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Libra *Summer School and Workshop 2024*

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University at Buffalo, SUNY

July 8, 2024

Libra Overview

Libra History

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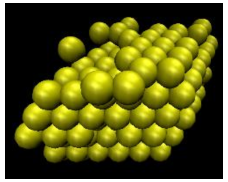
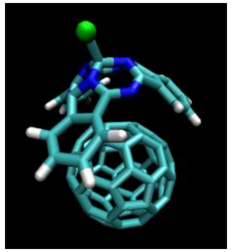
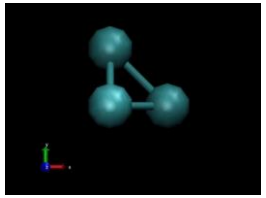
Classical MD





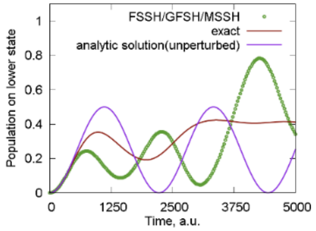
Rigid body MD

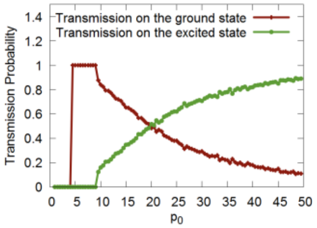


- Simplectic integrators for classical DOFs
- Thermostats
- Barostats
- Force fields
- ANN
- Chemical object representation

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

Ehrenfest & TSH



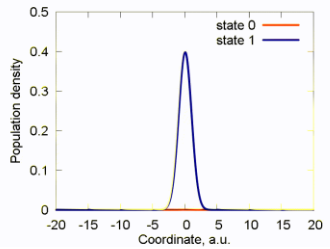


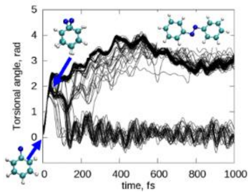
- Simplectic integrators for TDSE
- TSH, Ehrenfest, stand-alone scripts
- Decoherence methods
- Model problems
- Added HF and EHT to LCCCS
- Interface with VASP, then QE

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

DVR

Back-reaction



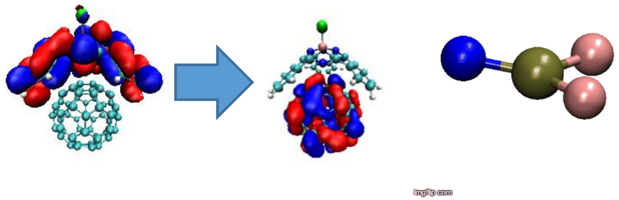


- Modularization and revision
- DVR methods
- Semiempirical Hamiltonians
- Molecular integrals
- Decoherence methods, TSH

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.

2007-2011 (LCCCS)

2011-2015 (Pyxaid)

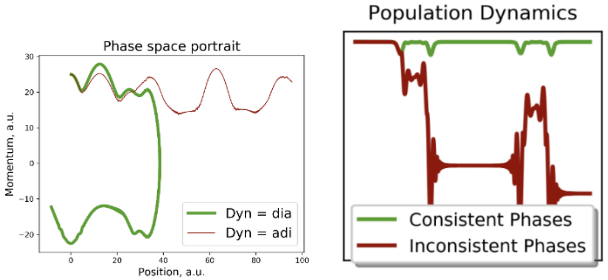
2015/2016 (Libra)

2018 (Pyxaid2, Libra-X)

Libra History

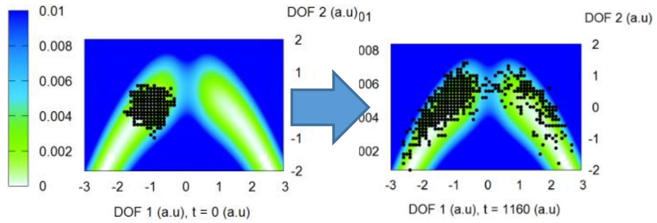
Phase correction for NACs

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



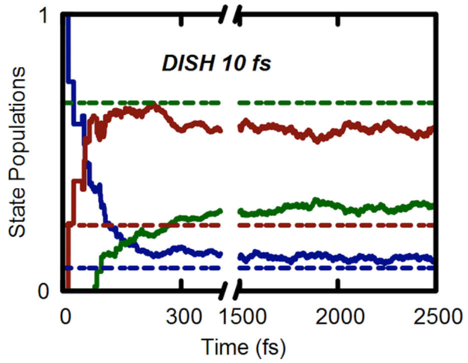
Entangled trajectories

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



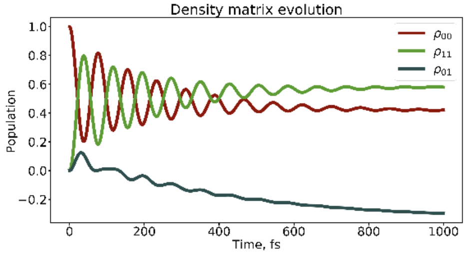
Bastida's Boltzmann-corrected Ehrenfest, mSDM

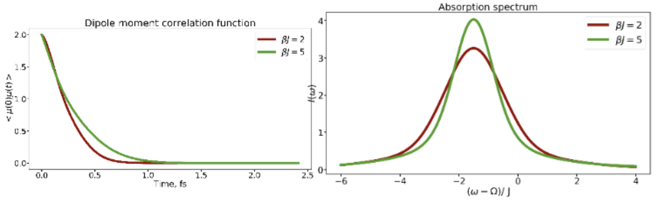
Smith; Akimov *JCP* **2019**, 151, 124107



HEOM

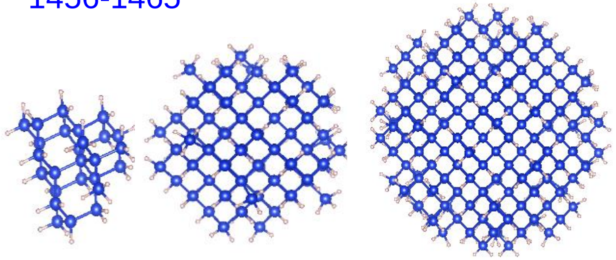
Temen, Jain, Akimov *Int. J. Quant. Chem.*, **2020**, 120, e26373





