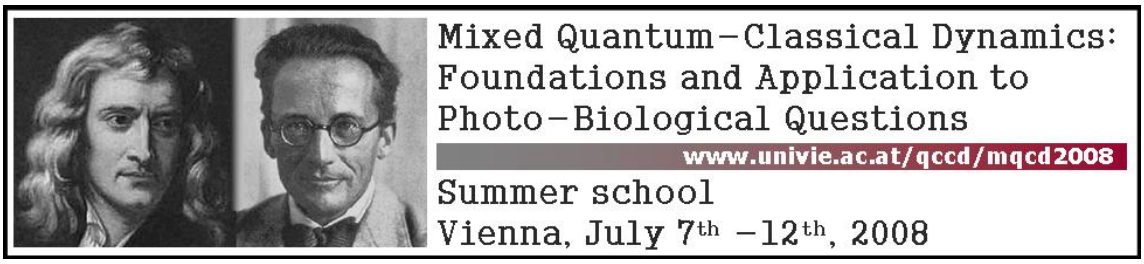
SCIENTIFIC REPORT



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1. Summary

Processes occurring in the excited states of organic molecules are of fundamental importance for photochemistry and photobiology underlying phenomena that range from the stabilization of nucleic acids to the molecular mechanism of vision. With the development of femtosecond spectroscopy, simulations of dynamics on multiple potential energy surfaces become a valuable tool for understanding such complex phenomena. Nevertheless, this kind of simulations applied to systems of biological interest is a new area still under development. While the simulation of ground state dynamics is well established, excited-state dynamics can be considered as the next frontier in the advances of the computational chemistry and it is at this point that this Summer School stands.

The purpose of the School has been to help forming a new generation of researchers able to apply the mixed quantum-classical dynamics (MQCD) methods to photo-chemical and photo-biological investigations. The School aimed at graduate students and researchers already holding some basis on quantum chemistry.

The programme of the School combined lectures on several methodological and phenomenological topics with intensive practical computational training. The computational training was projected as to present coherently all major steps during dynamics simulations. They were also planned to enforce the concepts discussed during the lectures. Extensive tutorials were written as support material for the School.

The School counted on a team of speakers of exceptional level, allowing the students to have direct contact with the developers of programs and methods. Among the speakers are developers of the program packages COLUMBUS (H. Lischka), CHEMSHELL (P. Sherwood), NEWTON-X (M. Barbatti), and GROMACS (G. Groenhof). The developer of some of the most important MQCD methods – the Fewest-Switches Surface Hopping (J. C. Tully) – lectured as well.

Forty nine people attended the Summer School; most of them graduate students (49%) and postdoc researchers (29%) from European universities (86%). A number of American students (4) also attended the School in the framework of the NSF-PIRE project, which co-sponsored the event. The number of female participants was 20%.

2. Description of the scientific content of and discussion at the event

Four major topics have been discussed during the School: (i) photochemistry phenomenology and ultrafast processes, (ii) mixed quantum-classical dynamics approaches, (iii) quantum chemistry methods for excited states, and (iv) hybrid methods and environmental effects. These topics were chosen as to consistently provide a global view of the current status and challenges in the field.

Photochemistry phenomenology

The solar radiation as the primary energy source left several fundamental marks in the evolutionary history of the Earth. Most different organisms have used this radiation not only to activate their own metabolic processes, but also to collect information about the environment and protect themselves against photochemical degradation. The initial step in these processes commonly involves the photo-activation of particular chromophore sites of proteins and nucleic acids. The photo-activation results in molecular transformations that end up in the conversion of the excess of electronic energy either into mechanical energy, electrical signal, or into photon emission. Nowadays, these processes can be monitored at the femtosecond time-scale through experiments that heavily rely on theoretical modeling to interpret the raw lab data. During the Summer School, these topics related to the phenomenological aspects of photochemistry were addressed from a theoretical point of view by Hans Lischka in his first lecture (L1 in Table I). Moreover, they also underlay most of other lectures, especially that held by Gerrit Groenhof (L10). The experimental point of view with emphasis on time resolved spectroscopy was brought by Werner Fuss (L5 and L11).

