Title: *Ab initio* and path integral molecular dynamics methodology for hydrogen-bonded systems in the condensed phase

Author: Kryštof Březina

Institute: Institute of Physics of Charles University

Supervisor: RNDr. Ondřej Maršálek, Ph.D., Institute of Physics of Charles University

Abstract: *Ab initio* molecular dynamics simulations with imaginary-time path integral representation of atomic nuclei provide valuable insight into the physics and chemistry of condensed-phase hydrogen-bonded molecular systems at a high level of descriptive accuracy. At the same time, such simulations often represent a methodological and computational challenge, especially once advanced electronic structure theories are required. In this work, we present our contributions to integrating machine learning potentials into the simulation workflow, focusing on employing active learning in the training set selection and on an efficient generation of the training geometries themselves. With this methodology, we performed advanced simulations of three different molecular systems. First, we explored the behavior of the benzene radical anion dissolved in liquid ammonia: a system with pertinence to Birch reduction chemistry. Motivated by our findings, we then performed an extensive study of π-hydrogen bonding in solutions of benzene liquid water and liquid ammonia with a particular focus on structure, dynamics, and vibrational spectroscopy. Finally, we transferred to surface physics to model proton-transfer reactions in nitrogen-based benzoquinone derivatives in the gas phase and on a gold surface and to describe the reactivity-defining role of nuclear quantum effects. The research is contained in five publications attached to this thesis.

Keywords: *ab initio* molecular dynamics, imaginary-time path integrals, density-functional theory, machine learning potentials, hydrogen bonds, condensed phase, chemical reactivity