Quantum Solvation of Reactive Species Enabled by Neural Networks

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Superfluid helium has not only fascinated scientists for centuries but is also the ideal matrix for the investigation of chemical systems under ultra-cold conditions in helium nanodroplet isolation experiments [1]. Together with related experimental techniques such as helium tagging photodissociation spectroscopy [2], these methods have provided unique insights into many interesting systems. Complemented by theoretical work [3], these techniques were able to greatly expand our general understanding of manifestations of superfluid behavior in finite sized clusters and their response to molecular impurities.
However, most theoretical studies up to now have not included the reactivity and flexibility of molecular systems embedded in helium. In this talk, the theoretical foundation of simulating fluxional molecules and reactive complexes in superfluid helium is presented in detail [4]. Special emphasis is put on recent developments for the converged description of both the molecular interactions and the quantum nature of the nuclei at ultra-low temperatures.
As a first step, our hybrid path integral molecular dynamics/bosonic path integral Monte Carlo method [5] is reviewed. Subsequently, methods for efficient path integral sampling tailored for this hybrid coupling scheme [6] are discussed while also introducing new developments to enhance the accurate incorporation of the solute-solvent coupling. Finally, highly accurate descriptions of the interactions in solute-helium systems using machine learning techniques are addressed. Our current automated and adaptive fitting procedures to parameterize high-dimensional neural network potentials [7] for both the full-dimensional potential energy surface of solutes and the solute-solvent interaction potentials are concisely presented [8, 9]. They are demonstrated to faithfully represent the interactions of chemically complex and reactive solutes in helium environments seamlessly from one He atom up to bulk helium at the accuracy level of coupled cluster electronic structure calculations.
Together, these advances allow for converged quantum simulations of fluxional and reactive solutes in superfluid helium under cryogenic conditions.

[1] J. P. Toennies, A. F. Vilesov, Angew. Chemie Int. Ed. **43**, 2622- 2648 (2004).
[2] A. B. Wolk, C. M. Leavitt, E. Garand, M. A. Johnson, Acc. Chem. Res. **47**, 202–210 (2014).
[3] D. M. Ceperley, Rev. Mod. Phys. **67**, 279-355 (1995).
[4] F. Brieuc, C. Schran, F. Uhl, H. Forbert, D. Marx, J. Chem. Phys. **152**, 210901 (2020)
[5] L. Walewski, H. Forbert, D. Marx, Comput. Phys. Commun. **185**, 884-899 (2014).
[6] C. Schran, F. Brieuc, D. Marx, J. Chem. Theory Comput. **14**, 5068–5078 (2018)
[7] J. Behler, M. Parrinello, Phys. Rev. Lett. **98**, 146401 (2007).
[8] C. Schran, F. Uhl, J. Behler, D. Marx, J. Chem. Phys. **148**, 102310 (2018).
[9] C. Schran, J. Behler, D. Marx, J. Chem. Theory Comput. **16**, 88–99 (2019)