Table I – Summary of the lectures during the MQCD 2008 Summer School.

	Lecturer	Topic	Field
L1	H. Lischka	Photochemistry and non-adiabatic phenomena	Photochemistry
L2	J. C. Tully	Mixed quantum-classical dynamics I: Fundamentals	MQCD
L3	H. Lischka	Multireference methods and non-adiabatic effects	Quantum chemistry
L4	M. Elstner	TD-DFT and TD-DFTB methods for excited states I	Quantum chemistry
L5	W. Fuss	Driving forces and momentum effects in photochemistry	Photochemistry
L6	J. C. Tully	Mixed quantum-classical dynamics II: Methods	MQCD
L7	M. Elstner	TD-DFT and semiempirical methods for excited states II	Quantum chemistry
L8	M. Barbatti	Pratical aspects in MQCD implementation	MQCD
L9	P. Sherwood	QM/MM I: classification of schemes and practical aspects	Hybrid methods
L10	G. Groenhof	Excited-state CASSCF/Force-field simulations	Hybrid methods
L11	W. Fuss	Dark states in photochemistry	Photochemistry
L12	P. Sherwood	QM/MM II: specialized approaches and recent developments	Hybrid methods
L13	I. Burghardt	Enviromental effects on a conical intersection I: models	Hybrid methods
L14	P. Slavíček	The Full Multiple Spawning	MQCD
L15	I. Burghardt	Enviromental effects on a conical intersection II: dynamics	Hybrid methods
L16	M. Persico	Open problems in MQCD methods	MQCD
L17	M. Persico	MQCD with semiempirical methods	MQCD

Mixed Quantum-Classical Methods

In the last years, theoretical investigations on excited-state processes have established themselves as fundamental for a deeper understanding of photo-biological processes. For the theoretician, this field is challenging, since the most advanced methods of quantum chemistry must be employed. Moreover, since time is an intrinsically important variable in these phenomena, conventional static approaches can only provide a very limited amount of information and dynamics simulations on excited states are an essential step. This is only now becoming feasible with present computational capabilities.

The ideal scenario would be to perform complete time-dependent quantum mechanical treatment of the systems. Such an approach is, however, applicable only to a very restricted subset of nuclear coordinates. MQCD approaches, in which the nuclear degrees of freedom are treated classically whereas the electrons are treated quantum mechanically, represent an effective gain in terms of reduction of computational effort in comparison with the full quantum-mechanical methods.

The methodological aspects of the MQCD approaches were the subject of the lectures by John C. Tully (L2 and L6). Open problems and recent advances in these methods were discussed by Maurízio Persico in one of his lectures (L16). Practical aspects of the implementation of the MQCD methods were addressed by Mario Barbatti (L8). The Full Multiple Spawning method was presented by Petr Slaviček (L14) and the wave packet approach (MCTDH) was addressed by Irene Burghardt in her first lecture (L13).

Quantum chemistry for excited states

The cost of computing excited-state properties is the main bottleneck for the MQCD simulations. Moreover, the method should allow the analytical computation of energy gradients and non-adiabatic coupling vectors at multi-reference level. Unfortunately, there is no ideal method that conjugates all these features, thus making the decision about which method to use dependent on each particular case. These topics were addressed in the lectures about TD-DFT and TD-DFTB methods held by Marcus Elstner (L4 and L7), in the second lecture about multi-reference methods held by Hans Lischka (L3), and in the lecture on semiempirical methods by Maurizio Persico (L17).

Environmental effects and Hybrid methods

Typical photochemical reactions proceed in specific environments (solvents, matrices, protein pockets) and, therefore, it is crucial to include their effect in the dynamics simulations. Since it is out of question to fully treat thousands of atoms, this is mainly done by means of hybrid methods, such as the QM/MM approach. The influence of the environment on the excited-state dynamics was discussed by Irene Burghardt in her second lecture (L15). The general principles of the QM/MM approach were explored by Paul Sherwood (L9), while advanced photo-biological applications conjugating MQCD and the QM/MM approaches were the subject of Gerrit Groenhof (L10) and of Maurizio Persico (L17). Recent developments in hybrid methods were discussed by Paul Sherwood (L12).