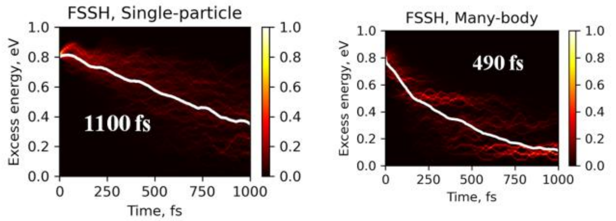
Belyaev-Lebedev LZ method

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



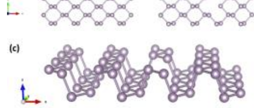
Many-body (TD-DFT) NA-MD

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

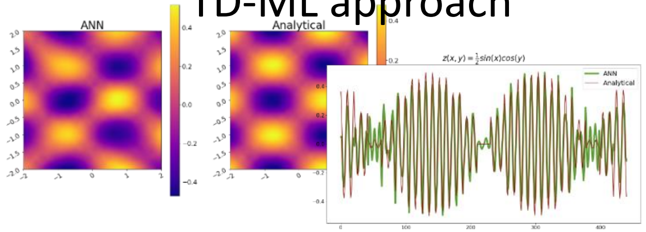


Revised DISH, new workflows

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



Machine Learning revised. TD-ML approach



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

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

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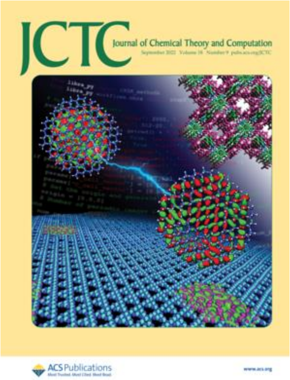
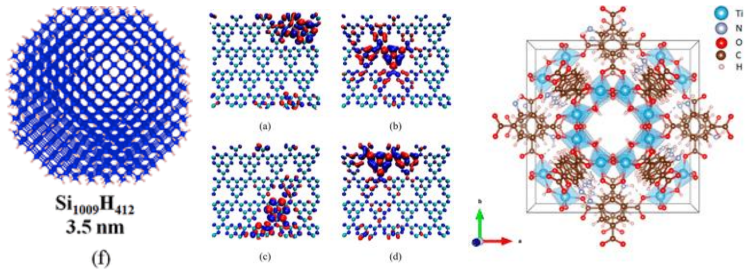
NA-MD with xTB – applications to large systems
Also: effect of spin-adaptation

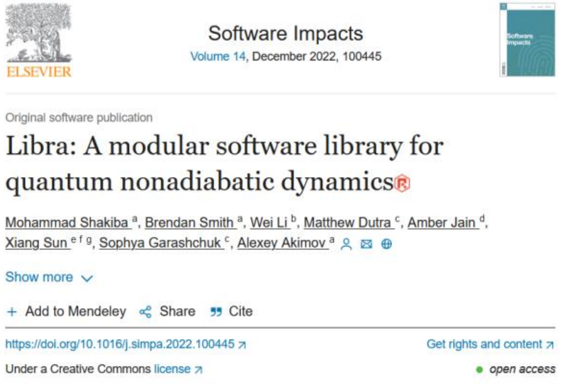
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157





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


Software Impacts
Volume 14, December 2022, 100445

ELSEVIER

Original software publication

Libra: A modular software library for quantum nonadiabatic dynamics

Mohammad Shakiba [a], Brendan Smith [a], Wei Li [b], Matthew Dutra [c], Amber Jain [d], Xiang Sun [e f g], Sophya Garashchuk [c], Alexey Akimov [a]

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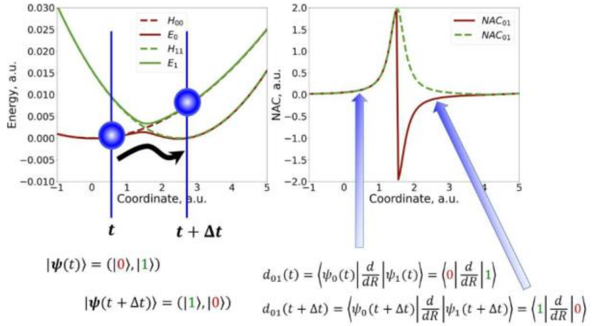
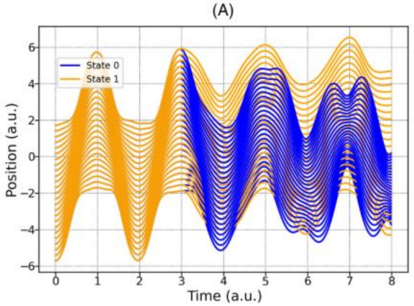
Generalized Local-Diabatization approach is adopted. New integrators. Liouville's formalism

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





QTAG added

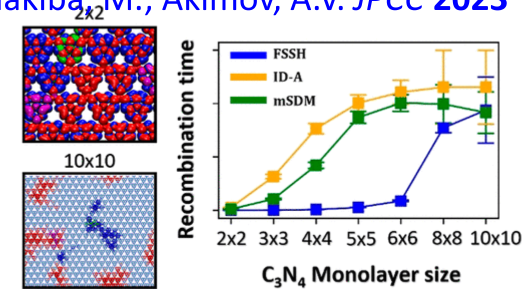
Dutra, M.; Garshchuk, S.; Akimov, A. *IJQC* **2023.** 123, e27078

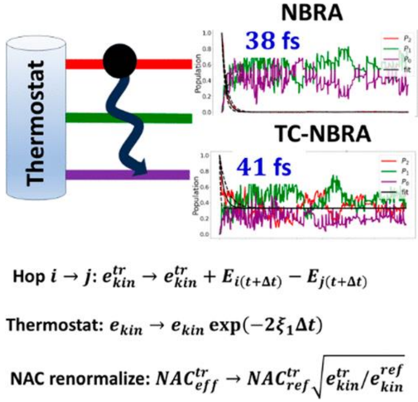
TC-NBRA workflow

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

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

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





2022

2023

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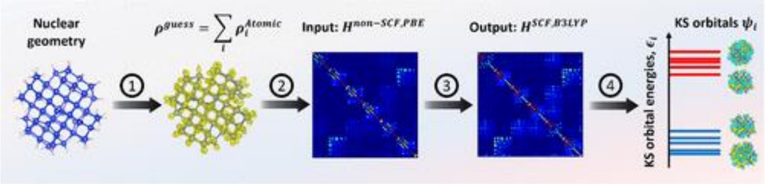
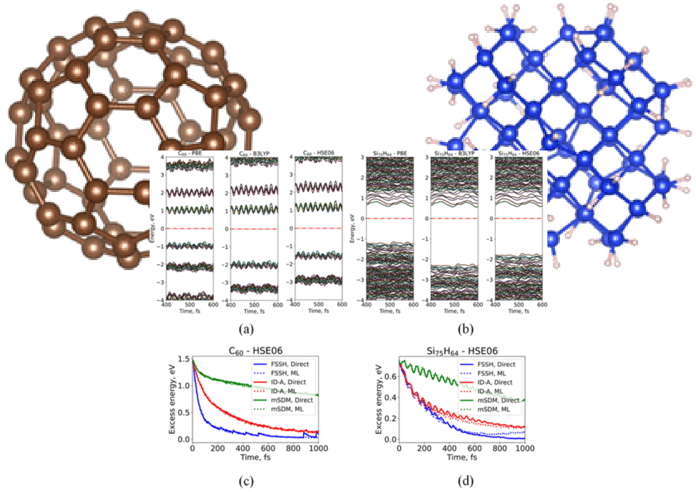
Theory of many methods available (and yet to be added) in Libra:

