



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich
Laboratorium für Physikalische Chemie

Einladung zu einem Kolloquium Hörsaal HCI J 3 ETH Zürich, Höggerberg

Datum/Zeit: **Dienstag, 29. November 2016, 16.45 Uhr**

Referent: **Prof. Jiri Vaníček**
Laboratory of Theoretical Physical Chemistry LCPT, EPFL,
Schweiz

Thema: **On-the-fly ab initio semiclassical dynamics for computing
vibrationally resolved electronic spectra**

Although many processes in nature exploit the quantum properties of both electrons and nuclei, until recently, the expression “ab initio molecular dynamics” has been typically used for methods using quantum mechanics only for electrons and treating the nuclear motion on electronic surfaces classically. Unfortunately, a full quantum dynamical simulation is difficult because the exact solution of the time-dependent Schrödinger equation scales exponentially with the number of atoms, and, accelerating computers even by orders of magnitude will not break this exponential barrier. In my talk, I will discuss the so-called on-the-fly ab initio (OTF-AI) semiclassical dynamics, a promising approach to address this exponential problem because the nuclear quantum effects are included at least approximately and the electronic structure is evaluated only where needed.

First, I will mention several efficient methods that simplify the quantum molecular dynamics problem by answering the following questions:

- 1) How many coupled electronic potential energy surfaces are required? [1]
- 2) Are these surfaces accurate not only “statically” but also “dynamically”? [2]
- 3) Can semiclassical dynamics be even cheaper than classical dynamics? [3]
- 4) Can semiclassical methods be systematically improved? [4]

I will illustrate these on photodissociation and time-resolved stimulated emission spectra.

In the second part, I will describe an OTF-AI implementation [5, 6] of Heller’s thawed Gaussian approximation (TGA) [7]. Despite its simplicity, the accuracy of the OTF-AI-TGA is sufficient to reproduce almost perfectly the experimental emission spectra of oligothiophenes with up to 105 vibrational degrees of freedom. To test its limitations, we applied the method to absorption and photoelectron spectra of ammonia—a prototype of floppy molecules, whose potential energy surfaces display strong anharmonicity. Finally, I will show how one can use a single semiclassical trajectory to obtain information about the importance of dynamical coupling between different vibrational degrees of freedom. This method allowed us to explain how the vibrational line shapes of the oligothiophenes change with an increasing number of rings.

- [1] T. Zimmermann and J. Vaníček, *comm.*, *J. Chem. Phys.* **132**, 241101 (2010).
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[3] C. Mollica and J. Vaníček, *Phys. Rev. Lett.* **107**, 214101 (2011).
[4] M. Šulc, H. Hernández, T. J. Martínez, and J. Vaníček, *J. Chem. Phys.* **139**, 034112 (2013).
[5] M. Wehrle, M. Šulc, and J. Vaníček, *J. Chem. Phys.* **140**, 244114 (2014).
[6] M. Wehrle, S. Oberli, and J. Vaníček, *J. Phys. Chem. A* **119**, 5685 (2015).
[7] E. J. Heller, *J. Chem. Phys.* **62**, 1544 (1975).

Gäste sind willkommen.

Nach der Veranstaltung laden wir Sie herzlich zu einem Apéro ein.