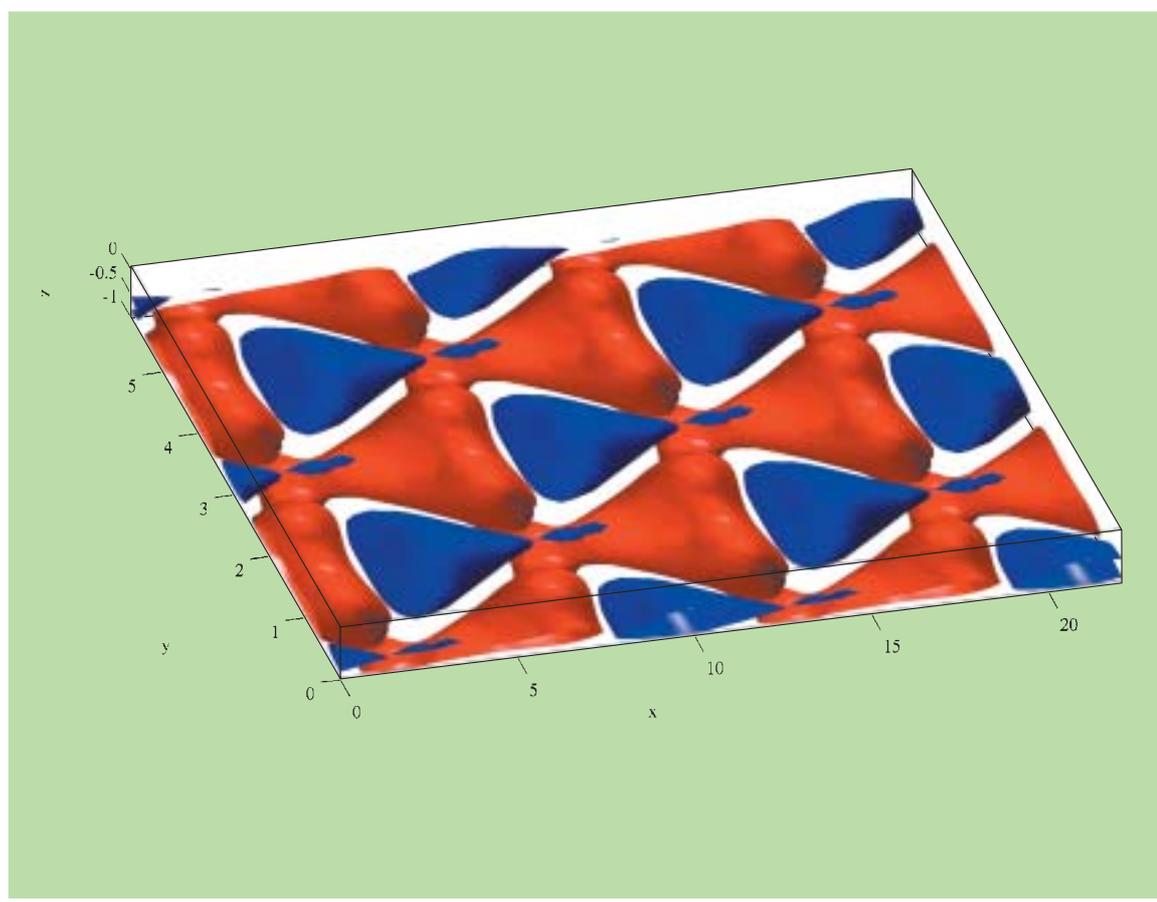


CSE

Computational Science and Engineering

Annual Report
2002/2003



CSE

Computational Science and Engineering

Annual Report 2002 / 2003

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Cover:

Visualization of the instantaneous velocity field taken from a simulation of laminar-turbulent (H-type) transition in plane channel flow. Shown are isocontours of positive (red) and negative (blue) streamwise disturbance velocity. The staggered pattern of the Λ -vortices can clearly be seen.

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G. Folkers	Pharmaceutical Sciences	45	189
J. Fröhlich	Theoretical Physics	28	191
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A. Gusev	Polymers	53	193
R. Hiptmair	Seminar for Applied Mathematics	60	
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Introduction

This is already the third Annual Report of Computational Science and Engineering (CSE) at the ETH. These reports have become a useful source of information for all persons interested in research and education in CSE, students and colleagues, visitors and people from other universities, to find out what is going on at the ETH in this exciting field. This new edition documents the changes that happened in the last year and gives a glimpse of the developments immediately ahead of us.

After last year's decision by the rector, Prof. K. Osterwalder, to redesign the diploma curriculum in CSE ("Rechnergestützte Wissenschaften") into a Bachelor and a Master program the major event of the reporting period is that this task has been completed. In fall of 2003 the first group of more than a dozen students has started with the Bachelor program. Details of this curriculum are described in Chapter 2. These students will receive their Bachelor degree in the fall of 2005 and will then have the possibility to continue in the Master program, which will start in that year. Soon the diploma studies CSE will be something of the past. The last group of students have started this year.

Since computer simulations become increasingly important in all fields of Science and Engineering again many new colleagues who use computing as an essential tool in their investigation have been hired by the ETH and the University of Zürich in the last year. This makes our curriculum even more attractive. At this point I should mention that our new colleague in Cosmology at the University Zürich, Prof. B. Moore, constructed a massively parallel supercomputer (see: <http://krone.physik.unizh.ch/~stadel/zBox/>) which was ranked in June 2003 to be number 144 on the top 500 list of fastest computers in the world!

At this point we thank the Schulleitung for supporting CSE in research and education. In particular, we thank the rector, Professor K. Osterwalder, for their financial support to produce this report. Moreover, we thank all those at the ETH who have contributed to this report.

Zürich, October 31, 2003

Rolf Jeltsch, Studiendelegierter und Mitglied des Ausschusses Rechnergestützte Wissenschaften

2

Education

In April 2003 the Schulleitung of the ETH Zürich has accepted the regulations (Studienreglement) of the Bachelor Curriculum in CSE. The new curriculum will start in October 2003 for students in their second year having done their first year's studies in another curriculum at the ETH Zürich or at another university. The first year's examinations are counted for 60 KP (credit points). In the subsequent two years of the Bachelor studies in CSE the students have to gather 120 KP in: mandatory Basic Courses (second year; the basics in Mathematics, Science and Engineering, Computer Science), Core Courses (third year; computational mathematical methods, advanced knowledge in Computer Science), Fields of Specialization (third year; more profound knowledge in one application area), Elective Courses (third year; emphasis on computational aspects), Bachelor Thesis (after third year; application oriented, computational). The overall requirement for getting the degree of a Bachelor of Science ETH in CSE is 180 KP in three years of studies.

The Bachelor diploma in CSE will allow students to continue their studies in a Master curriculum, in particular, in the Master Curriculum in CSE at the ETH Zürich which is in preparation and is planned to get started in October 2005. The Master studies will take one and a half years including the four months of the Master thesis and will lead to the degree of a Master of Science ETH in CSE.

The two and a half years Diploma curriculum in CSE existing since October 1997 will start for the last turn in October 2003 and will be replaced by the Bachelor /Master curricula in CSE.

In the academic year 2002/2003 5 new students have resumed their CSE studies at ETH; all students had taken their basic studies at ETH and in the following fields: Mathematics 1, Physics 2, Mechanical Engineering 1, Electrical Engineering 1.

The presentation of the CSE Diploma curriculum for ETH students of the 4-th semester of May 14 attracted around 60 persons; the presentation of the CSE Bachelor /Master curricula for ETH students of the second semester of May 28 was attended by around 90 persons. It is hoped that a fair number of them will start with the CSE studies this fall.

In the past academic year 6 students have successfully finished their CSE studies and have received a CSE diploma with very good scores. They chose the following fields of specialization: Fluid Mechanics, Scientific Computing, Software Engineering, Visualisation and Theoretical Physics. In the following list we give the name of the students, the title of the diploma thesis and, in parentheses, the name and the department/institute of the adviser.

Diploma Theses

- A. Adensamer Zweidimensionales Schmelzen
(M. Troyer, Theoretical Physics)
- M. Bergdorf A novel adaptive numerical method for convection-diffusion
equations
(P. Koumoutsakos, Computer Science)
- P. Häfliger Exploration of the suitability of 0-0 techniques for the design and
implementation of a numeric Math library using Eiffel
(B. Meyer, Computer Science)
- T. Hofmann Molecular Dynamics simulation of shock formation and reflection at
a solid wall
(T. Rösgen, Fluid Mechanics)
- R. Lauper Vergleich von Kollisionsdetektionsverfahren und deren Anpassung
für deformierbare Objekte
(M. Gross, Computer Science)
- C. Sigg Implementation of a computational framework for level set
representations
(M. Gross, Computer Science)

The total number of CSE students enrolled in the past academic year was 28. Listed below are the term papers written by the CSE students in the past two semesters.

Term Papers

- A. Burri Formulierung und Implementierung einer diskontinuierlichen
Galerkin-Methode für Konvektions-/Diffusionsprobleme
(C. Schwab, Applied Mathematics)
- A. Dobler Entwicklung eines Bildverarbeitungsalgorithmus zur Bestimmung
von Phasenumwandlungen
(T. Peter, Mechanical Engineering; H. C. Davis, Atmospheric
Physics)
- T. Kühne Impact of fixed-point effects in the performance of a soft-input
Viterbi decoder
(H. Bölskei, Electrical Engineering)
- St. Müller Plume-Rise in einem Lagrange'schen Partikelmodell
(M. Rotach, Atmospheric and Climate Science)
- M. Rüti Random number generator tests
(M. Troyer, Theoretical Physics)
- C. Sigg Parallel ray casting and isocontouring of very large volume data
(University of Texas, Austin)
- R. Veprek Multidimensionaler Suchalgorithmus für die Suche nach dem globalen
Minimum
(W. van Gunsteren, Computational Chemistry)

- G. Widmer Anordnung von dendritischen Verbindungen auf Graphit
(P. Nielaba, Physics, University of Konstanz)
- C. Winkelmann Formulierung und Implementierung einer diskontinuierlichen
Galerkin-Methode für Konvektions-/Diffusionsprobleme
(C. Schwab, Applied Mathematics)
- S. Wunderlich A simulation of an economy with a government bank and small
producer-consumer-agents
(K. Nagel, Computer Science)

Each semester on Thursdays, 15 - 17 hours, the CSE Case Studies Seminar takes place. Speakers from ETH, from other universities as well as from industry are invited to give a 2x45 minutes talk on an applied topic. The seminar talks of the past academic year are listed in Chapter 3 of the report. Beside the scientific talks the CSE students are asked to give short presentations (10 minutes) on published papers out of a list (containing articles from, e.g., Nature, Science, Scientific American, etc.). These presentations help the students to practise giving talks. Students are also asked to give talks on their term papers and voluntarily on their diploma theses (if there are free time slots).

Zürich, Oktober 3, 2003

Kaspar Nipp, Mitglied des Ausschusses Rechnergestützte Wissenschaften

For detailed information on the CSE curricula at the ETH Zürich see:
<http://www.cse.ethz.ch>

CSE Case Studies Seminar

The CSE Case Studies Seminar takes place each semester on Thursdays, 15 - 17 hours. Speakers from ETH, from other universities as well as from industry are invited to give a 2x45 minutes talk on an applied topic. The idea is to show the students a case study of an application problem containing the problem setting, the modelling, the mathematical approach and the simulation on a computer. In addition, such a case study should show what is going on in the field of CSE and what are the job perspectives for a CSE engineer. The seminars of the past academic year are given in the two following lists.

Case Studies Seminar WS02/03

- 31. 10. 02 M. Troyer, Theoretische Physik
Herausforderungen bei der Simulation von Phasenübergängen
- 14. 11. 02 R. Hiptmair, Seminar f"ur Angewandte Mathematik
Algorithmic Topology in Car Manufacturing
- 21. 11. 02 W. Krauth, ENS Paris
Monte Carlo Algorithmen für harte Kugeln und andere entropische Systeme: Gl"aser, Kolloide, Flüssigkristalle
- 28. 11. 02 K. Gates, Mathematik, Univ. of Queensland, Brisbane, AUS
The Tacoma Narrows Bridge Collapse
- 19. 12. 02 H.-J. Lüthi / G. Unger, Operations Research / McKinsey
Hedging Strategy and Electricity Contract Engineering
- 16. 1. 03 M. Konik, TIL-Consulting GmbH, Frankfurt
Mathematische Modellierung einer Umleitungssuche im Eisenbahnverkehr
- 23. 1. 03 S. Marrink, Biophysical Chemistry, Univ. of Groningen, NL
How to Simulate the Origin of Life Using Newton's Equations of Motion?

