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Electron-Nuclear Correlation: A Time-Dependent Perspective

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The Born-Oppenheimer (BO) approximation is widely employed to account for the electron-nuclear correlation when describing dynamical processes in molecular systems. It relies on the assumption that the typical time-scales of electronic and nuclear motion in a molecule are *adiabatically* separable. This hypothesis allows to write the full electron-nuclear wave function as a single product of an electronic eigenstate, for each fixed nuclear configuration, and a time-dependent nuclear wave function. Such an approximation is fundamental for our understanding of molecular processes. However, it is not suited when non-adiabatic effects due the coupling between the nuclear motion and excited electronic states become important, that are essential to understand phenomena such as vision, photovoltaic processes and Joule heating in molecular junctions.

The talk will show how the BO approximation can be made exact [1], by preserving the single product form of the full electron-nuclear wave function and accounting for electronic excitations. This *exact factorization* approach will be introduced and used as a tool [2] to interpret non-adiabatic processes beyond Ehrenfest dynamics [3], i.e. the uncorrelated product Anstatz for the electron-nuclear molecular wave function. Furthermore, algorithms will be derived [4, 5, 6] to describe electronic non-adiabatic processes employing a description of nuclear dynamics in terms of classical trajectories. Applications to model systems [4, 5] and to small molecules [6] will be presented to numerically validate such quantum-classical scheme.

References:

1. A. Abedi, N. T. Maitra and E. K. U. Gross, *Phys. Rev. Lett.,* **105**, 123002 (2010).
2. A. Abedi, F. Agostini, Y. Suzuki and E. K. U. Gross, *Phys. Rev. Lett.,* **110**, 263001 (2013).
3. F. Agostini, A. Abedi, Y. Suzuki, S. K. Min, N. T. Maitra and E. K. U. Gross, *J. Chem. Phys.*, **142**, 084303 (2015).
4. F. Agostini, A. Abedi and E. K. U. Gross, *J. Chem. Phys.*, **141**, 241101 (2014).
5. S. K. Min, F. Agostini and E. K. U. Gross, *Phys. Rev. Lett.,* **115**, 073001 (2015).
6. A. Scherrer, F. Agostini, D. Sebastiani, E. K. U. Gross and R. Vuilleumier, *J. Chem. Phys.*, **143**, 074106 (2015).