Dynamique Quantique des Systèmes Complexes
Vers les Nanostructures et les Environnements Biologiques

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Journée Annuelle de la Chimie 2009-2010
UFR de Chimie UPMC
Concepts/Models/Systems: From Polyatomics to Extended Systems
  Exciton Dissociation at Organic Semiconductor Junctions
  Excitation Energy Transfer (EET)
  Photobiological Systems

Methods: Quantum & Quantum-Classical Dynamics in Many Dimensions
  Multiconfigurational Methods
  Effective-Mode Models
  Quantum-Classical Phase-Space & Density Functional Methods

Perspectives - Towards Quantum and Classical Transport
  Exciton Dynamics
  Processes at Interfaces
  Classical Transport Phenomena
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Goals in a Nutshell

- Energy & Charge Transfer
- Non-Equilibrium Transport
- Microscopic Electronic Structure & Nuclear Dynamics
- Extended, Nano-Structured Biological & Material Systems e.g. for Photovoltaics
- Photonic Excitation, Dissipation, Decoherence
- Coherent Control

Understanding & Optimization
Can We Put to Use Our Knowledge of Reactivity & Photochemistry?

Many processes require (non-adiabatic) quantum dynamics
Landmark Topology: Conical Intersections (CoIn’s)

- CoIn topology highly anharmonic
- Extreme breakdown of the Born-Oppenheimer approximation
- Ultrafast decay (fs to ps scale)
- CoIn’s are ubiquitous (Truhlar/Mead: “Principle of non-rareness of CoIn’s”)
- Polyatomic molecules; Jahn-Teller effect in solids

CoIn = photochemical funnel


Photochemistry of “Complex” Systems

- polyatomic molecules
- solute-solvent systems
- biological chromophores & photoswitches
- extended systems, e.g., semiconducting polymers
- molecular nano-scale assemblies

- ultrafast processes (fs–ps)
- quantum coherence & decoherence
- special topologies, e.g., Coln’s
Methods for “Large” Systems

- Vibronic Coupling & Lattice Models; Accurate Multiconfigurational Techniques (MCTDH)
- Parametrized Model Hamiltonians & Accurate Quantum Dynamics
- Approximate Potentials & Approximate Dynamics
- Accurate Potentials & Accurate Quantum Dynamics
- On-The-Fly Electronic Structure & Classical / Semiclassical Dynamics
- High-Level or Semi-Empirical Electronic Structure Methods; Surface Hopping, Gaussian Wavepackets
Example 1: How Do Excitons Dissociate at a Polymer Interface (Heterojunction)?

exciton = electron + hole

→ photovoltaic devices, organic light-emitting diodes (OLED’s), ...

molecular-level understanding of interactions & dynamics at the polymer interface is required

collaboration with Eric R. Bittner (Univ. Houston)
Zeroth-Order Picture of a Heterojunction

- HOMO/LUMO $\leftrightarrow$ valence/conduction band
- 1st bound excited state: singlet exciton ($^1B_u^-$ in PPV); Frenkel type exciton
- @junction: compare band offset vs. exciton binding energy ($\varepsilon_B \sim 0.5$ eV)

polymer/polymer interface:

* F8BT 3.16 eV
  * PFB/TFB 1.92 eV
    * -2.75 eV (PFB)
    * -2.98 eV (TFB)
  * -3.54 eV
**Objective: Molecular-Level Perspective of Exciton Dissociation**

- initial photogeneration of an exciton state (XT, bright state)
- exciton decay to an interfacial charge transfer state (CT, exciplex)
- the XT → CT transition is mediated by electron-phonon coupling
3-State Electron-Phonon Coupling Model

\[ H = \sum_{i} H_i = \sum_{i} \frac{\omega_i}{2} \left( p_i^2 + x_i^2 \right) + V_{i}^{\text{lin}} \]

\[ V_{i}^{\text{lin}} = \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i^{(12)} x_i & \lambda_i^{(13)} x_i \\ \lambda_i^{(12)} x_i & \kappa_i^{(2)} x_i & \lambda_i^{(23)} x_i \\ \lambda_i^{(13)} x_i & \lambda_i^{(23)} x_i & \kappa_i^{(3)} x_i \end{pmatrix} \]

state 1 = exciton (XT) state
state 2 = charge transfer (CT) state
state 3 = intermediate (IS) state

phonons = C=C stretch + ring torsions

parameterization for TFB:F8BT:
polymer lattice model based on dimer;
TDDFT and semi-empirical (PM3) calculations
+ Wannier-function representation

