# Final report on CECAM/Marvel/Psi-k School on Path Integral Quantum Mechanics: From the Basics to the Latest Developments

https://www.cecam.org/workshop-1528.html

**Organisers:** *Michele Ceriotti, Tom Markland, Jeremy Richardson and Mariana Rossi*
**Dates:** 25-*29 June, 2018*

## 1. Summary

We convened a School on Path Integral Quantum Mechanics at the CECAM headquarters in Lausanne, Switzerland. The school gathered together 17 speakers (11 invited and 6 contributed) and 46 participants affiliated with 15 different countries. We received a total of 85 applications to attend the school and unfortunately could not accept more participants due to space constraints in the lecture room. This amount of applications, only two years after we had the last school on the same topic, underlines the growth of the community performing research on the theory and practice of Path Integral (PI) techniques for the atomic-scale modelling of the quantum behavior of materials and molecules

As in the last school, we explicitly asked the speakers to prepare pedagogic talks aimed at introducing the participants to the methods and simulation techniques to treat imaginary and real time path integrals, for both adiabatic and non-adiabatic dynamics. Invited and contributed speakers were encouraged to give lectures that explained the methods in great detail, so that the students could benefit the most from the school, even if this was their first contact with path integral methods.

Making use of the new CECAM headquarters infrastructure, all lectures were recorded and made available, through the CECAM website, to all participants that applied for the school, even the ones that were not accepted for participating physically in the event.

Hands-on sessions were mostly based on the i-PI (http://ipi-code.org) program. The i-PI code has recently hit its v2.0 release including many new features that allow more complex simulation setups using path integral methods. The participants could fully profit from the new infrastructure. Given the success we had in the last school of providing participants with a USB stick containing a full disk image that had the simulation environments pre-installed, we prepared that again. This time we also integrated our simulation environment in the Quantum Mobile (https://www.materialscloud.org/work/quantum-mobile), which benefits a much wider community.

Students could profit from direct interaction with the speakers and organizers through the poster session, the Q&A sessions, and a full afternoon dedicated to student projects where the organizers and the tutors were available to help the students with setting up their own simulations. The poster session had very high-quality posters and more than 20 students received help in setting up simulations regarding their research and also in coding new features into i-PI in the afternoon dedicated to that. The "anonymous" Q&A sessions, in which the participants would write questions on a piece of paper after the lectures and the speakers would answer all questions out loud by the end of the day, were also appreciated by the students.

We received generous funding from CECAM, Psi-k, and MARVEL. With this funding we were able to contribute to the participation costs of 24 participants, give four poster prizes, and provide useful conference items: personalized USB sticks (containing the software and exercise files and handouts) and personalized espresso cups that the participants could use to minimize the waste generated during the conference and take home as a token from the week they spent at this school. More details on our school follow below.

## 2. Goals and important outcomes from the school

Path integral quantum mechanics methods continues to be a topic that is often absent from the standard program of physics or chemistry undergraduate and graduate courses, and has become more important in the past decades. Our goal with this school was to make these methods accessible even for a person who was not at all familiar with path integral techniques. The pedagogical element of the lectures given by all speakers was fundamental in achieving this goal. We received feedback from the students that they found the level of the talks very good. We provided all the slides of the talks and the videos of the lectures to participants on site and also to the students that applied but were not accepted to attend. Most students that participated belonged to groups that had already started using path integral techniques or that had an explicit interest in starting to use them soon. This was in contrast to the last school, where we had many participants that belonged to groups where the technique had never been used or developed. We conclude that these schools are being successful in increasing the number of groups that are familiar and benefit from this technique. We received feedback that students would like more details and more time spent in the introductory lectures of more advanced path integral techniques.

Also this time, some of our participants were already quite knowledgeable in the field, but still could profit from our school's lectures on more advanced path integral techniques. An important aspect of this school was that it had more of a focus on path-integral techniques for non-adiabatic processes and several rather new techniques in this field that were developed in the last couple of years.

We encouraged social-media participation and advertisement of the school as well. We had a hashtag on Twitter (#PI18) that we used to post impressions from the school from both organizers and participants, and to advertise the poster prizes and their recipients. Students supported this idea.