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

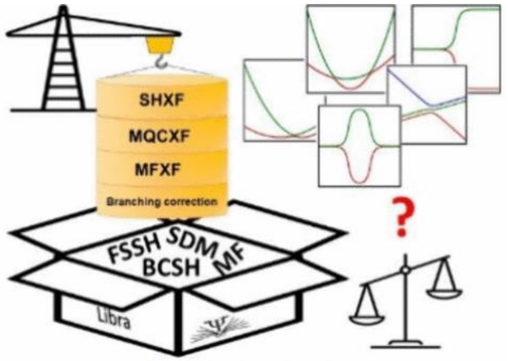
Shakiba, M.; Akimov, A.V. *JCTC* **2024** 20, 2992





Exact factorization
Also, re-validated Ehrenfest and integrators, state tracking and phases

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



Population scores:

SHXF > MQCXF >BCSH > SDM ≈ MFXF> FSSH ≈ MF

Coherence scores:

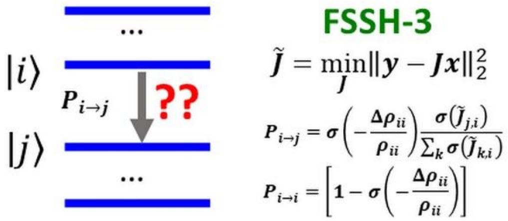
BCSH > SHXF > MQCXF > MFXF > SDM > FSSH ≈ MF

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

FSSH3, FSSH2

Akimov, A. V. *Mol. Phys.* **2024** (accepted)



Unpublished: MASH, QTSH, removal of rotation/translation, state selection

2024

Libra Philosophy/Vision

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- **modular**

Maximize and simplify the re-use, OOP

- **versatile**

linear algebra, integrals,
quantum and classical mechanics/dynamics,
nonadiabatic methods, surface hopping,
IO utilities, model preparation and analysis

- **“methodology discovery”** (prototyping)

  - Use with model problems and atomistic simulations
  - Python – for convenience, C++ - for efficiency

- **practical**

Fully-functional tool that can be applied to real (atomistic) systems to study materials

- **user-friendly & documented**

The code is convenient to users and they have plenty resources – examples and documentation

- **community tool**

  - A platform to adopt the past and latest developments
  - The developers can understand and contribute to the code

Versatile: Methods and Algorithms

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Dynamics:
- adiabatic
- Mean-field-like: Ehrenfest, MFSD, MASH
- TSH: FSSH, FSSH2, FSSH3, GFSH
- Exact factorization: SHXF, MQCXF, MFXF
- Decoherence: DISH, DISH_rev2023, IDA, IDF, SDM, mSDM, BCSH
- Coupled trajectories-like: ETHD, QTSH
- NAC-free: LZ, ZN, BLLZ
- Wavepackets: QTAG
- Exact grid: SOFT, Colbert-Miller
- Exact system-bath: HEOM

Representations:
- adiabatic
- diabatic

Representations:
- amplitudes (TD-SE)
- density matrix (Liouville)

Integrators:
- RK4 (electronic, general)
- rotations-based (electronic)
- exponentiation (electronic)
- Verlet (nuclear)

Integrators:
- NAC-based
- LD-based

Phase/state tracking:
- Phase correction
- Tracking: Munkres-Kuhn (Hungarian)/mincost

Initial conditions sampling:
- In adiabatic/in diabatic
- Momenta/coordinates
- Gaussian/Wigner/arbitrary
- Voronoi tessellation

Ensembles:
- NVE
- NVT (Nose-Hoover, Nose-Poincare)

Initial conditions sampling:
- In adiabatic/in diabatic
- Momenta/coordinates
- Gaussian/Wigner/arbitrary
- Voronoi tessellation

Other things:
- Force fields (UFF, GAFF, etc.)
- Semiempirics (INDO, EHT, etc.)
- Molecule transformations
- Rotation/translation removal
- Rigid body dynamics

Workflows: model and atomistic; NBRA or not

Interfaces with: CP2K, DFTB+, ORCA, Gaussian, GAMESS, eQE, QE, Ergo, etc.

Libra as a workhorse of our developments

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Implemented in **Libra: https://quantum-dynamics-hub.github.io/libra/index.html**
https://github.com/Quantum-Dynamics-Hub/libra-code

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

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

Some of the implemented methods:

Methods	Paper
Surface hopping schemes	Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061 (FSSH); Wang, L., et al. *JCTC* **2014**, 10, 3598 (GFSH); Akimov, A. V. et al. *J. Phys. Soc. Jpn.* **2015**, 84, 094002 (MSSH)
Decoherence schemes	Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114 (SDM); Nelson, T. et al. *J. Chem. Phys.* **2013**, *138*, 224111. (ID-A, ID-S); Jaeger, H. M. et al. *J. Chem. Phys.* **2012**, *137*, 22A545 (DISH)
Dephasing times calculations	Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107 Akimov, A. V.; Prezhdo, O. V. *J. Phys. Chem. Lett.* **2013**, *4*, 3857 Sifain, A. E.; Wang, L.; Tretiak, S.; Prezhdo, O. V. Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.
Neglect of back-reaction (NBRA)	Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Prog. Surf. Sci.* **2009**, *84*, 30
Boltzmann-corrected Ehrenfest	Bastida, A. et al. *Chem. Phys. Lett.* **2006**, *417*, 53 Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107
Phase corrections	Akimov, A. V *J. Phys. Chem. Lett.* **2018**, *9*, 6096
State tracking	Fernandez-Alberti, S.; et al. *J. Chem. Phys.* **2012**, *137*, 014512 (mincost); Temen, S.; AVA. *JPCL* **2021**, 12, 10587-10597 (stochastic)
Interfaces with ES codes	DFTB+ (Smith, B.; AVA *JPCL*. **2020**, 11, 1456), QE (Pradhan et al. *JPCM,* **2018**, 30, 484002), CP2K (Smith, B. A. et al. JCTC, 2021, 17, 678), Gaussian, GAMESS (Sato et al. *PCCP,* **2018**, 20, 25275)
Exact dynamics	Kosloff, D. and Kosloff, R. J. Chem. Phys. **1983**, *52*, 35-53 (SOFT); Colbert, D. T. and Miller, W. H. **1992**, *96*, 1982-1991 (Colert-Miller DVR)
HEOM	Temen et al. *Int. J. Quant. Chem.,* **2020**, 120, e26373

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
- Renner-Teller

  (Dual Rosen-Zener-Demkov, Dual Landau-Zener-Stuckelberg, Renner-Teller:) Sci. Rep. 6, 24198 (2016); J. Xu and L. Wang JCP 150, 164101 (2019)
- Dumbbell geometry (Subotnik)
- Double arch geometry (Subotnik)

  (Dumbbell geometry, Double arch geometry:) 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…

