Final Report on the Workshop

"Non-Adiabatic Dynamics at Surfaces"

Schloss Reisensburg, Günzburg, Germany
October 22-25 2007

Organized by Jörg Behler[1], Patrick Rinke[2,3], Karsten Reuter[3] and Matthias Scheffler[3,2]

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Summary

The workshop "Non-Adiabatic Dynamics at Surfaces" has focused on the theoretical investigation of dynamic processes in molecule-surface interactions that require approaches beyond the Born-Oppenheimer approximation. The main aim of the workshop was to bring together experts from many fields relevant for the accurate simulation of non-adiabatic processes in order to assess the status of the field and to stimulate progress in the development of new methods. For this purpose, the scientific program of the workshop focused on a variety of aspects of non-adiabatic dynamics at surfaces. This involved several methods ranging from the accurate calculation of the involved potential energy surfaces (PES) from first principles to the description of the dynamics of molecules interacting with surfaces on several PESs, which can be modeled for instance by mixed-quantum classical simulations employing surface hopping techniques or by full quantum dynamics. Other important aspects discussed were the energy dissipation at surfaces and results from novel experimental techniques, which should be addressed by theoretical studies. Several models for the mechanisms underlying the non-adiabaticity, like charge transfer or spin-effects have been covered in extended discussions.

The workshop took place at Schloss Reisensburg, the conference center of the University of Ulm, Germany, and has been carried out with financial support by the DFG and the Psi-K Network (ESF). The workshop program contained 18 invited talks covering mostly various theoretical aspects but also results by distinguished experimental groups (45 minutes including 10 minutes discussions), and 11 presented posters. Including speakers and organizers 32 scientists participated in the workshop, as well as 7 PhD students. The program started on Monday afternoon, October 22, and ended on Thursday, October 25, at noon. It was supplemented by a short excursion on Tuesday afternoon in order to stimulate informal discussions among the participants.

The workshop has clearly pointed out the recent advances in the theoretical description of non-adiabatic dynamics at surfaces, but also provided a good overview of open questions and new challenges to be addressed in future work.

Description of the Scientific Content and Discussions

The program was organized in several sessions on specific topics relevant for the description of dynamic processes at surfaces. In the first session on Monday afternoon the general focus of the workshop was introduced by two complementary talks addressing the experimental and theoretical state-of-the-art, respectively. Eckart Hasselbrink (U Duisburg-Essen, Germany) gave an overview on existing experimental evidence for non-adiabatic processes at surfaces and recent developments in experimental techniques for detecting excited electrons, which are created when a surface is exposed to a flux of gas phase atoms or molecules. In particular metal-insulator-metal layer sensors have shown to be valuable tools, which allow to detect the formation of electron-hole pairs and to follow the kinetics of surface chemical reactions. Geert-Jan Kroes (U Leiden, NL) gave a concise summary on the quality of electronically adiabatic calculations on reactive scattering of molecules from metal surfaces. In this context also current techniques to handle the multi-dimensional PESs involved in gas-surface dynamics were reviewed. A poster session on Monday evening provided the immediate opportunity for all participants to get-together and discuss in an informal atmosphere a wide range of topics including several DFT studies on the adsorption dynamics of molecules at metal surfaces.

On Tuesday morning, several approaches for the description of non-adiabatic dynamics at surfaces were presented and illustrated for specific systems.
David Bird (U Bath, UK) presented a time-dependent mean-field Newns-Anderson model, which employs a simplified description of the electronic structure allowing to derive an analytical expression for the non-adiabatic charge and energy transfer. Results for several exemplary systems, like H atoms approaching Cu and Au surfaces were given. George Darling (U Liverpool, UK) reported on a different source of non-adiabaticity in gas-surface dynamics, namely spin-forbidden reactions. He illustrated the role of spin for the adsorption of H atoms on graphene, which gives rise to complex atomic rearrangements at the surface.
The second half of the morning session was devoted on a particularly prominent model system for the study of non-adiabatic effects at surfaces, the oxygen dissociation at Al(111). Ronnie Kosloff (Hebrew University Jerusalem, IL) presented tests of DFT exchange-correlation functionals and developed model potentials for applications in quantum dynamics. Axel Groß (U Ulm, Germany) described studies based on mixed-quantum classical dynamics employing Tully's fewest switches algorithm for the same system. These simulations were performed using multidimensional DFT potential energy surfaces to investigate the role of spin transitions. Tuesday afternoon, Andreas Knorr (TU Berlin, Germany) presented an approach to study electron-phonon coupling by linking density-functional theory and density matrix theory and illustrated the method for the electron transfer from the bulk to surface states at Si(100).