Bittner et al., JCP 122, 214719 (2005)

Quantum Dynamics of Exciton Dissociation

- 3-state 28-mode model
- MCTDH calculations
- sample over relevant interface configurations
- intermediate states play a key role
- qualitative agreement with time-resolved photoluminescence

Interface Configurations: Role of Stacking

Eclipsed (E)

Staggered (S)

Note: F8’s electro-positive in F8BT but electro-negative in TFB
Example 2: Excitation Energy Transfer (EET)

→ photosynthesis, (artificial) light-harvesting systems

\[ H = \sum_i \frac{\omega_i}{2} \left( p_i^2 + x_i^2 \right) + \begin{pmatrix} \kappa_i^{(1)} x_i^{(1)} \\ V_{12}^{\text{Coulomb}} \end{pmatrix} \begin{pmatrix} V_{12}^{\text{Coulomb}} \\ \kappa_i^{(2)} x_i^{(2)} \end{pmatrix} \]

\[ V_{12}^{\text{Coulomb}} = \int dr_D dr_A \frac{\rho_D^{(eg)}(r_D) \rho_A^{(ge)}(r_A)}{|r_D - r_A|} \]

- inter-monomer couplings via transition densities
- generalization of Förster rate theory & transition dipole approximation
Ultrafast, Coherent Regime: Excitation Transfer Coupled to Porphyrin Effective Mode(s)

- significantly different from non-coherent, Förster (FRET) type transfer
EET in Functionalized Assemblies

e.g., carbon nanotubes (CNT) or quantum dots (QD) as donor/acceptor species

ANR project “Experimental and theoretical study of energy and charge transfer in nanotube/chromophore compounds”, submitted


- FRET\(^1\) labeling in biological/medical applications; photovoltaics
- again, pronounced non-Förster effects, esp. for elongated nano-objects

\(^1\)FRET = Fluorescence Resonance Energy Transfer
Example 3: Biological Switches, e.g., PYP

PYP = Photoactive Yellow Protein

isomerisation constrained by “protein nanospace”

- excited-state lifetime $\sim 700$ fs (in solution $\sim 10$ ps)
- the local amino acid environment is of key importance
- how is the chromophore’s quantum dynamics concerted with the environmental dynamics/fluctuations?
**A Complicated Photo-Switch ... Two Isomerisation Pathways**

- two $S_1$ minima; $\beta$ min. near a Coln
- charge distributions inverted at these two minima

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Gromov, Burghardt, Köppel, Cederbaum, JACS 129, 6798 (2007)
The Amino Acid Environment “Tunes” the Chromophore

CC2 supermolecular calculations

Impact of the active site amino acids
Hierarchical Treatment of Complex, Structured Systems

→ Hybrid methods for quantum dynamics & electronic structure

Primary zone:
- dominant modes in many-atom systems
- chromophore (in solution, protein)

Secondary zone:
- intramolecular “bath”
- first solvent shell (microscopic or mesoscopic description)
This book presents a collection of 14 review articles that cover the key topics addressed in the workshop Energy Flow Dynamics in Biomaterial Systems which was held in October 2007 in Paris. These reviews illustrate the many facets of today’s theoretical picture of electronic and vibronic dynamics and transport phenomena in biological, biomimetic, and molecular electronic systems. Part I focuses on excitation energy transfer in photosynthetic reaction centers and other multichromophoric systems, part II gives a tour d’horizon of DNA research, and part III addresses molecular electronics and quantum transport in organic materials. Finally, parts IV and V cover recent methodological developments in open system dynamics and hybrid quantum-classical methods. The scope of the book is deliberately broad in terms of physical systems studied and yet unified in the use of quantum dynamical methods to describe transient and often ultrafast energy and charge transfer events in complex systems.
Acknowledgments & Collaborations

- E. R. Bittner (University of Houston)
- L. Cederbaum, H. Köppel, E. Gromov, E. Gindensperger (University of Heidelberg)
- G. A. Worth (University of Birmingham, UK)
- K. H. Hughes (University of Bangor, UK)
- H. Tamura (ENS Paris, now Tohoku University)
- S. Zhao, P. Ramanathan, F. Martelli (Group ENS)

Thanks to: CNRS, ANR (France) for financial support