Case Studies Seminar SS03

- 17. 4. 03 Ben Moore, Theoretical Physics, Uni Z"urich
Simulating the Universe
- 24. 4. 03 J. Ostrowski, ABB
Simulation Induktionshärten
- 15. 5. 03 H. Van Swygenhoven, PSI Villigen
Atomistic Simulations in Nanocrystalline Metals as
a Guide for Experiments
- 22. 5. 03 P. Frauenfelder, Seminar für Angewandte Mathematik
Berechnung von Eigenwerten der Maxwell-Gleichungen
in 3D mit konformen Finite-Elemente-Methoden (FEM)
- 5. 6. 03 F. Nedelec, EMBL, Cell Biology and Biophysics, Heidelberg
Towards Simulating the Mitotic Spindle: Can We Explain
a Living Process from the Sum of its Parts?
- 12. 6. 03 K. Giebermann, Ahead Software AG, Karlsbad, Deutschland
Warum braucht Nero einen Mathematiker -- oder
wieviel Mathematik steckt in einem CD-Brennprogramm?

Computational Highlight

Numerical Simulation of Transitional and Turbulent Shear Flows

by Philipp Schlatter, Steffen Stolz and Leonhard Kleiser
Institute of Fluid Dynamics, ETH Zürich

A brief introduction to the numerical simulation of transitional and turbulent wall-bounded shear flows is presented. Important simulation strategies and numerical techniques like direct numerical simulation (DNS) and large-eddy simulation (LES) of incompressible transitional flows are reviewed. Furthermore, selected results for the test case of classical K-type transition in plane channel flow are given. For this flow configuration, a number of accurate experimental as well as highly-resolved numerical simulation data are available. Recent progress with the development of LES models within our group are outlined and the obtained results are shown and compared to highly-resolved DNS.

1 Introduction

Laminar-turbulent Transition The behavior and properties of fluid flows are important issues in different technical applications of the industrial world of today. One of the most relevant characteristics of a fluid is the flow state in which it is moving: laminar, turbulent, or the transitional state in between. Laminar flow is a well structured, predictable and layered flow (Latin *lamina*: layer, sheet, leaf), which usually exercises significantly less frictional resistance to solid bodies and much lower mixing rates than the chaotic, swirly and fluctuating fluid state of a turbulent flow. Understanding and predicting both turbulent and laminar flow is crucial in a variety of technical applications, e.g. flows in boundary layers on aircraft wings, around cars, intermittent flows around turbine blades, and flows in chemical reactors or combustion engines. The evolution of an initially laminar flow into a fully developed turbulent flow is called *laminar-turbulent transition*. This process and specifically the triggering mechanisms of transition are not fully understood even today, after a century of research.

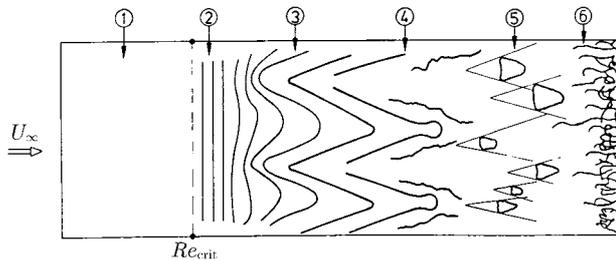


Figure 1: Schematic view of laminar-turbulent transition over a flat plate.

flow remains a solution of the governing equations at all Reynolds numbers, this solution becomes unstable to disturbances at some finite *critical* Reynolds number Re_{crit} . Mostly a sequence of linear and nonlinear (primary, secondary, higher-order) instabilities leads, through a more or less extended transitional state, to the *fully developed* turbulent state.

The history of transition research dates back to the classical experiments made by Osborne Reynolds already in the 19th century. By injecting ink into the flow in a glass tube he discovered that the change-over from laminar to turbulent flow is basically dependent upon the above-mentioned non-dimensional Reynolds number. Since the discovery of the classical mechanisms of perturbation growth of modal instability solutions (the classical K- (Klebanoff) and H- (Herbert) type breakdowns, see figure 3 and front page), many different transition scenarios have been proposed and verified, e.g. oblique transition (O-type) and bypass transition triggered by ambient high-level turbulence, see e.g. Brandt et al. (2002).

The essence of laminar-turbulent transition is sketched in figure 1 for the canonical case of the flow over a flat plate (boundary-layer transition). The fluid flows along the plate (position ①) until at a certain downstream position, indicated by Re_{crit} , it becomes unstable. Further downstream, two-dimensional disturbances are generated within the boundary layer (pos. ②), which rapidly evolve into three-dimensional perturbations (pos. ③). These in turn tend to break down into local turbulent spots (pos. ④), which grow

The crucial non-dimensional parameter determining whether a flow will likely be laminar or turbulent is the Reynolds number Re , which can be defined as the ratio of inertial to viscous forces acting on the flow particles. Flows at low Re are laminar. Flow through a pipe with circular cross-section, for example, will be turbulent above Reynolds numbers of a few thousands, with the precise value depending mainly on the level of disturbances at the inlet. Reynolds numbers of practically important flows may be as high as millions or even billions. This behaviour is generic: Although the laminar

and merge together to form a fully turbulent boundary layer (pos. ⑤-⑥), indicated by the downstream position Re_{tr} .

Numerical Simulation The governing equations for laminar, transitional and turbulent flows are the *Navier-Stokes* equations, which have been known for almost 200 years. Except for a few simple laminar flow cases, no closed analytical solutions to these nonlinear equations are known. Therefore, one needs to resort to numerical simulation techniques in order to get at least an approximate solution of a given fluid dynamics problem. Increasing the Reynolds number Re leads to the excitation of smaller and smaller turbulent scales down to a lower limit. These smallest, so-called *Kolmogorov scales* need to be resolved in numerical simulations; the simulation accuracy strongly depends on the spatial and temporal resolution employed. The fully resolved direct solution of the Navier-Stokes equations, referred to as *direct numerical simulation* (DNS), is therefore extremely expensive even for moderate Re , since the required CPU time roughly scales as Re^3 . Practical high Reynolds-number calculations thus need to be performed using simplified *turbulence models*. One commonly used possibility is to solve the Reynolds-averaged Navier-Stokes equations (RANS). Although this technique may require a number of *ad-hoc* adjustments of the turbulence model to a particular flow situation, quite satisfactory results can be obtained for some specific cases.

A technique with a level of generality in between DNS and RANS is the large-eddy simulation (LES). The eddies (turbulent vortices) above a certain size are completely resolved on the numerical grid, whereas the smaller scales are only modeled. The idea behind this scale-separation is that the smaller eddies are more homogeneous and isotropic and depend little on the specific flow situation, whereas the the energy-carrying large-scale vortices are strongly affected by the particular flow conditions (geometry, inflow, etc.). Moreover, the self-similarity of the small scales is often supposed to allow an easier modeling. Since for LES not all scales have to be resolved on the computational grid, only a fraction of the computational cost compared to DNS is needed (typically of order 1%). The success of a LES is essentially dependent on the quality of the underlying sub-grid scale (SGS) model and the applied numerical solution scheme. Substantial research efforts during the past 20 years have led to more universal SGS models, see Lesieur and Métais (1996); Domaradzki and Adams (2002).

Transitional flows have been the subject of intense experimental and numerical research. Since the beginning of the 1980's, with the increasing power of computers, and reliability and efficiency of numerical algorithms, it was tried to simulate the breakdown to turbulence in simple incompressible shear flows. One of the first well-resolved simulations to calculate through 3D transition into fully developed turbulence was presented in the DNS work of Gilbert and Kleiser (1990), who considered fundamental K-type transition in plane Poiseuille flow. Comprehensive review articles on the numerical simulation of transition can be found in Kleiser and Zang (1991) and Rempfer (2003).

In transitional flows one is typically dealing with stability problems where small initial disturbances with energies many orders of magnitude smaller than the energy of the steady base flow may evolve into turbulent fluctuations. After disturbance growth and breakdown, the resulting energy of the turbulent fluctuations can be of the same order as that of the base flow. Moreover, the spatial and temporal evolution of various sorts of wave disturbances and their nonlinear interactions need to be computed accurately over many disturbance cycles. For these reasons, high-order numerical schemes that accurately capture small-amplitude wave propagation have to be employed (Rempfer, 2003). These specific challenges make simulations of laminar-turbulent transition one of the most demanding problems of numerical fluid dynamics. High accuracy and stability of the underlying numerical scheme is mandatory to obtain meaningful results. Therefore, numerical schemes that are used for transition simulations often rely on spectral methods (Canuto et al., 1988) or higher-order finite-difference methods. All of the methods that are currently in use apply spatial discretizations that are at least fourth-order accurate. For time integration, typically third- and fourth-order schemes are used.

2 Large-Eddy Simulation

The governing equations for transitional and turbulent flows are the *Navier-Stokes* equations for the velocity components u_i ($i = 1, 2, 3$) and the pressure p , given here for an incompressible flow, complemented

with the incompressibility constraint,

$$\frac{\partial u_i}{\partial t} + \frac{\partial u_j u_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{1}{Re} \frac{\partial^2 u_i}{\partial x_j \partial x_j} \quad \text{and} \quad \frac{\partial u_i}{\partial x_i} = 0 . \quad (1)$$

(Note that the Einstein summation convention for repeated indices has been used.) These equations have to be solved numerically on a domain \mathcal{V} with boundary and initial conditions. In the LES approach, these equations are spatially filtered by a low-pass filter G with the filter width Δ . The filter operation yields the so-called *LES equations*

$$\frac{\partial \bar{u}_i}{\partial t} + \frac{\partial \bar{u}_j \bar{u}_i}{\partial x_j} = -\frac{\partial \bar{p}}{\partial x_i} - \frac{\partial \tau_{ij}}{\partial x_j} + \frac{1}{Re} \frac{\partial^2 \bar{u}_i}{\partial x_j \partial x_j} \quad \text{and} \quad \frac{\partial \bar{u}_i}{\partial x_i} = 0 . \quad (2)$$

The low-pass filtered velocity is given by

$$\bar{u}(x) = G * u := \int_{\mathcal{V}} G(x, x', \Delta) u(x') dx' . \quad (3)$$

These equations govern the evolution of the large, energy-carrying scales of motion. The effect of the non-resolved small scales appears through a subgrid-scale (SGS) term

$$\tau_{ij} = \bar{u}_i \bar{u}_j - \bar{u}_i \bar{u}_j \quad (4)$$

which is not closed (i.e. cannot be obtained from the computed quantities \bar{u}_i) and must thus be modeled. The most prominent SGS models are the eddy-viscosity models, in which

$$\tau_{ij} - \frac{\delta_{ij}}{3} \tau_{kk} = -2\nu_T \bar{S}_{ij} , \quad (5)$$

where \bar{S}_{ij} is the large-scale strain-rate tensor $\bar{S}_{ij} = (\partial \bar{u}_i / \partial x_j + \partial \bar{u}_j / \partial x_i) / 2$. The eddy-viscosity ν_T is usually modeled according to Smagorinsky (1963) yielding the widely-used *Smagorinsky* model

$$\nu_T = (C_S \Delta)^2 |\bar{S}| \bar{S}_{ij} \quad , \quad |\bar{S}| = (2\bar{S}_{ij} \bar{S}_{ij})^{1/2} . \quad (6)$$

The constant C_S has to be determined empirically and is dependent on the particular flow situation.

A SGS model suitable to simulate transition should be able to deal equally well with laminar, transitional and turbulent flow states. The model should leave the laminar base flow unaffected and only be effective, in an appropriate way, when nonlinear interactions between the resolved modes and the non-resolved scales become important. The initial slow growth of the instability waves is mostly sufficiently resolved even on a coarse LES grid. Due to the possibly intermittent character of transitional flows (e.g. spatial simulations, bypass transition), spatial averaging of the model coefficients (a common practice with the dynamic Smagorinsky model) should be avoided. Furthermore, for the sake of generality, a three-dimensional formulation of the model is required. Ideally, the SGS model should require no *ad-hoc* adaptation to a specific flow situation.

The classical variants of eddy-viscosity models, e.g. the above-mentioned Smagorinsky model or the popular structure function model (Métais and Lesieur, 1992) with constant model coefficients, fail to correctly predict transition. *Ad-hoc* remedies used are, e.g., transition functions or special near-wall treatment. However, such methods are designed for special flow configurations only.

Through the introduction of spatial filters to separate the turbulent scales from the (laminar) base flow, Ducros et al. (1996) successfully applied the filtered structure function model to weakly compressible boundary-layer flow. High-pass-filtered eddy-viscosity models and their application to transitional and turbulent flows with constant model coefficient have been studied in Stolz et al. (2003).

Another possibility is the use of dynamic LES models, which were introduced by Germano et al. (1991); Lilly (1992). These models, mostly used in the form of the dynamic Smagorinsky model (DSMAG), attempt to adapt the local model coefficient automatically to different flow situations, e.g. laminar, transitional, and turbulent flows. However, in general they do not correctly predict the laminar base flow. Moreover, averaging of the dynamic model coefficient in the homogeneous directions has usually to be employed for turbulent flows in order to minimize the occurrence of singularities.

Alternatively, Stolz and Adams (1999) proposed the approximate deconvolution model (ADM) for the LES of incompressible and compressible flows. The model is based on an approximate deconvolution of the filtered data by a truncated series expansion of the inverse filter. It easily provides an approximation for all SGS-terms using the computed approximation of the unfiltered field. Furthermore, a relaxation term which acts only on the scales close to the numerical cut-off is used to model the interaction of the resolved scales with those not represented numerically. The coefficient of the relaxation term can be estimated by a dynamic procedure from the instantaneous solution. For transition in an incompressible channel flow, the results of Schlatter et al. (2003a) demonstrate that it is well possible to simulate transitional flows on the basis of the ADM approach. Models of this type will be discussed in the next section.