A last important goal we wanted to achieve again with this school was to make the practical sessions as easy as possible to start, and as easy as possible to keep after the school was over. We asked all participants to bring their own laptops -- the ones who were unable to do this could use the computers in CECAM. We provided USB keys with the whole environment and software needed for the exercises pre-installed. Since last time there were problems with the speed of the USB data transfer, we asked the participants to prepare for the school by ensuring they had enough space on their hard-disks and asking them if possible, to download and install the image from a web-link even before the school started. The ones that were unable to do this simply transferred the image from the USB stick to their computers. This setup worked very well, with minor problems in the VirtualBox software in a few computer environments.

## 3. Topics covered in the lectures

Below we provide a summary of the topics covered in the school. We stress that very recent developments in this field were widely represented, so that the participants could have a taste of the state-of-the-art of the community -- even if starting from the very basics.

**Invited lectures:**

***M. Parrinello - Path Integrals: Past, Present and Future***

- History of the topic
- Examples of modern sampling techniques, e.g. metadynamics

***T. Markland - Introduction to Imaginary-Time Path Integrals***

- Derivation of imaginary time path integral expression
- Reinserting the momenta and PIMD - mass matrix etc.
- Evolving the ring polymers - normal modes and staging transformations, a brief recap on developing integrators using Liouville operator splitting and resonance barriers in PIMD
- Thermostatting of PIMD - non ergodicity challenges etc., targeted thermostatting schemes PILE and NHC, GLE as a thermostat for PIMD

***O. Marsalek - Path Integral Estimators***

- Position-dependent operators
- Kinetic energy - primitive and virial
- Free energy change upon isotope substitution

***M. Ceriotti - Accelerated Path Integral Techniques & Advanced PIMD***

- A brief introduction to Generalized Langevin Equation thermostatting
- Generalized Langevin Equations for path integrals
- High-order path integrals
- Ring-polymer contraction and multiple time stepping

***D. Ceperley - Path Integrals for Indistinguishable Particles***

- Path integral exchange (formulation)
- Important examples of exchange in quantum processes

- He phase diagram
- PIMC sampling
- Fermion sign problem
- Possible routes around the sign problem

***M. Rossi - Ab initio PIMD***
- DFT and other ab initio methods
- Particular points with regard to simulation of PIMD
- Challenges and examples

***X-Z. Li - Applications of PIMD***
- Hydrogen phase diagram
- Discussion of important future applications

***S. Bonella - Real-time path integrals***
- Path integral representation of the real time propagator, semiclassical limit, and the sign problem

***M. Rossi - RPMD and CMD Approaches to Quantum Dynamics***
- Brief recap on correlation functions
- How CMD and RPMD approximate correlation functions
- Caveats with the approximations
- How TRPMD approximates correlation functions
- How a typical calculation works
- Examples of successes and failures of the methods

***S. Althorpe - Matsubara Dynamics***
- Motivation: quantum Boltzmann statistics with classical dynamics underpins CMD, RPMD, TRPMD, etc.
- Recap of linearized semiclassical approx (i.e. classical Wigner) & its failure to satisfy detailed balance
- Sketch of Matsubara dynamics derivation and demonstration that it satisfies db
- Origin of CMD and RPMD.
- Use of Matsubara to generate alternative db-satisfying quantum stat/classical dynamics methods

***J. Richardson - RPMD rate theory***
- Classical and quantum rate constants from the flux correlation function
- Classical and quantum transition state theories

- Dividing surfaces and recrossing

***J. Richardson - Ring polymer instanton approaches***

- Derivation of semiclassical instanton theory
- Numerical methods for computing ring-polymer instanton
- Connection to RPMD
- Examples of instanton calculations on molecules

***N. Ananth - Non-Adiabatic and Semiclassical Dynamics***

- Deriving the Van Vleck propagator from the real-time propagator
- Initial Value representation and flavors; HK-IVR, EFB-IVR, FB-IVR
- LSC-IVR
- Mixed quantum-classical IVR
- Brief look at nonadiabatic dynamics in the SC-IVR framework
- Semiclassical non-adiabatic dynamics: Mapping formalism and linearization

**Contributed talks speakers and titles:**

***Venkat Kapil:*** *Advanced Path Integral Methods - Beyond the Benchmark*

***Fabien Brieuc:*** *Tackling reactive molecules at ultralow temperatures using modern path integral simulation techniques*

***Richard Remsing:*** *Effective Mass Path Integral Simulations: Applications to Excitons in Disordered Systems and Charge Carrier Trapping in 2D Materials*

***Kenneth Jung:*** *Inclusion of nuclear quantum effects in second order response spectroscopy*

***George Trenins:*** *Mean-field Matsubara dynamics: bending the curve on the curvature problem*

***Joseph Lawrence:*** *The non-adiabatic to adiabatic transition in reaction rates*

**Posters and Flash Talks**

Each participant presenting a poster also presented a 90s flash talk. This was an opportunity to advertise their poster to the other participants for the upcoming poster session.