On Wednesday morning several methodological approaches for the calculation of potential energy surfaces were presented. First, Nicola Marzari (MIT, USA) discussed the strengths and shortcomings of DFT for applications to the description of processes at surfaces, e.g., the accuracy of electron-transfer processes and of potential energy surfaces involving different spin multiplicities. Troy Van Voorhis (MIT, USA) presented a constrained DFT scheme for the calculation of diabatic PESs from first principles by introducing suitable constraints on the electron distribution in the system. The second half of the morning session was devoted to many-body approaches. Michael Rohlfing (U Osnabrück, Germany) reported results obtained on dynamics of electron-hole excitations at surfaces by ab-initio many-body perturbation theory in form of the GW approach. Steven Louie (UC Berkeley, USA) presented a Wannier

functions technique to non-adiabatic transitions and electron-phonon interactions in condensed systems and its practical realization in the framework of DFT.

The Wednesday afternoon session was opened with a contribution by Angel Rubio (DIPC, Spain) on structural dynamics in the excited state employing time-dependent DFT. Oliver Kühn (FU Berlin, Germany) then reported the results of non-adiabatic quantum dynamics studies of matrix-isolated molecules, in particular for dihalogen molecules, and suggested further experiments in this context. Non-adiabatic dynamics results based on a different approach employing QM/MM techniques using ab initio, semiempirical and force field methods were then detailed by Maurizio Persico (U Pisa, Italy). A semiclassical surface hopping approach was applied to several photochemical reactions. The afternoon session was closed by Thorsten Klüner (U Oldenburg, Germany). He presented studies on the photodesorption of small molecules from oxide surfaces by first principles, in particular the desorption of NO and CO from a NiO(100) surface by wave packet calculations. The underlying PESs were determined by accurate correlated quantum chemical methods like CASPT-2 and CCSD(T).

The Thursday morning session focused on future challenges in the field. Alec Wodtke (UC Santa Barbara, USA) reported on recent experimental results on the vibrationally promoted electron emission from metal surfaces, which is a direct evidence for the break-down of the Born-Oppenheimer approximation and whose exact mechanism is still debated. Bill Gadzuk (NIST, USA) talked about STM-induced atom transfer on surfaces, which allows to study the effect of an energetic hot electron flux on the site-to-site transfer of adsorbed atoms. The workshop was closed with a contribution of Eckhard Pehlke (U Kiel, Germany), who presented results on simulations of electronic energy dissipation processes within time-dependent density-functional theory.

Assessment of Results and Impact of the Event

In summary, the presented results, the talks as well as the posters, provided a comprehensive overview on the current status of the field. A close contact between groups employing different methods to the study of non-adiabatic processes at surfaces has been established, which was one of the main purposes of the workshop. The rather small size of the workshop and the informal atmosphere provided room for many fruitful discussions, which allowed to assess the scope and limitations of the various approaches and to identify new important challenges for the field. In particular density-functional theory due to its efficiency still has a central in the description of molecule-surface interactions, and a large effort is spent to assess the accuracy and applicability to various systems. Extensions to deal with excited states, like time-dependent density-functional theory or the GW approximation, but also constrained-DFT techniques are of increasing importance and essential in the description of non-adiabatic processes. A higher accuracy is provided by quantum chemical methods, which are still prohibitively expensive for a variety of systems. In parallel, the description of dynamics on several PESs, either in form of a surface-hopping scheme or by quantum dynamics is very important for the study of dynamic phenomena, but in turn relies on accurate potential energy surfaces underlying the trajectories. A key aspect of the dynamics is also the energy dissipation by the creation of electron-hole pairs or a coupling to phonons. In addition to the detailed discussion of the various theoretical approaches to these problems several contributions by experimentalists pointed out new future challenges.