Libra in Materials Research: Quantum Dots and Molecules

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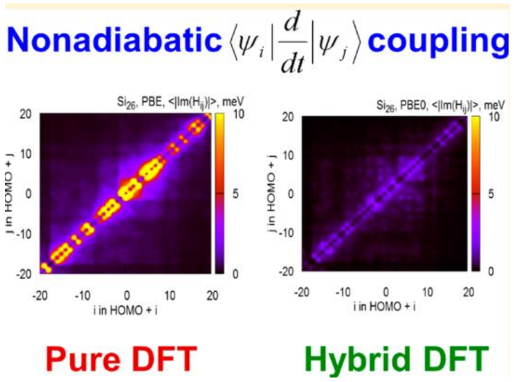
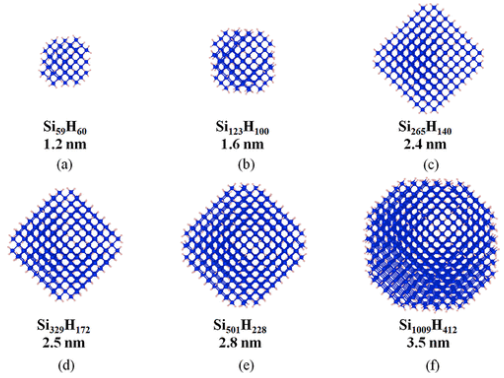
Bare and hydrogenated Si clusters

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



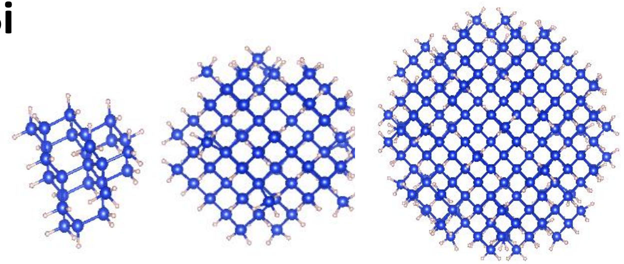
Si nanoclusters: xTB approach

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



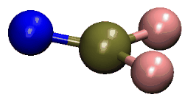
H- and F-terminated Si nanoclusters: BLLZ

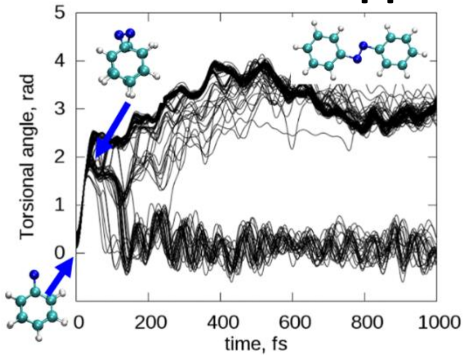
Smith, B.; Akimov, A. V *JPCL* **2020**, 11, 1456-1465



Azobenzene and HFCO: Delta-SCF approach

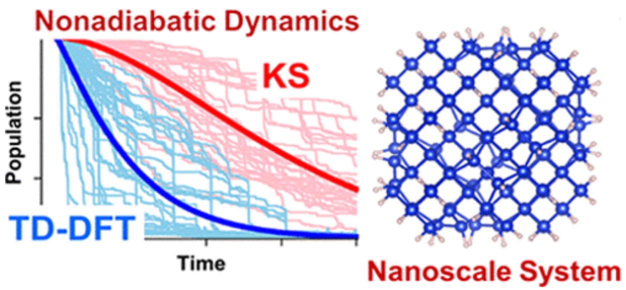
Pradhan et al. *JPCM,* **2018**, 30, 484002





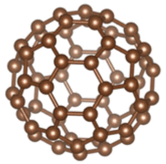
Si and CdSe nanoclusters: TD-DFT vs. KS

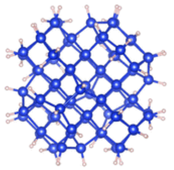
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157

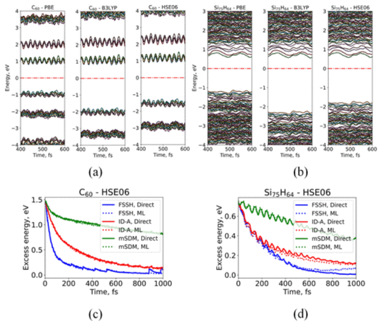


Si nanoclusters and C_{60}: ML KS Hamiltonian mapping

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







Libra in Materials Research: 2D materials and heterojunctions

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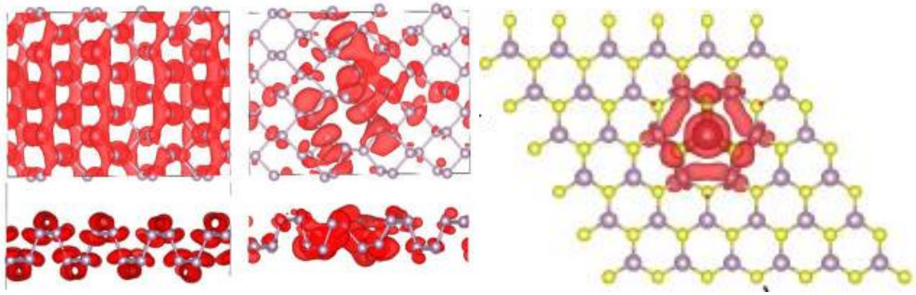
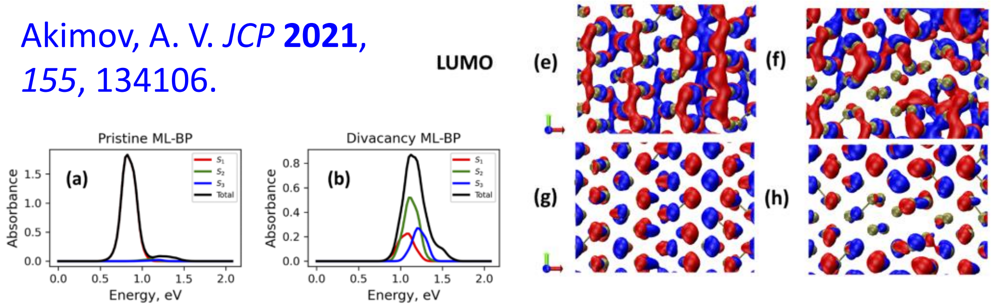
Black phosphorus monolayers (Phosphorene)

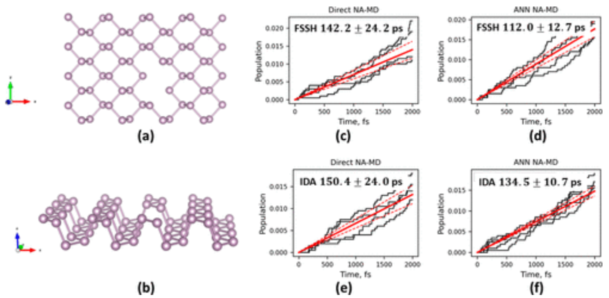
Long el al. *JPCL* **2016**, *7*, 653.



