Assessment of the PhD thesis:

"Ab initio molecular dynamics with non-adiabatic and spin-orbit effects applied to time-dependent fluorescence"

submitted by

Marek Pederzoli

Supervisor:
Dr. Jirí Pittner (Charles University)

The thesis presented by the PhD candidate Marek Pederzoli is based on a compendium of four international peer-reviewed publications on the field of non-adiabatic dynamics and applications. The four papers deal with different development advances that will enrich the Newton-X non-adiabatic program package, as well as four applications of different complexity, from gas phase to complex environments. On the development side, the candidate has extended the simulation of non-adiabatic dynamics to use several single-reference quantum chemical methods, to include spin-orbit couplings, and to bypass the calculation of non-adiabatic couplings via wavefunction overlaps.

The thesis is composed of five chapters. After a brief preface to the field of molecular modelling, chapter 2 presents the main methodological aspects of non-adiabatic molecular dynamics the candidate dealt with, with emphasis on the inclusion of spin-orbit, and using
embedding approaches to deal with excitations of a chromophore within an environment. This chapter is succinct and written in a very general form, which in some cases lacks formalism, e.g. the nomenclature of wavefunctions is not uniform (compare the electronic wavefunction of eq. 2.4, 2.6 and 2.9). Chapter 3 introduces the general concepts of fluorescence spectroscopy, lying the foundation of the physical concepts the applications deal with, chapter 4 summarizes the work of the four papers of the applicant and chapter 5 concludes.

In paper I, the candidate presents surface-hopping simulations of 9H-Adenine using ADC(2) in gas phase, after arguing why CC2 and TD-DFT are lesser suitable quantum chemical methods for this task. The simulations show that C2 deformations are the main deactivation channel in the dynamics, providing kinetics in good agreement to the experimental values. This paper in an application of the implementation of CC2, ADC(2) and TD-DFT dynamics within Newton-X, using wavefunction overlaps as an estimation of non-adiabatic couplings.

In paper II, a dynamical study of thiophene and selenothiophene is presented, where both non-adiabatic and spin-orbit couplings are included. As shown in the literature, dynamics including spin-orbit couplings is more convenient to be done in the diagonal or spin-mixed representation and this paper proposes an improvement of the original 3-step propagator scheme proposed in SHARC, a program that pioneered the calculations of non-adiabatic dynamics including spin-orbit couplings. The calculations of thiophene and selenothiophene, both in gas phase and solution, nicely show the importance of including spin-orbit couplings in the modeling of photophysics.

Paper III details a QM/MM study of the absorption spectrum of PRODAN, a fluorescence probe, in water. To this aim, different models including up to 5 explicit water molecules and 300 classical waters are tested. The best agreement is achieved when a polarizable force field is employed, demonstrating that solvent polarization effects are necessary to describe PRODAN excited states in water.

Paper IV deals with another fluorescence probe, LAURDAN, a derivative of PRODAN. The aim was to calculate its absorption and emission spectra upon insertion in a lipid bilayer membrane. The results show that the probe is not drastically affected by the environment.

The four papers illustrate the very broad education and impressing maturity
reached by Mr. Pederzoli, who has touched very different aspects of non-adiabatic dynamics, from development to application, from gas phase to solution and bio-environments simulations, and from the command of advanced ab initio methods to classical molecular dynamics.

Additional to the papers presented, the candidate has developed a gradient selection method to ease the application of the spin-mixed representation, which is not detailed in the thesis, and has simulated the light-driven dynamics of 2,4-dithiothymine and 2-thiouracil, also not presented in the thesis.

The developments achieved within this thesis represent important advances in the field, and foremost broad the application of the program package Newton-X. The thesis is in general very well written and it shows that an excellent theoretical background on non-adiabatic dynamics has been acquired by the candidate. Thus, Mr. Pederzoli is prepared to undertake research independently and I recommend this doctoral thesis for oral examination.

Fazit: I recommend without any restriction this doctoral thesis for the degree of Doctor of Philosophy of the Charles University of Prague.

Prof. Dr. Dr. h.c. Leticia González