3 LES of Plane Channel Flow Transition

The physics of forced transition involving modal growth of the disturbances (the classical transition problem) is now understood quite well. Due to its simplicity and the availability of reliable experimental results and – nowadays – also highly-resolved simulation data, this transition scenario is still an important test bed for turbulence models (see e.g. Germano et al. (1991) or Schlatter et al. (2003a)).

Geometry and Implementation The geometry for the simulations presented in this chapter is given in figure 2a. The *temporal framework* is adopted, i.e. the disturbances grow in time rather than in space. Therefore, periodic (homogeneous) boundary conditions can be applied in both the spanwise and the streamwise direction. No-slip conditions are enforced at the solid walls. The simulations use a fully spectral method with Fourier representation in the periodic wall-parallel directions and a Chebyshev-tau approximation in the wall-normal direction (Gilbert and Kleiser, 1990). The nonlinear advection terms of the Navier-Stokes equations are computed with full dealiasing employing the 3/2-rule in all spatial directions (Canuto et al., 1988). The divergence-free condition is enforced exactly by an influence-matrix technique (Kleiser and Schumann, 1980). Time advancement is achieved by a semi-implicit second-order Runge-Kutta/Crank-Nicolson scheme.

The initial disturbances for the transition simulations consist of a two-dimensional (stable) Tollmien-Schlichting (TS) wave with maximum amplitude of 3% and two superimposed weak oblique (stable) three-dimensional waves with amplitude 0.1% and the same fundamental streamwise wavelength as the two-dimensional disturbance. The parameters are the same as in the fully resolved DNS by Gilbert and Kleiser (1990). The Reynolds number based on bulk velocity and channel half-width is $Re_b = 3333$. For the statistically stationary results of fully-developed turbulent channel flow the data is statistically averaged well after transition.

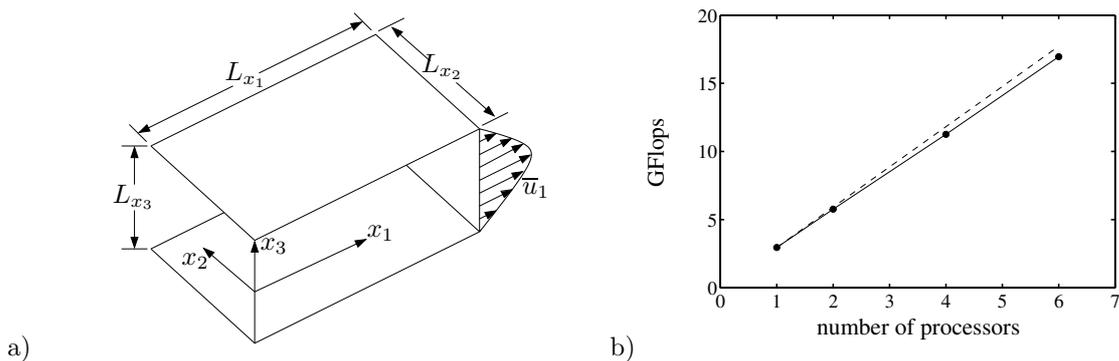


Figure 2: *Left*: Sketch of the channel flow configuration. The coordinates $x = x_1$ denote the streamwise, $y = x_2$ the spanwise, and $z = x_3$ the wall-normal direction, respectively. *Right*: — Speed-up of the fully spectral code used for channel simulations. Performance data for shared memory version on the NEC SX/5 at the CSCS, Manno. ---- linear speed-up.

The actual implementation is written in Fortran 77 and is completely parallelized using the shared-memory approach with OpenMP compiler directives. 70% of the CPU time is spent in FFT routines for

which the self-adapting FFTW library was adopted (Frigo and Johnson, 1999). Performance data for the NEC SX/5 are shown in figure 2b. It can be seen that for up to 6 processors a nearly linear speed-up could be attained. Similar speed-ups could also be measured on other architectures, e.g. the IBM SP-4 and dual-processor Linux PC's. An extension of the algorithm to massively-parallel architectures is in progress.

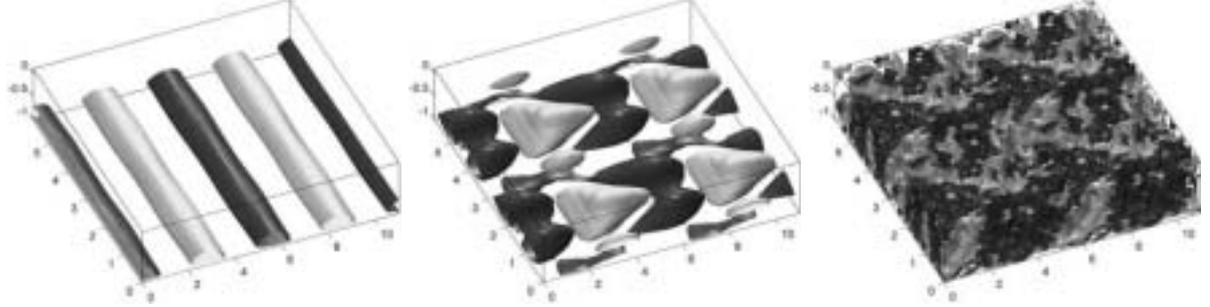


Figure 3: Visualization of the instantaneous flow structures during K-type channel flow transition. Shown are isocontours of positive (light color) and negative (dark color) streamwise disturbance velocity u' . From left to right: $t = 0$ (disturbed laminar), $t = 100$ (transitional), $t = 500$ (turbulent). Only the lower channel half is plotted.

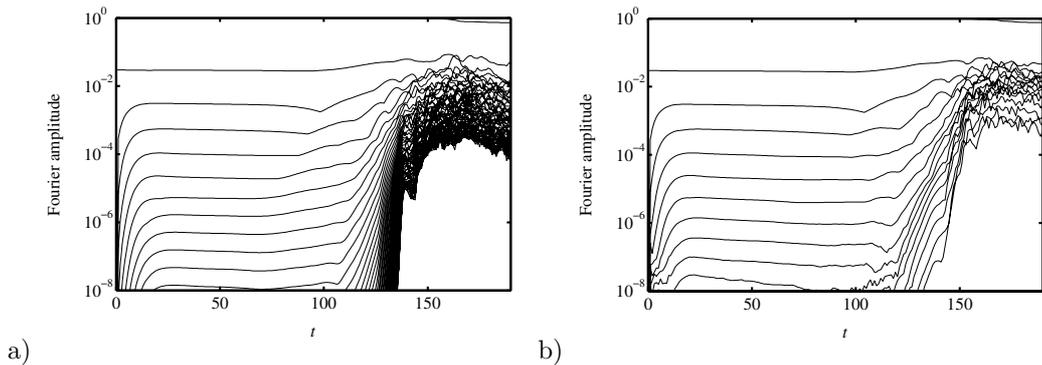


Figure 4: Evolution of the wall-normal maximum of the 2D Fourier amplitudes $\max_{x_3} |\hat{u}_1(k_i, 0, x_3, t)|$ corresponding to two-dimensional waves during the transitional phase ($Re_b = 3333$). *Left*: fully-resolved DNS on $160^2 \times 161$ grid. *Right*: LES RT model, $32^2 \times 33$ grid.

DNS results In figure 3, a visualization of the K-type transition process is shown taken from our DNS with resolution $160^2 \times 161$. Moreover, in figure 4a the evolution of different Fourier modes can be followed during the transitional phase. For $t < 100$, the initial 2D-TS-wave evolves into a saturated 2D wave, the harmonics of which exhibit a geometric progression with increasing wavenumbers, with each of the Fourier modes slowly decaying in time (Gilbert and Kleiser, 1990). During that stage, all the integral quantities like the skin friction (Re_τ) remain on their respective laminar value. The flow then becomes unstable to three-dimensional disturbances ($t \approx 125$). The changeover from two-dimensional to three-dimensional disturbances is referred to as *secondary instability* (Herbert, 1988). Three-dimensional structures are formed which appear as peaks and valleys of the fluctuation amplitude in dependence on the spanwise direction. Pronounced shear layers are formed by the development of Λ -shaped vortices. The shear layers generated by the Λ -vortices roll up into new, smaller-scale vortices with areas of strong shear, and narrow spikes in the instantaneous velocity signal are appearing. This highly dynamic transient state soon leads to localized breakdown into turbulent spots.

LES Model In the ADM approach, the filtered Navier-Stokes equations with approximately deconvolved quantities u_i^* used in the unclosed terms and a relaxation term added to the right-hand side are

Table 1: Temporally and spatially averaged skin friction Re_τ obtained for the different simulations of fully developed turbulent channel flow. All DNS results are grid-filtered to $32^2 \times 33$ grid points.

Re_τ for $Re_b =$	2800	3333	
ADM-2D $32^2 \times 33$, 2D filtering and deconvolution	177.5	214.0	----
RT $32^2 \times 33$, only 3D relaxation term	174.9	207.5	—
DSMAG $32^2 \times 33$, dynamic Smagorinsky	165.8	200.1
no-model LES $32^2 \times 33$	203.1	221.1	—
fully-resolved DNS $128^2 \times 129$	178.6	205.7	●
filtered with G	176.6	203.6	○

used together with the filtered incompressibility constraint (Stolz et al., 2001a),

$$\frac{\partial \bar{u}_i}{\partial t} + \frac{\partial \overline{u_j^* u_i^*}}{\partial x_j} + \frac{\partial \bar{p}}{\partial x_i} - \frac{1}{Re} \frac{\partial^2 \bar{u}_i}{\partial x_j \partial x_j} = -\chi (I - Q_N * G) * \bar{u}_i \quad \text{and} \quad \frac{\partial \bar{u}_i}{\partial x_i} = 0, \quad (7)$$

where \bar{u}_i and \bar{p} are the filtered velocity and pressure, respectively. Here, an overbar denotes filtered quantities $\bar{u}_i := G * u_i$, a star stands for the approximately deconvolved quantities $u_i^* := Q_N * \bar{u}_i$, G is the discrete primary low-pass filter and Q_N its approximate inverse (Stolz and Adams, 1999).

$$Q_N = \sum_{\nu=0}^N (I - G)^\nu = (I - G)^{N+1} \approx G^{-1}. \quad (8)$$

The definition of G is given in Stolz et al. (2001a).

Two alternative variants of the standard ADM (Stolz et al., 2001a) have been developed, both of which were found to be suitable for LES of transitional channel flow on grids as coarse as $32^2 \times 33$ (Schlatter et al., 2003a), i.e. less than 1% of the DNS. It has been shown in Schlatter et al. (2003a) that this resolution, particularly in the wall-normal direction, is just sufficient for capturing the key elements of channel flow transition.

- *ADM-2D*: Instead of using three-dimensional filtering and deconvolution, only two-dimensional filtering in the homogeneous (wall-parallel) directions is applied, resulting also in a two-dimensional formulation of the relaxation term. The two-dimensional deconvolution operator is maintained all the way through the transitional and turbulent phases. Herewith the advantages of the ADM technique are retained, although this model is not as general as the original formulation since it is restricted to filtering in two dimensions only. Note that in most transition simulations involving homogeneous directions, the SGS model is restricted to these directions (Germano et al., 1991; Ducros et al., 1996)
- *RT*: The three-dimensional filter definition is used to evaluate the relaxation term, but the non-linear terms are evaluated as $\frac{\partial \bar{u}_j \bar{u}_i}{\partial x_j}$, as in a no-model calculation. Different from standard ADM and ADM-2D, within this procedure the quantity \bar{u}_i has to be considered as filtered by sharp spectral cut-off to grid resolution (grid-filter). This modification is still as general as the standard ADM procedure but does not use deconvolved quantities for the non-linear terms. A more detailed examination of these so-called *relaxation-term (RT) models* can be found in Schlatter et al. (2003b) together with an investigation of the influence of aliasing errors.

For both options, a dynamic determination of the relaxation parameter χ according to Stolz et al. (2001b) is applied.

