

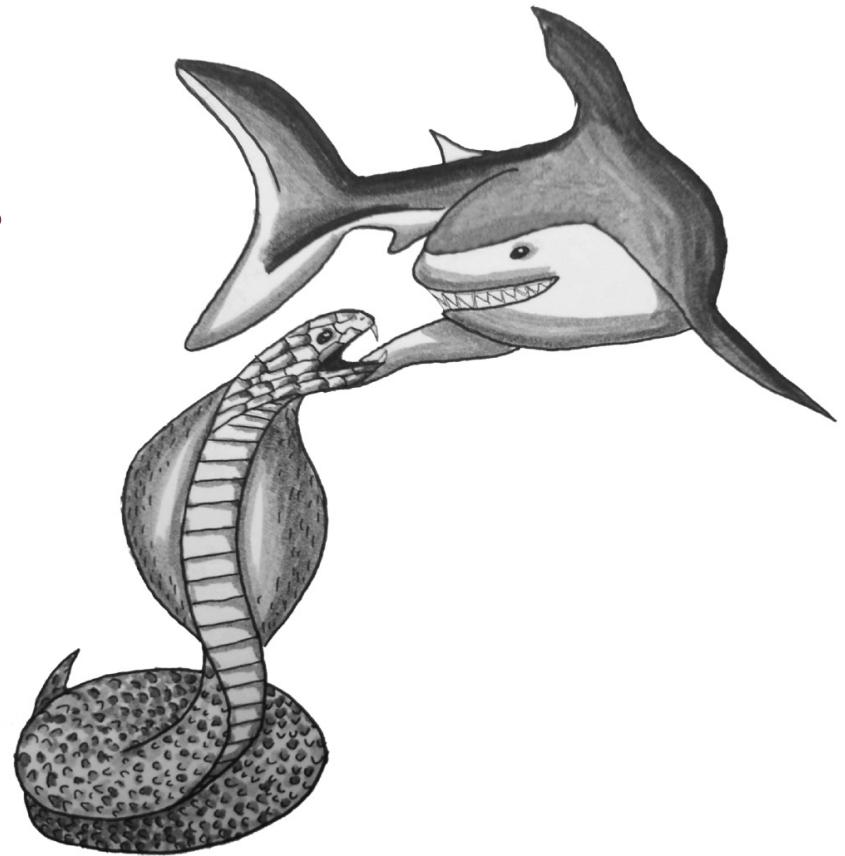


# The SHARC-COBRAMM Interface for QM/MM Trajectory Surface Hopping Simulations with Arbitrary Couplings

Davide Avagliano



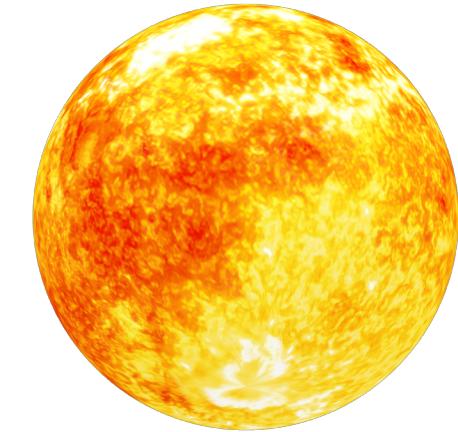
ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA





# Introduction

# Photo-induced processes





# Introduction

# Excited states dynamics

## nonadiabatic dynamics

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

---

quantum dynamics:

nuclear and electronic wave functions

highly expensive

reduced dimensionality – difficult for complex environment

---

mixed quantum-classical methods:

classical nuclei/quantum electrons

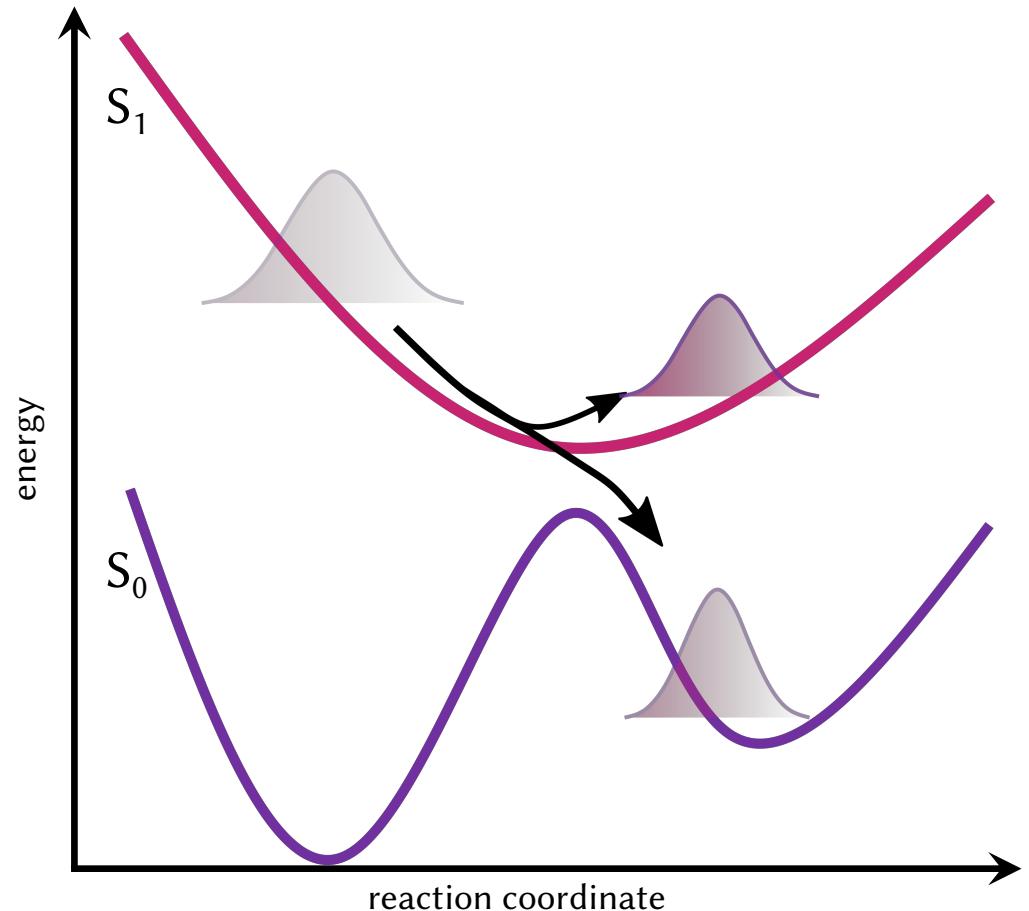
Trajectory Surface Hopping



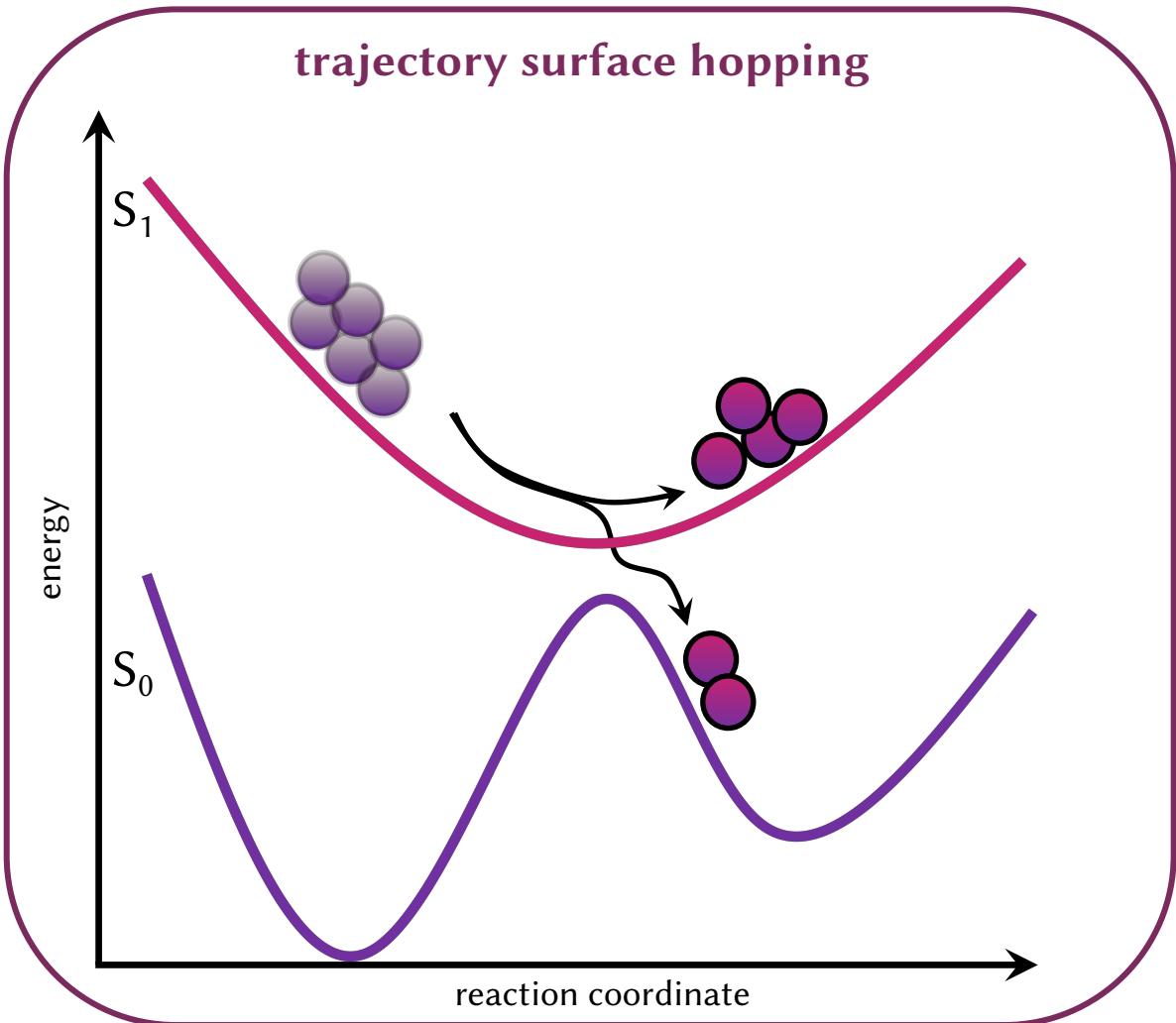
# Introduction

# Excited states dynamics

wave packet dynamics



trajectory surface hopping

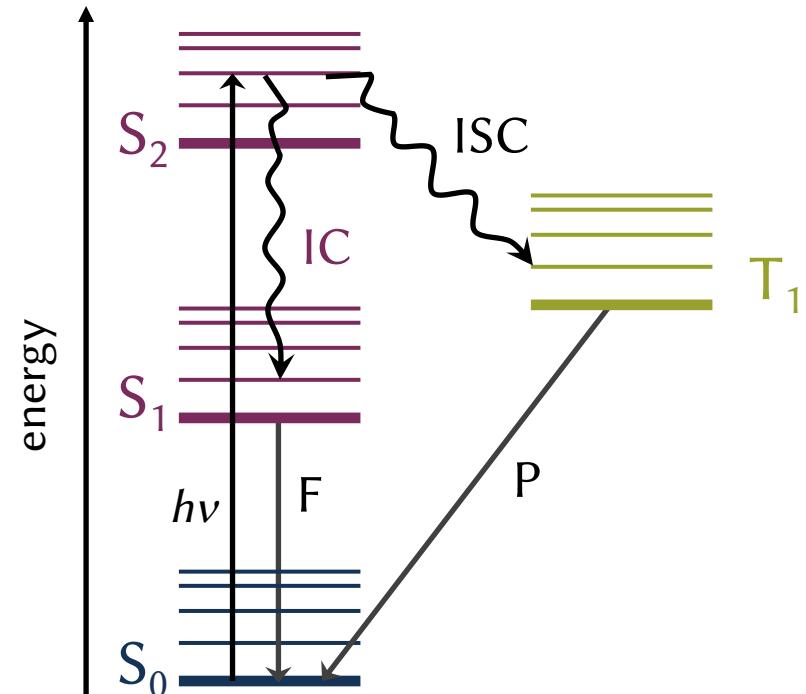




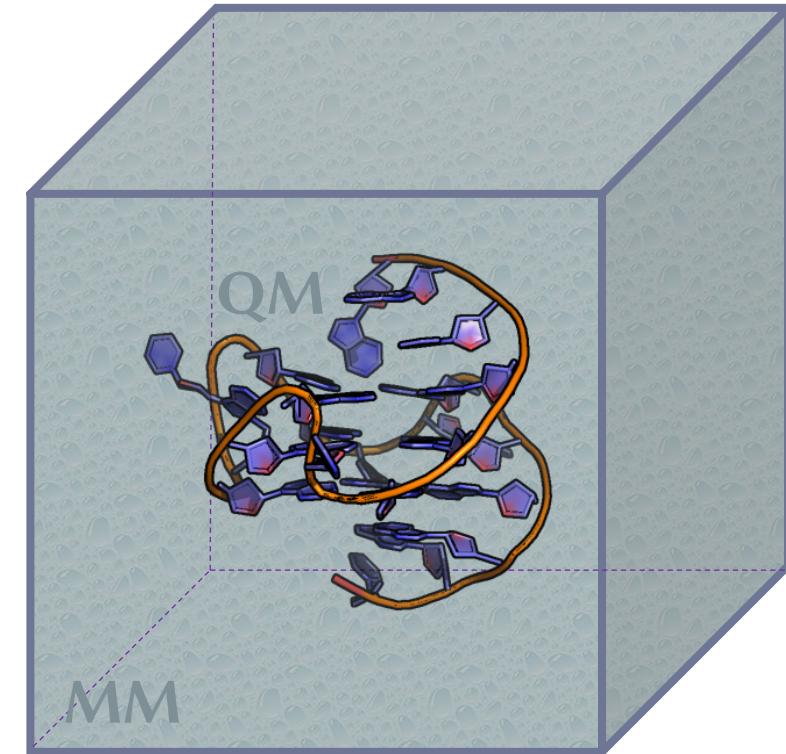
# Introduction

Goal

combine two additional elements



including arbitrary couplings

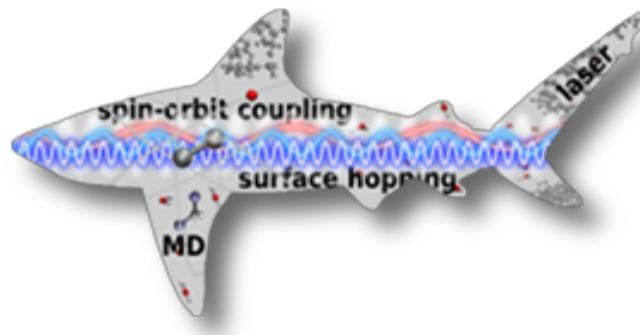


treating complex environments



# Software

SHARC



SHARC2.1

Surface Hopping including ARbitrary Couplings

developed by the González group



universität  
wien



# Software

SHARC

$$\hat{\mathcal{H}}_{full} = \hat{\mathcal{H}}_{MCH} + \hat{\mathcal{H}}_{add}$$

$\hat{\mathcal{H}}_{MCH}$  molecular coulomb Hamiltonian      kinetic, Coulombic

$\hat{\mathcal{H}}_{add}$  additional Hamiltonian      relativistic effects

What changes?