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



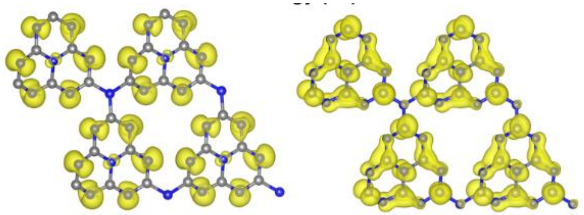
Akimov, A. V. *JPCL* **2021**, *12*, 12119–12128.



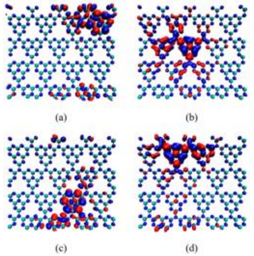
Yet another one is in progress (Hamid Zabihi)

g-C_3N_4

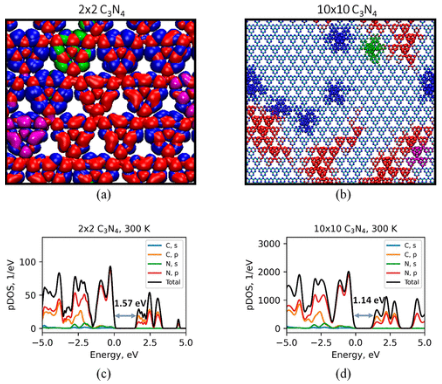
Agrawal, S.; Lin, W.; Prezhdo, O. V.; Trivedi, D. J. *J. Chem. Phys.* **2020**, *153*, 054701.



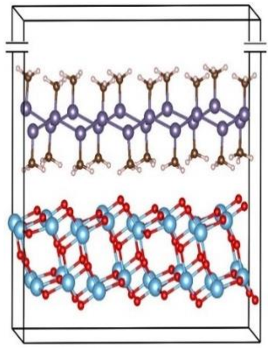
Shakiba, M.; Stippel, E.; Li, W.; Akimov, A. V. *JCTC* **2022** 18, 5157



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



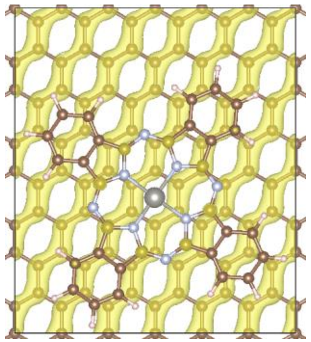
SiR/TiO_2 and GeR/TiO_2



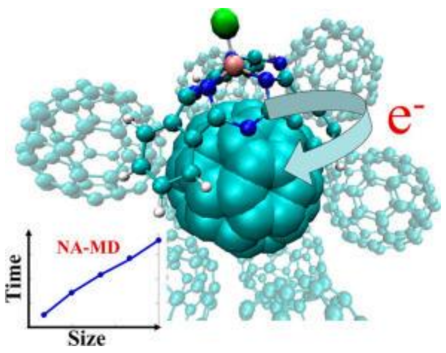
Nijamudheen, A.; AVA *JPCC*, **2017**, *121*, 6520

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}



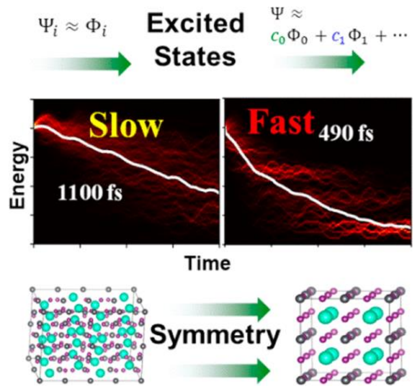
Akimov, A. V. *JCTC* **2016**, *12*, 5719–5736

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

Libra in Materials Research: Periodic Solids

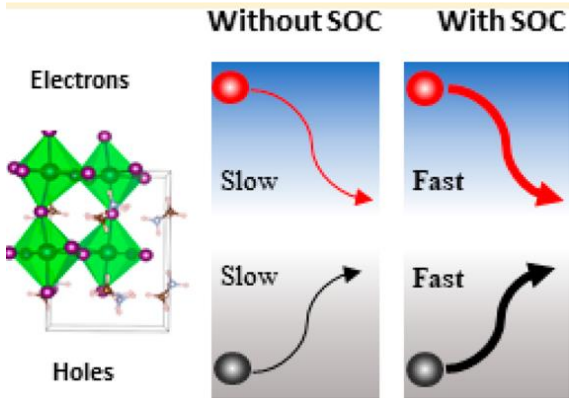
Lead halide perovskites: MB effects

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



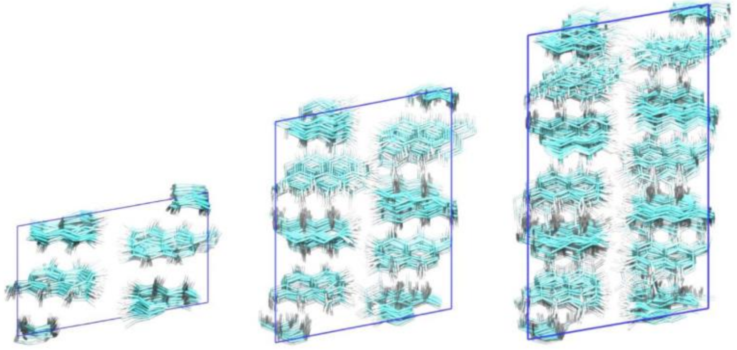
Lead halide perovskites: SOC effects

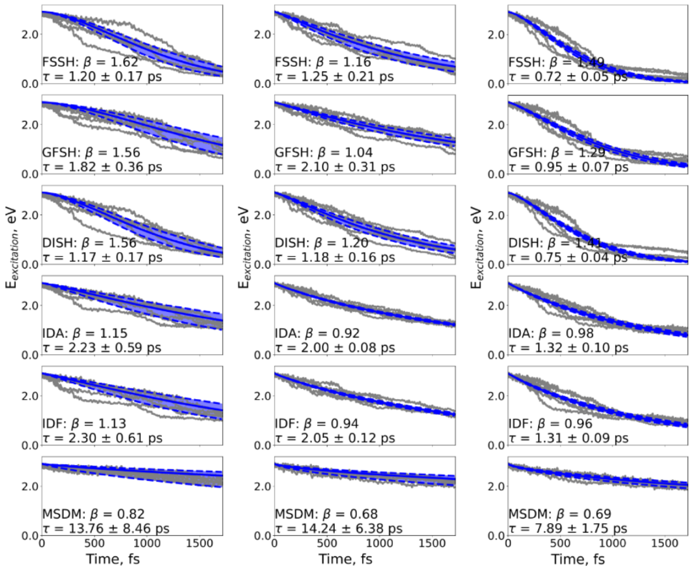
Li, W.; Zhou, L.; Prezhdo, O. V.; Akimov, A. V. *ACS Energy Lett.* **2018**, *3*, 2159–2166.



