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Towards ab-initio Molecular Dynamics without Born-Oppenheimer Potential-Energy Surfaces

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The correlated motion of electrons and ions is a challenging problem yet one that is increasingly topical due to the advent of experimental techniques that allow to visualize the "molecular movie". Theoretical methods mostly rely on the Born-Huang expansion of the molecular wavefunction. Hence, the concepts of Born-Oppenheimer potential-energy surfaces (BOPES) and nonadiabatic couplings
(NAC) arise naturally, suggesting the picture of a nuclear wavepacket evolving on many static BOPESs. This approach is, however, very expensive due to the computational costs associated to the calculation (and parametrization) of all BOPESs and NACs involved in the dynamics.

We propose an alternative approach to molecular dynamics based on the use of conditional wavefunctions [1]. The exact electron-nuclear dynamics is described by means of an ensemble of single, time-dependent, potential energy surfaces (C-TDPESs) that drive each component of the total wavefunction. While keeping the theory at the full configuration level, this approach allows for the use of trajectory-based techniques to circumvent the calculation of the BOPESs and NACs, and allows to draw clear connections between different exact frameworks [2]. We have investigated features of the C-TDPESs in the presence of strong nonadiabatic couplings and proposed a universal mechanism for the explanation of quantum nonadiabatic effects [3]. The paradigm shift associated with the transition from the many static BOPESs to the single time-dependent potentials can open new avenues in the understanding of quantum dynamics. Furthermore, the combination of the CD approach with the inherent scalability of other techniques such as TDDFT could lead to a breakthrough in the efficiency of ab-initio molecular dynamics methods.

[1] G. Albareda et al., Phys. Rev. Lett. 113, 083003 (2014).
[2] G. Albareda et al., J. Phys. Chem. Lett. 6, 1529 (2015).
[3] G. Albareda et al., arXiv:1512.08531 (2015).

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