- energy
- number and position of hops
- number of states

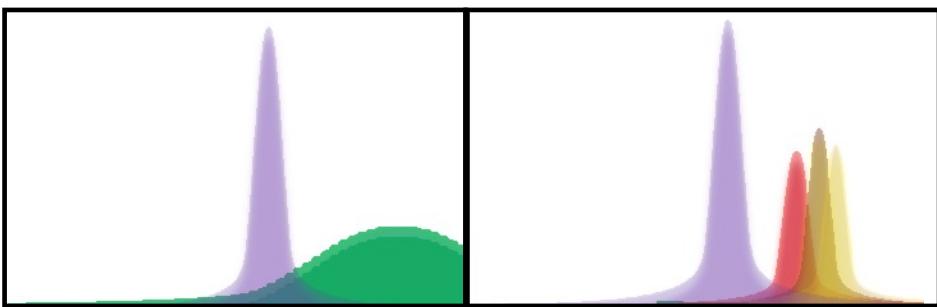
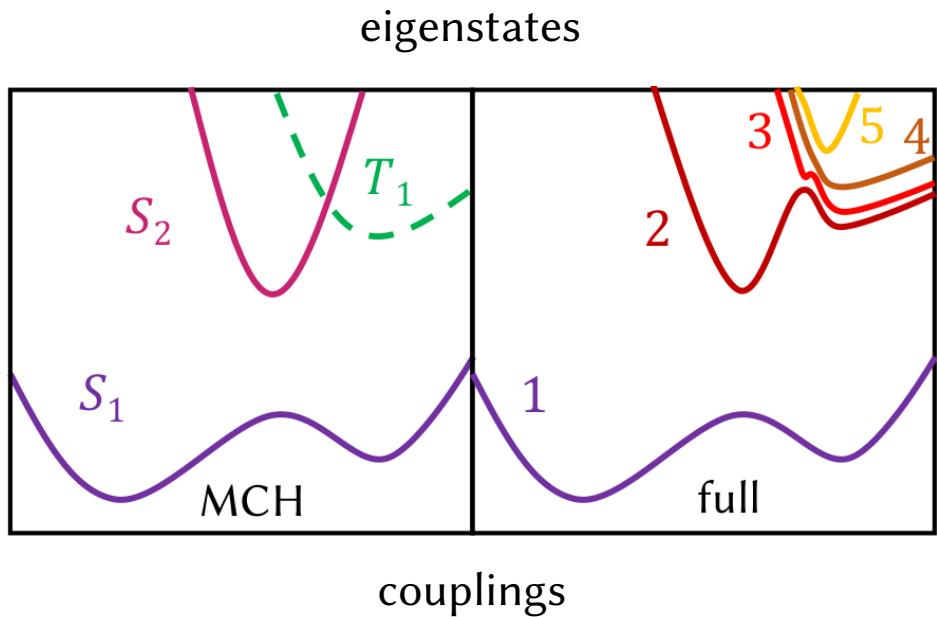
Advantages of full:

- localized couplings
- less hops
- more accurate energies

Disadvantages:

- QM programs give MCH

modification to the algorithm to work in full Hamiltonian

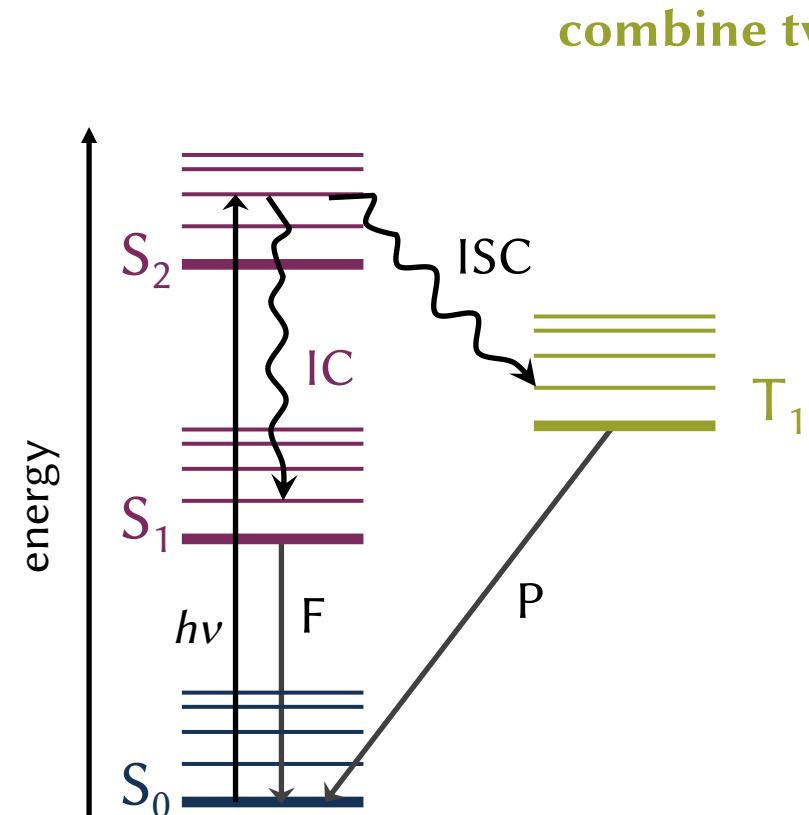


S. Mai, P. Marquetand, L. González, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 8, e1370, (2018)

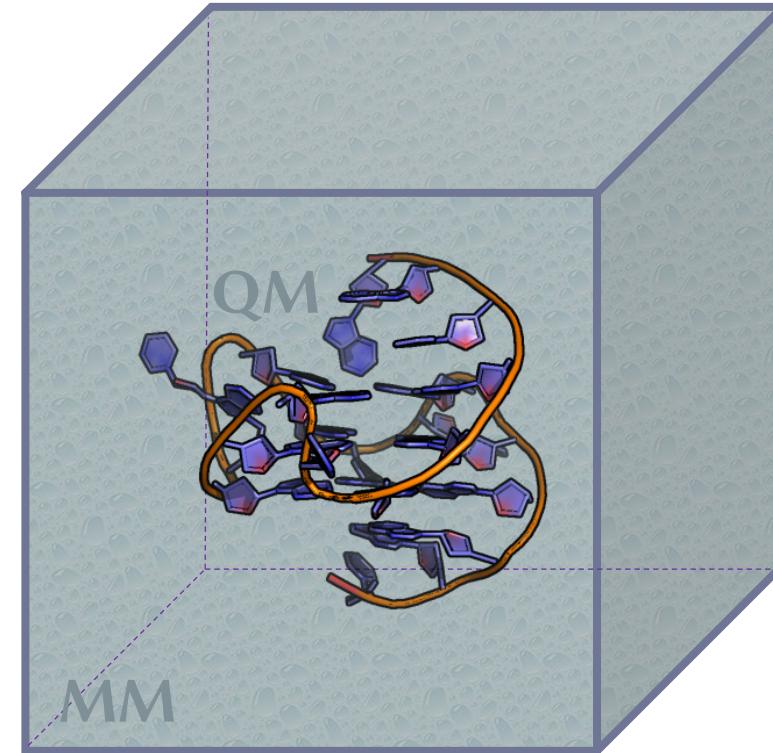


# Software

COBRAMM



combine two additional elements



including arbitrary couplings

treating complex environments



# Software

COBRAMM

COBRAMM 2.3

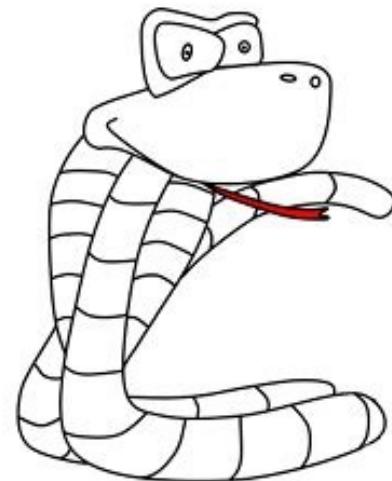
Cobramm is Optimize in Bologna to  
Run Ab-initio and Molecular Mechanics calculations

<https://site.unibo.it/cobramm/en>

developed by Garavelli group



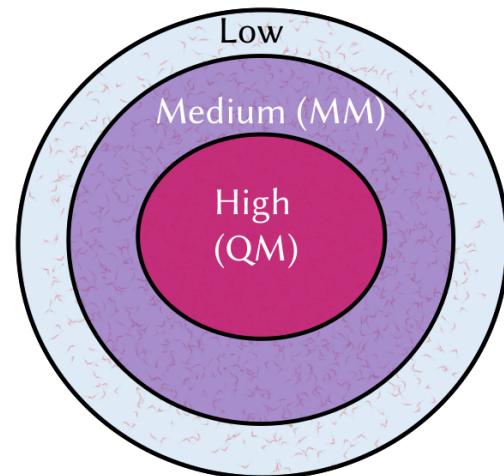
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# Software

# COBRAMM



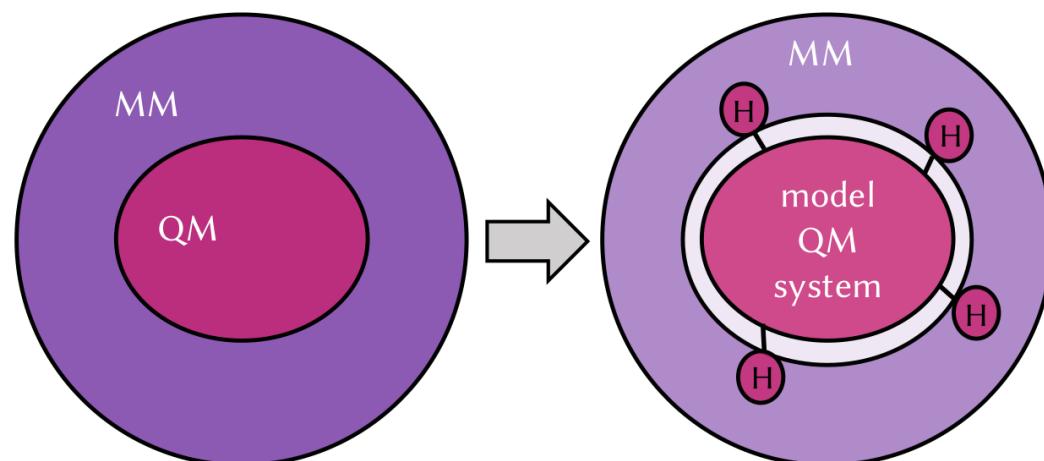
divide the system in regions treated at different levels of theory

e.g. quantum mechanically (QM) and classically (MM)

subtractive schemes:

$$E_{QM/MM} = E_{QM} + E_{MM} - E_{MM(QM)}$$

allows generalization to more layers (ONIOM-like)



QM/MM couplings included  
electrostatic embedding

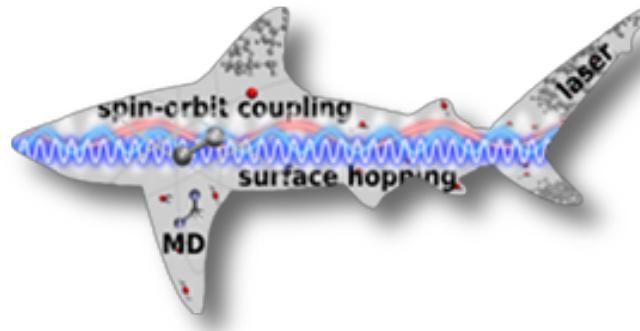
MM point charges incorporated in the Hamiltonian  
QM  $e^-$  density polarized by the charges  
state specific MM gradient