List of Participants

1	Abufager, Paula	(U Rosario, Argentine)
2	Behler, Jörg	(Ruhr-Uni Bochum, Germany)
3	Beltran, Juan	(Fritz-Haber-Institut Berlin, Germany)
4	Bird, David	(U Bath, UK)
5	Bücking, Norbert	(TU Berlin, Germany)
6	Carbogno, Christian	(U Ulm, Germany)
7	Darling, George	(U Liverpool, UK)
8	Gadzuk, Bill	(NIST, USA)
9	Gavnholt, Jeppe	(TU Denmark, Denmark)
10	Groß, Axel	(U Ulm, Germany)
11	Gross, Hardy	(FU Berlin, Germany)
12	Hasselbrink, Eckart	(U Duisburg-Essen, Germany)
13	Holloway, Stephen	(U Liverpool, UK)
14	Juanes-Marcos, Juan Carlos	(U Leiden, The Netherlands)
15	Klüner, Thorsten	(U Oldenburg, Germany)
16	Knorr, Andreas	(TU Berlin, Germany)
17	Kosloff, Ronnie	(Hebrew U Jerusalem, Israel)
18	Kroes, Geert-Jan	(U Leiden, The Netherlands)
19	Kühn, Oliver	(FU Berlin, Germany)
20	Louie, Steven	(UC Berkeley, USA)
21	Marzari, Nicola	(MIT, USA)
22	McKenna, Keith	(UCL, UK)
23	Meyer, Jörg	(Fritz-Haber-Institut Berlin, Germany)
24	Mizielinski, Matthiew	(U Bath, UK)
25	Olsen, Thomas	(TU Denmark, Denmark)
26	Pehlke, Eckhard	(U Kiel, Germany)
27	Persico, Maurizio	(U Pisa, Italy)
28	Persson, Mats	(U Liverpool, UK)
29	Reuter, Karsten	(Fritz-Haber-Institut Berlin, Germany)
30	Rinke, Patrick	(UC Santa Barbara, USA)
31	Rohlfing, Michael	(U Osnabrück, Germany)
32	Rosini, Marcello	(U Modena, Italy)
33	Rubio, Angel	(DIPC San Sebastian, Spain)
34	Scheffler, Matthias	(Fritz-Haber-Institut Berlin, Germany)
35	Schiotz, Jakob	(TU Denmark, Denmark)
36	Timmer, Matthias	(U Duisburg-Essen, Germany)
37	Van Voorhis, Troy	(MIT, USA)
38	Wodtke, Alec	(UC Santa Barbara, USA)
39	Yu, Chol Jun	(RWTH Aachen, Germany)

Program

Monday 22. October 2007

-16:00 arrival and registration

Afternoon Session: Chair: **Jörg Behler**

16:00 Opening Remarks

16:15-17:00 Eckart Hasselbrink
"Non-adiabaticy in surface chemical process studied using metal-insulator-metal sensors"

17:00-17:45 Geert-Jan Kroes
"The quality of electronically adiabatic calculations for reactive and non-reactive scattering of H_2 from metal surfaces."

18:00 Dinner

20:00 Poster Session

Tuesday 23. October 2007

8:00-9:00 Breakfast

Morning Session: Chair: **Stephen Holloway**

9:00-9:45 David Bird
"Electron-hole pair excitation in adsorption"

9:45-10:30 George Darling
"Spin forbidden reactions on graphite"

10:30-11:00 Coffee Break

11:00-11:45 Ronnie Kosloff
"Dynamics of oxygen dissociation on an Al surface"

11:45-12:30 Axel Gross
"Mixed quantum-classical simulations of gas-surface dynamics"

12:30-14:00 Lunch

Afternoon Session: Chair: **Karsten Reuter**

14:00-14:45 Andreas Knorr
"Linking density-functional and density matrix theory: picosecond electron relaxation at the Si(100) surface"

15:00 Excursion

18:30 Dinner

Wednesday 24. October 2007

8:00-9:00 Breakfast

Morning Session: Chair: **Patrick Rinke**

9:00-9:45 Nicola Marzari
"Teaching new tricks to an old dog"

9:45-10:30 Troy Van Voorhis
"Constrained DFT for diabatic electron dynamics"

10:30-11:00 Coffee break

11:00-11:45 Michael Rohlfing
"Dynamics of electron-hole excitations at surfaces described by ab-initio many-body perturbation theory"

11:45-12:30 Steven Louie
""Wannier functions approach to non-adiabatic transitions or electron-phonon interactions in condensed matter

12:30-14:00 Lunch

Afternoon Session: Chair: **Hardy Gross**

14:30-15:15 Angel Rubio
"Structural dynamics in the excited state within a tddft formalims"

15:15-16:00 Oliver Kühn
"Nonadiabatic quantum dynamics of matrix-isolated molecules"

16:00-16:30 Coffee break

16:30-17:15 Maurizio Persico
"Nonadiabatic dynamics on the fly with ab initio, semiempirical and QM/MM methods"

17:15-18:00 Thorsten Klüner
"Photodesorption of small molecules from oxide surfaces: New insight from first principles"

18:30 Dinner

Thursday 25. October 2007

8:00-9:00 Breakfast

Morning Session: Chair: **Matthias Scheffler**

9:00-9:45 Alec Wodtke
"Electronic excitations induced by molecule-surface interactions"

9:45-10:30 Bill Gadzuk
"STM-induced atom transfer on surfaces: hot electrons, vibrations, or tunneling?"

10:30-11:00 Coffee break

11:00-11:45 Eckhard Pehlke
"Simulation of electronic energy dissipation processes within time-dependent density-functional theory"

11:45-13:00 Lunch and Departure