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

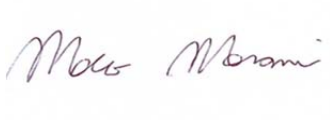
SCIENTIFIC REPORT

Dr Marco Marazzi
Université de Lorraine - Faculté des Sciences et Techniques
UMR 7565, SRSMC Théorie-Modélisation-Simulation
Nancy, France

Subject: Short Term Scientific Mission
Reference: COST Action CM1405
Host institution: Institute of Theoretical Chemistry, University of Vienna
Period: 22/02/2016 to 12/03/2016
Reference code: COST-STSM-ECOST-STSM-CM1405-220216-071273

During the short stay at the group of Prof. Dr. Leticia González in the University of Vienna, the following tasks were performed:
- As first, a TD-DFT benchmark of the complex benzophenone (BP)-DNA was performed, applying functionals available in the DALTON package (PBE0, BLYP, B3LYP and CAM-B3LYP). Both BP-DNA binding modes (double insertion and minor groove binding) were taken into account, using the structures optimized along a simplified reaction coordinate in a previous study (Dumont, E.; Wibowo, M.; Roca-Sanjuán, D.; Garavelli, M.; Assfeld, X.; Monari, A. J. Phys. Chem. Lett. **2015**, *6*, 576–580.). More in detail, a first test was conducted on a minimal model (i.e. BP and the nearest guanine) in vacuum. Subsequently, the electrostatic environment was included by using the QM/MM module available in DALTON. The CAM-B3LYP was found to be the most suitable functional, as compared to the CASPT2 and RASPT2 results given in the mentioned publication.
- Because of the present limitations encountered in the DALTON code, three different possibilities were explored to build the most suitable and reliable SHARC-DALTON interface:
1) Build an interface by that SHARC can read the excited-state energy gradients from Linear Scaling (LS) DALTON and the Spin-Orbit Coupling (SOC) matrix elements from DALTON2016 (see http://www.daltonprogram.org/);
2) Build an interface that includes only the newer LS-DALTON code through the OpenRSP project, presently under development by the DALTON group and, since March 2016, by the groups of Antonio Monari and Leticia González. Indeed, OpenRSP would allow the open-ended calculation of response properties (see http://openrsp.readthedocs.org/en/latest/), as the required excited-state transition dipole moments and SOC elements;
3) Build an interface that will read only the excites-state energy gradients from LS-DALTON, while the SOC elements are calculated by an external SHARC module, as suggested by Dr. Felix Plasser in Vienna.
Option 1 was found to be the less efficient, since two calculations per trajectory time-step are required. Moreover, since LS-DALTON and DALTON2016 are two separate codes, small numerical differences can give rise to energy conservation instabilities. Option 2 can solve the problems found in option 1. TD-DFT energy gradients were already tested by the grantee within the OpenRSP project. Additional work is ongoing to obtain the SOC elements as an OpenRSP tool. Option 3 is in principle valid as option 2. Moreover, it could make SHARC independent of the particular quantum mechanics code for the extraction of the SOC elements. In the technical point of view, all the modules required by SHARC to call LS-DALTON and/or OpenRSP are now available.
Also, the first QM/MM dynamics tests between LS-DALTON and AMBER were successfully conducted in order to include the electrostatic embedding in the SHARC-DALTON interface.

Nancy, 22/03/2016



(Dr. Marco Marazzi)

Confirmation of the host of the successful execution of the STSM

I confirm that Marco Marazzi from Université de Lorraine worked in our laboratories at the University of Vienna from 22/02/2016 to 12/03/2016.
The visit has been successful and the results obtained are described above.

(Prof. Dr. Leticia González)