link atom approach

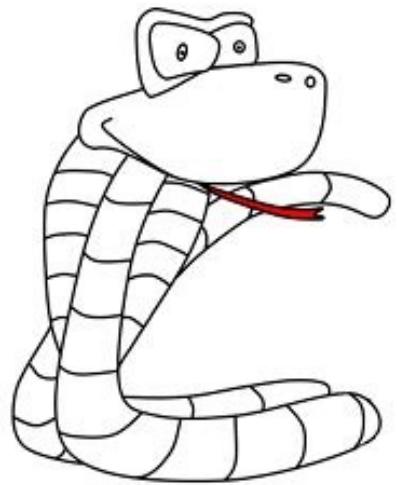
treating covalent bonds



# Software



# The interface





## Software



## The interface



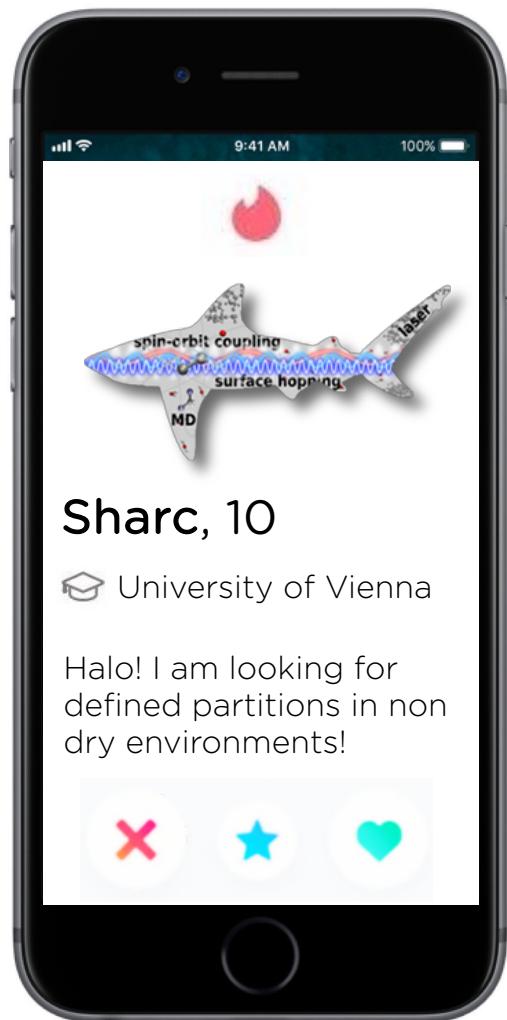
# Software

# The interface



# Software

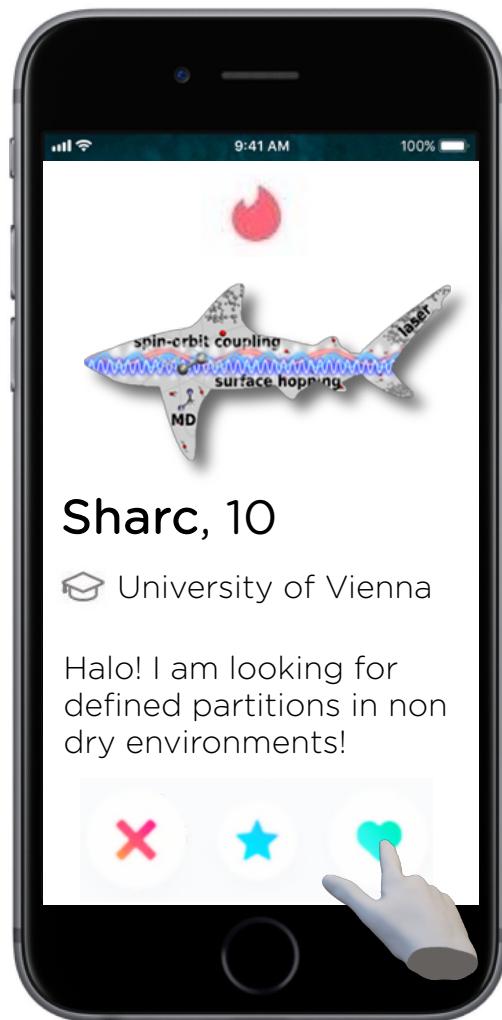
# The interface





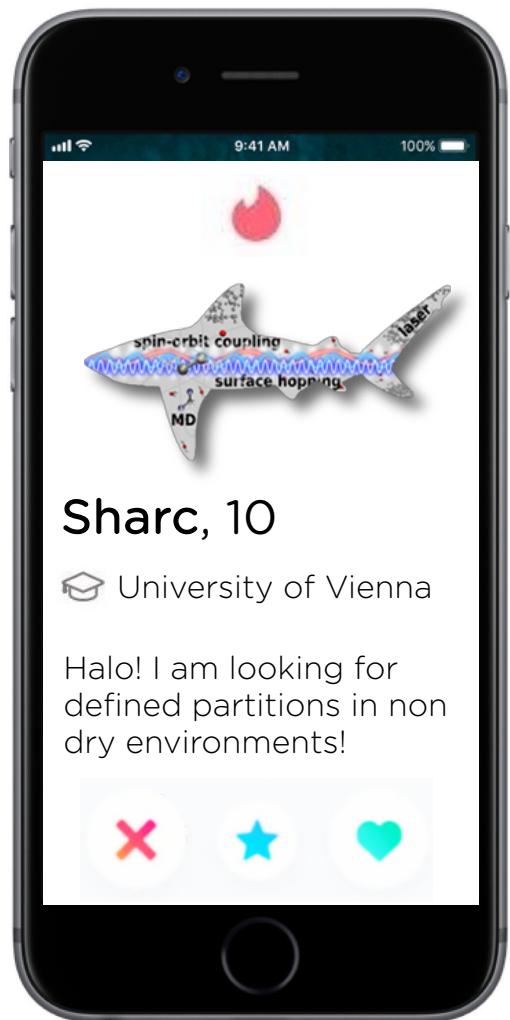
# Software

# The interface





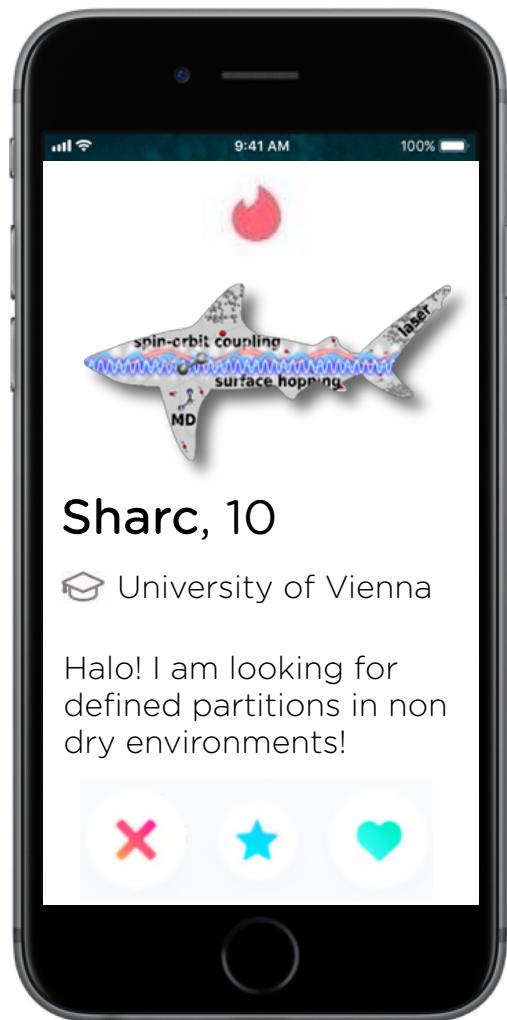
# Software



# The interface



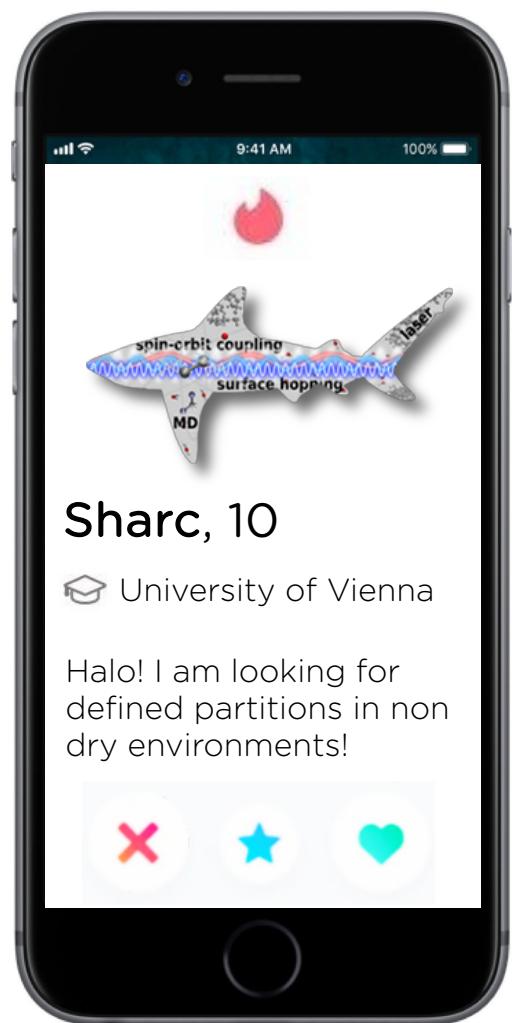
# Software



# The interface



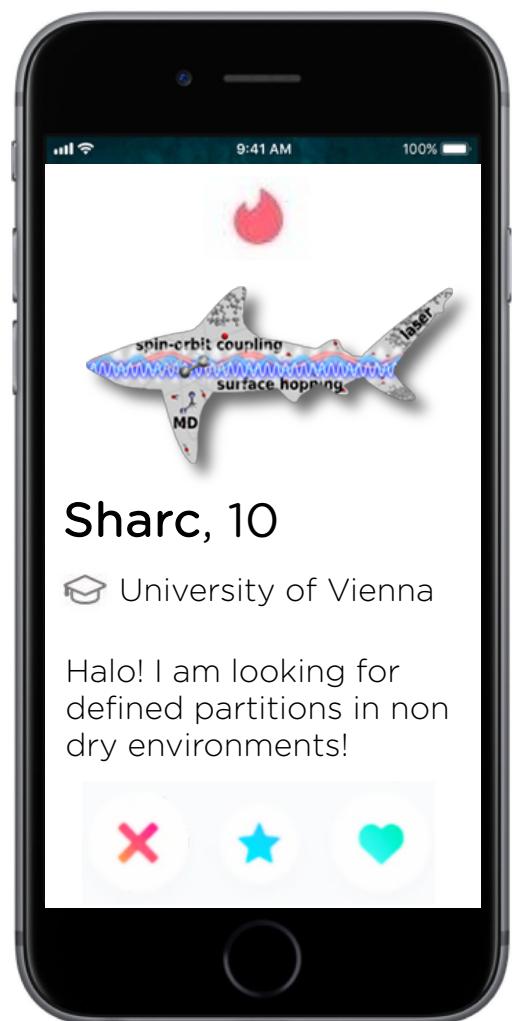
## Software



## The interface



## Software



**Sharc, 10**

University of Vienna

Halo! I am looking for defined partitions in non dry environments!



**Cobramm, 13**

University of Bologna

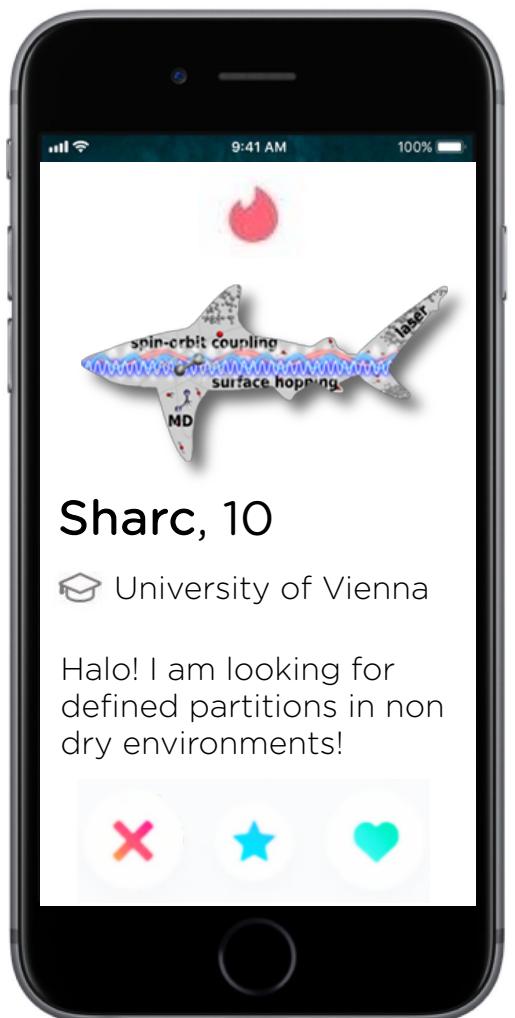
Ciao! I am looking for arbitrary couplings!



## The interface



## Software



**Sharc, 10**

University of Vienna

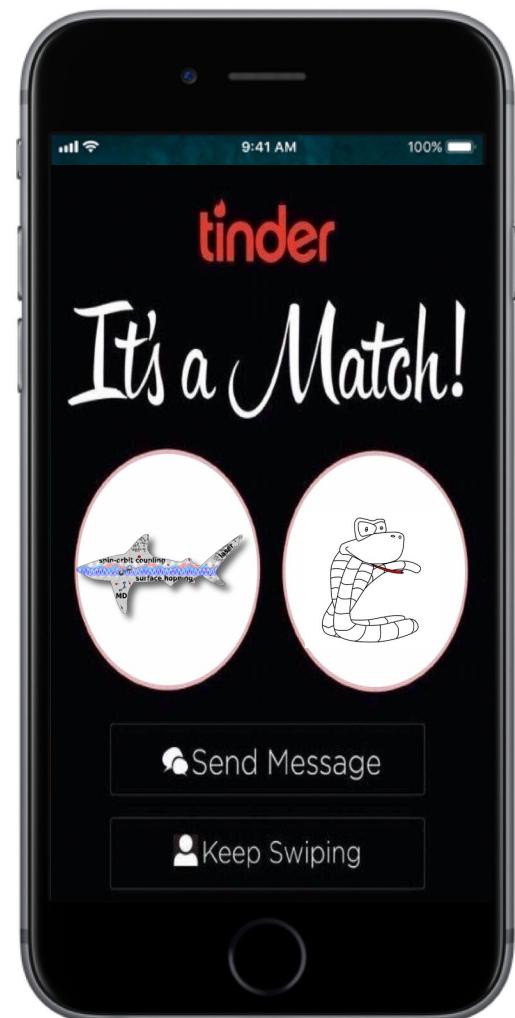
Halo! I am looking for defined partitions in non dry environments!



**Cobramm, 13**

University of Bologna

Ciao! I am looking for arbitrary couplings!



Send Message

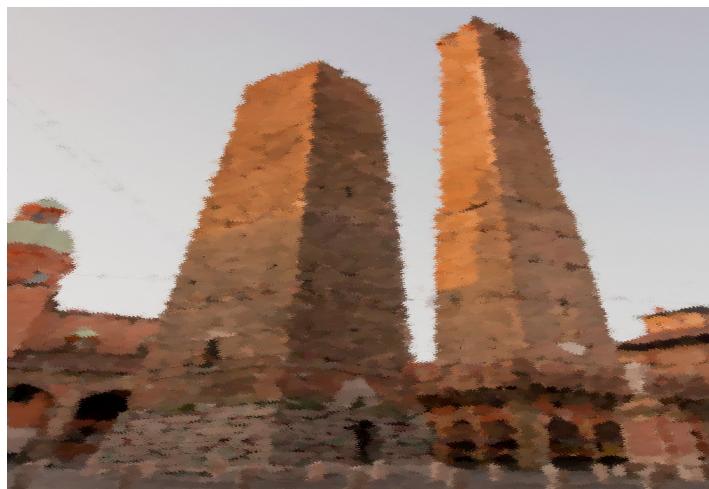
Keep Swiping

## The interface





## Software



## The interface





# Methodology

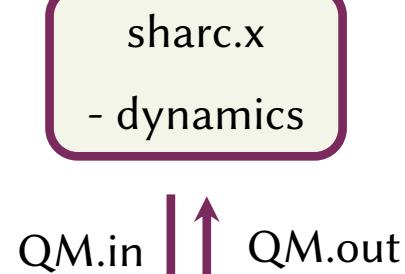
# Development



# Methodology

# Development

## SHARC

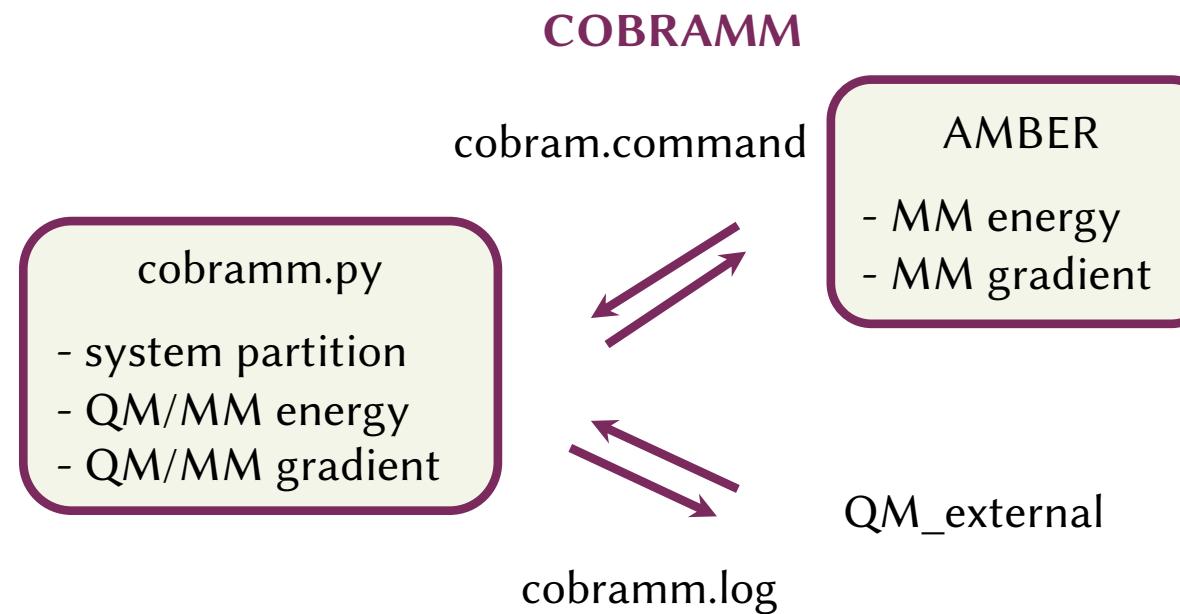
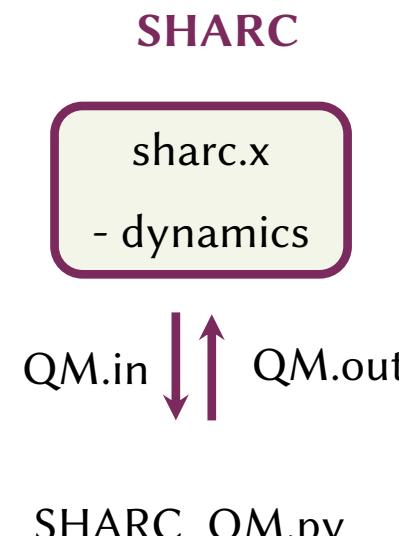


