

# Anharmonic Nuclear Quantum Effects and their Interplay with the Electronic Structure of Weakly Bonded Systems

Mariana Rossi<sup>a</sup>

<sup>a</sup>*Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin*  
rossi@fhi-berlin.mpg.de

In this talk, I will discuss our recent efforts to include quantum nuclear effects in first-principles simulations of various high-dimensional systems containing weakly bonded organic components.

The quantum nature of the nuclei can often impact the atomic structure, nuclear dynamics, and the electronic structure of a given system at finite temperature. From a theoretical point of view, this requires simulations that treat electrons and nuclei as quantum particles, and that are also able to describe the coupling between them. Nuclear motion is most easily captured in the harmonic approximation, and improvements can be achieved by further perturbative expansions. However, in flexible organic systems, the anharmonic perturbation is typically large, such that the full anharmonic nature of the nuclear interactions has to be accounted for. In that respect, methods based on the path integral formulation of quantum mechanics arise as a good choice to treat anharmonic nuclear quantum effects in these systems.

I will present methodology to accelerate path-integral molecular dynamics of weakly bonded interfaces and to improve approximations to nuclear quantum dynamics [1,2] in a manner that allows their use with on-the-fly energy and force evaluations from first-principles methods [3]. We find important changes in the atomic structure, vibrational spectra, and reaction rate constants in the deep tunnelling regime for a wide class of systems comprising isolated molecules, organic-inorganic interfaces and molecular crystals [4-6]. In particular, we show that in weakly bonded interfaces anharmonic nuclear fluctuations can considerably change the electronic density of states and lead to isotope effects in the work-function of functionalized metallic surfaces.

## References

1. Y. Litman, D. Donadio, M. Ceriotti and M. Rossi, *J. Chem. Phys.* **148** 102320 (2018).
2. M. Rossi, V. Kapil, M. Ceriotti, *J. Chem. Phys.* **148**, 102301 (2018).
3. V. Kapil *et al.*, *Comp. Phys. Comm.* **236**, 214 (2019).
4. Y. Litman, T. Kumagai, J. Richardson and M. Rossi, *J. Am. Chem. Soc.* **141**, 2526 (2019).
5. M. Rossi, P. Gasparotto, M. Ceriotti, *Phys. Rev. Lett.* **117**, 115702, (2016).
6. J. Li, *et al.*, *J. Phys. Chem. Lett.* **9**, 3969-3977 (2018).