LES Results The above LES models have been implemented in the simulation code and calculations have been performed at the substantially reduced resolution of $32^2 \times 33$ grid points. Although the Λ -vortices can be identified in all the different simulations, the time of breakdown is notably different for the various computations. This is shown in figure 5a which depicts the temporal evolution of the Reynolds number Re_τ based on the friction velocity and the channel half-width, averaged over the two walls. The onset of transition and the initial growth of Re_τ is still comparable for all simulations summarized in table 1, while they begin to separate during the spike stage ($t = 140$). Furthermore, the skin friction

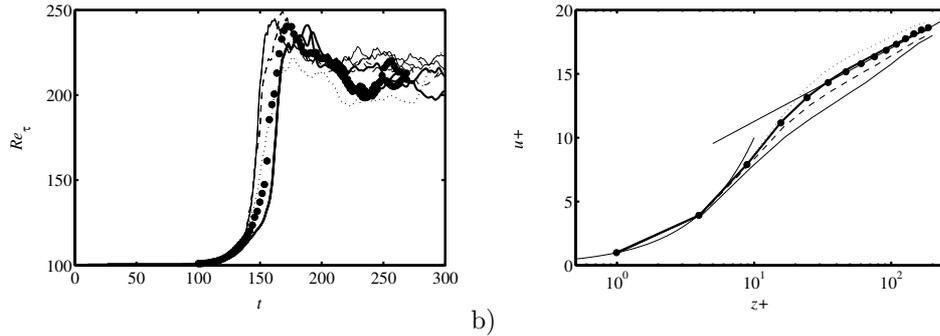


Figure 5: *Left*: Evolution of the non-dimensional wall shear stress Re_τ averaged over the wall planes during the transitional phase ($Re_b = 3333$). *Right*: Averaged streamwise velocity profile u^+ scaled in wall units in the fully turbulent regime ($Re_b = 3333$). Line caption see table 1.

peak value is similar and the well-known overshoot of Re_τ of about 15% is visible for DNS, ADM-2D and RT. The formation of fully developed turbulence largely proceeds on the same time scale for all models. The stationary values of Re_τ after transition ($Re_b = 3333$) are given in table 1.

It is obvious that the no-model LES overpredicts the stationary value of Re_τ by approximately 10% compared to the resolved DNS. Both SGS model calculations ADM-2D and RT provide a much better prediction of the wall friction. The dynamic Smagorinsky model (DSMAG) does similarly, although it seems to be slightly too dissipative at this coarse resolution.

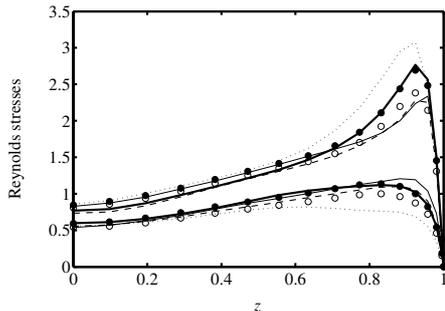


Figure 6: RMS velocity fluctuations (Reynolds stresses) $\sqrt{u'_1 u'_1} / u_\tau$ and $\sqrt{u'_2 u'_2} / u_\tau$ in the fully turbulent case. Line caption see table 1.

A similar conclusion can be drawn from the mean velocity profile depicted in figure 5b; especially RT agrees very well with the fully-resolved DNS.

The predictions of the velocity fluctuations (figure 6) with the dynamic Smagorinsky model DSMAG are not very accurate, whereas the ADM cases ADM-2D and RT show a substantial improvement. Again, the RT model (no deconvolution) is very close to the values of the fine-grid DNS calculation. ADM-2D is less accurate, leading to the conclusion that capturing of three-dimensional effects in the relaxation and deconvolution are important (see also the three-dimensional filtering and deconvolution in Stolz et al. (2001a)).

4 Conclusions

In this contribution, the basic difficulties of LES of transitional flows have been discussed. Results of several large-eddy simulations of transitional incompressible channel flow have been presented. In order to facilitate the use of deliberately chosen coarse grids, the standard ADM methodology had to be adapted. Two recent variants of the original ADM algorithm have been described and compared to no-model LES and fine-grid DNS calculations as well as to results of the dynamic Smagorinsky model.

The results obtained indicate that it is well possible to simulate transitional wall-bounded flows on the basis of the modified ADM method while preserving the accuracy of the original for the turbulent phase. During the early stages of transition, the results of no-model LES calculations, which have sufficient resolution for this stage of flow development, are recovered. This confirms that the LES model is inactive there. During the rapid mean flow development, the model contributions are beginning to provide additional dissipation. The results demonstrate that a proper treatment of each spatial direction should be used in order to faithfully represent the relevant physical features such as the local gradients. Moreover, in the three-dimensional case the SGS model is formulated in a more general way.

The neglect of deconvolution in the RT model is a step towards a more simple subgrid model which provides dissipation based on a high-pass filtering approach. A further study aiming at a more versatile procedure for an easier determination of the relaxation parameter χ has been investigated in Schlatter et al. (2003b).

The LES models presented herein are completely dynamic in space and time such that no ad-hoc constants or adjustments are needed. This self-adaptation to the current local flow situation is very important for all types of transitional flows. An interesting extension of the present work will be spatial simulations of transition with more complex flow situations including separation.

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CSE Research Projects

Title: Frustrated Quantum Spin Systems

Researchers: G. Schmid, S. Wessel, M. Troyer, M. Sigrist *
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Institute/Group: *Theoretische Physik, ETH Zürich
** Université de Toulouse

Description:

Frustrated quantum spin systems offer the possibility to study the appearance of unusual quantum phases, driven by competing interactions and large fluctuations. In recent experiments on insulating cuprate materials evidence for substantial cyclic four-spin exchange interactions was accumulated. Higher order spin interactions are poorly understood in general. We investigated the overall phase diagrams of systems with such interactions and witnessed a surprisingly rich phase diagram already on the simple ladder structure. Among the different phases we discover the long sought staggered spin current phase.

We are also interested in the phase diagram of the generalized Shastry-Sutherland model (which seems to be realized in $\text{SrCu}_2(\text{BaO}_3)_2$). Our results indicate that the phase between the usual Neel order and the exact dimer phase is actually a Valence Bond Crystal with a plaquette covering.

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A. Läuchli, S. Wessel and M. Sigrist, Phys. Rev. B **66**, 014401 (2002)

Title: Numerical investigation of strongly correlated systems

Researchers: C. Honerkamp, Th. Siller, M. Indergand, S. Wessel,
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*** Theoretische Physik, Universität Leipzig, Germany
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Description:

The physics of strongly correlated electrons is one of the most active research fields in condensed matter physics. Next to technologically relevant developments such as high-temperature superconductors and colossal magnetoresistance materials, the field raises many important and difficult questions to basic research such as new exotic states of matter and the breakdown paths of the more conventional metallic or ordered states. We analyze the latter issue by means of extensive numerical renormalization group calculations for two-dimensional electron systems. Furthermore novel correlation phenomena like the binding of holes or magnetic excitations with impurity sites are investigated using modern numerical techniques such as density matrix renormalization group and exact diagonalization.

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E. Koch, O. Gunnarsson, S. Wehrli and M. Sigrist, Preprint, submitted to Phys. Rev. B
A. Lauchli, C. Honerkamp and T.M. Rice, Preprint, submitted to Phys. Rev. Lett.
H. Kusunose and T.M. Rice, Preprint, submitted to Phys. Rev. B
C. Honerkamp and T.M. Rice, J. Low Temp. Phys. **131**, 159 (2003).

Title: Quantum Antiferromagnetism in Quasicrystals

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A. Jagannathan **
S. Haas **

Institute/Group: * Theoretische Physik, ETH Zürich
** University of Southern California , Los Angeles, USA

Description:

Quantum magnetic phases of low-dimensional antiferromagnetic Heisenberg systems show various degrees of disorder caused by zero-point fluctuations. In our study we explore how non-periodic environments, such as provided in quasicrystal structures, further affect the magnetic properties of quantum magnets. In particular we study the Heisenberg model on a two-dimensional bipartite quasiperiodic lattice. The distribution of local staggered magnetic moments is determined, using the stochastic Series Expansion Quantum Monte Carlo method. A non-trivial inhomogeneous ground state is found. For a given local coordination number, the values of the magnetic moments are spread out, reflecting the fact that no two sites in a quasicrystal are identical. A hierarchical structure in the values of the moments is observed which arises from the self-similarity of the quasiperiodic lattice. Furthermore, the computed spin structure factor shows antiferromagnetic modulations that can be measured in neutron scattering and nuclear magnetic resonance experiments. Our generic model is a first step towards understanding magnetic quasicrystals such as the recently discovered Zn-Mg-Ho icosahedral structure.

References:

S. Wessel, A. Jagannathan and S. Haas, Phys. Rev. Lett. 90, 177205 (2003).

Title: Solitons in the nonlinear Hartree Equation

Researchers: W.H Aschbacher, J. Fröhlich, G. Interlandi, M. Troyer,

Institute/Group: Theoretische Physik, ETH Zürich

Description:

This project concerns minimizers (lowest energy eigenfunctions) of the Hartree energy functional with attractive Hartree interaction. Among the most important findings is a symmetry breaking of the ground state wave function when the interaction is sufficiently strong. We also investigate the time evolution of such soliton-like minimizers in an external potential. As a particular application of these results and as a motivation for the investigation of the Hartree functional, we propose a generalization of the Gross-Pitaevskii functional of Bose-Einstein condensation for *attractive* interatomic forces that overcomes the breakdown of this theory at the collapse point of the condensate.

References:

W.H. Aschbacher, J. Fröhlich, G.M. Graf, K. Schnee, M. Troyer,
J. of Math. Phys. **43**, 3879 (2002)

Title: Vortices in superconductors

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** Landau Institute, Moscow, Russia

Description:

Vortices in type-II superconductors, caused by the intrusion of a magnetic field, form a new and unusual form of matter, so-called “vortex matter”. Using numerical simulations we investigate two aspects in particular. The first are equilibrium ground state vortex configurations close to the quantum phase transition between type-I and type-II superconductors at $\kappa=1/\sqrt{2}$. The second project concerns the dynamics of vortex collisions, as a basis of a microscopic description of vortex lattice melting. Numerical simulations show that when two vortices collide, they recombine twice, and thus effectively cross.

References:

F. Mohamed, M. Troyer, G. Blatter and I. Luk'yanchuk, Phys. Rev. B **65**, 224504 (2002)

Title: Phase Diagrams of 2D Bosonic Systems

Researchers: G. Schmid, S. Todo, M. Troyer *
G.G. Batrouni, K. Bernardett, F. Hebert **
A. Dorneich, W. Hanke ***
R.T. Scalettar ****

Institute/Group: * Theoretische Physik, ETH Zürich
** Université de Nice, France
*** Universität Würzburg, Germany
**** University of California, Davis

Description:

The behavior of bosons in two dimensions is of major current interest for several reasons. Such systems describe, for example, Helium adsorbed on surfaces. They can also be mapped (approximately) to models for Josephson junction arrays, which can be manufactured and studied experimentally. In addition, a Hamiltonian describing a system of hardcore bosons, can be mapped exactly onto models of spin-1/2 Heisenberg quantum antiferromagnets. Such quantum spin models are of great theoretical and experimental interest: There are several recently discovered materials, exhibiting a variety of interesting properties such as magnetization plateaus, which are very well described by these Hamiltonians. In addition, such bosonic models can be used as effective models for fermionic systems where the bosonic Cooper pairs are well formed. In several extensive simulations we could determine the ground state and finite temperature phase diagram of the bosonic hardcore Hubbard model. Previously conjectured supersolid phases turned out to be phase separation instead. Unusual reentrant behavior and ordering upon *increasing* the temperature have been found.

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A. Dorneich, *et al.*, Phys. Rev. Lett. **88**, 057003 (2002).
G. Schmid and M. Troyer, preprint, submitted to Phys. Rev. Lett.

Title: Quantitative modeling of quantum magnets

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** Ames Laboratories, Ames, Iowa
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Description:

Unusual behavior is observed in materials where quantum effects are strong. These materials typically consist of low-dimensional structures, such as weakly coupled chains or planes. The most prominent examples are the high temperature superconductors, which consist of doped copper oxide layers. While we are still far from a complete understanding of these doped systems, we could make rapid progress on the undoped parent compounds, which are quantum magnets. Modern quantum Monte Carlo algorithms allow quantitative comparisons between models and experimental measurements on these quantum magnets. These comparisons allow the determination of microscopic coupling constants and the explanation of unusual magnetic properties of low-dimensional quantum magnets, such as copper and vanadium oxide materials.

References:

D.C. Johnston, Matthias Troyer, S. Miyahara, D. Lidsky, K. Ueda, M. Azuma, Z. Hiroi, M. Takano, M. Isobe, Y. Ueda, M.A. Korotin, V.I. Anisimov, A.V. Mahajan, and L.L. Miller, Preprint, submitted to Phys. Rev. B

Title: Quantum criticality

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Description:

In low dimensional systems, such as layered materials quantum fluctuations are especially strong. They can lead to a destruction of an ordered ground state, just as thermal fluctuations can destroy order at finite temperatures. In the vicinity of a quantum critical point (a continuous phase transition in the ground state of a quantum system at zero temperatures) universal quantum critical behavior can be observed. This is similar to classical critical behavior observed near classical phase transitions at finite temperatures. Universal here means that the behavior does not depend on details of the system, material, lattice structure, but only on the symmetries of the phases and on the dimensionality. Simulations on simple models can thus provide results valid for a large class of materials. In the determination of universal classical critical behavior (characterized by universal critical exponents and amplitude ratios) numerical simulations were essential. The biggest challenge for these simulations is that the relevant length scales diverge at the phase transition, requiring extremely large lattices for accurate and reliable results. Recent breakthroughs in algorithmic developments for quantum systems now allow similar calculations to be performed near quantum critical points.