SHARC\_QM.py



# Methodology

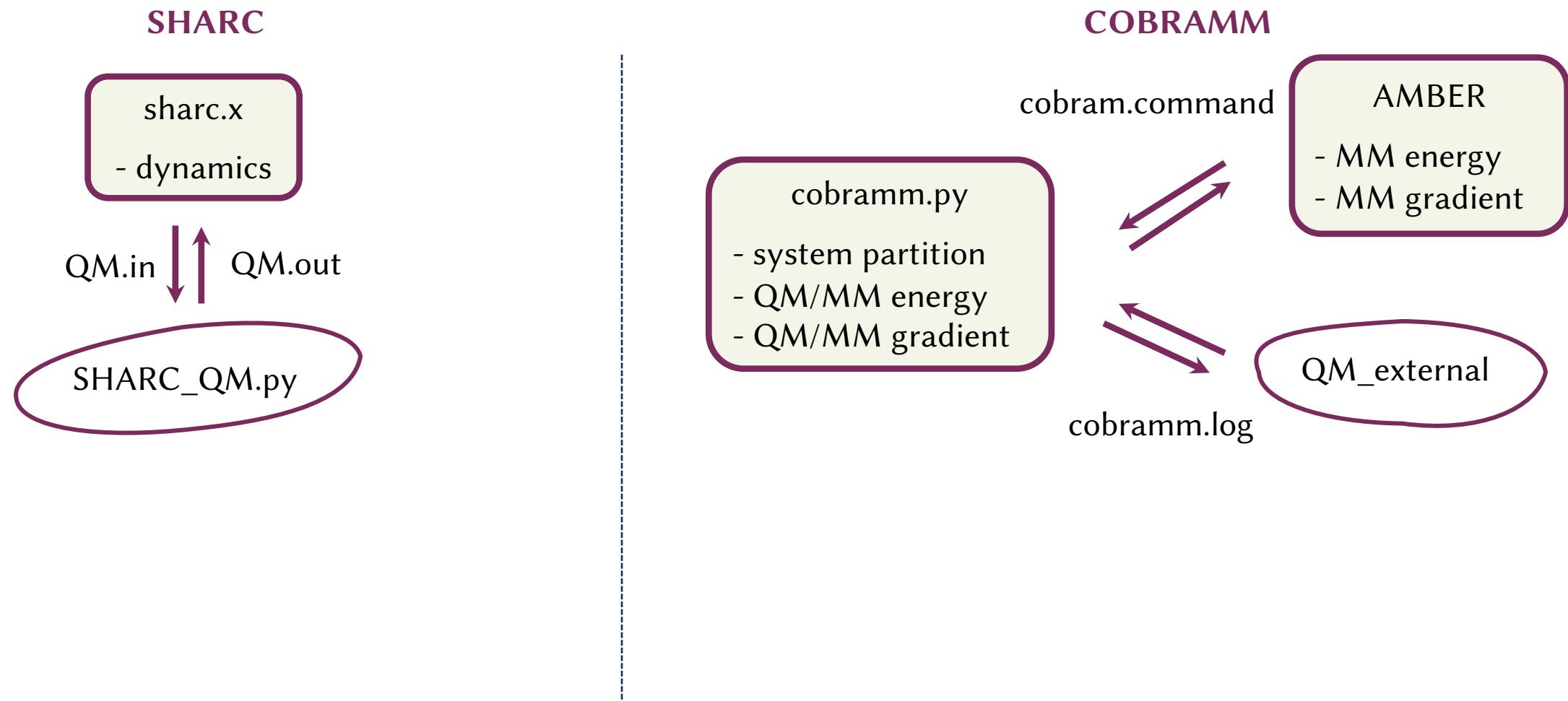
# Development





# Methodology

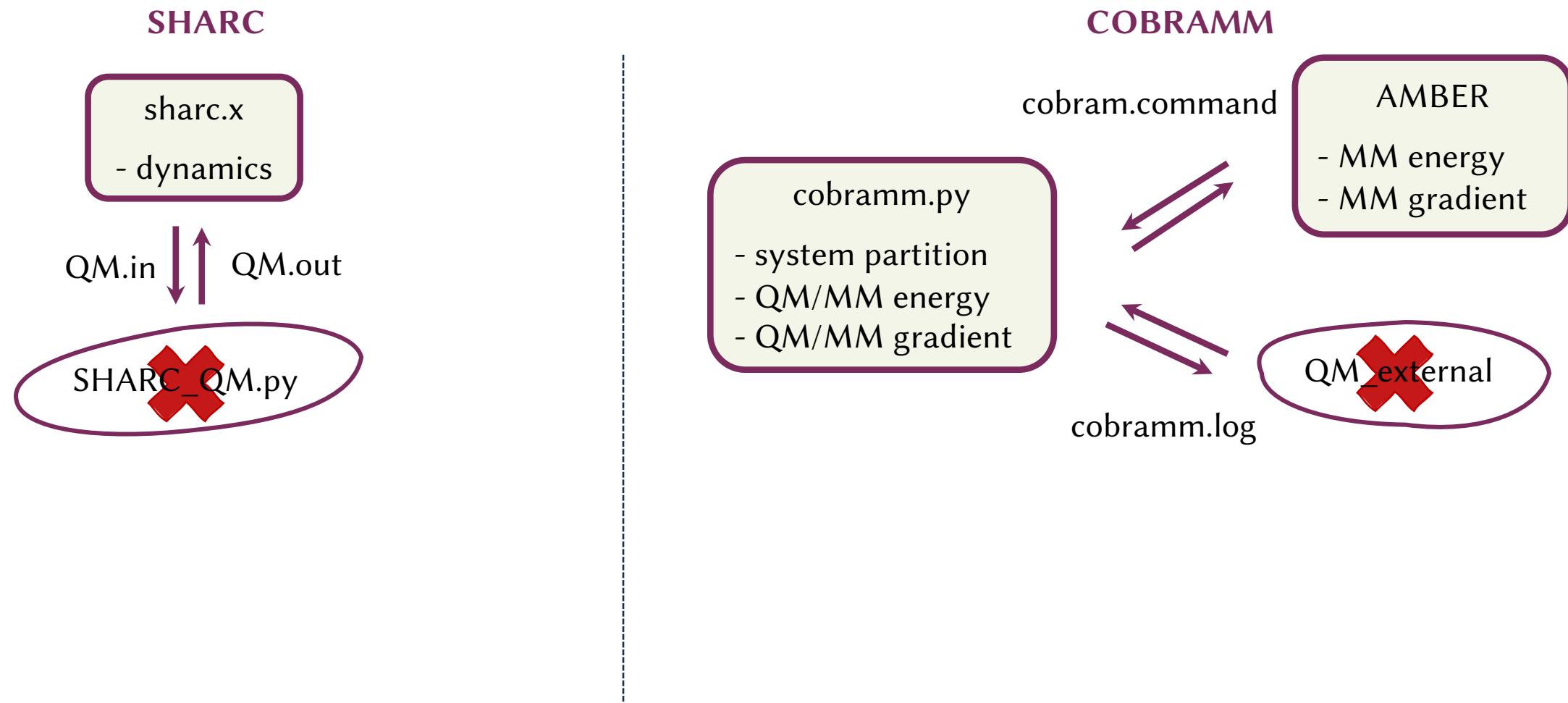
# Development





# Methodology

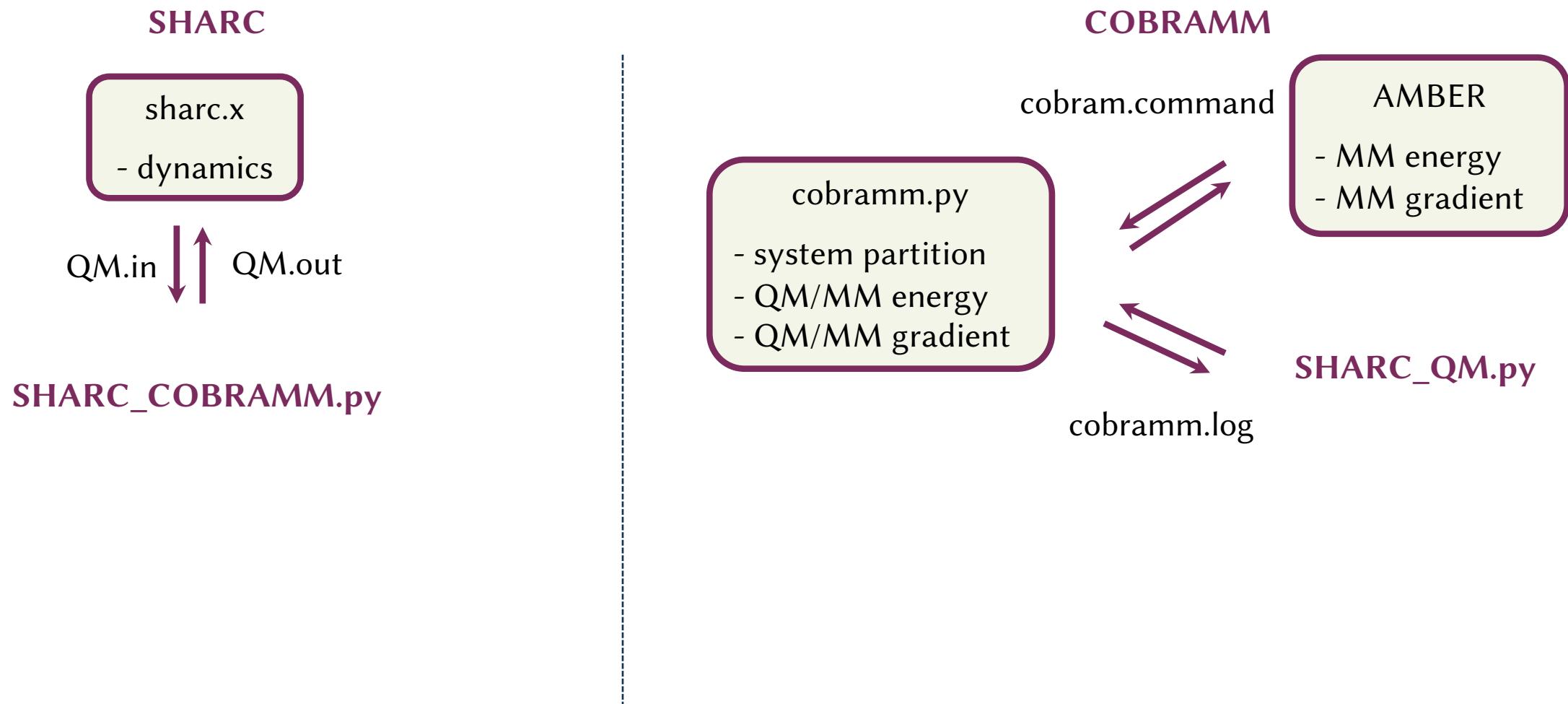
# Development





## Methodology

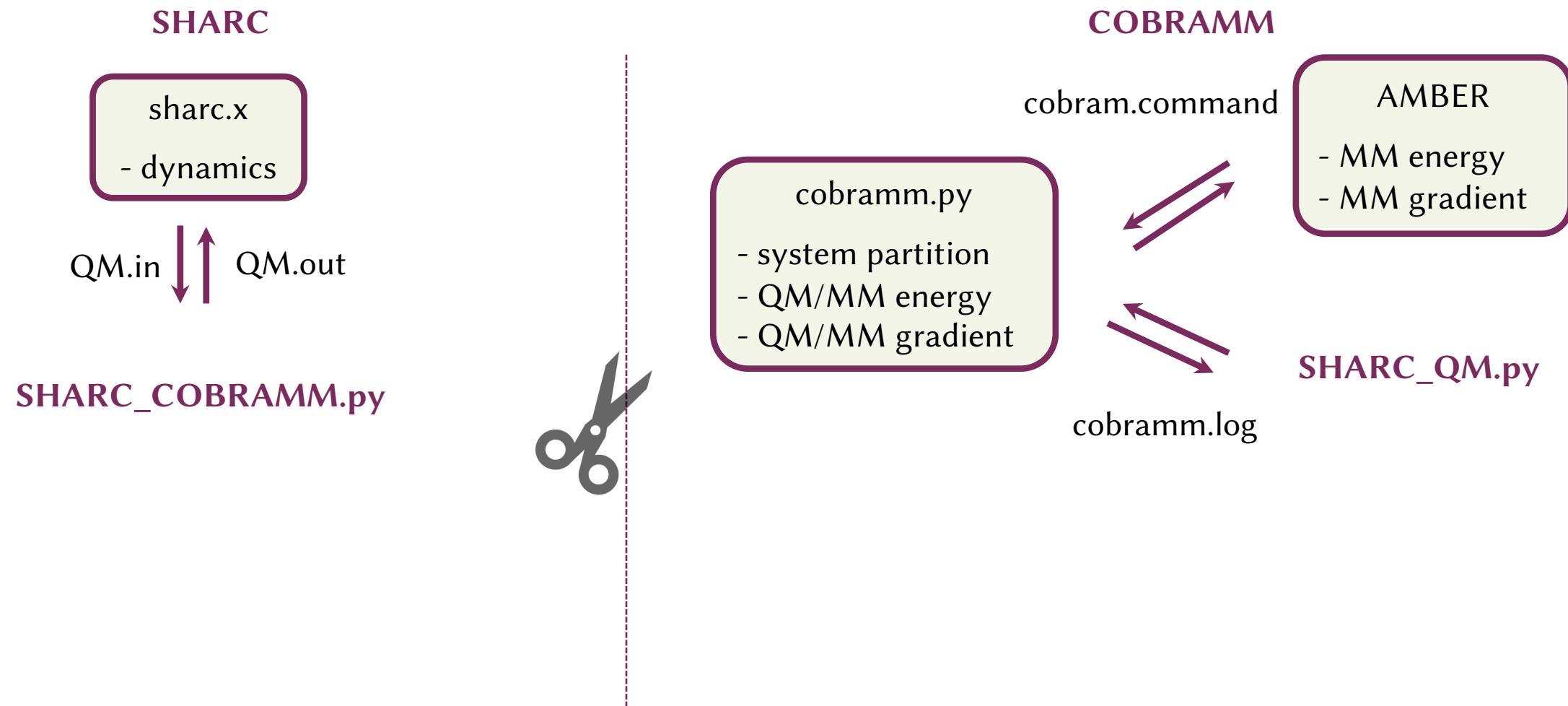
# Development





# Methodology

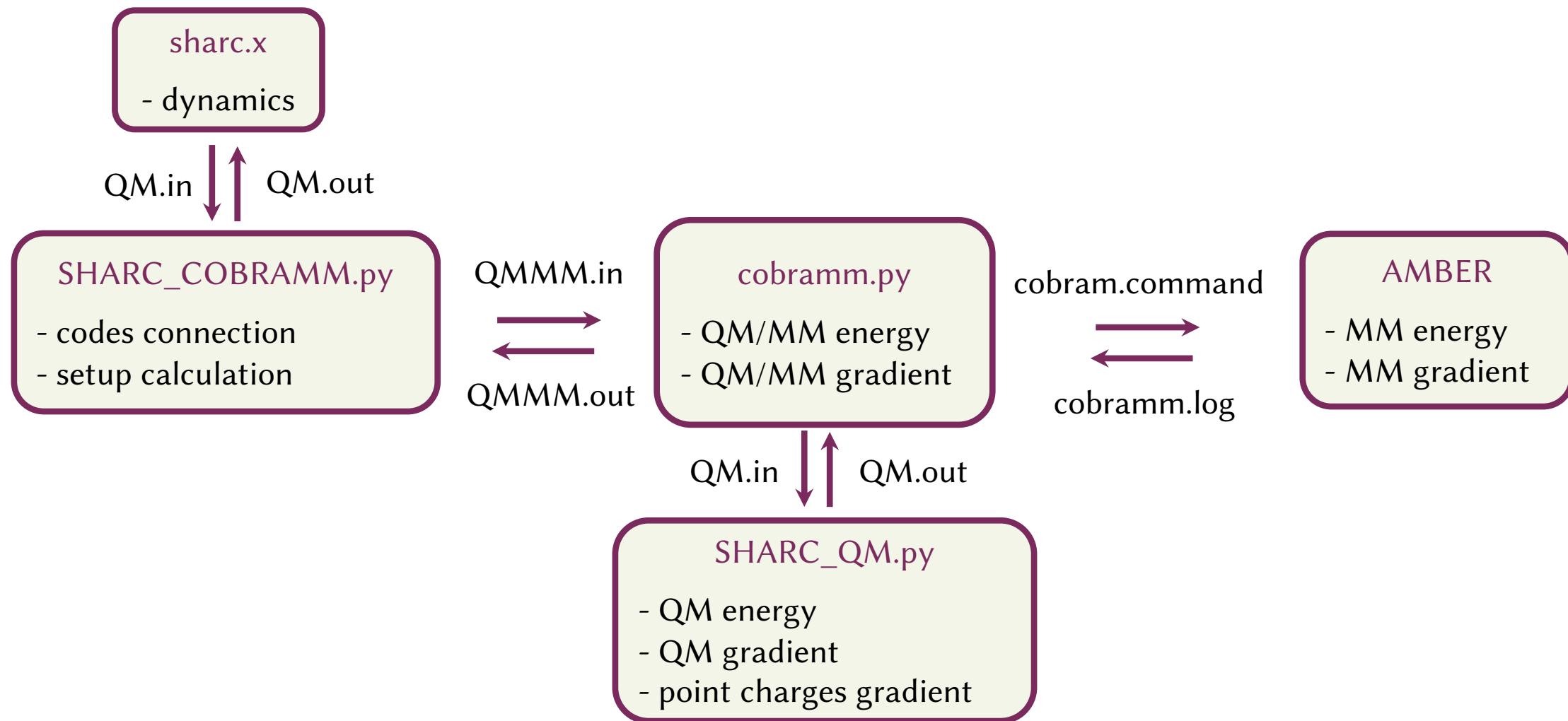
# Development





# Methodology

# Workflow



# Methodology

# Workflow

## SHARC\_COBRAMM.py

- codes connection
- setup calculation

## sharcCalculator.py

- call QM calculation
- return QM energy and gradient

**MOLCAS (CASSCF)**  
**TURBOMOLE (ADC(2))**  
**ORCA (TD-DFT)**

QM energy:

MM energy:

QM/MM energy:

QM gradient:

MM gradient:

MM gradient due to QM:

QM/MM gradient:

Nuclear propagation:

modification in SHARC:

modification to specific SHARC\_QM.py interfaces:

- include the point charges in the calculation
- give back the state-specific MM gradient contribution due to QM

## WHO DOES WHAT:

QM software via SHARC\_QM.py via sharcQMcalculator.py  
AMBER via amberCalculator.py  
cobramm.py