Crystalline pentacene

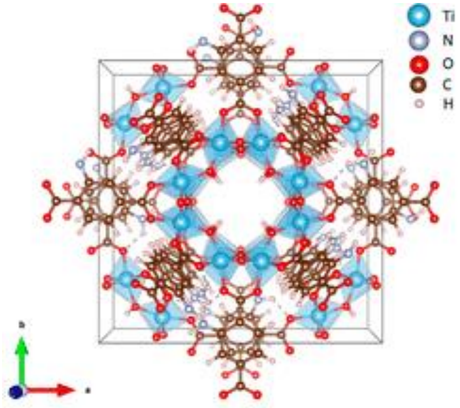
Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *JPCM* **2024**, 36, 385901





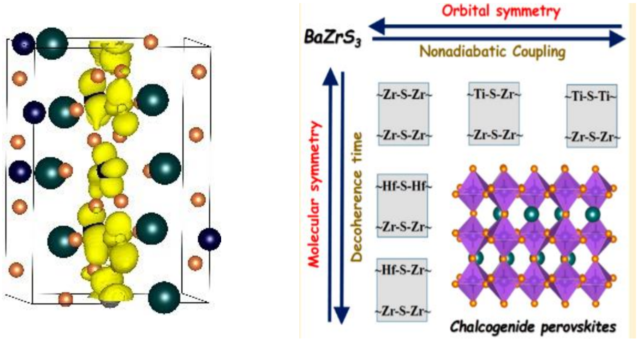
MOFs: With xTB

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

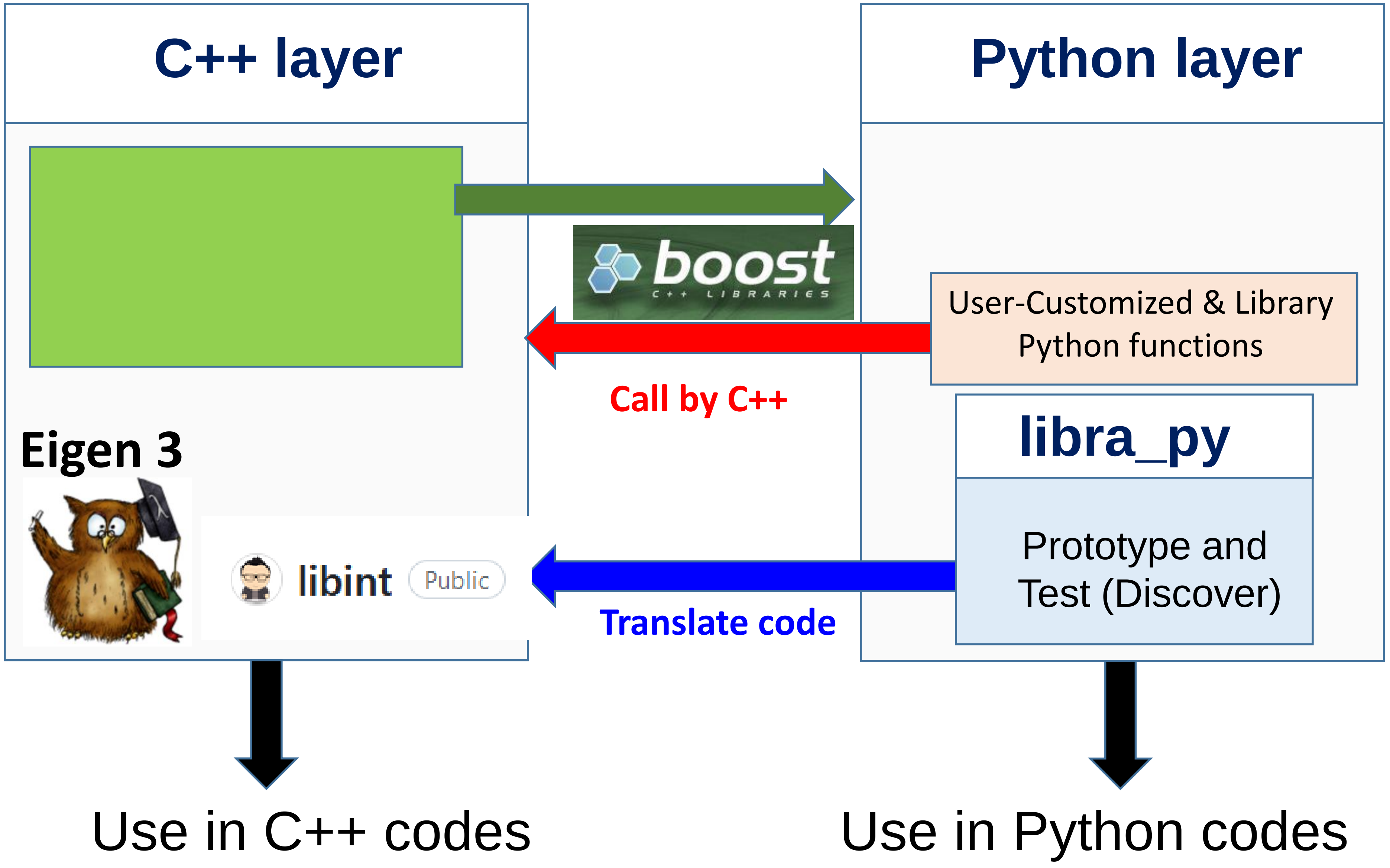


BZTS perovskites

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



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



Modularity: API Diversity and User-friendliness

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- The goal is to suite the needs of the **users of various levels**
- Find a balance between **simplicity** and **flexibility**

Developer/Efficiency

```
double gaussian_overlap( AO* AOa, AO* AOb,int
is_normalize, int is_derivs,  VECTOR& dIdA, VECTOR& dIdB,
vector<double*>& auxd,int n_aux);

double gaussian_overlap( AO* AOa, AO* AOb,int
is_normalize, int is_derivs, VECTOR& dIdA, VECTOR& dIdB );

double gaussian_overlap(AO* AOa, AO* AOb,int
is_normalize);

double gaussian_overlap(AO* AOa, AO* AOb);
```