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- M. Troyer, Sup. Prog. Theor. Phys. (2003)

Title: Topologically protected quantum bits

Researchers: D. Ivanov, P. Dayal, M. Troyer, G. Blatter *
L. Ioffe **
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Description:

We propose an implementation of a topologically protected quantum bit based on Josephson junction arrays. A topologically protected quantum bit has the huge advantage that no error correction is needed, since it is stable to disorder because of its topological nature. Unfortunately the implementation of a topologically protected quantum bit has remained unclear so far. Based on numerical investigations of strongly correlated systems, we show how their developing an isolated two-fold degenerate quantum dimer liquid groundstate can be used in the construction of topologically stable qubits and discuss their implementation using Josephson junction arrays

Our most recent work concentrates on a more practical device which still has some of the valuable topological features preserved. We propose a design for a qubit involving four superconducting islands in the topology of a symmetric tetrahedron, uniformly frustrated with one-half flux-quantum per loop and one-half Cooper-pair per island. This structure emulates a noise-resistant spin-1/2 system in a vanishing magnetic field. The flux-frustration boosts quantum fluctuations and relieves the constraints on junction fabrication. Variability of manipulation and optimized readout through single-shot measurements are additional benefits of this design. For specific limits, the spectrum of this '3-body' quantum system can be found analytically using quasi-classical methods, but an accurate and general determination requires numerical solution. This has been implemented successfully using exact diagonalization techniques (Lanczos) both in the charge and phase representation of the Hamiltonian.

References:

L. Ioffe, M.V. Feigel'man, A. Ioselevich, D. Ivanov, M. Troyer and G. Blatter
Nature **415**, 507 (2002).

M.V. Feigel'man, L.B. Ioffe, V.B. Geshkenbein, P. Dayal, and G. Blatter, Preprint, submitted to Phys. Rev. Lett..

Title: Quantum Monte Carlo Study of Randomness-Driven Quantum Phase Transitions in Two-Dimensional Antiferromagnets

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Description:

We investigate effects of randomness, such as site dilution and bond randomness, on the ground state of two-dimensional Heisenberg antiferromagnets and also the nature of randomness-driven quantum phase transitions by means of the quantum Monte Carlo method.

References:

M. Matsumoto, C. Yasuda, Syngge Todo, and Hajime Takayama,
Phys. Rev. B **65**, 014407 (2002)

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J. Phys. Chem. of Solids, **63**, 1607 (2002)

Masaaki Nakamura and Syngge Todo, Phys. Rev. Lett. **89**, 077204 (2002)

Title: Electronic Structure of Strongly Correlated Materials

Researchers: T.M. Rice, M. Sigrist *
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Description:

Modifications of standard density functional theory are needed to calculate the electronic structure in the presence of strong correlations among the electrons. One method known as LDA+U, allows the treatment of broken symmetries in spin and orbital degrees of freedom. A second method combines the local density approximation with the dynamical mean field theory to describe systems without a broken symmetry. These methods are applied to materials of high current interest.

References:

V.I. Anisimov, I.A. Nekrasov, D. Ekondkov, T.M. Rice and M. Sigrist,
Eur. J. Phys. B **25**, 191 (2002).

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Title: New Quantum Monte Carlo Algorithms

Researchers: M. Troyer *
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F. Alet *
S. Wessel *
E. Sorensen ***

Institute/Group: * Theoretische Physik, ETH Zürich
** Universität Würzburg, Germany
*** Mc Master University, Canada

Description:

Great algorithmic progress for quantum Monte Carlo simulations has been achieved in the past years, shadowing the growth of processor power by many orders of magnitude. Still, many problems remain intractable and further algorithmic progress is needed. We have developed an algorithm to measure offdiagonal and time-dependent Green's function in the Stochastic Series Expansion (SSE) Quantum Monte Carlo algorithm.

A possible break-through was achieved by an adaptation of Wang-Landau sampling to quantum systems. This algorithm has the potential of overcoming the problems associated with tunneling through energy barriers at first order transitions and for disordered and glassy systems.

We also investigated the generalization of detailed balance equations required during the Quantum Monte Carlo simulations. We obtain accordingly improved "directed loop" algorithms, which are shown to be more efficient than conventional ones.

We have developed a continuous time worm algorithm to study quantum lattice models with nearest-neighbor interactions.

References:

M. Troyer, S. Wessel and F. Alet, Phys. Rev. Lett. **90**, 120201 (2003).
F. Alet and E. Sorensen, Phys. Rev. E **68**, 026702 (2003).
F. Alet, S. Wessel, M. Troyer, submitted to Phys. Rev. E.

Title: Flat-Histogram Algorithms

Researchers: P. Dayal, S. Trebst, M. Troyer, S. Wessel, D. Wuertz *
S. Sabhapandit, S. Coppersmith **

Institute/Group: *Theoretische Physik, ETH Zürich
** Department of Physics, University of Madison, USA

Description:

When studying phase transitions the traditional Metropolis algorithm becomes inefficient when the temperature approaches the critical temperature of the transition. For second order phase transitions the problem of "critical slowing down" -- a rapid divergence of the number of Monte Carlo steps needed to obtain a subsequent uncorrelated configuration -- was solved more than a decade ago by cluster update algorithms. At first order transitions and in systems with many local minima of the free energy, such as frustrated magnets or spin glasses, there exists the similar problem of long tunneling times between local minima. Recently proposed flat histogram methods produced promising results to effectively study first order phase transitions in these systems as well.

By studying the optimal scaling of flat-histogram methods with system size for classical 2D Ising models we determined a lower algorithmic bound for all flat-histogram methods such as Wang-Landau sampling, multicanonical sampling, tempering and broad histograms. For the 2D spin glass we found severe limitations in the form of exponential scaling and fat-tailed Frechet distributions of the tunneling time, the relevant time scale when sampling the full energy range in a multicanonical simulation.

References:

P. Dayal, S. Trebst, S. Wessel, D. Wuertz, M. Troyer, S. Sabhapandit, S.N. Coppersmith,
Preprint, submitted to Phys. Rev. Lett.

Title: Simulations of novel exotic phases of matter

Researchers: F. Alet, S. Trebst, M. Troyer

Institute/Group: Theoretische Physik, ETH Zürich

Description:

Novel states of matter with fractional quantum numbers, where an electron effectively splits up into smaller parts, each carrying only parts of the mass or charge of the original electron, have been a vivid research topic within condensed matter physics, propelled by the discovery of high temperature superconductivity and the fractional quantum hall effect.

The central role of excitations carrying a fractional charge in these novel quantum phases has been addressed in theoretical works over the years. Related topological states have recently been found to be promising candidates for the physical implementation of qubits, the elementary building units of a quantum computer. What has been missing so far are detailed numerical investigations if these proposed exotic phases are actually realized in realistic model.

We develop novel quantum simulation algorithms to study microscopic models and search for these fractionalized states with explicit macroscopic topological order to obtain the needed definitive proof of existence of these phases through high-performance numerical work.

Title: NP-hardness of the negative sign problem of quantum Monte Carlo simulations

Researchers: M. Troyer *
U.-J. Wiese **

Institute/Group: * Theoretische Physik, ETH Zürich
** Universität Bern

Description:

Quantum Monte Carlo simulations, while being efficient for bosons and non-frustrated quantum magnets, suffer from the infamous "negative sign problem" when applied to fermions or frustrated magnets -- causing an exponential increase of the computing time with the number of particles. A polynomial time solution to the sign problem is highly desired, since it would provide an unbiased and numerically exact method to simulate correlated quantum systems. Here we argue, however, that such a solution is almost certainly unattainable, by showing that it is NP-hard, implying that a generic solution of the sign problem would also solve all NP-complete problems in polynomial time.

References:

M. Troyer and U.-J. Wiese, Preprint

Title: Numerical Simulation of Chemically Reactive Flows

Researchers: Christos E. Frouzakis
Konstantinos Boulouchos

**Institute/
Group:** Aerothermochemistry and Combustion Systems Laboratory

Description:

The numerical simulation of chemically reactive flows, although still severely limited by the availability of resources for application on problems of practical interest, can provide in-depth understanding of fundamental problems in combustion. In addition, simulation results are essential for the proper modeling of turbulent combustion. Our numerical simulation codes are based on a high-order time splitting scheme for the time-accurate integration of the conservation equations in their low Mach number form. Spatial terms are discretized with the spectral element method, giving us the geometric flexibility needed for flows in complex geometries. The 2-D code can include chemical kinetics and transport models of various complexities. Using detailed chemistry and transport, it has been employed in the study of the transition from diffusion to premixed flames and the role of edge flames in a hydrogen/air opposed-jet burner. During the last year, a lot of effort has also been invested on the implementation of the algorithm on a 3-D parallel code, which is currently used to study cell formation and oscillatory phenomena observed experimentally in jet diffusion flames close to extinction.

References:

- A.K. Chaniotis, C.E. Frouzakis, J.C. Lee, A.G., D. Poulikakos, and K. Boulouchos, Remeshed smoothed particle hydrodynamics for the simulation of laminar chemically reactive flows, *J. Comp. Phys.*, **191**(1), pp. 1-17, 2003
- C. E. Frouzakis, A. G. Tomboulides, J. Lee, K. Boulouchos, From diffusion to premixed flames in an H₂/air opposed-jet burner: the role of edge flames, *Combust. Flame*, **130**(3), pp. 171-184, 2002
- C. E. Frouzakis, A. G. Tomboulides, J. Lee, K. Boulouchos, Transient phenomena during diffusion/edge flame transitions in an opposed-jet hydrogen/air burner", *Proc. Combustion Inst.*, **29**, pp. 1581-1587, 2002

Title: Computational Solid State Electronics

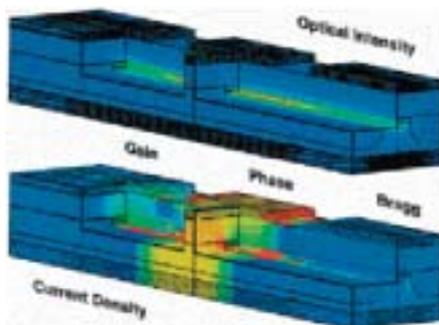
Researchers: Wolfgang Fichtner
Andreas Schenk
Andreas Witzig
Jens Krause
Eduardo Alonso
Dölf Aemmer

Institute/ Group: Integrated Systems Laboratory/
Technology Computer Aided Design (TCAD) Group

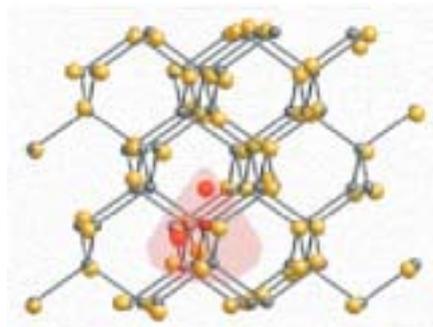
Description:

For the development of novel micro- and opto-electronic processes, devices and circuits, the use of advanced numerical simulation tools has become indispensable. With the continuing advances in semiconductor technology, and the trend to further scaling of the active device dimensions, computational solid state electronics has reached an extremely high level of physical and numerical sophistication. As we are rapidly approaching nanoscale dimensions, effects at the atomistic or quantum-mechanical level are becoming dominant.

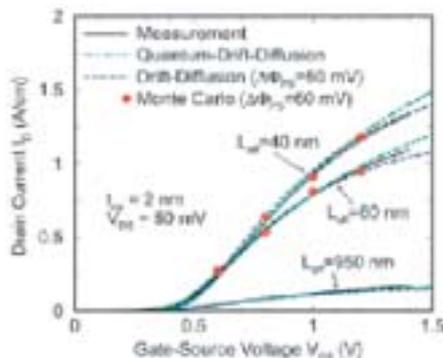
We are performing research in a variety of fields in the computational solid state electronics domain. Current projects include the development and utilization of new simulations tools for molecular dynamics studies in material diffusion, novel devices such as single-electron transistors, and optoelectronic devices such as LEDs and laser diodes. For all of our projects, the main emphasis lies in the exploration how accurate physical models can be pragmatically combined with state-of-the-art numerical algorithms. These simulations were carried out on compute-servers of our laboratory, but now we will also use the IBM SP4 system at CSCS Manno in a *Large User Project*. The following pictures illustrate some of our activities:



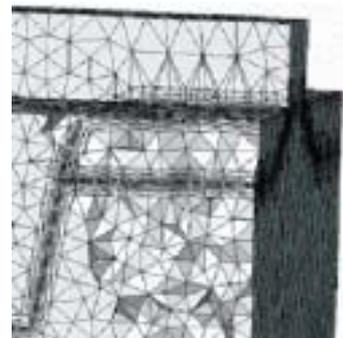
Coupled electro-optical 3D Simulation of a semiconductor laser.



Ab initio molecular dynamics simulation of dopant diffusion in silicon.



Monte Carlo Simulation of Nanoscale MOSFETs.



Anisotropic 3D meshing in semiconductor device and process simulation.