QM software via SHARC\_QM.py via sharcQMcalculator.py  
AMBER via amberCalculator.py  
QM software via SHARC\_QM.py via sharcQMcalculator.py  
cobramm.py

sharc.x

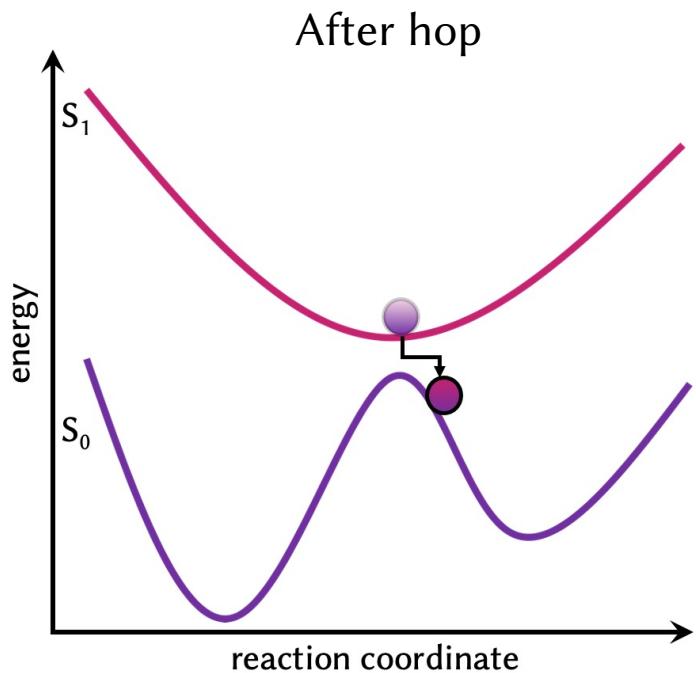
modification in COBRAMM:

new external calculator

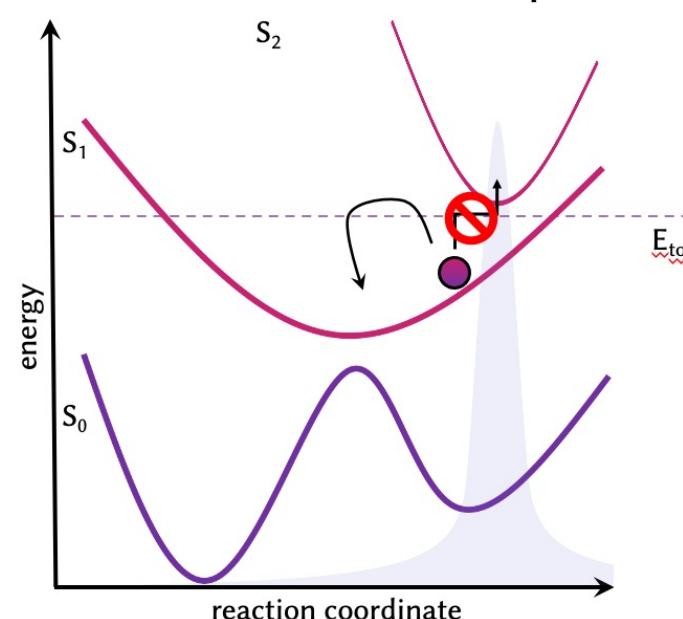
# Methodology

# Atom masking

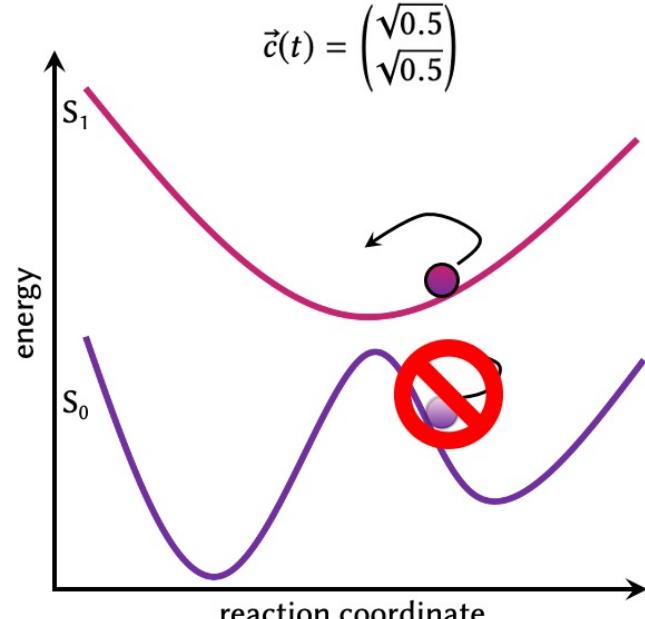
Velocity rescaling (if through velocity vector)



After frustrated hop



KE difference to dump electronic coefficients

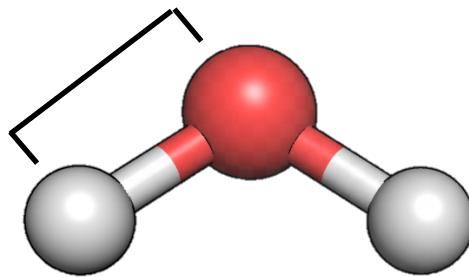


procedure extended to all the atoms by default

**MM atoms need to be excluded  
inclusion of an atom masking**



# Methodology



SO<sub>2</sub> water  
B3LYP/def2-SVP//TIP3P  
SHARC/COBRAMM//ORCA/AMBER

constraints in molecular dynamics:

accelerate calculations

increase the time step

prevent wrong description (like TIP3P water)

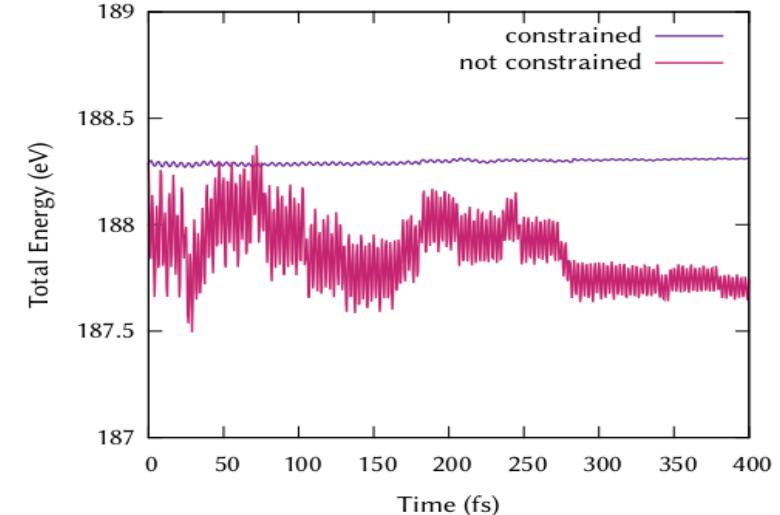
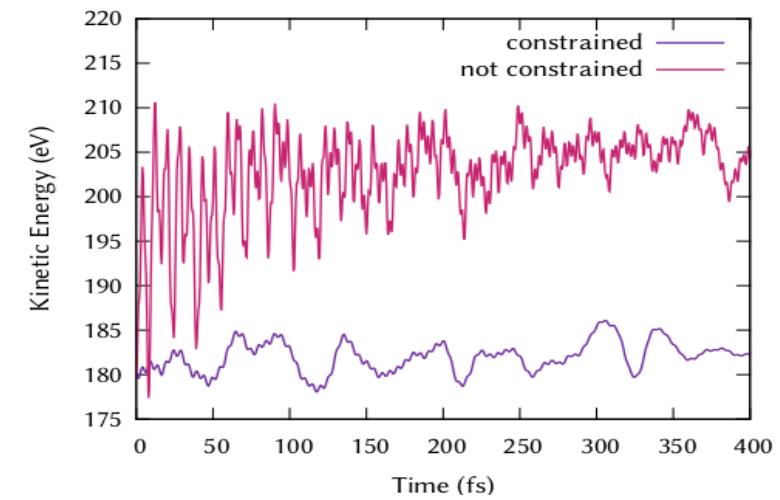
RATTLE algorithm for Velocity Verlet

first corrects the positions  
then corrects the velocities

constrain O-H bonds

better to use flexible FF

RATTLE





# Application

Acrolein



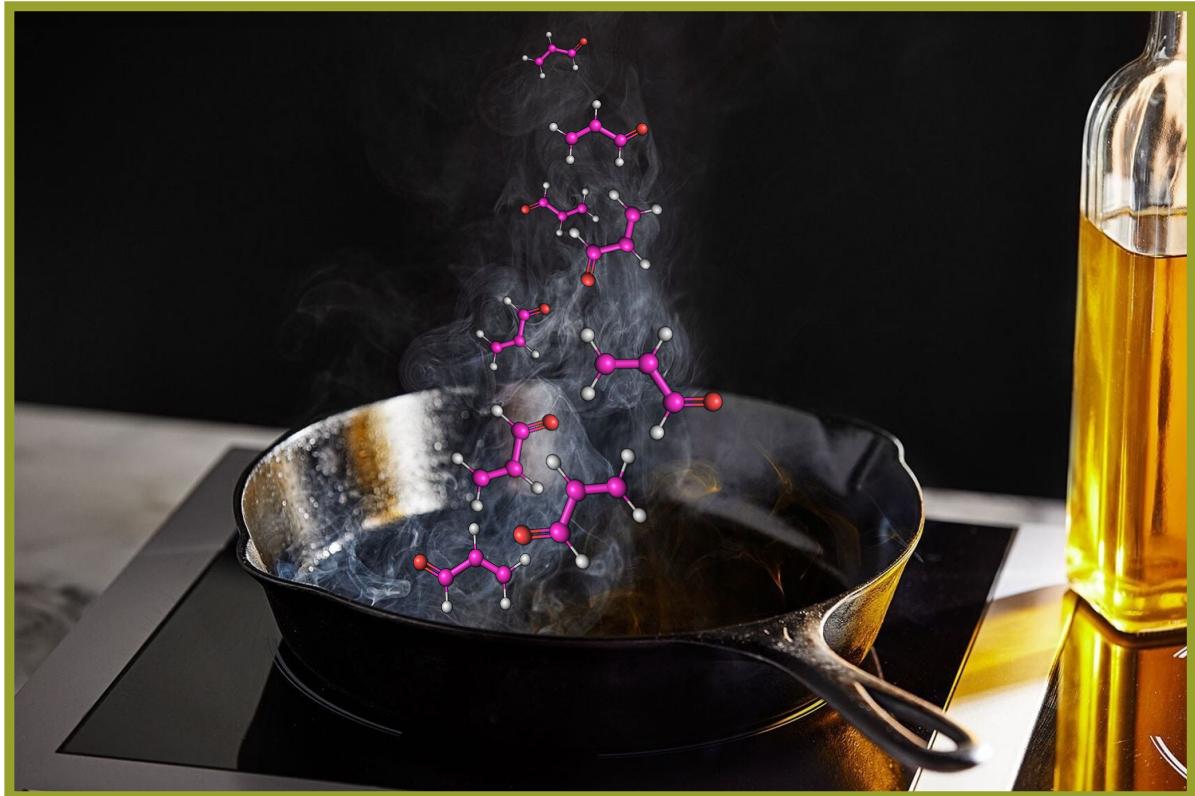
fried food is the best in the world





# Application

Acrolein



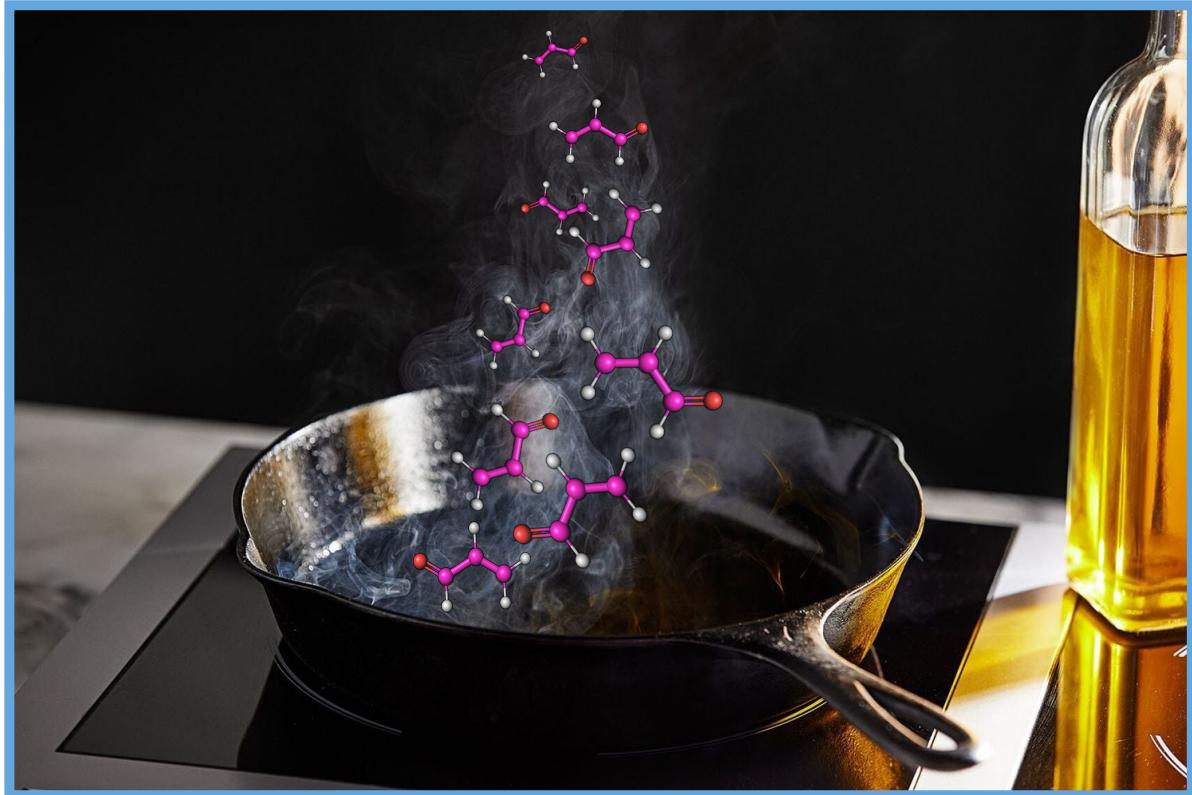
be careful: smoking point!

smoke point:	butter (Vienna)	130-170°
	animal fat (Bologna)	180-210°
	oil (compromise)	165-190°



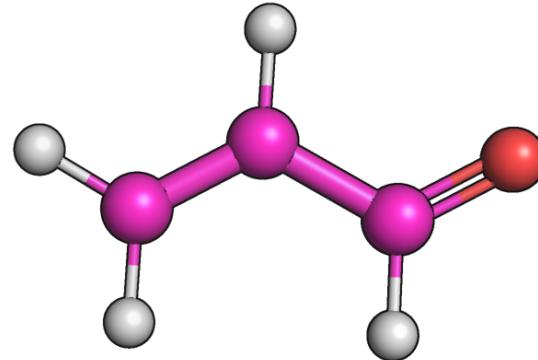
# Application

## Acrolein



be careful: smoking point!

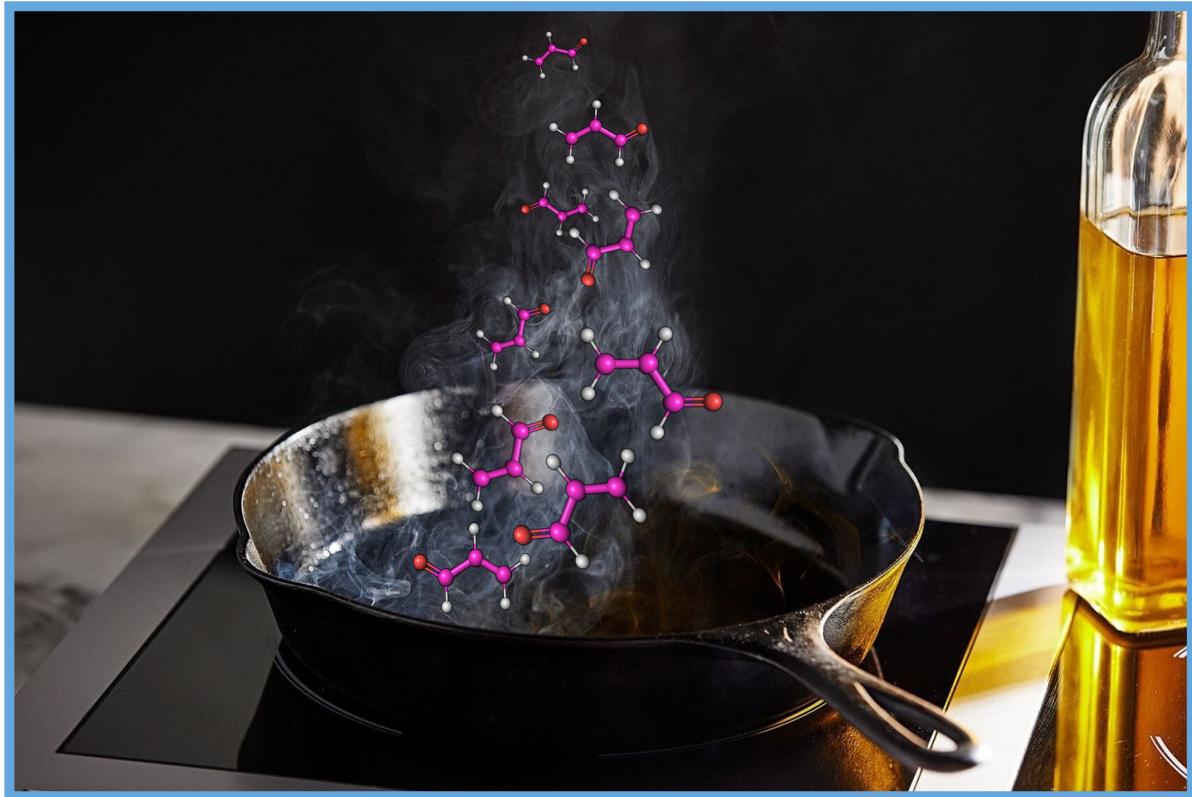
smoke point:	butter (Vienna)	130-170°
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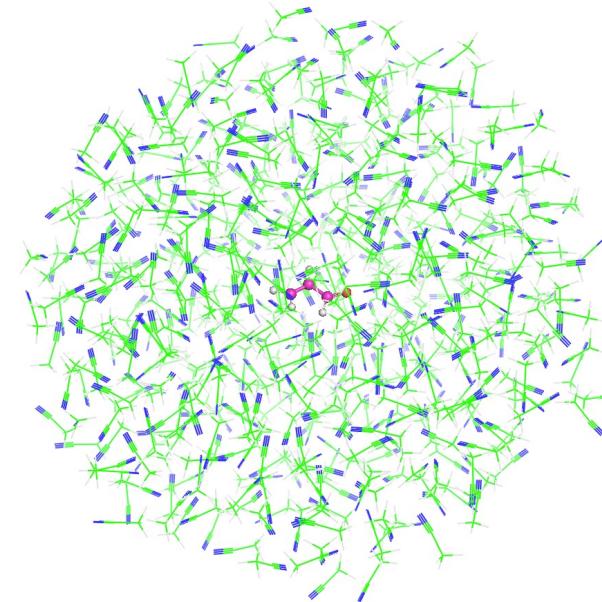
# Application

# Acrolein



be careful: smoking point!

