Final Report

Workshop "Energy Flow Dynamics in Biomaterial Systems"
Paris Research Center
2-5 October 2007

Organizers:

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Web sites:

`http://www.chimie.ens.fr/UMR8642/Quantique/Workshop2007/`

`http://www.clas.ufl.edu/PRC/`

1. Summary

This workshop has been the second meeting of a prospective series of "PRC Workshops" held at the Paris Research Center (PRC) of the University of Florida. The first PRC workshop, on the topic of "Quantum Dynamics of Complex Molecular Systems", was held on May 18-20 2005, and was organized by I. Burghardt (ENS Paris) and D. A. Micha (University of Florida). This first workshop event attracted a considerable number of internationally renowned scientists and has led to the publication of a Proceedings volume in the Springer Chemical Physics series (Quantum Dynamics of Complex Molecular Systems, Eds. D. A. Micha and I. Burghardt, Springer (2006)).

This year's second PRC Workshop, held on October 2-5 2007, continues the general focus on quantum dynamical phenomena, but aims specifically to investigate the role of these phenomena in biological and nano-structured systems. The workshop thus aims to contribute to developing a unified theoretical picture of electronic excitation energy transfer in biological systems, molecular electronic materials, and biomemetic systems. To this end, the workshop has drawn together researchers from the following fields:

- Energy transport and quenching in DNA and light-harvesting systems
- Energy and charge transfer in organic materials and interfaces
- Quantum and mixed quantum/classical dynamics methods for processes in condensed phases, at surfaces, and in spatially extended systems
- Quantum chemistry of non-adiabatically coupled systems
- Time-resolved ultrafast spectroscopies and multidimensional techniques

The general orientation of the workshop was markedly interdisciplinary. While most of the participants were theoretical chemists, physicists and biologists, an important aim was to explicitly make contact to the experimental side. We have therefore invited several leading experimentalists in the field.

One of the distinguishing feature of this workshop was that we invited a number of the speakers to give more broad "overview" talks that would touch upon both their work and provide a unified background for the subsequent talks in that session. This proved to be a very stimulating approach when coupled with breakout sessions and social interactions at the Paris Research Center. Altogether, we had close to 50 participants from 9 countries, a number of whom were postdoctoral fellows and students of senior participants.

Finally, all participants are invited to contribute to a Proceedings volume to be published in Springer's notable "Lecture Notes in Physics" series and many participants have graciously uploaded the slides from their talk to the workshop's web page. We have further been invited to document the workshop event in an article for the Newsletter of the European Photochemistry Association (EPA).

2. Description of scientific content and discussion at the event

The scientific scope of the workshop was deliberately broad in terms of physical systems studied yet unified in the use of spectroscopic techniques, quantum dynamical methods, or a combination thereof to study transient and often ultrafast energy or charge transfer events in complex systems. By and large, the systems of focus by most of the participants were assemblies of conjugated organic polymers in light-emitting or photovoltaic cells or chromophores in biological systems such as light-harvesting complexes or DNA.

The meeting was structured into nine sessions:

- From molecular systems to biomaterials (Session 1.1)
- Dynamics in DNA and biomolecular systems (Session 1.2)
- Multidimensional spectroscopy and its applications (Session 1.3)
- Excited-state electronic structure and dynamics (Session 2.1)
- Quantum properties and dynamics in many dimensions (Session 2.2)
- Mixed quantum-classical methods (Session 2.3)
- Electronic dynamics in materials systems (Session 3.1)
- Energy transfer: Förster theory and beyond (Session 4.1)
- Molecular electronics (Session 4.2)

Each session was started with an overview talk and comprised two to three additional, shorter presentations. In addition, a poster session with brief oral presentations was part of the program. In the following, brief summaries of each session will be given; while these focus on the overview talks, the importance of all other contributions should be no means be diminished. We refer to the workshop schedule for the complete list of presentations.

The overview talk by Greg Scholes (University of Toronto) which started session 1.1, provided an excellent overview of how theoretical and experimental research has made subtle shift in paradigm over the past number of years. Previously, the role of theory has been to *explain* experimental results or to *predict* new effects. However, both experimental and theoretical techniques have advanced to the point that now experimentalists are beginning to design experiments that interrogate specific aspects of theoretical models.