Title: Including energetically favorable tautomers of nucleobase derivatives in molecular docking applications

Researchers: Pavel Pospisil
Patrick Ballmer
Leonardo Scapozza
Gerd Folkers

Institute/Group: Institute of Pharmaceutical Sciences
Department of Chemistry and Applied Biosciences, ETH Zürich

Description:

The therapeutically important Herpes simplex virus type 1 thymidine kinase (HSV1 TK) is able to accommodate several pyrimidine and purine bases in its active site. Tautomers of known nucleobase analogs of diverse viral thymidine kinases were docked into the active site using the programs AutoDock and FlexX. Additionally, different rotameric states of the Gln125 amino acid side chain crucial for ligand binding were considered. In order to perform further investigations using an extended library of drug-like purine and pyrimidine analogs, a program to generate all tautomers of each database entry (AGENT) was developed. The tautomers of several compounds achieved different scores as compared to earlier screenings in which tautomerism and rotameric states were disregarded. Subsequent comparative ranking and scoring of compounds versus their corresponding tautomers revealed an increased amount of detected hits. Best-ranked tautomers were submitted to semiempirical calculations (using MOPAC) of their heat of formations and the favorable binding of the docked tautomers was predicted. The results showed the impact of tautomerism in predicting ligand-binding orientation.

References: A manuscript is in preparation.

P. Pospisil, P. Ballmer, L. Scapozza and G. Folkers. Tautomerism in Computer-Aided Drug Design J Recept Signal Transduct Res 33:(4) (2003) in press

Title: A molecular dynamics study of reovirus attachment protein $\sigma 1$ reveals conformational changes in $\sigma 1$ structure

Researchers: Andrea Cavalli
Gerd Folkers
Leonardo Scapozza

Institute/Group: Institute of Pharmaceutical Sciences
Department of Chemistry and Applied Biosciences, ETH Zürich

Description:

Two protocols of 5 ns each of molecular dynamics simulations in explicit water were performed using the recently determined crystal structure of the reovirus attachment protein, $\sigma 1$ (PDB code 1KKE) (in total, about 45,000 atoms). These studies were conducted to improve an understanding of two unique features of $\sigma 1$ structure: the protonation state of Asp345, which is buried at the $\sigma 1$ trimer interface, and the flexibility of the protein at a defined region below the receptor-binding head domain. The results indicate that protonation of Asp345 is essential to the integrity of the head trimer structure seen by X-ray crystallography. This was further confirmed carrying out electrostatic calculations using the finite difference Poisson-Boltzmann method. Deprotonation induces structural changes that destabilize the trimer interface.

Moreover, increased mobility was observed for three polar residues (Ser291, Thr292, and Ser293) located within an insertion between the second and third β -spiral repeat of the crystallized portion of the $\sigma 1$ tail. These amino acids likely interact with water molecules of the solvent bulk and are responsible for a swaying movement of the head with respect to the tail of $\sim 50^\circ$ during 5 ns of simulations.

Our studies show that protonation of Asp345 is crucial for the stability of the trimer. Besides, our findings provide new insights about the conformational dynamics of $\sigma 1$, which is able to undergo more dramatic bending than observed in the crystal structure. We speculate that these $\sigma 1$ design features play important roles in reovirus attachment and cell entry.

References: A. Cavalli, A. E. Prota, T. Stehle, T. S. Dermody, M. Recanatini, G. Folkers and L. Scapozza A molecular dynamics study on reovirus attachment protein $\sigma 1$ reveals conformational changes in $\sigma 1$ structure Biophysical Journal (2003) submitted

Title: Molecular mechanisms of resistance to imatinib in Ph⁺ leukemias:
A molecular dynamic study

Researchers: Marc Gasser
Thomas Kuoni
Carlo Gambacorti
Leonardo Scapozza

Institute/Group: Institute of Pharmaceutical Sciences
Department of Chemistry and Applied Biosciences, ETH Zürich

Description:

Imatinib, a tyrosine kinase inhibitor, is an innovative treatment modality for the Ph⁺ leukemias and gastrointestinal stromal tumors. Imatinib complexes selectively the Abl tyrosine kinase with a 100fold higher binding affinity to the inactive conformation (7mM) compared to the active form (38nM). Binding of the inhibitor seems to stabilize the inactive form of the enzyme and the inhibition induces the transformed cells to apoptosis. However, the problem of resistance to imatinib became quickly evident after imatinib entered clinical use, due to mutations within the kinase domain of Bcr-Abl.

In order to explore the effect of these mutations, molecular dynamic studies were performed including the wild type and mutated tyrosine kinase domain using AMBER 5. The distant mutations seem to have a common mechanism, that is the modification of the equilibrium between inactive and active conformation by conserving the stability of the active structure while the inactive conformation is destabilized. Despite the different locations, molecular dynamic simulation suggested that these mutations decrease the binding affinity of imatinib without affecting the kinase activity.

References: A manuscript is in preparation.

Title: The RET Tyrosine Kinase – Homology Modeling and Docking Study

Researchers: Thomas Kuoni
Carlo Gambacorti
Leonardo Scapozza

Institute/Group: Institute of Pharmaceutical Sciences
Department of Chemistry and Applied Biosciences, ETH Zürich
Department of Experimental Oncology
Istituto Nazionale Tumori, Milan, Italy

Description:

Protein tyrosine kinases play a central role in various biological processes such as control of metabolism, cell growth, differentiation and apoptosis. The RET proto-oncogen encodes for a receptor tyrosine kinase, that causes Multiple Endocrine Neoplasia MEN2A, MEN2B, medullary thyroid carcinoma and Hirschsprung disease. A selective inhibitor that can block the RET activity could be a promising approach in cancer therapy. To date, the three-dimensional structure of RET is still unsolved. Therefore we created two models of the RET kinase with homology modeling using the phosphorylated insulin receptor tyrosine kinase (PDB: 1IR3) as template for the active form and the Abl kinase (PDB: 1FPU) for the inactive form, respectively. Both models were refined using AMBER 6 for computing molecular dynamic simulations. The binding mode of published inhibitors was evaluated by molecular docking. Furthermore, virtual screening was performed, using DOCK 4, FlexX and GOLD on the models. Some hits were selected and are in testing.

References: A manuscript is in preparation.

Title: The Jacobi–Davidson algorithm for solving large sparse symmetric eigenvalue problems Inverses

Researchers: Roman Geus
Peter Arbenz

**Institute/
Group:** Institute of Computational Science

Description:

The Maxwell equations for the strength of the electric field are solved by a mixed method with quadratic finite edge elements for the field values and corresponding node-based finite elements for the Lagrange multiplier. This approach avoids spurious modes that are introduced if the divergence-free condition for the electric field is not treated properly. The Jacobi-Davidson (JD) algorithm has been implemented for solving the resulting large sparse symmetric matrix eigenvalue problem. A two-level hierarchical basis preconditioners are employed for the efficient solution of the correction equation that is at the heart of the JD algorithm. The solver is implemented stably and efficiently. It is able to handle very large eigenvalue problems of orders above 7 millions on a single-processor workstation.

The software is implemented as Python modules. The time-critical computations are realized as extension modules written in C.

References:

P. Arbenz and R. Geus: *Multilevel preconditioners for solving eigenvalue problems occurring in the design of resonant cavities*. Technical Report 396, Institute of Computational Science, ETH Zürich, April 2003.

R. Geus and P. Arbenz: *PySparse and PyFemax: A Python framework for large scale sparse linear algebra*. Contributed paper at PyCon03, Washington DC, USA, 26-28 March, 2003.

R. Geus, *The Jacobi–Davidson algorithm for solving large sparse symmetric eigenvalue problems*, ETH Zürich, PhD Thesis No. 14734, 2002.

R. Geus and P. Arbenz: *PYFEMAX: A Python Finite Element Maxwell Solver*. PSI-Annual Report, VI:51-53, 2002, Paul Scherrer Institute, CH-5232 Villigen-PSI.

Title: Jacobi–Davidson algorithms for the complex symmetric eigenvalue problem

Researchers: Oscar Chinellato
Peter Arbenz

**Institute/
Group:** Institute of Computational Science

Description:

The development and optimization of modern optoelectronic semiconductor lasers, such as vertically-cavity surface-emitting lasers (VCSELs) require the solution of the three-dimensional homogeneous Maxwell equations describing the optical field. Their numerical discretization by finite element methods lead to large sparse generalized complex-symmetric matrix eigenvalue problems.

The stable and accurate computation of these matrices is investigated. Variants of the Jacobi–Davidson method are derived and implemented that can exploit their complex-symmetric structure. The correction equations are solved by conjugate-gradient-type algorithms preconditioned by hierarchical basis preconditioners based on Nédélec elements.

References:

P. Arbenz and M. Hochstenbach: *Jacobi–Davidson Method for Solving Complex-Symmetric Eigenvalue Problems*. July 2002. Accepted for publication in SIAM J. Scientific Computing (2003)

O. Chinellato and W. Gautschi: *Improved and Stabilized Modification Algorithms for Orthogonal Polynomials*. Paper in preparation.

Title: CSE-SEP project TH-1/02-4: Large Scale Eigenvalue Problems in Opto-Electronic Semiconductor Lasers and Accelerator Cavities

Researchers: Peter Arbenz*
Wolfgang Fichtner†
Hansruedi Fitze‡
Olaf Schenk§

**Institute/
Group:** *Institute of Computational Science
†Integrated Systems Laboratory
‡Paul Scherrer Institute
§Department of Informatics, University of Basel

Description:

For the development and optimization of both modern and future optoelectronic semiconductor lasers, such as vertically-cavity surface-emitting lasers (VCSELs), and of particle accelerator cavities, computer aided design became an indispensable tool building a tremendous challenge for researchers in physics, computational science, and engineering. Though both problems differ in their technical background and their dimensions by several orders of magnitude (a few micrometers versus a few meters) they both require the solution of the three- dimensional homogeneous Maxwell equations describing the optical and electromagnetic field, respectively. Their numerical discretization by finite element methods lead to large sparse generalized eigenvalue problems which are hard to solve on contemporary computer architectures with respect to memory constraints and simulation time. In laser simulation these eigenvalue problems describe only a part of the physical description, i.e. they are naturally imbedded into a much more complex nonlinearly coupled optoelectronic model.

The aim of this project is the extension of an existing Maxwell equation eigensolver to very large scale problems and its integration into an semiconductor laser simulator bringing research and development of computational science and engineering together.

References:

O. Chinellato, P. Arbenz, M. Streiff and A. Witzig: *Computation of Optical Modes Inside Axisymmetric Open Cavity Resonators*. Technical Report 402, Institute of Computational Science, ETH Zürich, June 2003. Accepted for publication in Future Generation Computer Systems.

Title: Parallel Multigrid Methods using Sparse Approximate Inverses

Researchers: Oliver Bröker*
Marcus J. Grote†

Institute/ *Institute of Scientific Computing
Group: † Department of Mathematics, University of Basel

Description:

We consider combining sparse approximate inverses with geometric and algebraic multigrid, see Trottenberg et al. (2001) and Ruge and Stüben (1987). The approximate inverses are based on the SPAI-Algorithm by Grote and Huckle (1997). For a given matrix A , a sparse approximate inverse M is computed by minimizing $I - MA$ in the Frobenius norm. Various choices for the sparsity pattern of M yield a new hierarchy of smoothers: SPAI-0, where M is diagonal; SPAI-1, where M has the sparsity pattern of A ; and SPAI(ε), where the sparsity pattern of M is determined automatically by the SPAI-Algorithm. The approximate inverses can be used as smoothers. The performance of SPAI-1 smoothing is comparable to that of the Gauss-Seidel iteration, while SPAI(ε) may be used when the simpler SPAI-0 and SPAI-1 smoothers fail. We investigate further reductions of the sparsity of the approximate inverses and further use of the approximate inverses as the definition for strong connections and incorporation in the Galerkin coarse grid projection. Essential advantages of combining multigrid with SPAI are: improved robustness, inherent parallelism, ordering independence, and possible local adaptivity.

References:

O. Bröker: *Parallel Multigrid Methods using Sparse Approximate Inverses*, ETH Zürich, PhD Thesis No. 15129, May 2003.

O. Bröker and M. J. Grote:
Sparse Approximate Inverse Smoothers for Geometric and Algebraic Multigrid.
Appl. Numer. Math. **41** (2002), pp. 61–80.

O. Bröker, M. J. Grote, C. Mayer, and A. Reusken:
Robust Parallel Smoothing for Multigrid via Sparse Approximate Inverses.
SIAM J. Sci. Comput. **23** (2002), pp. 1396–1417.

Title: Finite Element Predictions for the Thermoelastic Properties of Nanotube Reinforced Polymers

Researchers: Hans Rudolf Lusti
Andrei A. Gusev

Institute/Group: Institute of Polymers, Department of Materials, ETH

Description:

The overall effective thermoelastic properties of nanotube reinforced polymers (NRP) were calculated numerically by using a finite element based procedure. 3D multi-inclusion periodic computer models were built for 3 different nanotube orientation states, namely, unidirectional, 2D random in-plane and 3D random states. The enhancement of the Young's modulus as well as the decrease of the thermal expansion coefficient was calculated numerically, assuming technologically relevant combinations of nanotube aspect ratio and volume fraction. Maximal changes of the thermoelastic properties can be achieved in the longitudinal direction of unidirectional NRPs whereas 2D random in-plane and 3D random composite morphologies exhibit more moderate enhancements but in more than one specific direction. Numerical predictions for the in principle possible enhancements of the thermoelastic properties confirmed that carbon nanotubes are considerably more effective for the stiffening of polymers than conventional glass or carbon fibers.