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# Application

# Acrolein

*“193 nm photodynamics of acrolein in acetonitrile: The dominant reaction channel was found to be 1,3-hydrogen migration in the  $T_1$  state (78%), accompanied by some  $\alpha$  C–H cleavage in the  $S_1$  state (12%)”*

Wu et al. J. Chem. Phys. 132, 124510, 2010



# Application

Acrolein

CASSCF (8,7)/6-31G MOLPRO

G. Cui and W. Thiel J. Chem. Phys. 141, 124101 (2014)

*“193 nm photodynamics of acrolein in acetonitrile: The dominant reaction channel was found to be 1,3-hydrogen migration in the  $T_1$  state (78%), accompanied by some  $\alpha$  C–H cleavage in the  $S_1$  state (12%)”*

Wu et al. J. Chem. Phys. 132, 124510, 2010



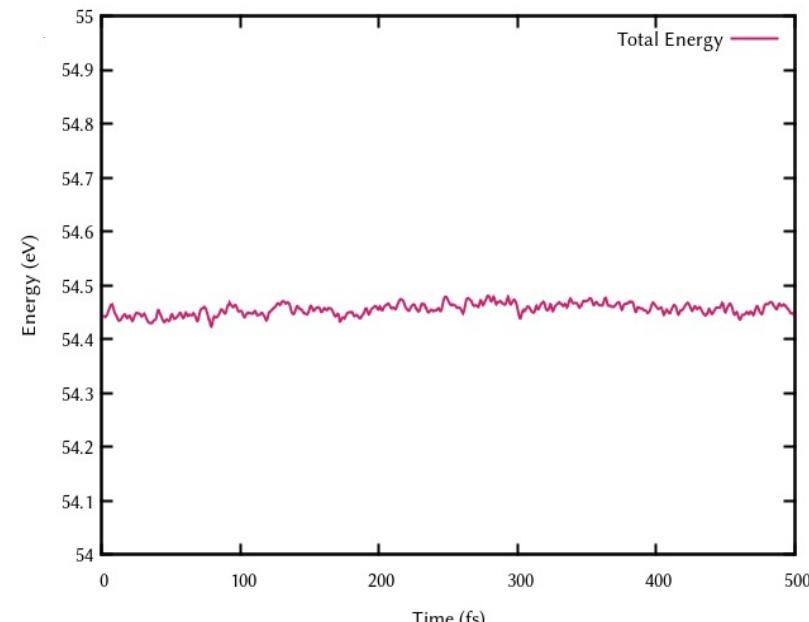
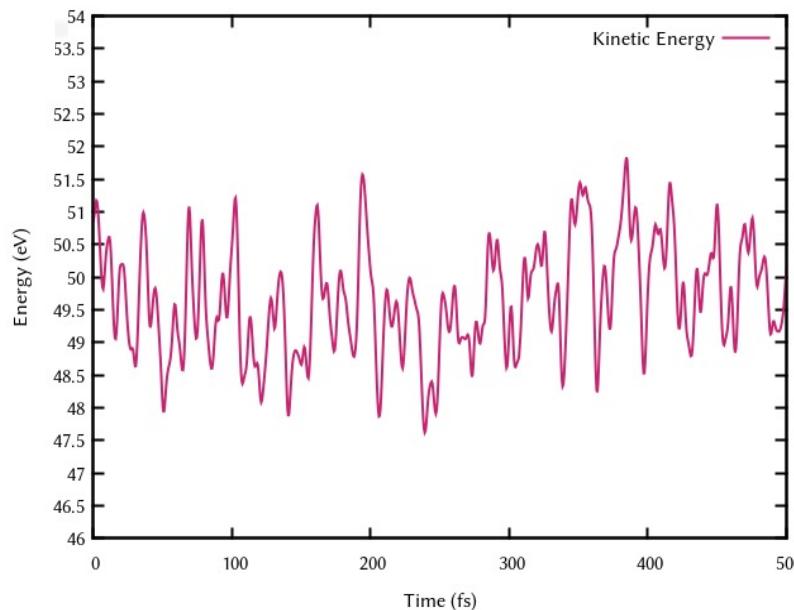
# Application

Acrolein

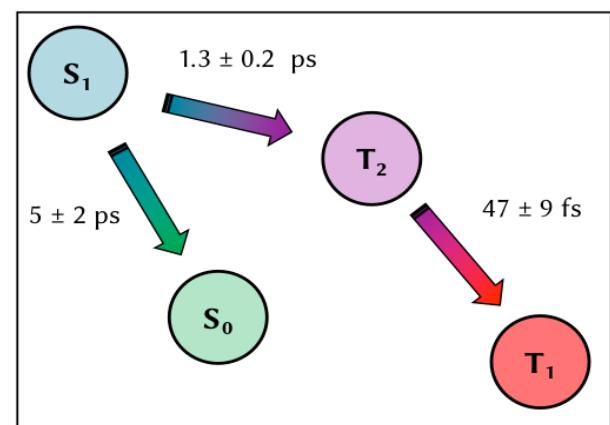
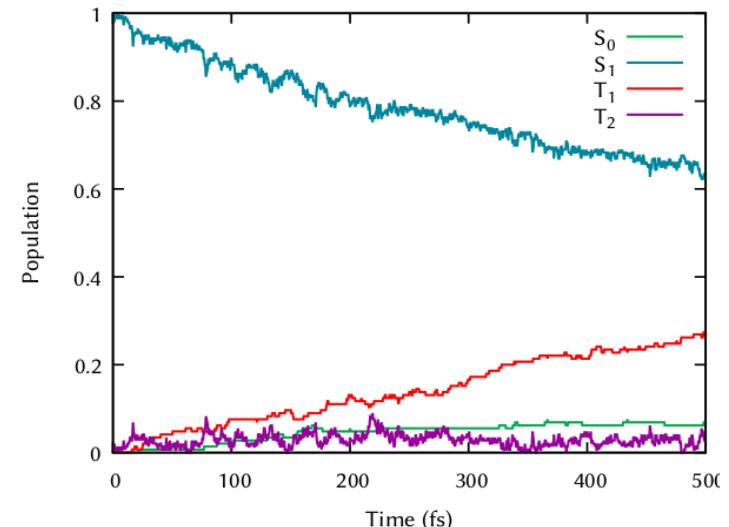
SHARC/COBRAMM//MOLCAS/AMBER

CASSCF(8,7)/cc-pVDZ//GAFF

146 trajectories



SHARC/COBRAMM working test





# Application

## Initial Conditions

Initial conditions generation is a delicate yet fundamental process

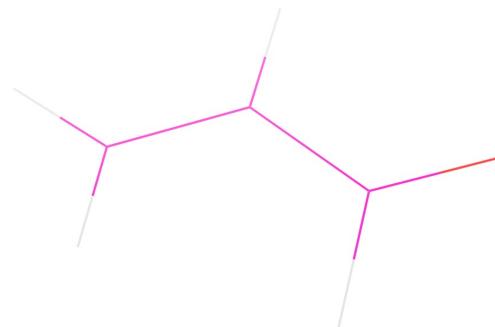
Name	Task	Location
wigner.py	calculate QM Wigner distribution	\$SHARC
cobramm-solvatedchromo.py	solvate the QM geometries	\$COBRAM_PATH
cobramm-equilibration.py	equilibrate the solvent (AMBER)	\$COBRAM_PATH
amber_to_initconds.py	convert amber to sharc format	\$SHARC
combine_init.py	include Wigner velocities	\$SHARC
cobramm-droplet.py	create droplet and layers	\$COBRAM_PATH
cobramm_rattle.py	create rattle file information	\$COBRAM_PATH
setup_cobramm_init.py	setup initial conditions	\$SHARC
excite.py	excite initial conditions	\$SHARC
setup_cobramm_traj.py	setup trajectories	\$SHARC



# Application

# Initial Conditions

optimized geometry + frequency (PCM)



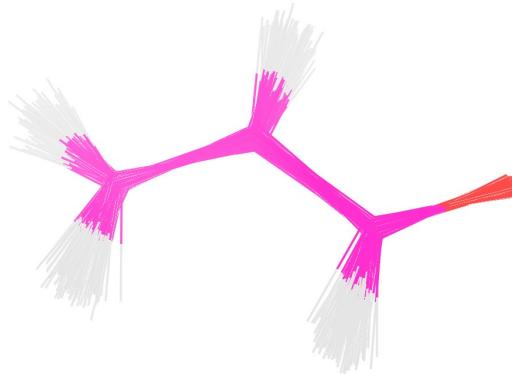


# Application

# Initial Conditions

optimized geometry + frequency (PCM)

Wigner distribution (PCM)





# Application

# Initial Conditions

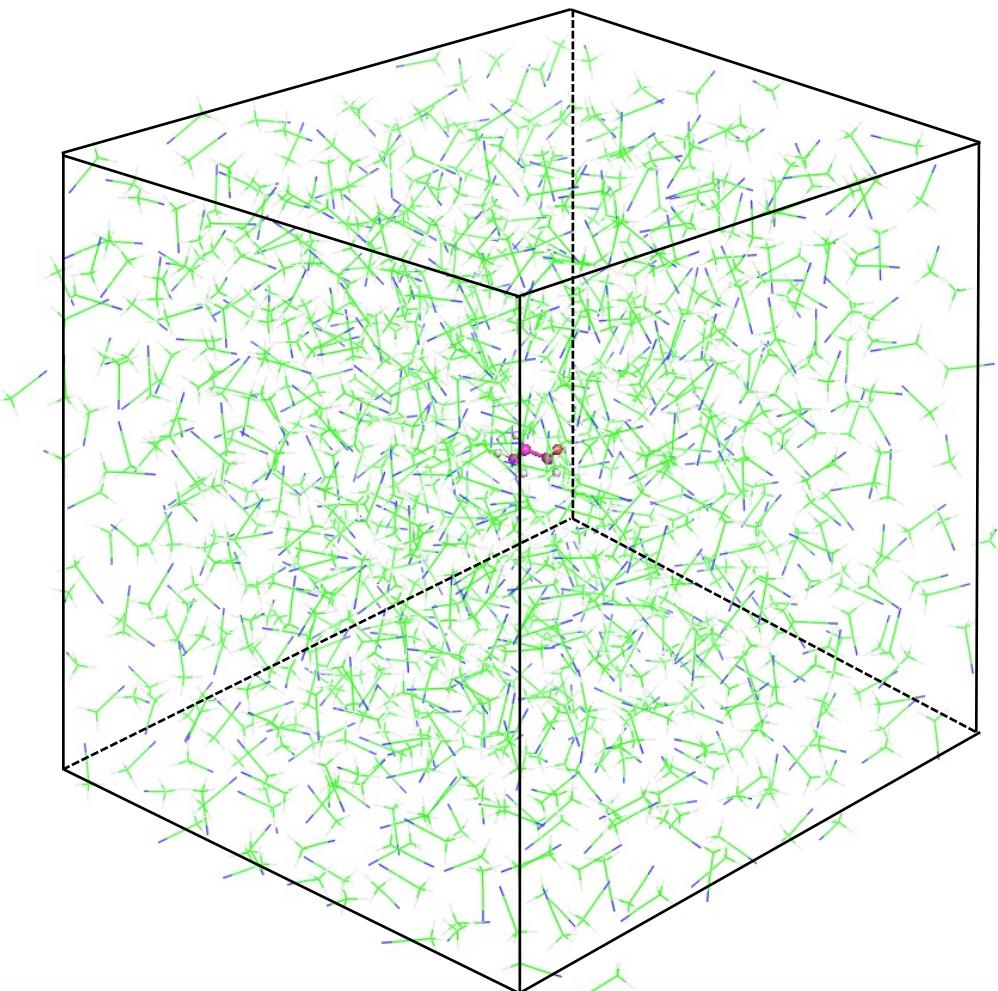
Wigner distribution (PCM)  
↓  
solvation





# Application

# Initial Conditions

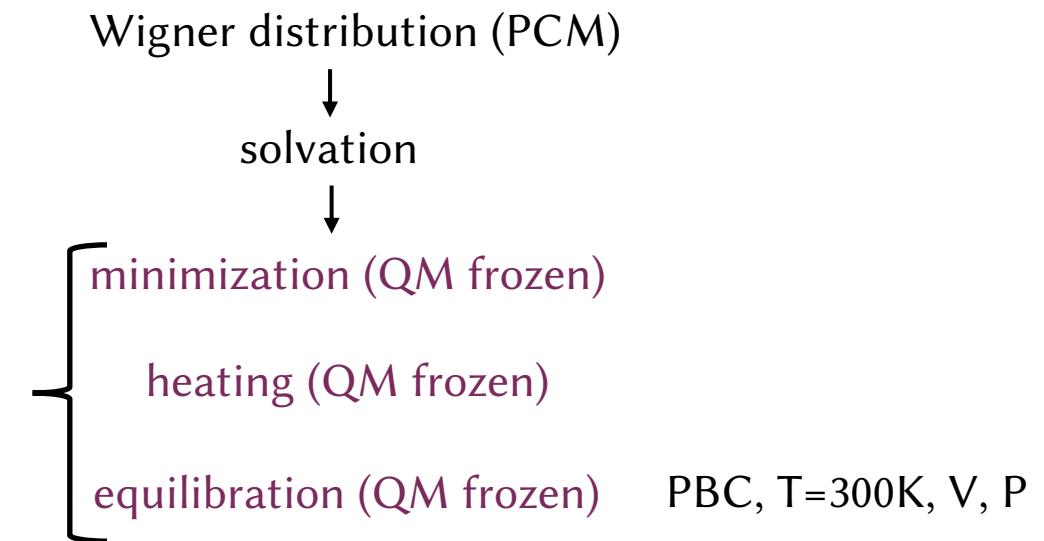
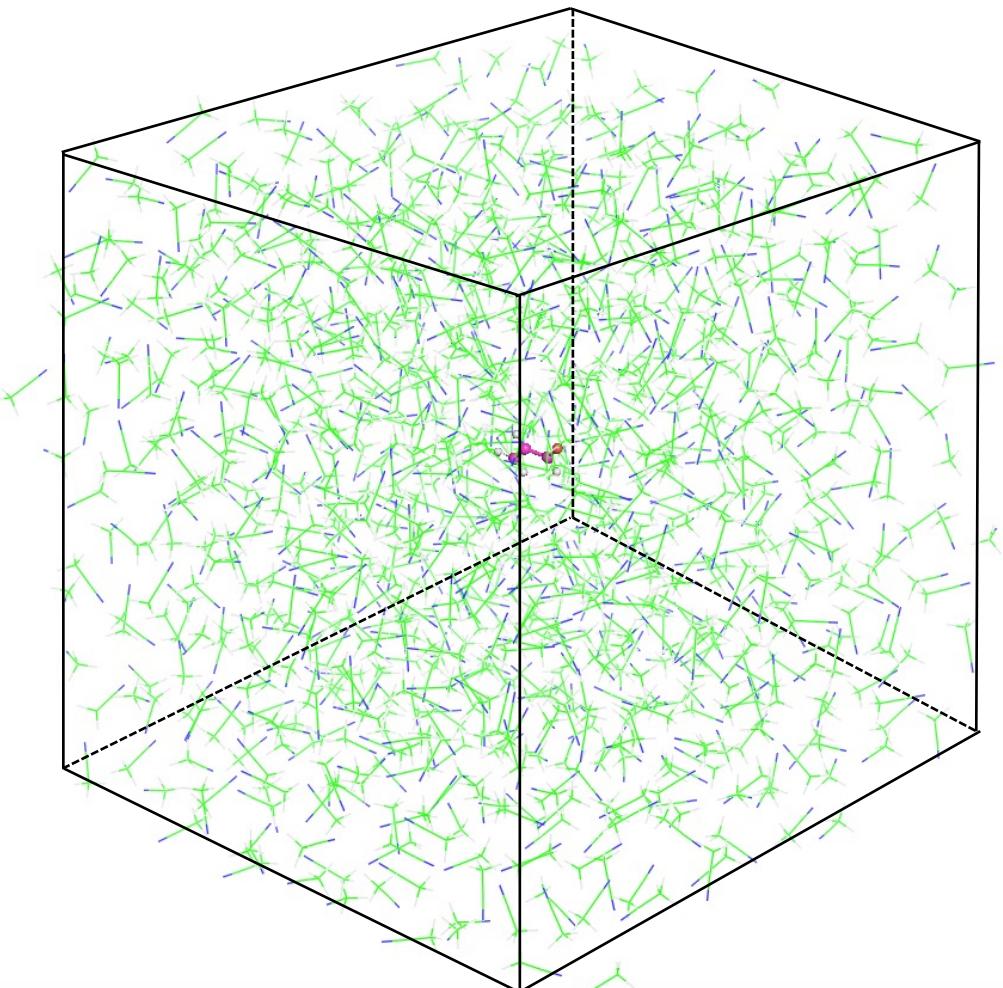


