

Development of a SHARC-DALTON Interface to Study Excited-state Dynamics of DNA Photosensitization

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Fast intersystem crossing (ISC) mechanisms occurring in organic molecules have been extensively studied in the last decades, especially by time-resolved experimental techniques [1,2]. Nevertheless, it is only in the last years that reliable computational methods were developed in order to study the dynamical details of such processes [3,4]. At this purpose, the SHARC (Surface Hopping including Arbitrary Couplings) code was recently developed by the González group at the University of Vienna, as an *ab initio* molecular dynamics (MD) software package devoted to the excited-state dynamics of molecules [5]. Especially, the SHARC code has interfaces to MOLPRO, MOLCAS and COLUMBUS *ab initio* programs.

One of these interfaces (SHARC-MOLCAS) was recently used by the applicant in order to study at the multiconfigurational level of theory (CASSCF [6]) the mechanism of ultrafast triplet population in benzophenone (BP), a paradigmatic organic molecule for photosensitization [7].

Nevertheless, if a molecular system of larger size is studied, the time dependent - density functional theory (TD-DFT) is nowadays one of the most reliable methods, overcoming the too high computational expenses of the multiconfigurational approach. Accordingly, the SHARC code should be interfaced with a program that can provide the required TD-DFT properties (energy, gradients, spin-orbit couplings) to perform MD.

Among the available TD-DFT suites of programs, the DALTON code [8] was selected for its capability to calculate efficiently the necessary spin-orbit couplings between excited states and the versatility of the (free distributed) code. Indeed, at the Université de Lorraine the Monari's group is presently developing a DALTON-AMBER interface in order to include the effects of complex environments (solvent, proteins, DNA [9]) by hybrid quantum mechanics/molecular mechanics calculations, hence potentially obtaining a SHARC-DALTON-AMBER interface.

In the framework of a project describing photoinduced processes as energy transfer and hydrogen-abstraction between BP and the thymine base pair (Thy) of DNA, promising mechanistic descriptions (*i.e.* minimum energy paths not including dynamics) were obtained at the TD-DFT level of theory [10,11].

Indeed, BP is a fundamental photosensitizer to investigate DNA lesions [12], and therefore the development of a SHARC-DALTON interface can finally make possible the study of the excited-state dynamics mechanisms. This will provide crucial data, as the reaction time scale and the quantum yield.

More in general, the SHARC-DALTON interface will supply a valuable tool to study the excited-state of complex molecular systems, allowing to get insights into bio-molecular complex functions and materials properties.

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