References: Submitted to Model. Simul. Mater. Sci.

Title: Matching thermal expansion of mica-polymer nanocomposites and metals

Researchers: Olga Guseva***
Hans Rudolf Lusti*
Andrei A. Gusev*

Institute/Group: * Institute of Polymers, Department of Materials, ETH
** Laboratory for Metallic Materials, EMPA, Dübendorf

Description:

Hybrid polymer-metal structures are indispensable today in various demanding applications. For example, polymer-based coatings and paints are widely used to protect the metal bodies of aircrafts and automobiles whereas polymer films are employed as interlayer dielectrics and packaging materials in microelectronics. As polymers and metals have different thermal expansion, temperature changes lead to the appearance of internal stresses that diminishes the structures' service life and causes shape stability problems. Aluminosilicates such as clays and mica have an order of magnitude lower thermal expansion coefficients than organic polymers. One can therefore reduce the thermal expansion by filling polymers with aluminosilicates.

We have carried out finite element numerical simulations to show that by the dispersing of small amounts of exfoliated muscovite mica platelets in a polymer one can considerably reduce and eventually match the thermal expansion of metal and polymer parts. This mismatch reduction can extend the service life of metal-polymer joint structures. For the identification of the potential of mica-polymer nanocomposites, a finite-element-based numerical route was used. We studied computer models comprised of a random dispersion of fully aligned round muscovite mica platelets. A most striking finding is that the decrease of the thermal expansion for such nanocomposites is controlled by the product of the aspect ratio a (ratio of the platelet diameter to its thickness) and the volume fraction f of the mineral platelets, and that the decrease can accurately be described by a master curve in the form of a stretched exponential function. This master curve behavior facilitates the task of designing nanocomposites with tailored thermal expansion coefficients for advanced applications.

References: Submitted to Model. Simul. Mater. Sci.

Title: The numerical prediction of the elastic and thermoelastic properties of multiphase materials

Researchers: Peter Hine**
Hans Rudolf Lusti*
Andrei A. Gusev*

Institute/Group: * Institute of Polymers, Department of Materials, ETH
** IRC in Polymer Science and Technology, University of Leeds, UK

Description:

Computer aided design offers the potential for the rapid development of new multiphase materials with interesting and novel behavior. The advantage of a validated numerical simulation is clear, as it allows a large number of potential variables to be studied before proceeding to a manufacturing stage, reducing cost and risk accordingly. This is vital for there are a large number of variables available to the materials designer including the reinforcement shape (cylinders, platelets, discs, spheres or any combination of these), the elastic anisotropy of the reinforcement and matrix phases, and any distributions of reinforcement orientation and size. We describe a new finite element based approach of Gusev for the numerical prediction of the properties of multiphase materials. We illustrate the importance of building physically representative computer models based on microstructural parameters measured on real materials, and show that, in particular, real injection molded and extruded materials show orientation distributions close to a maximum entropy prediction (i.e. most random) and that mechanical properties are well predicted by a constant strain assumption between the phases.

References: Accepted by Comp. Sci. Tech.

Title: Putting titania shells in a polymer: which properties can be achieved?

Researchers: Ilya A. Karmilov
Andrei A. Gusev

Institute/Group: Group of polymer chemistry, Institute of polymers, ETH

Description:

In this work we have used a finite element based approach for predicting the overall elastic and dielectric properties of shell-egg-particle reinforced polymers. Multiscale tetrahedra-based meshes were employed for reproducing the morphology. The particles were approximated by core-shell spheres with the walls of different thickness. For the particles, typical titanium dioxide properties were assumed in calculations. We investigated the dependence of macroscopic properties on the inclusion volume fraction, thickness of the titanium dioxide walls, and aspect ratio of the spheroids. It appears that the core-shell-particle reinforced polymers exhibit a unique portfolio of technological properties that can be indispensable in various demanding weight-saving applications. The optimal wall thickness was found.

References: A.A. Gusev, I.A. Karmilov, *Macromol. Theory Simul.* **2002**, *11*, 247-249

Title: Finite element approaches to generation of complex morphological states in block copolymer systems

Researchers: Ilya A. Karmilov^a
Andrei A. Gusev^a
Glen H. Fredrickson^b
Frank S. Bates^c
Hsuan-Yi Chen^d

Institute/Group: ^aInstitute of Polymers, Department of Materials, ETH
^bMitsubishi Chemical Center for Advanced Materials and Departments of Chemical Engineering & Materials, University of California, Santa Barbara
^cDepartment of Chemical Engineering and Materials Science, University of Minnesota
^dDepartment of Physics, National Central University of Taiwan

Description:

In this work we have developed and implemented a finite element based version of Self-Consistent Field Theory for predicting the morphologies of complex block copolymer systems. As a first application, we generated an ensemble of morphological states realizable in symmetric poly(styrene-*b*-isoprene-*b*-ethylene oxide) triblock copolymers, and compared the predicted mesoscopic crystals with experimental data. The principal objective of this study is to use a combination of experimental data and numerical predictions for gaining in-depth understanding of the morphologies realizable in this ABC triblock system.

References: A manuscript is in preparation

Title: Numerical prediction of light scattering in photonic glasses

Researchers: Martin Heggli
Andrei A. Gusev

Institute/Group: Institute of Polymers, Department of Materials, ETH

Description:

The scattering of light by a random arrangement of titania spheres in a polymeric matrix has been studied. 3D computer models of randomly dispersed non-overlapping identical spheres have been created by a Monte Carlo procedure. Maxwell's equations have been solved on a regular cubic grid by a finite element based procedure. A single raised cosine pulse has been used as excitation and the reflected and transmitted light has been recorded. The response was then Fourier transformed to the frequency domain. The procedure allowed to study the reflection and transmission coefficient in dependence of a wide range of sphere diameters with a single calculation. By systematically varying the lateral dimensions and the thickness of the simulation box we have identified the representative volume element size for this problem.

References: A manuscript is in preparation

Title: Voltage breakdown in random composites

Researchers: Andrei A. Gusev¹
Olga A. Guseva²

Institute/Group: ¹ Institute of Polymers, Department of Materials, ETH-Zentrum,
Universitätsstrasse 6, CH-8092 Zürich, Switzerland
² Swiss Federal Laboratory for Materials Testing and Research,
Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Description:

Voltage breakdown is a critical phenomenon involving a catastrophic increase in the electric conductivity of a dielectric body, induced by an external electric field. Here, we studied the voltage breakdown phenomenon in a composite comprised of a random dispersion of metal spheres in a polymer matrix, based on periodic Monte Carlo realizations with a varying number of spheres. We gradually increased the electric field and collected the individual voltage breakdown estimates, predicted numerically, on the basis of morphology-adaptive unstructured meshes and by using an iterative finite element solver. At all the concentrations studied, the individual estimates obtained with computer models of 1000 spheres were rather uniform. But strikingly, already with a dozen spheres, the ensemble minimum estimates obtained with a given number of spheres were practically the same as those obtained with 1000 spheres. Our results suggest that in random composites the voltage breakdown is a locally controlled phenomenon, and that estimates obtained with incredibly small computer models are representative for much larger, laboratory samples.

References: Advanced Engineering Materials 2003 (in print)

Title: Computation of Maxwell Eigenvalues using hp -Version
Edge Elements

Researchers: P.D. Ledger*
J. Coyle**

**Institute/
Group:** *Seminar for Applied Mathematics, ETHZ
**Dept. Mathematics, Monmouth University USA

Description:

The accurate calculation of Maxwell eigenvalues is important for the design of microwave devices and cavity resonators. Realistic cavities have complex geometries and may contain many dielectric layers. For such problems the finite element procedure is well suited.

We employ a hierarchical edge element discretization which allows for both h and p refinements. For a series of challenging benchmark problems we are able to obtain the theoretical predicted exponential rates of convergence when the refinements are carefully selected.

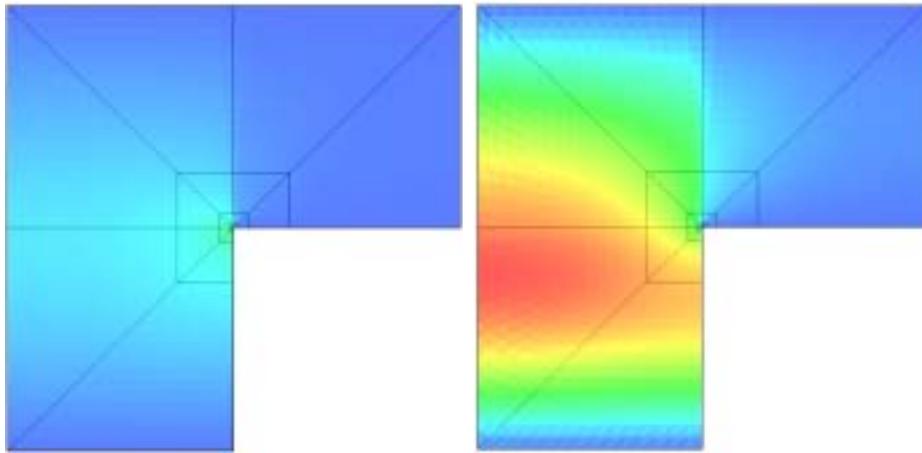


Figure 1: Contours of the electric field for two eigenmodes of an L-shape cavity

References:

P.D. Ledger and J. Coyle , “Evidence of exponential convergence in the computation of Maxwell eigenvalues,” *Computer Methods in Applied Mechanics and Engineering* submitted 2003.

Title: Effect of mutations involving charged residues on the stability of staphylococcal nuclease : A continuum electrostatics study.

Researchers: Ulf Börjesson*
Philippe H. Hünenberger*

Institute/ * Laboratory of Physical Chemistry
Group:

Description :

A continuum electrostatics model is used to calculate the relative stabilities of 117 mutants of *Staphylococcal* nuclease (SNase) involving the mutation of a charged residue to an uncharged one. The calculations are based on the crystallographic structure of the wild-type protein, but take implicitly into account the effect of the mutations in the denatured state by assuming a linear relationship between the free energy changes caused by the mutation in the native and denatured states. A good correlation (linear correlation coefficient of about 0.8) is found with published experimental relative stabilities of these mutants. The results suggest that in the case of SNase (*i*) electrostatic interactions involving charged residues contribute significantly to the stability of the native state, and (*ii*) the denatured state of SNase is characterized by strong native-like electrostatic interactions. The continuum electrostatic method is only moderately sensitive to model parameters, and leads to quasi-predictive results for the relative mutant stabilities (error of about $k_B T$), except for mutants in which charged a residue is mutated to glycine.

References: A manuscript has been submitted to Protein Eng.

Title: Influence of cutoff truncation and artificial periodicity of electrostatic interactions in molecular simulations of ions: A continuum electrostatics study.

Researchers: Michael Bergdorf*
Christine Peter*
Philippe H. Hünenberger*

Institute/ * Laboratory of Physical Chemistry
Group:

Description :

A new algorithm relying on finite integration is presented that solves the equations of continuum electrostatics for truncated (and possibly reaction-field corrected) solute-solvent and solvent-solvent interactions under either non-periodic or periodic boundary conditions. After testing and validation by comparison with existing methods whenever possible, the algorithm is applied to investigate the effect of cutoff truncation and artificial periodicity in explicit-solvent simulations of ionic solvation and ion-ion interactions. Both cutoff truncation and artificial periodicity significantly alter the polarization around a spherical ion and thus its solvation free energy. The nature and magnitude of the two perturbations are analyzed in details, and correction terms are proposed for both effects. Cutoff truncation is also shown to induce strong alterations in the potential of mean force for ion-ion interaction. These observations help to rationalize artifacts previously observed in explicit-solvent simulations, namely spurious features in the radial distribution functions close to the cutoff distance and alterations in the relative stabilities of contact, solvent-separated and free ion pairs.

References: A manuscript has been submitted to J. Chem. Phys.

Title: Influence of artificial periodicity and ionic strength in molecular dynamics simulations of charged biomolecules employing lattice-sum methods.

Researchers: Mika Kastenholtz*
Philippe H. Hünenberger*

Institute/ * Laboratory of Physical Chemistry
Group:

Description :

Lattice-sum methods are nowadays routinely used to calculate electrostatic interactions in explicit-solvent simulations of biomolecular systems. These methods account for the long-range component of Coulomb interactions by assuming that they are exactly periodic within the simulated system. When lattice-sum methods are applied to inherently non-periodic systems such as solutions, it is legitimate to question the validity of this assumption. The present study investigates the nature and magnitude of periodicity-induced artifacts in a set of twelve independent explicit-solvent molecular dynamics simulations of a small protein and an oligonucleotide, at different temperatures and ionic concentrations. Configurations sampled during these simulations are analyzed using continuum electrostatics to evaluate the corresponding periodicity-induced perturbation of the electrostatic free energy. The results suggest that, for the systems considered, artificial periodicity induces a non-negligible free-energy bias in the sampled ensembles, but that this energetical bias results in no major structural perturbation. The perturbation is also found to be smallest when a minimal (neutralizing) set of counterions is included during the simulation.