Wigner distribution (PCM)  
↓  
solvation



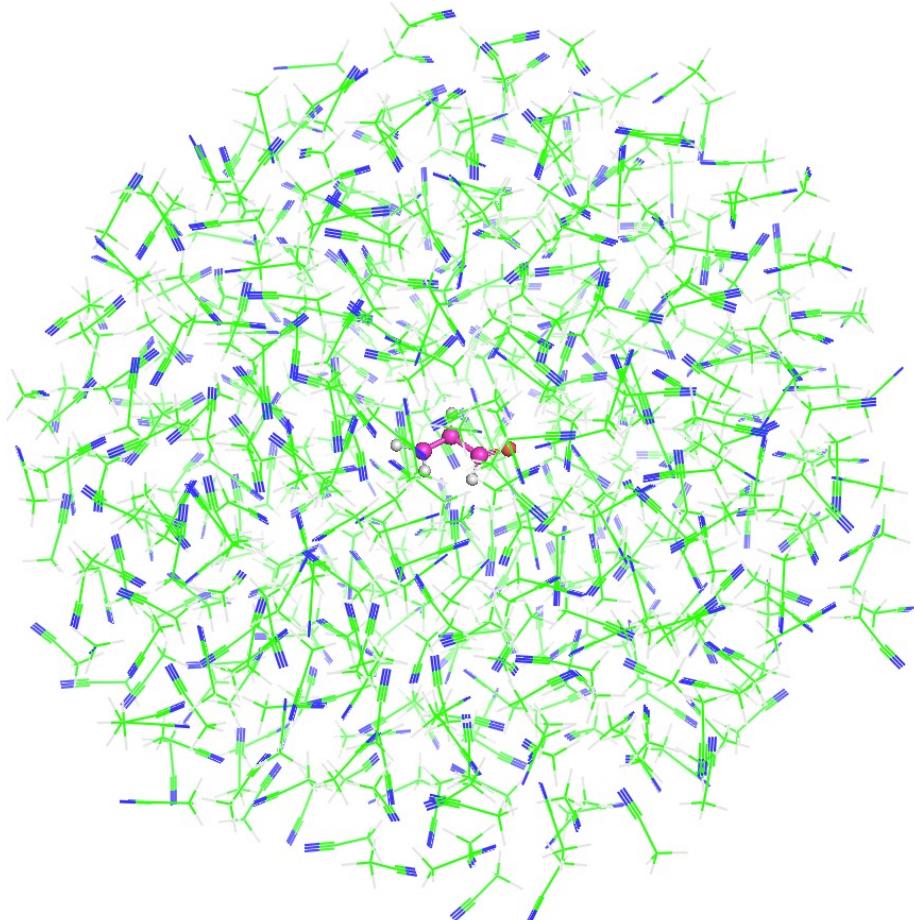
# Application

# Initial Conditions

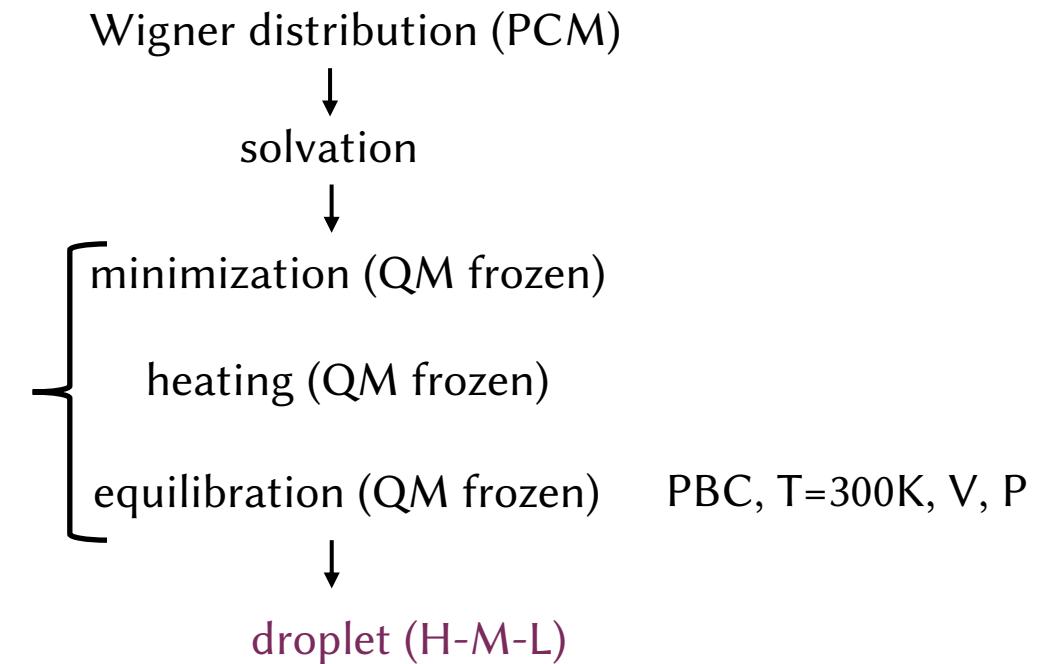




# Application

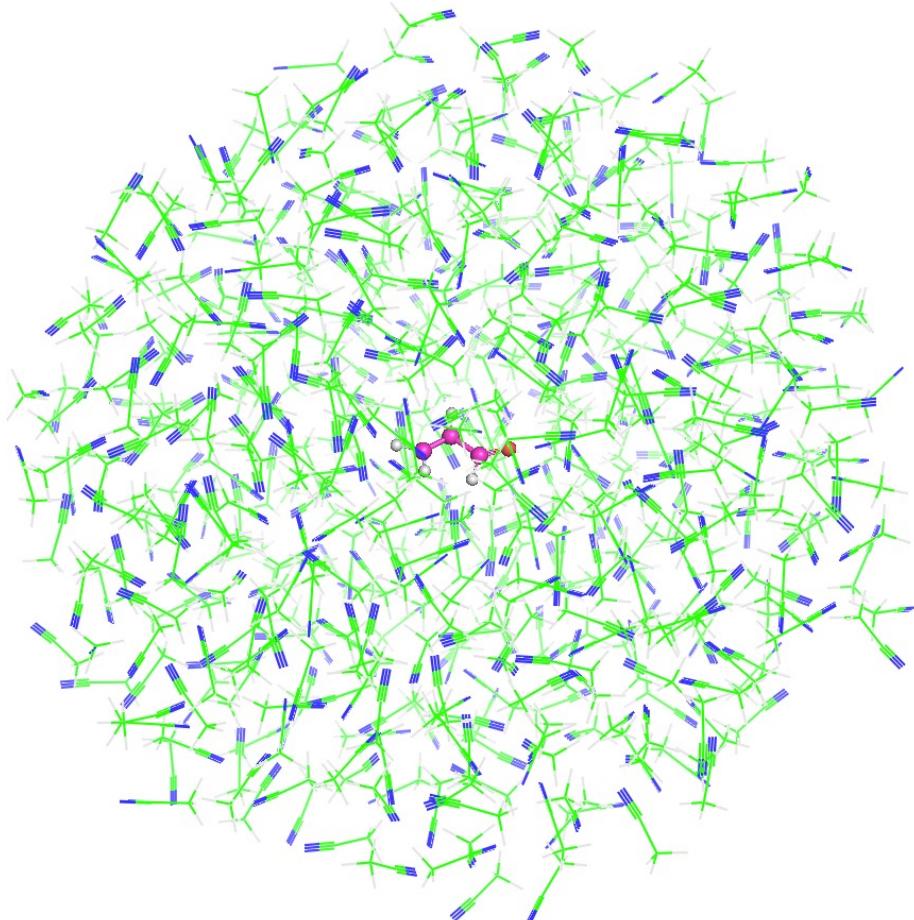


# Initial Conditions

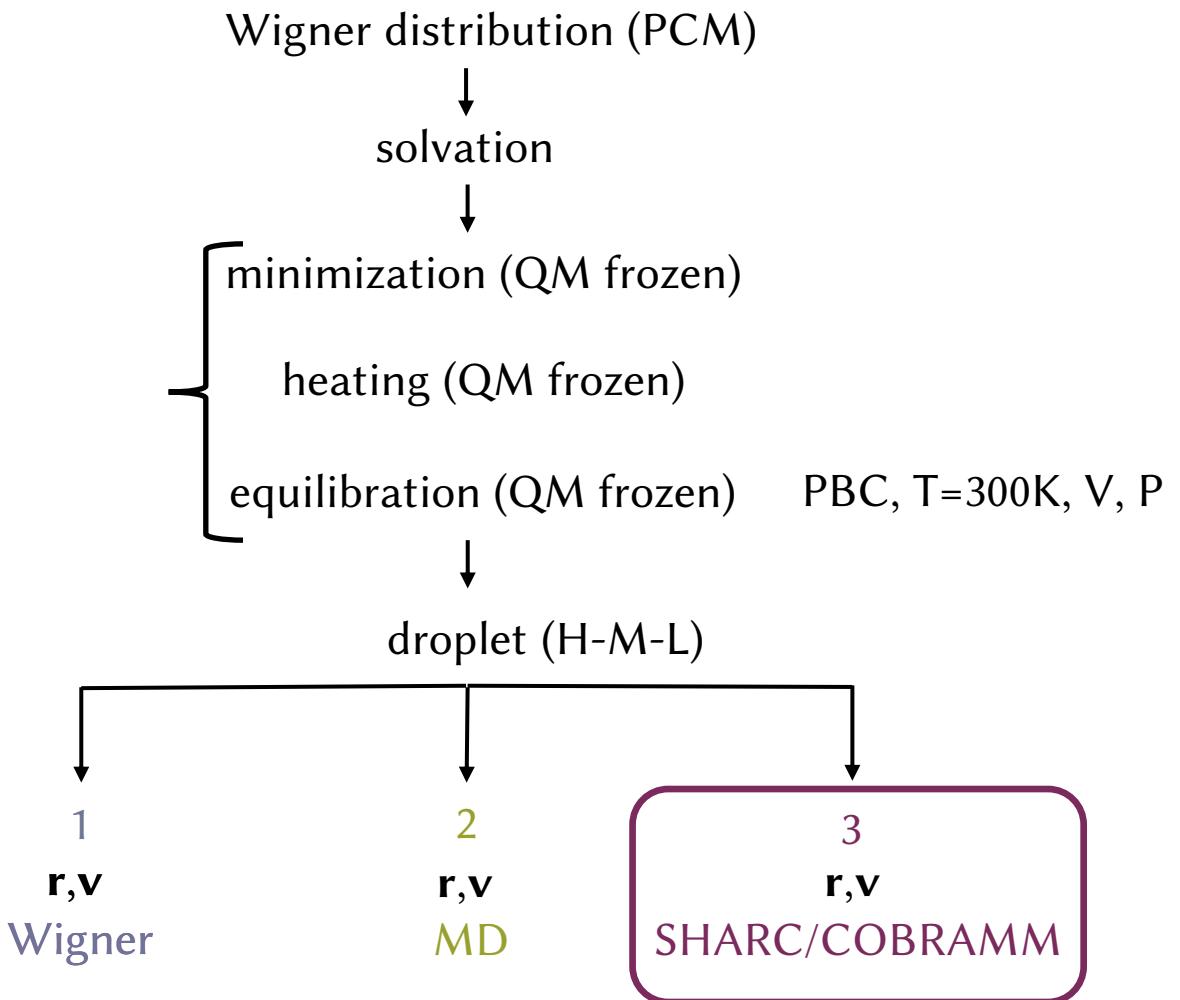




# Application

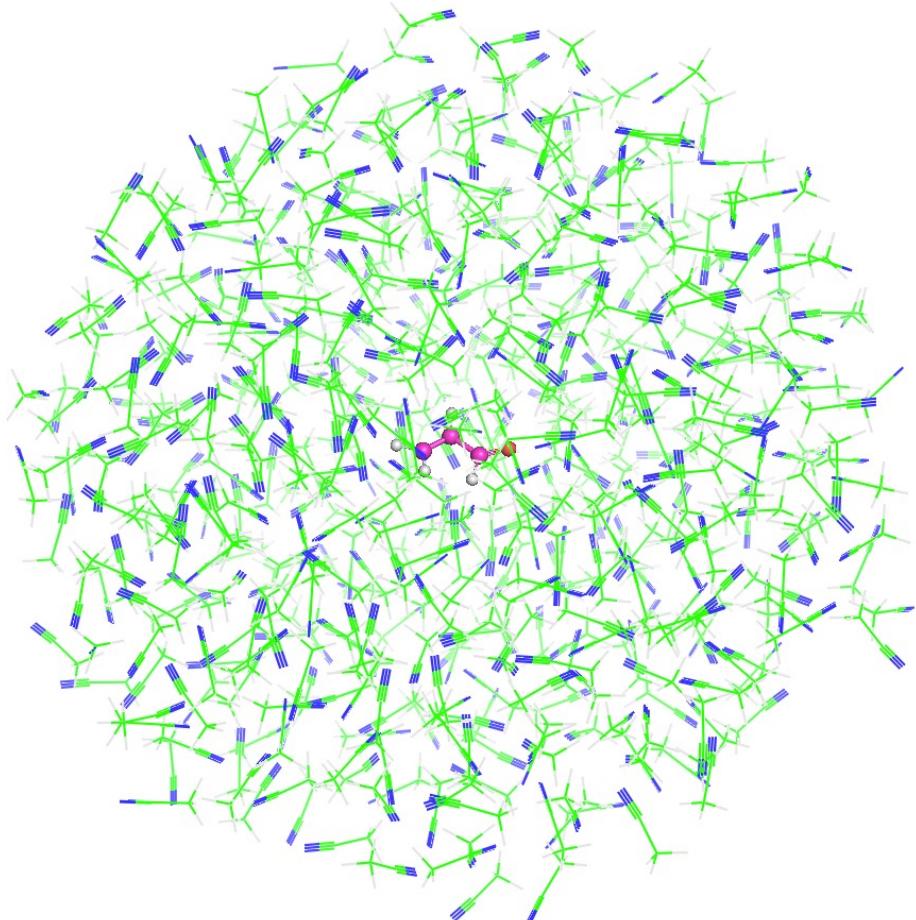


# Initial Conditions

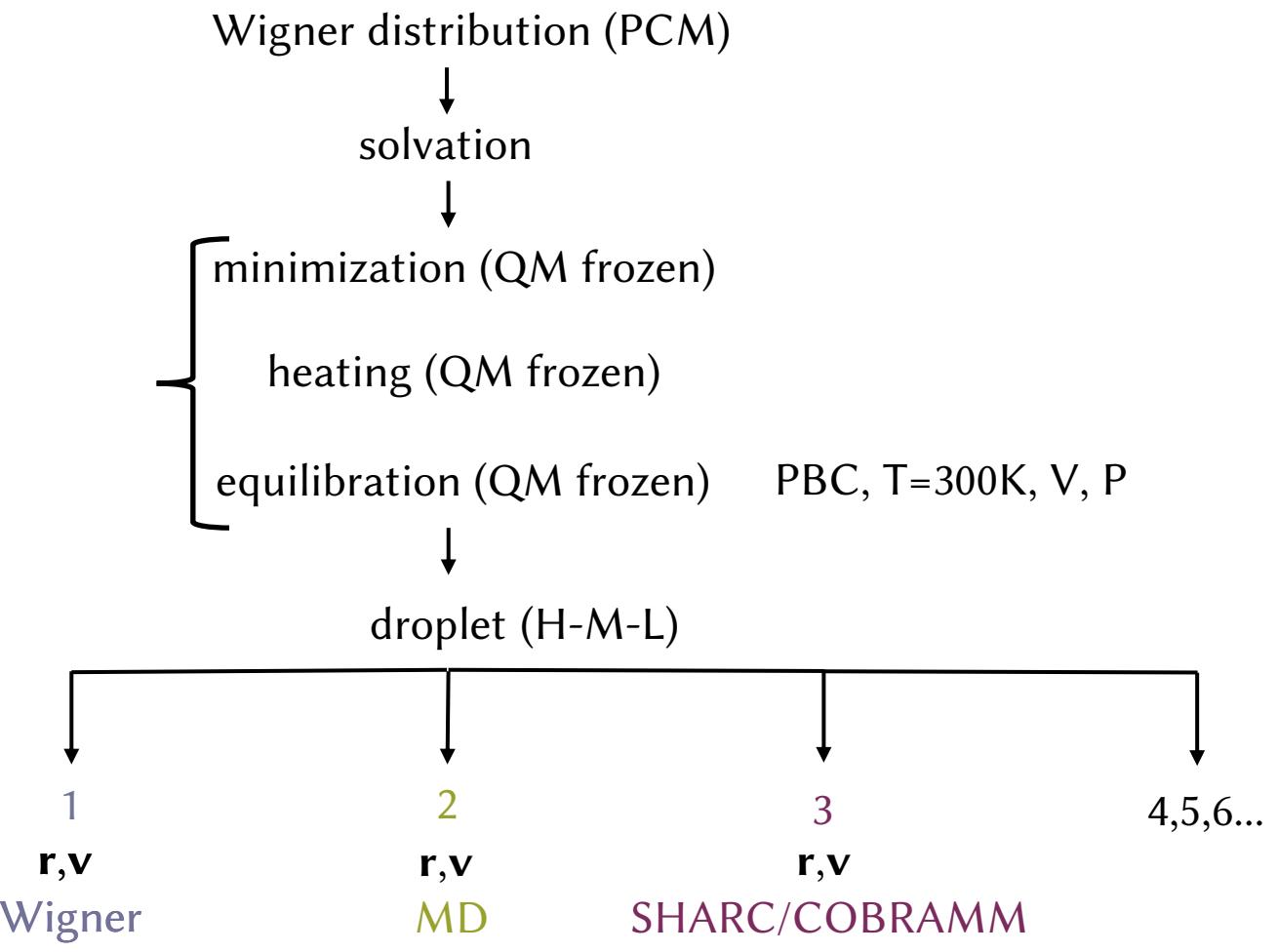




# Application



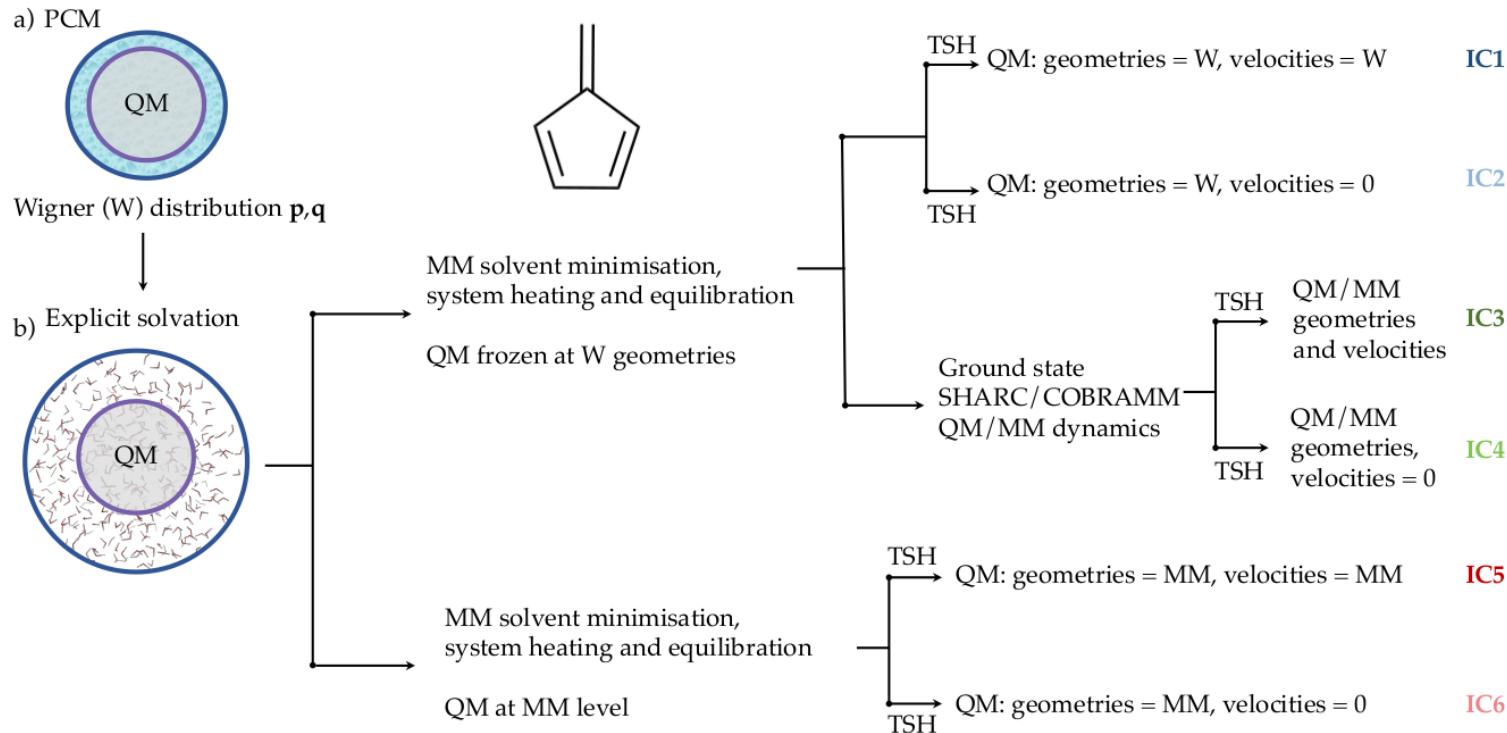
# Initial Conditions



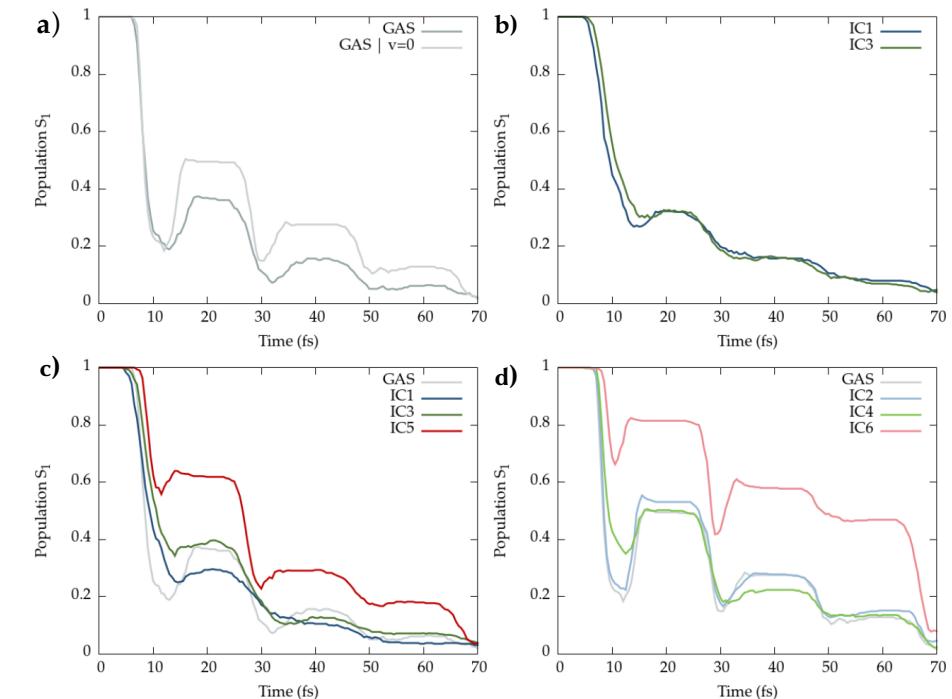


# Application

# Initial Conditions



Extensive comparison  
of the sampling in QM/MM TSH





# Conclusion

# Summary

## Why choosing SHARC/COBRAMM interface?

ISC in complex environment

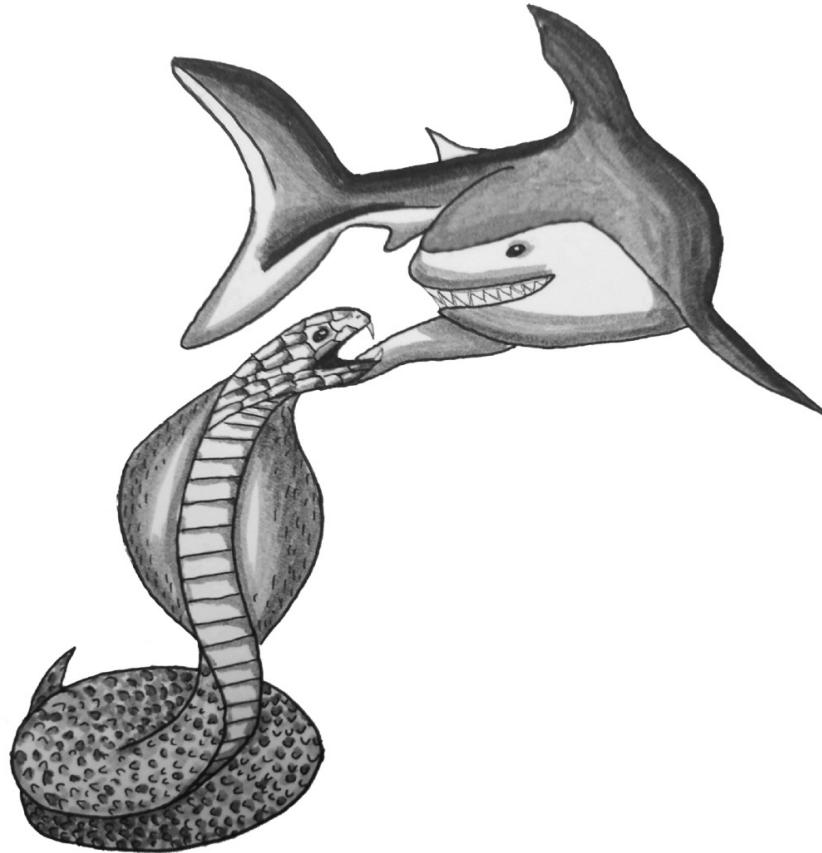
several levels of theory

auxiliary scripts

benefit from independent future developments