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| Suraj Kannath | Path-integral approach to hydrogen atom abstraction from<br>Ethanol by atomic hydrogen in aqueous solution |
| Pablo Videla | Understanding isotopic segregation " in aqueous systems |
| Kelly Hunter | Coupling Effects in the Infrared and Raman Spectra of Liquid Water |
| Mandal Arkajit | Quasi-diabatic representation for nonadiabatic dynamics |
| Manish Thapa | Breakdown of Wolynes Theory |
| Pablo del Mazo | Neural Networks for PES fitting |
| Juha Tiihonen | Simulating dynamic molecular polarizabilities<br>at finite temperature with path-integral Monte Carlo |
| Aran Lamaire | NQEs in metal-organic frameworks |
| Sohag Biswas | First Principles Molecular Dynamics Study of Aqueous<br>Solution of SO4 2- and S2O3 2- with Dispersion Correction:<br>Structural, Dynamical and Spectral Properties of Water |
| Laura Duran Caballero | Microsolvation of Water and Protonated<br>Water in Superfluid pH 2 and 4 He |
| Maksim Orekhov | Fluctuation enhancement of ion diffusivity in liquids |
| Thomas Fay | Quantum master equations for non-adiabatic electron transfer reactions of radical pairs: The role of coherence, energy shifts and dephasing |
| Muhammad Qaisrani | Mysterious Fluorescence in proteins aggregates |
| Tim Burd | Quantum dyanmics of atmospheric reactions |
| Deepak Ojha | Nuclear Quantum Effects on Vibrational Dynamics of Air-water Interface |
| Karen Fidanyan | Vacancy diffusion in bcc metals:<br>Beyond the NEB precision |
| Yair Litman | Temperature and Tunneling Influence on<br>Intramolecular Double Hydrogen<br>Transfer Reactions |
| Yashoj Shakya | Comparative study on environmental<br>effects in light harvesting complexes |
| Huziel Sauceda | Path Integral Molecular Dynamics Simulations<br>with Machine-Learned Force Fields |
| Hagen-Henrik Kowalski | Strong Anharmonic and Quantum-Nuclear Effects in the<br>Low Temperature Dyamics of CsCl |

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| Venkat Kapil | Efficient computation of particle momentum distribution |
| Rich Remsing | Statistical Mechanical Modeling of Quasiparticles in Condensed Phases |
| Juraj Hasik | Quantum and classical ripples in graphene |
| Jiri Suchan | Photodynamical simulations with CW laser |

## Conference program:

| | Monday | Tuesday | Wednesday | Thursday | Friday |
|---|---|---|---|---|---|
| 8:30-9:00 | Registration | | | | |
| 9:00-10:00 | Welcome (9:00-9:30)<br>Path Integrals: Past, Present and Future (Parrinello) | Accelerated Path Integral Techniques (Ceriotti) | Applications of PIMD (Li) | Matsubara dynamics (Althorpe) | Practical III |
| 10:00-10:30 | | Coffee Break | Contributed Talk III | Contributed Talk V | |
| 10:30-11:00 | Coffee Break | Advanced PIMD (Ceriotti) | Coffee Break | Coffee Break | Coffee Break |
| 11:00-12:00 | Introduction to Imaginary-Time Path Integrals (Markland) | Contributed Talk I | Real-time path integrals (Bonella) | RPMD rate theory (Richardson) | Practical III |
| 12:00-12:30 | | Q/A & Discussion | Lunch | Contributed Talk VI | |
| 12:30-13:15 | Lunch | Lunch | | Lunch | Lunch |
| 13:15-13:45 | | | Real time correlations from CMD and (T)RPMD (Rossi) | | |
| 13:45-14:45 | Practical PIMD simulation (Marsalek) | Path integrals for indistinguishable particles (Ceperley) | Contributed Talk IV | Ring polymer instanton approaches (Richardson) | Students' projects |
| 14:45-15:30 | Practical I | Contributed Talk II (14:45-15:15) | Practical II | Non-adiabatic semiclassical methods (Ananth) | |
| 15:30-16:00 | Coffee Break | Coffee Break | Coffee Break | Coffee Break | Coffee Break |
| 16:00-17:00 | Practical I | Ab initio PIMD (Rossi) | Practical II | Non-adiabatic semiclassical methods (Ananth)<br>Q/A & Discussion | Students' projects |
| 17:00-18:00 | | Poster Flash Talks | | Summary and future directions of the field | |
| Evening | Q/A & Discussion | Conference Dinner | Poster Session | | |

