Analysis and benchmark of Non-Adiabatic Dynamics with NRPMD

Danilo Calderini[1], **Jeremy Richardson**[1]

[1] *ETH Zürich, Department of Chemistry and Applied Biosciences, Laboratory of Physical Chemistry, Vladimir-Prelog-Weg 1-5/10 8093 Zürich Switzerland*

Thanks to its capability of including quantum effects in a classical dynamics, Ring-Polymer Molecular Dynamics (RPMD) has focused the interest of researchers from many different theoretical fields. Firstly used to reproduce time correlation functions [1] and the rate of chemical reactions[2], RPMD has been connected to the instantons formalism [3] and used to describe nonadiabatic dynamics [4] with the support of mapping approach [5]. This allow us to use a set of continouos (i.e. classical) variables to approximately describe the evolution of a quantum system.

In the Nonadiabatic RPMD (NRPMD), the Hamiltonian can be written as

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + U_N(\mathbf{x}) + \frac{1}{2\Lambda}\sum_{i=1}^{N}\sum_{\alpha=1}^{\Lambda} X_{i\alpha}^T V(x_i) X_{i\alpha} + P_{i\alpha}^T V(x_i) P_{i\alpha} - \mathrm{tr} V(x_i) \tag{1}$$

where $\mathbf{p}$ and $\mathbf{x}$ are the momentum and position vectors of the RP beads with elements p_i and x_i; $X_{i\alpha}$ and $P_{i\alpha}$ are the electronic mapping variables vectors, which contain the positions and the momentums components of all the PES involved (usually two, i.e. $X_{i\alpha} = \{X_{i\alpha,0}, X_{i\alpha,1}\}$), while U_N is the RP potential.

In the classical ($N = 1, \Lambda = 1$) mapping variables methods, during the propagation the electronic system tends to exit from their physical subspace, namely the Single Excited Oscillators (SEO) subspace, leading to ambiguity and inaccuracy.

As shown in [6], the introduction of many mapping variables ($\Lambda \to \infty$) ensures that the system is initialized onto the correct SEO. We study the applicability and the accuracy of this method at longer times against a benchmark model for nonadiabatic phenomena, the two level, linear potential Hamiltonian. Special attention will be dedicated to dynamical effects, especially for electronic population statistics and for conservation of the classical phase-space Boltzmann distribution, $e^{-\beta \hat{H}}$, which represents a critical condition that NRPMD has to meet in order to produce reliable results.

This efforts are motivated by the lack of theoretical proofs about the behaviour of the NRPMD Hamiltonian in the long time limit.

[1] I. R. Craig, D. E. Manolopoulos, J. Chem. Phys. **121**, 3368 (2004).
[2] I. R. Craig, D. E. Manolopoulos, J. Chem. Phys. **122**, 084106 (2005).
[3] J. O. Richardson, S. C. Althorpe, J. Chem. Phys. **131**, 214106 (2009).
[4] J. O. Richardson, M. Thoss, J. Chem. Phys. **139**, 031102 (2014).
[5] G. Stock, M. Thoss, Phys. Rev. Lett. **78**, 578 (1997).
[6] J. O. Richardson, P. Meyer, M. Pleinert, M. Thoss, Chem. Phys. **482**, 124 (2017).