comparison with their own implementation

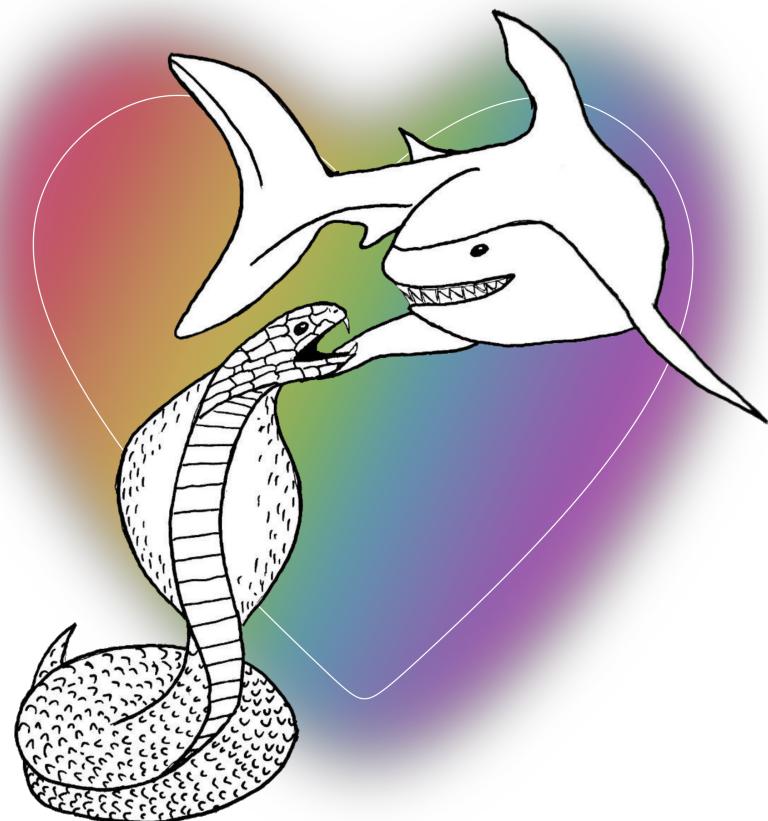
both open source





## Conclusion

## Summary



**SHARC & COBRAMM interfaced**

**MOLCAS, ORCA, TURBOMOLE  
interfaces available**

**efficient nonadiabatic dynamics  
including ISC and environment**



## Conclusion

## Summary

**Final version and documentation available  
Try it out!**

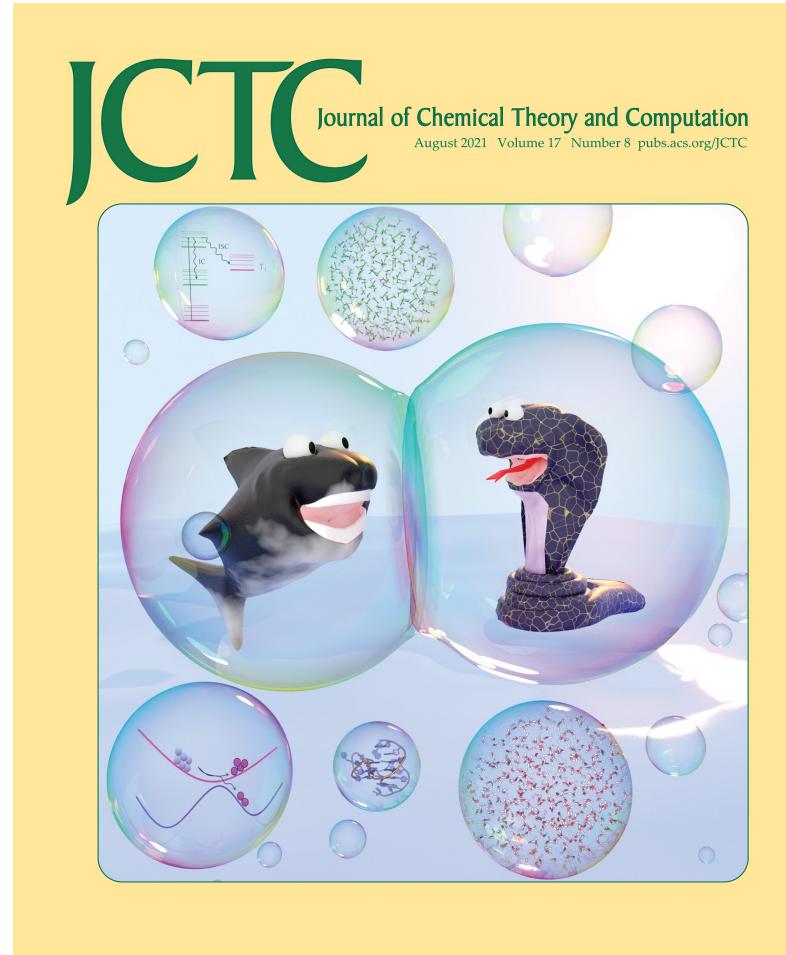
[https://github.com/sharc-md/sharc\\_cobramm\\_interface](https://github.com/sharc-md/sharc_cobramm_interface)

D. Avagliano, M. Bonfanti, M. Garavelli, L. González,  
*J. Chem. Theory Comput.* 2021, 17, 8, 4639–4647

for any feedback, comments, bugs report, questions:



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# Conclusion



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Thank you for your attention!