Ultrafast photodynamics simulations with *ab initio* multiple cloning approach

D.V. Makhov[a,b] and D.V Shalashilin[a]

[a] *School of Chemistry, University of Leeds,* [b] *School of Mathematics, University of Bristol*
d.makhov@leeds.ac.uk

We present the recent developments and applications of our *ab initio* multiple cloning (AIMC) method [1,2]. The idea of the method is to run non-adiabatic molecular dynamics on the fly using the basis of Gaussian coherent states moving along branching Ehrenfest trajectories thus combining some best features of Multiple Spawning [3] and Ehrenfest approaches [4].

We apply AIMC method to simulate processes of ultrafast photodynamics in a number of molecular systems. In particular, we have performed extensive simulations [5,6] of the photodissociation dynamics for various heterocyclic amines, such as pyrrole, imidazole, pyrazole, 2-ethylpyrrole, *etc* along with their selectively deuterated species. Our calculations reproduce well the main features of experimental TKER spectra and VMI images, as well as dissociation times and isotope effects, providing detailed insights into the experimental results.

Another area of our simulations is the intramolecular energy transfer in light-harvesting dendrimers. We have run AIMC simulations of the excitation dynamics for a set of different combinations of a chain of linked dendrimer building blocks [7]. The calculations show that the efficiency of the energy transfer strongly depends on the way how multiple chromophoric units have been assembled. The comparison between the results of AIMC and Ehrenfest dynamics demonstrates the importance of the wave function bifurcation in the case of larger dendrimers, which is accounted by the cloning procedure in the AIMC approach.

References

1. D.V. Makhov, W.J. Glover, T.J. Martinez, D.V. Shalashilin , J. Chem. Phys. **141** (2014), 054110.
2. D.V. Makhov, K. Saita T.J. Martinez, D.V. Shalashilin, Chem. Phys. **493** (2017), 200.
3. M. Ben-Nun and T. J. Martinez, Adv. Chem. Phys. **121** (2002), 439.
4. D. V. Shalashilin, Faraday Discuss. **153** (2011), 105.
5. J.A. Green, D.V. Makhov, N.C. Cole-Filipiak, C. Symonds, V.G. Stavros, D.V. Shalashilin, Phys. Chem. Chem. Phys., **21** (2019), 3832.
6. C. Symonds, D.V. Makhov, N.C. Cole-Filipiak, J.A. Green, V.G. Stavros, D.V. Shalashilin, Phys. Chem. Chem. Phys., **21** (2019), 9987.
7. V.M. Freixas, D. Ondarse-Alvarez, S. Tretiak, D.V. Makhov, D.V. Shalashilin , S. Fernandez-Alberti, J. Chem. Phys. **150** (2019), 124301.