User/Convenience

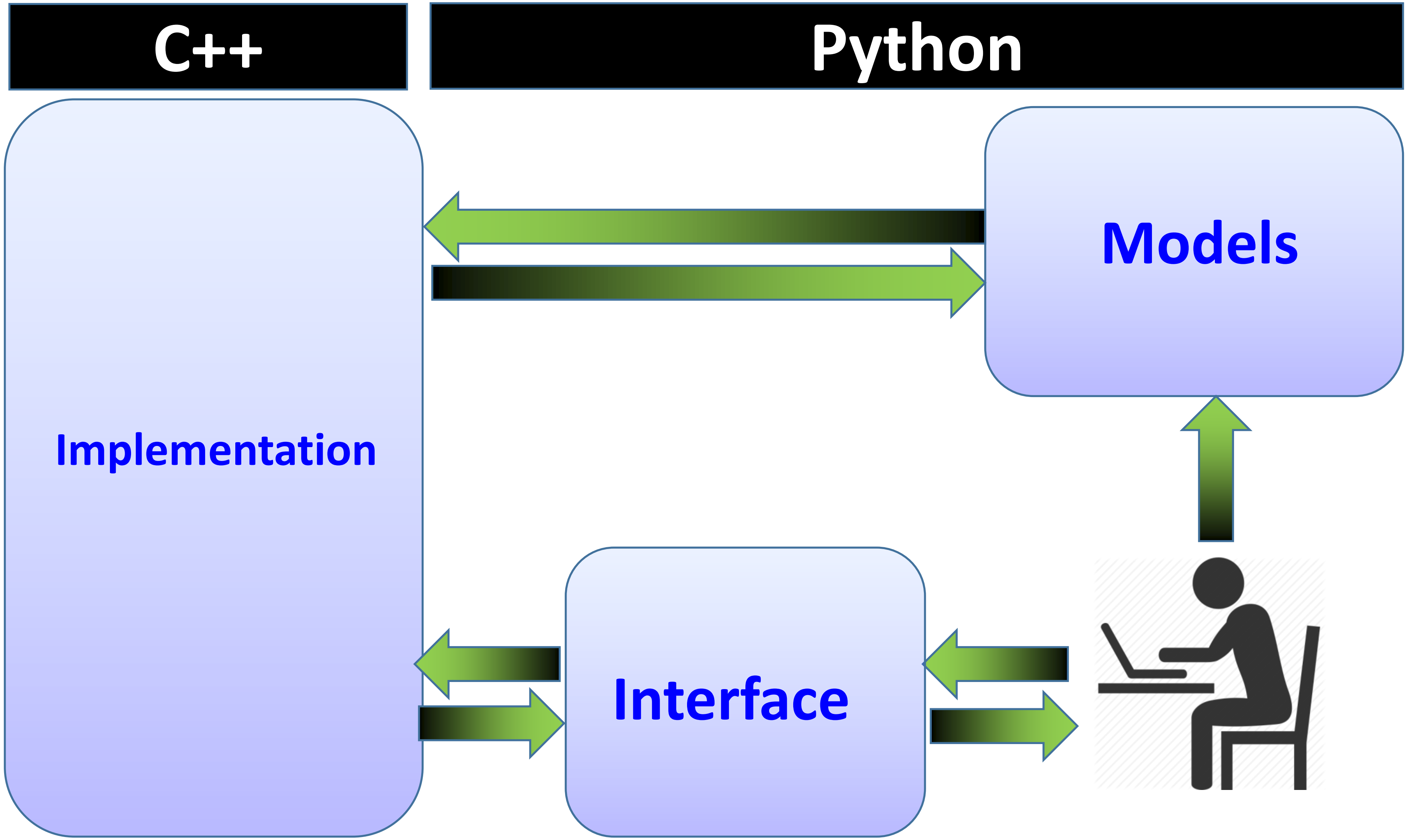
Computing kinetic energy between Gaussians

```
g1 = PrimitiveG()
g2 = PrimitiveG()
g1.init(n1,m1,k1, a1, VECTOR(x1, y1, z1))
g2.init(n2,m2,k2, a2, VECTOR(x2, y2, z1))

kin = kinetic_integral(g1,g2)
```

Benchmarked against PyQuante

```
p1 = PyQuante.PGBF.PGBF(a1,(R1.x,R1.y,R1.z),(n1,m1,k1))
p2 = PyQuante.PGBF.PGBF(a2,(R2.x,R2.y,R2.z),(n2,m2,k2))

val_ref = p1.kinetic(p2)
```

Passing Python functions



How it works with Sampling

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```
vector<MATRIX> metropolis_gau
(Random& rnd, bp::object target_distribution,
MATRIX& dof, bp::object distribution_params,
int sample_size, int start_sampling, double gau_var){
```

```
def test():
    q  = MATRIX(ndof, 1)
    output = metropolis_gau( piab, q, params, ...)
```

User calls the sampling

Output

Metropolis Algorithm

```
double p_old =
bp::extract<double>( target_distribution(s_old,
distribution_params) );

...
}
```

```
def piab(q, params):
```

User defines the probability density

C++

Python

Sampling Example

User defines how to run the MC sampling

```
q = MATRIX(1,1);  q.set(0, 0.5)
params = {"k":1.0, "m":2000.0, "states":[0], "coeffs":[1.0]}
Nsamp = 1000000; Nstart = 50000
sampling = metropolis_gau(rnd, HO_sup, q, params, Nsamp,Nstart, 0.05)
bin(sampling, -1.5, 2.0, 0.01, 0, 0, "_distrib-1.txt")
```

User defines what probability distribution function is to be sampled

