

# Adiabatic and nonadiabatic dynamics with conditional wave functions

Guillermo ALBAREDA

Departament de Química Física. Universitat de Barcelona

I will present an exact trajectory-based scheme to decompose the coupled electron-nuclear motion in terms of conditional wave functions<sup>1</sup>. By projecting the time-dependent Schrödinger equation on the configuration of an ensemble of generally defined trajectories, non-unitary equations of motion for the nuclei (or electrons), that depend parametrically on the electronic (or nuclear) degrees of freedom can be obtained. These equations do not rely on tracing-out degrees of freedom and no prior knowledge of Born-Oppenheimer potential-energy surfaces nor of the nonadiabatic couplings is required. By choosing the trajectories to be quantum (Bohmian) particles, the formulation acquires an additional interpretative value. Remarkably, for this particular choice, the resulting propagation scheme does not require the computation of the quantum potential, in this way overcoming one of the main difficulties of sampling approaches based on the quantum Hamilton-Jacobi equation<sup>2</sup>.

The above formalism can be made specific for adiabatic dynamics by tracing out electronic degrees of freedom and taking the Born-Oppenheimer limit. The evolution of the N-body nuclear wave function moving on a 3N-dimensional Born-Oppenheimer potential-energy hyper-surface is then rewritten in terms of single-nuclei wave functions evolving nonunitarily on a 3-dimensional potential-energy surface<sup>3</sup>. The use of conditional wave functions can be then exploited to circumvent the calculation and storage of many-body quantities (e.g., wave function and potential-energy surface) whose size scales exponentially with the number of nuclear degrees of freedom.

As a proof of concept, we present numerical results for both adiabatic and nonadiabatic molecular dynamics of a 2-dimensional model porphine<sup>4</sup> and the Shin-Metiu<sup>5</sup> model respectively.

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