Session 1.2 focused upon new experiments by Steve Bradforth (University of Southern California) and Dimitra Markovitsi (CEA) in probing how photoexcitations migrate and localize within DNA chains. One of the crucial issues at hand was how photoexcitations are quenched in DNA as to prevent photodamage leading to carcinogenesis. Does π-stacking or base-pairing determine the fate of an exciton in DNA?

Session 1.3 addressed new developments in the theory of multidimensional optical spec-

troscopy by Shaul Mukamel (University of California at Irvine) who is certainly the key developer of much of the theoretical tools used by ultrafast experimentalists in designing new multicolor experiments.

Peter Rossky's (University of Austin) overview starting session 2.1, entitled "Simulation of Condensed Phase Electronic Dynamics", focused upon the development of mixed quantum classical techniques and path-integral methods to study relaxation of photoexcited species such as the solvated electron and organic dye molecule in solution.

Session 2.2 was started by Michael Thoss (Technical University of Munich) who gave an overview of his work with Haobin Wang (University of New Mexico) in developing a multilayer multi-configurational time-dependent Hartree method for simulating the quantum dynamics of molecular systems with many degrees of freedom.

Session 2.3 on mixed quantum-classical schemes was headed by Raymond Kapral (University of Toronto), who discussed the implications of various mixed quantum-classical dynamics approaches with the goal of providing a unified mechanical basis for performing such simulations.

We also had a number of experimental talks summarized by Laura Herz from Oxford University. Her talk "Electronic Dynamics in Materials Systems" (Session 3.2) again emphasized the theme of how quantum dynamical effects and molecular structure play a crucial role in the microscopic operation of optical electronic devices fabricated from molecular scale materials.

Session 4.1 was headed by Eitan Geva (University of Michigan), with a talk on "Energy Transfer: Förster Theory and Beyond", discussing how Förster's theory of energy transfer needs to be modified to take into account both dynamic and structural inhomogeneity.

Finally, in the session on molecular electronics (session 4.2.), the overview talk by Gianaurelio Cuniberti addressed his theoretical investigation of molecular conductance using density functional theory for open systems, and how one can "Tune the Conductance of a Molecular Switch".

These brief summaries should highlight the diversity of topics and the interdisciplinary nature of the workshop. By the composition and program, we believe that we have succeeded in creating an active dialogue between theorists and experimentalists, as well as between theorists specialized in different domains.

As a whole, the workshop had a very relaxed and collegial feel, no doubt accentuated by the choice of venue. The PRC center at Reid Hall features a beautiful courtyard with the conference room off to one side. During the breaks and before the workshop began each day, one could usually find groups of participants having discussions over a cup of coffee. The mix between theoretical researchers and experimentalists was good. As organizers, we specifically invited experimentalists who enjoyed talking to theoreticians and mostly vice

versa. Overall, the workshop had the general feel of a Gordon Research Conference.

Besides the scientific activities, the workshop included a group "cultural event" to the Île de la Cité, with a visit to the Sainte Chapelle, the Musée d'Orsay, and a walk through the St. Germain district before the conference dinner.

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

We believe that this workshop event has been highly successful in stimulating discussions and future collaborations between theorists and experimentalists, as well as between theorists of different directions. The workshop has certainly met its central objective, i.e., to draw together researchers from various fields in order to foster communication and pave the way to the development of new approaches to the unified theoretical treatment of quantum phenomena in biological and nano-structured materials.

We have received very positive feedback from many participants, who explicitly suggested that this workshop will likely have an important influence upon their future research activities and collaborations. A majority of participants have stated enthusiastic interest for a follow-up workshop with a similar direction that would again take place at the PRC in two years' time.

We thus hope to have a series of workshops following the developments in this field. These workshops should preserve a certain continuity (e.g., there was roughly a 50% overlap of participants between this year's workshop and the one held 2 years ago) while encouraging new themes and shifts of focus.

As mentioned previously, we are preparing a Proceedings volume to document the discussion and developments in this field. As editors, we have asked the contributors to make their contributions to be as pedagogical as possible to provide a good introduction to the field to new researchers and bring future graduate students, postdocs, and scientists up to speed in this rapidly evolving field.