The computational training was projected as to present coherently all major steps during dynamics simulations. They were also planned to enforce the concepts discussed during the lectures. One single molecule was consistently used throughout the exercises. First, the students were first familiarized with excited-state calculations using the MRCI and MCSCF methods (PW1 and PW2 in Table II). The COLUMBUS program system was used. Following, they were tutored on initial conditions generation and spectrum simulations using the NEWTON-X program (PW3). After that, they carried out surface hopping dynamics at MCSCF level (PW4) and performed the statistical analysis of the results (PW5), again using the NEWTON-X program. Finally, they carried out full multiple spawning dynamics simulations at MCSCF level (PW6 and PW7), using the FMS and the MOLPRO programs.

Table II – Practical computational works during the Summer School.

	Subject	**Topic**	**Program**
PW1	Quantum chemistry	MCSCF calculations	COLUMBUS
PW2	Quantum chemistry	MRCI calculations	COLUMBUS
PW3	Surface hopping dynamics	Initial conditions and spectrum simulation	NEWTON-X/ COLUMBUS
PW4	Surface hopping dynamics	Dynamics simulations	NEWTON-X/ COLUMBUS
PW5	Surface hopping dynamics	Analysis of the dynamics results	NEWTON-X
PW6	Full multiple spawning	Dynamics simulations	FMS/MOLPRO
PW7	Full multiple spawning	Analysis of the dynamics results	FMS

3. Assessment of the results and impact of the event on the future direction of the field

- The MQCD 2008 Summer School provided advanced information on topics of quantum chemistry, non-adiabatic processes, and excited-state dynamics simulations to a public formed mainly by graduate students (Table III).

- The School has contributed to form a new generation of researchers able to apply new concepts and methodologies to photo-chemical and photo-biological investigations in a rigorous way.

- The practical training using specialized programs (COLUMBUS, MOLPRO, NEWTON-X) should teach the students the routine usage of non-black-box programs packages, resulting in an increased quality of the produced quantum-chemical data.

- Extensive tutorials for the COLUMBUS and NEWTON-X programs were written as support material for the School. They are now also available at the homepages of these programs.

- Slides and summaries of all lectures will remain available on-line at the Summer School homepage www.univie.ac.at/qccd/mqcd2008.

- The direct participation of researchers and students connected to the NFS-PIRE project (pire-europe.chem.ttu.edu) had the effect of strengthening inter-European (Vienna – Pisa – Santiago de Compostela) scientific collaborations as well as the collaborations between these European groups and the American groups at Yale, Iowa State, and Texas Tech Universities. Other collaborations are expected to have been strengthened as a result of the meeting.

Table III – Statistics on the participants of the Summer School (excluding the lecturers).

Participants	Total number	**49**
Qualification	Post doc / researcher / lecturer	14
	Graduate students	24
	Undergraduate students	11
Sex	Male	39
	Female	10
Origin	Europe (contributing countries)	35
	Europe (non-contributing countries)	7*
	America	4*
	Asia	3*

* Most of these participants were supported by other sources than the ESF funds. The number of participants from non-contributing countries funded by the ESF budget was restricted to 10% of the total.

4. Final programme of the MQCD 2008 Summer School

	Jul 7	Jul 8	Jul 9	Jul 10	Jul 11	Jul 12
9:00 – 9:45		L3. Lischka	L6. Tully	L9. Sherwood	L12. Sherwood	L15. Burghardt
9:45 – 10:30		L4. Elstner	L7. Elstner	L10. Groenhof	L13. Burghardt	L16. Persico
10:30 – 11:00		Coffee break				
11:00 – 11:45		L5. Fuss	L8. Barbatti	L11. Fuss	L14. Slavíček	L17. Persico
11:45 – 14:00		Lunch time				
14:00 – 16:00		PW1	PW3	PW5	PW6	
16:00 – 16:30	Registration	Coffee break			Coffee break	
16:30 – 18:00		PW2	PW4		PW7	
17:45 – 18:00	Opening					
18:00 – 18:45	L1. Lischka					
18:45 – 19:30	L2. Tully					

	Total time (h)
L – Lectures	13:00
PW – Practical computational work	12:30

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