Mathematical questions of quantum dynamics

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15:30 – Loïc Joubert Doriol

Title: Understanding and accounting for geometric phase effects in direct dynamics near conical intersections

Abstract: The Born-Oppenheimer approximation is at the origin of our understanding of numerous chemical processes. Going beyond this approximation becomes necessary when potential energy surfaces approach each other or cross. Very frequently, such crossings have a conical topography and are therefore named conical intersections (CIs). CIs play a central role in photochemical phenomena by allowing radiationless electronic transitions. It has also been known that electronic states participating in a CI acquire an additional phase, known as the Berry or geometric phase (GP), when they are transported along a close path encircling a CI. We considered two questions associated with GP: 1) How does GP affect molecular dynamics? and 2) How one can include GP in quantum dynamics simulations?

To address the first question, we systematically explored the impact of GP on the dynamics of model systems in different regimes, and then searched for molecules representing interesting model regimes. It was found that in low energy dynamics, GP slows down tunnelling processes, and in excited state dynamics, GP enhances radiationless transitions between electronic states [1].

The second question poses a problem because construction of Hamiltonian models becomes too cumbersome or even impossible for large molecules. However, the understanding obtained in studying model problems led us to a new approach that naturally accounts for GP in simulations without resorting to a Hamiltonian model [2].

References:

[1] I. G. Ryabinkin, L. Joubert-Doriol, and A. F. Izmaylov, *Acc. Chem. Res.* **50**, 1785 (2017)

[2] L. Joubert-Doriol, J. Sivasubramanium, I. G. Ryabinkin, and A. F. Izmaylov, *J. Phys. Chem. Lett.* **8**, 452 (2017); L. Joubert-Doriol and A. F. Izmaylov, *J. Chem. Phys.* **148**, 114102 (2018)