Energy flow dynamics in biomaterial systems

Oct. 02 2007 to Oct. 05 2007

Workshop schedule

Tuesday 2 October

Session 1.1: (10:30-12:30) From molecular systems to biomaterials

- 10:30-10:45: Welcome/Introduction to PRC
- 10:45-11:30 **Motivation/Perspective**: From molecular systems to biomaterials (Organizers)
- 11:30-12:15 **Greg Scholes** Overview talk: Charge and energy transfer dynamics in nanostructured systems

Lunch (12:30-13:45)

Session 1.2: (13:45-16:00) Dynamics in DNA and Biomolecular Systems

- 13:45-14:30: **Steve Bradforth** Overview talk
- 14:30-15:00: **Casey Hynes** On the Mechanism of Drug Intercalation into DNA
- 15:00-15:30: **Dimitra Markovitsi** Excited states and energy transfer in DNA double helices
- 15:30-16:00: **William Barford** The Role of Chlorophyll Dimers in the Photoprotection Mechanisms of Light Harvesting Complexes

Break (16:00-16:30)

Session 1.3 (16:30-18:15) Multidimensional Spectroscopy and its applications

- 16:30-17:15: **Shaul Mukamel** Overview talk
- 17:15-17:45: **Yoshitaka Tanimura** Two-dimensional infrared spectroscopy for frustrated system below and above the freezing temperature
- 17:45-18:15: **Anne Goj** Protein dephasing in a confined environment

Discussion (18:15-18:45)

Reception at PRC

Wednesday 3 October

Session 2.1 (10:30-12:20) Excited state electronic structure and dynamics

- 10:30-11:15: **Peter Rossky** Overview talk
- 11:15-11:45: **Marco Garavelli** Modelling light induced events in complex molecular architectures: moving towards an accurate computational photochemistry/photobiology
- 11:45-12:15: **Victor Batista** The MP/SOFT methodology for simulations of nonadiabatic quantum dynamics

Lunch (12:30-13:45)

Session 2.2: (13:45-15:45) Quantum properties and dynamics in many dimensions

- 13:45-14:30: **Michael Thoss** Overview talk
- 14:30-15:00: **Oliver Kuehn** Multidimensional Vibrational Dynamics of Double Hydrogen Bonds
- 15:00-15:30: **Ulrich Kleinekathofer** Absorption spectra for light-harvesting systems using non-Markovian theories
- 15:30-16:00: **Peter Saalfrank** Vibrational energy transfer from adsorbates to surfaces

Break (16:00-16:30)

Session 2.3 (16:30-18:30) Mixed quantum-classical methods

- 16:30-17:15: **Ray Kapral** Overview talk
- 17:15-17:45: **Giovanni Ciccotti** Do we have a consistent non-adiabatic quantum-classical mechanics?
- 17:45-18:15: **Sophya Garashchuk** Description of ZPE and nonadiabatic effects with approximate quantum trajectories
- 18:15-18:45: **David Coker** An Iterative mixed quantum-classical scheme for modeling quantum transitions in condensed phase dynamics

Discussion (18:45-19:15)

Thursday 4 October

Session 3.1 (10:30-12:15) Electronic dynamics in materials systems

- 10:30-11:15: **Laura Herz** Overview talk
- 11:15-11:45: **Carlos Silva** Exciton dynamics in supramolecular semiconductors
- 11:45-12:15: **Masanori Tachiya** Stochastic Approach to Exciton Annihilation Dynamics in Quantum Dots and Carbon Nanotubes

Lunch (12:30-13:30)

Poster session (13:30-15:30): oral presentations (5-10 min. talks) + discussion

Tour or excursion + Workshop Dinner

Friday 5 October

Session 4.1 (10:30-12:45) Energy transfer: Forster theory and beyond

- 10:30-11:15: **Eitan Geva** Overview talk
- 11:15-11:45: **Biman Bagchi** Non-radiative resonance energy transfer in systems involving nanoparticles
- 11:45-12:15: **Alexandra Olaya Castro** Quantum interference and the efficiency of excitation transfer in a light-harvesting system
- 12:15-12:45: **Emmanuelle Hennebicq/David Beljonne** Singlet excitation transport in conjugated materials: Beyond Forster

Lunch (12:45-14:15)

Session 4.2: (14:15-15:30) Molecular Electronics

- 14:15:15:00 **Gianaurelio Cuniberti** Overview talk
- 15:00-15:30: **Eran Rabani** Inelastic effects in Aharonov-Bohm molecular rings: Nonequilibrium Green's function and a real-time path integral approach

Discussion + Outlook (15:30-16:30)

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