VISTA Seminar, April 26, 2023

Topic: A Mapping Approach to Surface Hopping

Presenter: Prof. Jeremy O. Richardson, Laboratory of Physical Chemistry, ETH Zurich, Switzerland

Summary:

In this presentation, a new approach was presented for nonadiabatic dynamics which is a combination of the Tully’s fewest switches surface hopping (FSSH) approach and the quasiclassical mapping called Mapping Approach to Surface Hopping (MASH). The presenter first showed the derivation of MASH which from the exact quantum mechanics theory and the quantum-classical Liouville equations.

The similarity of MASH and FSSH is that it popagates the nuclear wavepacket on the active adiabatic potential energy surface but the transition between these surfaces happens when the electronic mapping variables evolve on the nonadiabatic coupling regions of the electronic phase space.

The derivation of this approach helps to a rigorous prescription for momentum rescaling and frustraded hops. The presented framework helps for deriving the approximate decoherence corrections which is one of the main issues in surface hopping where cross terms in the wavefunction expansion in the Born-Oppenheimer approximations are ignored and the wavepackets are collapsed onto one surface. One of the issues that the presenter bolds for decoherence corrections is the huge number of these schemes presented by the quantum dynamics community for surface hopping.

The presenter explained that their method, MASH, includes decoherence inherently. After showing the derivation procedure, which is very specific with some complicated mathematical formulas, the application of MASH to famous quantum dynamics problems is shown. In fact, MASH is based on spin mapping and maps the spin-sphere into distinct regions which each of them corresponds to an adiabatic surface. These problems are spin-boson models, Tully model problems, and Marcus theory. The presenter shows a comparison of MASH with FSSH and Ehrenfest dynamics. MASH showed comparable results to FSSH and was better than Ehrenfest dynamics. However, the presenter told that their method is only applicable to two-level systems but it will be generalized to three-level systems soon. One of the thing that other attendees asked was about why they did not add decoherence corrections to their methods and the response of the presenter was “which one should we use among the zoo of decoherence schemes?” and that answer was kind of satisfying but not quite a lot. This question from the attendees arose because even though their method was able to capture the Marcus theory well but it wasn’t exactly the same and the presenter agreed with the ones who questioned that and said that we expect that this problem will be solved if we can include the decoherence correction to it.

Another point that the presenter was talking about was MASH can finally turn into one global approach for surface hopping and replace FSSH. One of the attendees however, disagreed and said one approach to work for different model problems may not be possible. One of the other questions was about the computational cost of the presented method which the presenter told that the computational time is comparable to FSSH which I guess that this method is slower than that since he used the word “comparable”. Overall, this meeting was a challenging meeting where many questions were asked and answered.