The Spin-Mapping RPMD, a new approach to study non-adiabatic dynamics

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ABSTRACT

In this presentation, we propose to present a Ring Polymer Molecular Dynamics (RPMD) method for non-adiabatic reactions. The RPMD methods present the advantage of mixed quantum-classical methods, by including quantum effects with a classical dynamics [1], hence having an advantageous numerical cost compared to exact calculations. This method, based on the isomorphism between the canonical partition function of a quantum system and the canonical partition function of a classical system in an extended phase space (representing the system as a fictitious ring polymer, its beads connected by classical harmonic springs) has been recently investigate in the case of non-adiabatic dynamics. Its most promising extension considers a mapping of the electronic states as continuous variables, a manner to treat on the same footing nuclear and electronic degrees of freedom. To this extent, the Meyer-Miller-Toss-Stock (MMST) [2-4] approach is usually used, based on the mapping of the electronic degrees of freedom onto position/momentum variables from the coherent states of the harmonic oscillator [5-6].

We present here a mapping onto the spin coherent states, the mapping variables being the angles projecting the spin states onto the Bloch sphere, based on the representation of the Hamiltonian on spin operator basis. This approach allows to work onto a basis of same size as the natural basis of the system [7], contrarily to the MMST approach which has a basis of larger size and requires further projections.
We derive spin-mapping RPMD partition functions and present position and population auto-correlation functions for standard 1D non-adiabatic models compared to exact results.

References

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