VISTA Seminar

Seminar 14

March 17, 2021

9:30 – 11:00 am EDT / 1:30 – 3:00 pm GMT / 2:30 pm – 4:00 pm Paris

TOC:

Zombie Cats on the Quantum-Classical Frontier

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In this talk we revisit a simple problem from a fundamental perspective: the nuclear evolution of an initially prepared quantum coherence between two uncoupled electronic states. This is the iconic Schrodinger's Cat problem realized in a molecular system. We consider a simple model of two electronic states each with a harmonic one-dimensional vibrational potential. These potentials are shifted with respect to each other and possess frequencies that are different in general. We study the problem using the Wigner-Moyal formalism in both the exact and semiclassical limit. It is well-known that quantum dynamics on a single potential surface in the Wigner representation correspond to purely classical evolution of the Wigner function. The coherence between two such states, however, not purely classical. Despite this the exact dynamics of the electronic coherence in the Wigner representation can be analyzed analytically. In particular, a ``thawed Gaussian'' ansatz in phase space for the coherence is an exact representation, and the equations of motion for the parameters are closed due to the truncation of the Moyal expansion after the first nonclassical term for the harmonic case. A beautiful picture emerges from the perspective of Schrodinger's cat: the simultaneously alive and dead cats of the exact quantum dynamics become a ``zombie'' cat in the semiclassical limit – an averaged behavior, neither alive nor dead. As well as being an amusing but accurate metaphor, this perspective directly illustrates the well-known and experimentally observable errors of the semiclassical approximation in its application to dynamics and spectroscopy.
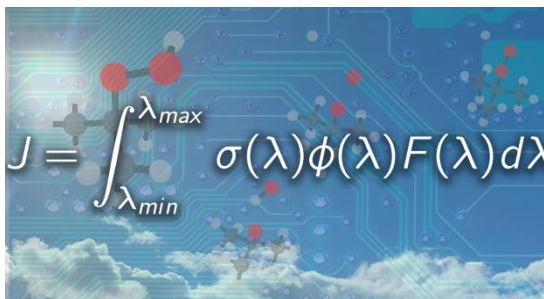
In silico determination of photolysis rate constants for transient atmospheric molecules

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Volatile organic compounds (VOC) are ubiquitous atmospheric molecules which generate a complex network of chemical reactions in the troposphere, often triggered by absorption of sunlight. Since the short lifetime of some transient VOCs poses significant challenge for accurate experimental and spectroscopic measurements, there is an urgent need for predictive computational approaches to study VOC, in particular when it comes to their photochemistry and photophysics.

Here, we show how recent advances in computational photochemistry allow us to calculate *in silico* photolysis rate constants.[1] Such rate constants are utilized in general atmospheric models used to predict the accurate composition of atmosphere but are often not experimentally available for transient VOCs. Photolysis rate constants depend on three key pieces of information: the flux of the radiation source, the absorption cross section of the molecule and the wavelength-dependent photolysis quantum yield. We show how one can evaluate the sought-for ingredients – and consequently the corresponding photolysis rate constants – by combining state-of-the-art electronic structure methods (XMS-CASPT2) and nonadiabatic molecular dynamics methods (surface hopping). We carefully compare the different strategies available to determine *in silico* absorption cross-sections and wavelength-dependent quantum yields, allowing us to propose error bars for the computational results. We benchmark our protocol with the photolysis of *tert*-butyl hydroperoxide, a compound for which reliable experimental data are available.[2] The protocol proposed here can be straightforwardly extended to account for hot ground-state reactivity following nonradiative decay or reactions involving intersystem crossing processes.

References:

[1] A. Prlj, L. M. Ibele, E. Marsili and B. F. E. Curchod, *J. Phys. Chem. Lett.* **11**, 5418 (2020).
[2] M. Baasandorj, D. K. Papanastasiou, R. K. Talukdar, A. S. Hasson and J. B. Burkholder, *Phys. Chem. Chem. Phys.* **12**, 12101 (2010).

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