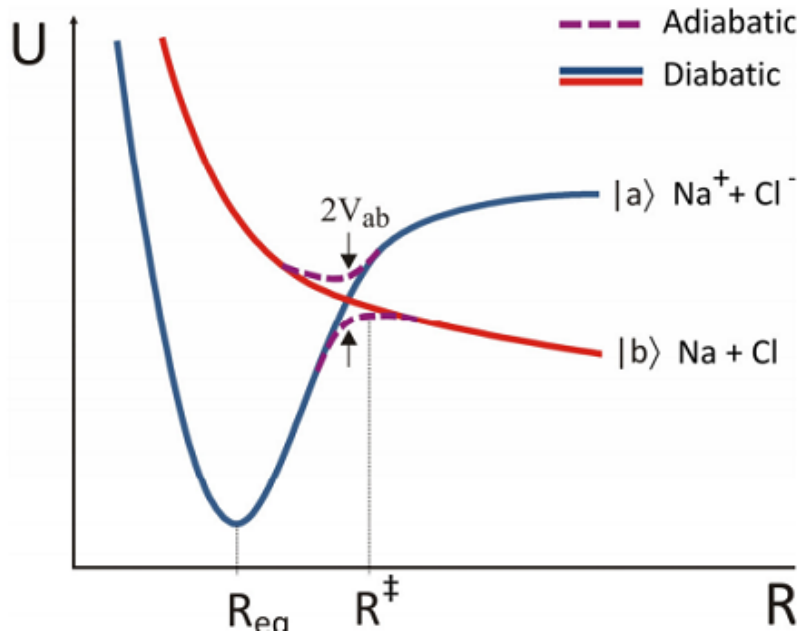
$$\langle \psi_{adi,i} | \hat{H}_{el} | \psi_{adi,j} \rangle = 0, \forall i \neq j$$

(Quasi-)Diabatic

- non-unique, infinite # of possibilities
- Is not an eigenstate of molecular Hamiltonian
- usually chosen to be chemically-intuitive

Diabatic (NACs are exactly zero):

$$\langle \psi_{dia,i} | \nabla_{\boldsymbol{R}} | \psi_{dia,j} \rangle = 0, \forall \boldsymbol{R}$$



https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Time_Dependent_Quantum_Mechanics_and_Spectroscopy_(Tokmakoff)/06%3A_Adiabatic_Approximation/6.03%3A_Diabatic_and_Adiabatic_States

Equations of Motion with Different Ansatze

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Example 1: BO with quantum nuclei

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

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R})$$

In the **adiabatic basis**

Diagonal BO correction to the PES!
(ZPE of electrons)

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}D^{(2)}_{ij,\alpha}\chi_j$$

$D^{(1)}_{ij,\alpha} = \langle\Phi_i|\nabla_\alpha\Phi_j\rangle$ first-order nonadiabatic couplings (NAC) - vector

Describes how a nuclear DOF α couples electronic state i and j
This is what determines the rates of nonadiabaatic transitions.

$D^{(2)}_{ij,\alpha} = \langle\Phi_i|\nabla^2_\alpha\Phi_j\rangle$ second-order NAC - scalar

Example 2: BO with wavepacket-dressed trajectories

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

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(\boldsymbol{t}))$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t))\right]\chi_i - i\hbar\sum_j\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j$$

$$\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle = \sum_{j,\alpha}\left\langle\Phi_i\left|\frac{\partial}{\partial\boldsymbol{R}_\alpha}\right|\Phi_j\right\rangle\frac{\partial\boldsymbol{R}_\alpha}{\partial t} = \sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\boldsymbol{P}_\alpha}{M_\alpha}$$

This terms appears because Φ is an implicit function of time, via $\boldsymbol{R}(t)$

Classical Path Approximation

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Example 3: BO with trajectories

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

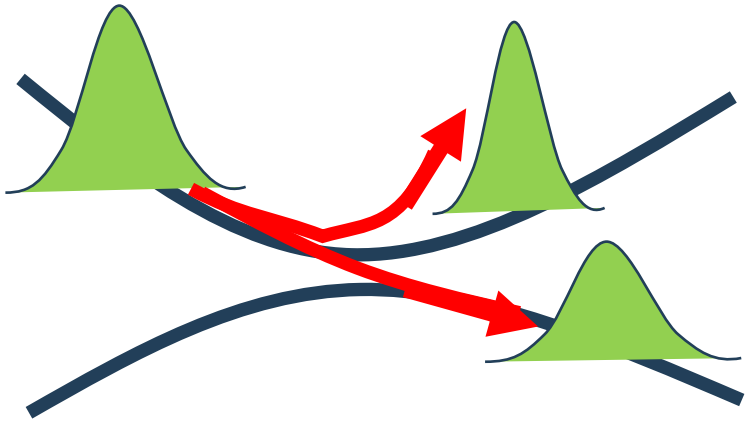
$$\Psi(t,\boldsymbol{r};\boldsymbol{R}(t)) = \sum_i c_i(t)\Phi_i(\boldsymbol{r};\mathbf{R}(\boldsymbol{t}))$$

$$i\hbar\frac{\partial}{\partial t}c_i = E_i(\boldsymbol{R}(t))c_i - i\hbar\sum_j \left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle c_j$$

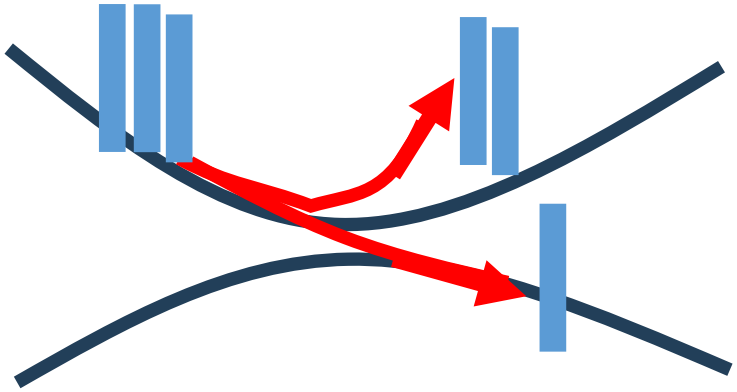
$c_i(t)$ – state amplitudes (electronic coordinates)

$$\dot{\boldsymbol{R}}_\alpha(t) = \frac{\boldsymbol{P}_\alpha}{M_\alpha} \qquad \dot{\boldsymbol{P}}_\alpha(t) = \boldsymbol{F}_{\alpha,i}$$

$\{\boldsymbol{R},\boldsymbol{P}\}$ - nuclear coordinates and momenta



Quantum Nuclei: Wavepackets



Classical Trajectories