```
def HO_sup(q, params):
    k = params["k"];    m = params["m"];
    states = params["states"];    coeffs = params["coeffs"]
    x = q.get(0)
    sz = len(states)
    p = 0.0
    for n in xrange(sz):
        p = p + coeffs[n] * ket_n(x, states[n], k, m)
    p = p * p
    return p
```

The dynamical algorithm is in C++, but…

Don’t need to implement the model in C++

Initial Conditions: Metropolis Sampling

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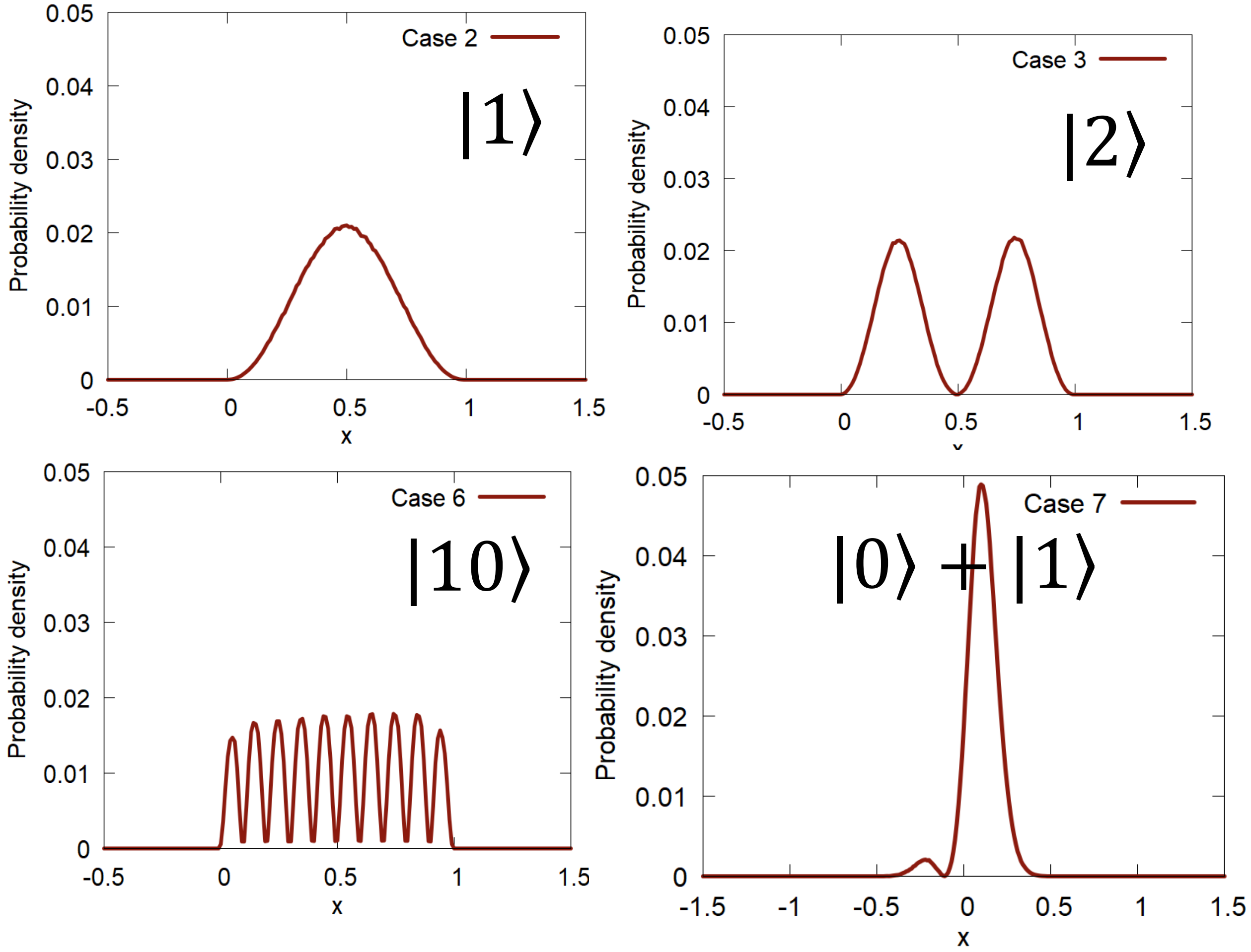
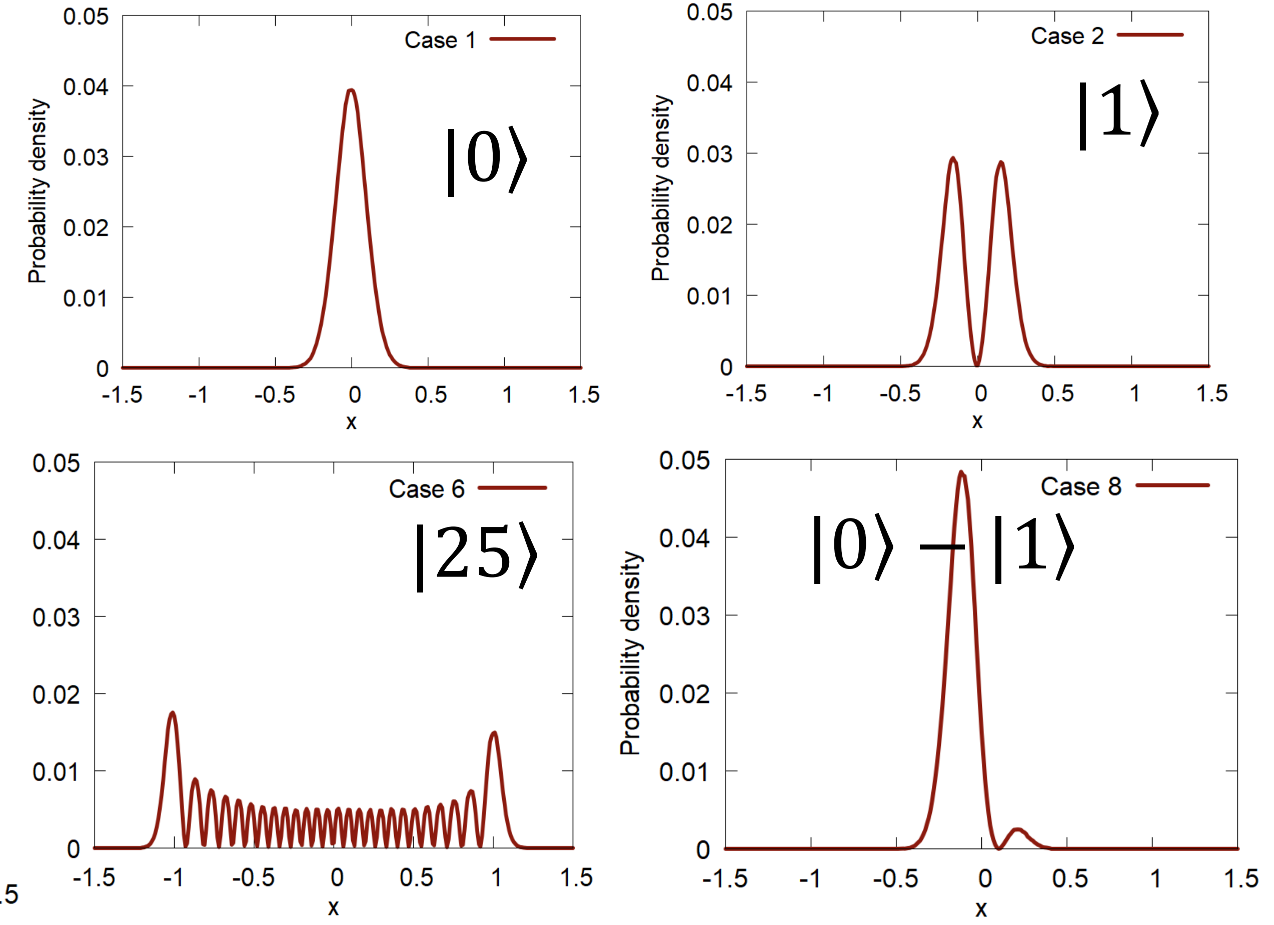
Particle in a box

$$\psi_n(q) \sim sin\left(\frac{\pi n q}{L}\right)$$



Harmonic oscillator

$$\psi_n(q) \sim H_n(q\sqrt{\alpha}) \exp\left(-\frac{\alpha q^2}{2}\right)$$



Community Tool: Code Contributions/Integration

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Sophya Garaschchuk – quantum trajectory guided Gaussians (QTAG)	src/libra_py/dynamics/qtag
Amber Jain – Hierarchical Equations of Motion (HEOM) https://github.com/amber-jain-group-iitb/heom_amber	src/dyn/heom
Xiang Sun – (Non)-equilibrium Fermi Golden Rule (FGR) https://github.com/tsiangsun/FGR	src/fgr
Craig Martens – quantum trajectory surface hopping (QTSH)	in progress
Nandini Ananth – Initial value representation (IVR) https://github.com/AnanthGroup/SC-IVR-Code-Package	src/ivr
Rebecca Gieseking – INDO NACs in MOPAC https://github.com/Devon333	in progress

… and more