## 4. Set up of hands-on session


The idea of using a virtual machine as the platform to perform all of the tutorials, that we pioneered during the 2016 edition of this school, was very successful and triggered the development of more professional implementations of the concept. For this school we used the “quantum mobile” https://materialscloud.org/quantum-mobile as the basis to prepare the environment, that we complemented with i-PI, CP2K, LAMMPS, and the tutorial files, that are also available from a github repository, https://github.com/epfl-cosmo/pimd-tutorial. The topics covered on the 3 hands-on session were:

1. Introduction to PIMD simulations
2. Advanced PIMD simulations
3. RPMD and CMD simulations
4. For those who finished the 3 tutorials quickly, there was an extra tutorial on instanton theory.

The software used was all open source, based on the interface of the i-PI (http://ipi-code.org/) program with LAMMPS (http://lammps.sandia.gov/) and CP2K (https://www.cp2k.org/).

## 5. Q&A sessions at the event

Students were encouraged to interrupt during the lectures to ask questions whenever they occurred. However, our Q&A sessions where the lecturers would answer questions written on pieces of papers anonymously by the students continued to be effective and initiated a great deal of discussion. We also had good feedback from this format of discussion. The feedback we got from students was that they would prefer us to try to answer as many possible interpretations of the questions that we felt were not very clear, since we could not ask the students what they meant with them (after all, it was anonymous).

## 6. Poster session and poster prizes

Due to generous funding, we were able to award poster prizes to the participants. Four posters were chosen by the jury made up of speakers at the school. The main poster prize went to Arkajit Mandal, who was awarded 200 CHF. Three runner-up prizes (100 CHF each) were also given to Yair Litman, Thomas Fay and Jiri Suchan.

The poster session was very lively and we set up a screening of the World Cup games that were happening that night in the poster session. Participants stayed to watch the games and further discuss the posters until 10 p.m. All posters presented and the corresponding abstracts can be found in the conference website.


## 7. Impressions from the participants

CECAM gathered feedback from many of the participants, as well as suggestions for further improvements that we have incorporated in the discussion above. A selection of the comments in the questionnaire follow:

*There was ample room for discussion after the talks, and during the discussion and poster sessions.*

*I really appreciated that the organizers were open for discussions during and after the session, it brought a really nice scientific atmosphere through the workshop.*

*I'd like to thank the organizers for an excellent workshop!*

## 8. Full list of participants

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| Markland | Tom |
| Richardson | Jeremy |
| Rossi | Mariana |
| Ceriotti | Michele |
| Althorpe | Stuart |
| Ananth | Nandini |
| Bonella | Sara |
| Ceperley | David |
| Li | Xinzheng |
| Marsalek | Ondrej |

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|---|---|
| Parrinello | Michele |
| Basdogan | Yasemin |
| Benson | Raz |
| Biswas | Sohag |
| Brieuc | Fabien |
| Burd | Timothy |
| Bussy | Augustin |
| Camisasca | Gaia |
| del Mazo Sevillano | Pablo |
| Duran Caballero | Laura |
| Fay | Thomas |
| Fidanyan | Karen |
| Hasik | Juraj |
| Heindel | Joseph |
| Hunter | Kelly |
| Jung | Kenneth |
| Juraskova | Veronika |
| Kannath | Suraj |
| Kapil | Venkat |
| Kowalski | Hagen-Henrik |
| Lamaire | Aran |
| Lawrence | Joseph |
| Lesnicki | Dominika |
| Libbi | Francesco |
| Lidberg | Andrea |
| Litman | Yair |
| Mandal | Arkajit |
| Menkah | Elliot |
| Ojha | Deepak |
| Orekhov | Maksim |
| Ortega Guerrero | Andres Adolfo |
| Öström | Jonatan |
| Pauletti | Michela |
| Ple | Thomas |
| Qaisrani | Muhammad Nawaz |
| Ranya | Srinath |
| Remsing | Richard |
| Sauceda | Huziel E. |
| Shakya | Yashoj |
| Suchan | Jiri |
| Thapa | Manish |
| Tiihonen | Juha |
| Trenins | George |

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|---|---|
| Vassilev | Valentin |
| Videla | Pablo |
| Willatt | Michael |
| Wu | Yantao |