References: A manuscript has been submitted to J. Phys. Chem. B

Title: A fast-Fourier-transform method to solve continuum-electrostatics problems with truncated electrostatic interactions: Algorithm and application to ionic solvation and ion-ion interaction.

Researchers: Christine Peter*
Wilfred F. van Gunsteren*
Philippe H. Hünenberger*

Institute/ * Laboratory of Physical Chemistry
Group:

Description :

An iterative algorithm based on fast Fourier transforms is presented, that solves the equations of continuum electrostatics for systems of heterogeneous dielectric permittivity (*e.g.* solute cavity in a solvent) under periodic boundary conditions. The method makes explicit use of the charge-dipole and dipole-dipole interaction tensors, and is thus applicable both to Coulombic interactions (Ewald scheme) and to cutoff-based electrostatic interactions described by any polynomial function (including a Coulombic r^{-1} term), as commonly used in molecular dynamics simulations. The latter case includes in particular straight truncation of Coulombic interactions and truncation including a reaction-field correction. After testing and validation by comparison with existing methods (whenever possible), the algorithm is used to investigate the effect of cutoff truncation and artificial periodicity in explicit-solvent simulations of ionic solvation and ion-ion interactions. Both cutoff truncation and artificial periodicity are found to significantly affect the polarization around a spherical ion and thus, its solvation free energy. The nature and magnitude of the two perturbations are analyzed in details, and approximate analytical correction terms are derived to be applied to the results of explicit-solvent simulations. Cutoff truncation is also shown to induce strong alterations in the potential of mean force for the interaction between two spherical ions. The present observations based on continuum electrostatics help to rationalize artifacts previously reported from explicit-solvent simulations involving cutoff truncation, and in particular the unphysical attraction of like charges, the unphysical repulsion of opposite charges, and the corresponding alterations in the relative stabilities of contact, solvent-separated and free ion pairs.

References: A manuscript has been submitted to J. Chem. Phys.

Title: Solving Dirichlet Problems Numerically
Using the Feynman Kac Representation.

Researchers: Fabian M. Buchmann
Wesley P. Petersen

Institute/ Seminar for Applied Mathematics
Department: Dept. of Mathematics, ETHZ

Description:

A significant limitation of finite element and finite difference schemes for partial differential equations (PDEs) is that when the spatial dimension is larger than two, simulation of any non-trivial problem may easily become an industrial scale task. For elliptic and parabolic problems in high dimensional spaces, therefore, Monte-Carlo methods are very attractive. The basic idea is to simulate independent sample paths of a stochastic differential equation (SDE), whose drift and diffusion coefficients are taken from the PDE. The solution of the PDE is given by expectations (averages) of functions of these sample paths. Non-linear and complex problems can also be treated. For elliptic problems with Dirichlet boundary conditions, one of the most challenging problems is determining the "first exit time" of each sample path and its position on the boundary upon exit.

We have explored two procedures for boundary finding: (1) a bounded increment approach, wherein the step-size is chosen so that paths are never allowed to leave the domain but stop within a "stopping layer" whose thickness is smaller than the truncation error of the integration rule; and (2) an estimated excursion method, wherein the Brownian increments are Gaussian, but statistical estimates of the exit time are made based on Brownian Bridge. All high dimensional tests were run on our Beowulf cluster named *Asgard*.

References: Manuscript to be published in *BIT*, October, 2003.

Title: Finite volume dynamical core for decadal-scale climate simulations

Researchers: William Sawyer*
Rolf Jeltsch*
Shian-Jiann Lin**
Kevin Yeh***

Institute/ *Seminar for Applied Mathematics, ETHZ
Group: **Geophysical Fluid Dynamics Laboratory
***Global Modeling and Assimilation Office, NASA GSFC

In this stage of our collaboration we have investigated the use of pentagonal/hexagonal grids for the solution of the shallow water equations on the sphere (SWES). Such grids avoid problems due to converging points near the pole. The shallow water formulation of Lin for rectangular latitude-longitude grids could be adapted for these non-orthogonal grids, although an additional set of wind variables had to be employed. Radial basis functions (RBFs) were used to provide high-quality interpolations at non-grid points, and also for the reconstruction of the pressure thickness (height) field as seen in Figure 1.

The resulting algorithm can be shown to be mass- and vorticity-conserving in the discrete sense. It does, however, depend on a high quality scalar advection algorithm for the P/H grids, which is currently being developed.

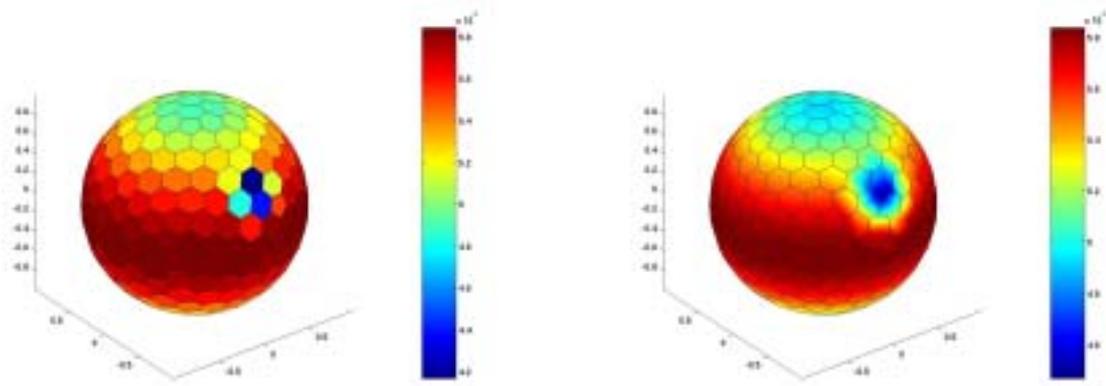


Figure 1: The finite volume means of the pressure thickness (on left) over a large mountain are used for a more accurate radial basis function reconstruction (right).

References:

- [1] W. Sawyer and R. Jeltsch, *A Finite-Volume Mass- and Vorticity-conserving Solver of the Shallow-Water Equations on the Sphere using Penta-/Hexagonal Grids*, Proc. European Conf. on Num. Math. and Adv. Appl. 2003, in preparation.
- [2] S.-J. Lin, *A "vertically Lagrangian" finite-volume dynamical core for global models*, Monthly Weather Review, submitted.

Title: Genuine Multidimensional, Divergence-free Numerical Methods for the Equations of Magnetohydrodynamics

Researcher: Manuel Torrilhon
Dr. Michael Fey
Prof. Rolf Jeltsch

Institute: Seminar for Applied Mathematics
ETH Zürich

Description:

The equations of magnetohydrodynamics describe the flow of plasmas in interaction with a magnetic field. A major issue in instationary magnetohydrodynamic simulations is the control of the divergence of the magnetic field. In this project locally divergence-preserving finite volume methods are developed and analysed. The methods freeze the initial value of the discrete divergence exactly which corresponds to the properties of the analytical evolution operator. Together with a special solenoidal initialization we obtain a divergence-free magnetic field during the entire simulation.

The figure shows a magnetized cloud which has been run over by a shock wave from the left to the right. The dense cloud is initially circular and magnetized by a perpendicular electric current. The secondary flow behind the shock wave deforms the cloud, while the magnetic field lines try to maintain a circular shape. Similar flow problems arise in electric arc simulations for circuit breakers.

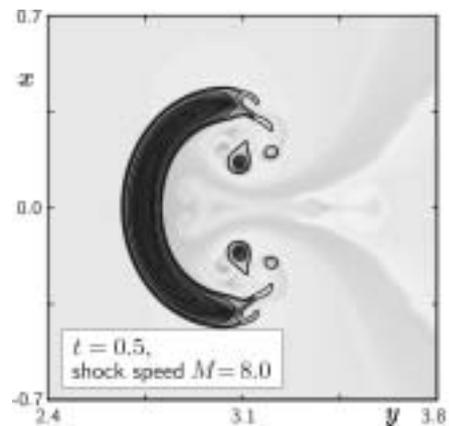


Figure 1: Deformation of a circular plasma cloud hit by a shock wave. The plot shows magnetic field lines with underlying density contours.

References:

- [1] M. Torrilhon and M. Fey, *Constraint-Preserving Upwind Methods for Multidimensional Advection Equations*, SIAM J. Num. Anal. (2003), submitted
- [2] R. Jeltsch and M. Torrilhon, *Discrete Solenoidal Initialization for Locally Divergence-free MHD Simulations*, Proc. Intl. Conf. High Performance Scientific Computing, Springer (2003), in press

Title: Inverse aerodynamic shape design for turbine components

Researchers: Rolf Jeltsch
Andreas Troxler

Institute/Group: Seminar for Applied Mathematics, ETHZ

Description:

In inverse aerodynamic shape design the geometry of a flow device is defined in terms of specified surface flow data, because many loss mechanisms are correlated with surface pressure distributions.

The present approach starts from the system of ordinary differential equations obtained after spatial discretisation of the unsteady flow equations, which forms, together with the design constraints, an initial value problem of differential–algebraic equations. A half–explicit multistage scheme is employed to reach a steady state solution. The algorithm is implemented as an extension of an existing flow analysis code. Underlying flow models range from two–dimensional inviscid up to three–dimensional viscous and turbulent.

The method is applied to redesign of compressor and turbine blade profiles subject to specified distributions of blade thickness and pressure loading. Results of a reproduction test case are shown in Figure 1. The increase in computational effort amounts to roughly 20% with respect to a pure analysis calculation.

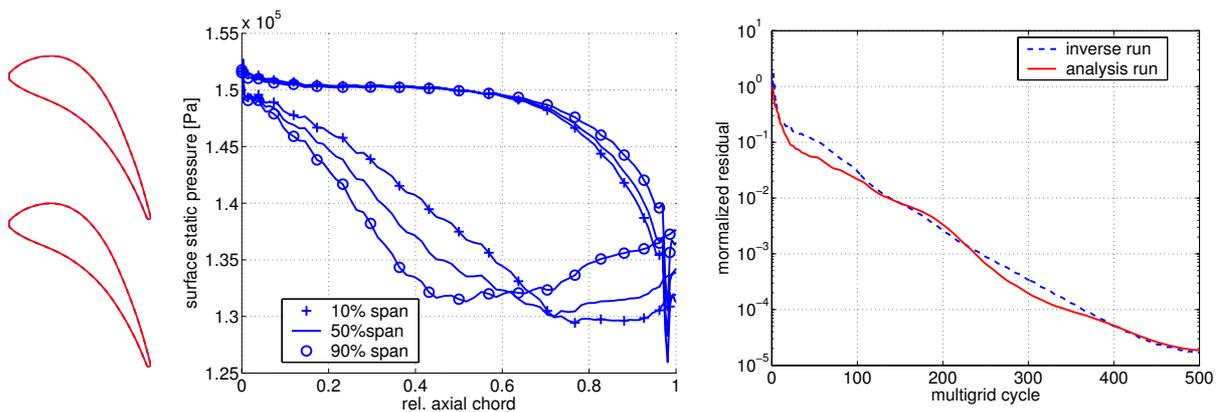


Figure 1: From left to right: Blade profile at midspan; surface pressure distributions at different span locations; comparison of convergence histories.

References:

A. Troxler: “A Differential–Algebraic Approach to Inverse Aerodynamic Shape Design of Gas Turbine Blades”, PhD. thesis, ETH Zurich, 2003 (in preparation).

**Institut für Hydromechanik und Wasserwirtschaft (IHW),
ETH Hönggerberg
Arbeitsgruppe W. Kinzelbach**

Abstracts of projects involving computational science

1.) Stochastic modelling of well catchments

The project is part of the European Project W-SAHARA (2000-2003) on 'Stochastic Analysis of Well Head Protection and Risk Assessment' comprising nine partners. Wellhead protection zones serve as an effective protection of groundwater against pollution by regulating human activities in areas around drinking wells. Stochastic computational methods are developed for the delineation of well catchments in aquifers of random heterogeneity, which may be conditioned on available measurements. The main task is to quantify the uncertainty in the extent of the well catchments. The methods comprise numerical Monte Carlo techniques, alternative methods of particle tracking, analytical stochastic approximations, as well as stochastic inverse modelling. The methodologies are applied to benchmarks and selected real-world cases. The results are conceived to serve as a basis to delineate wellhead protection zones. Furthermore, the methods will be used to develop a strategy for reducing the uncertainty of the results.

Contacts:

Harrie-Jan Hendricks Franssen, IHW ETH Zürich; Fritz Stauffer, IHW,ETH Zürich;
Wolfgang Kinzelbach, IHW ETH Zürich.

Publications:

Stauffer F., und W. Kinzelbach, 'Zuströmbereiche für Grundwasserfassungen. Bestimmung in Lockergesteinsgrundwasserleitern'. gwa 81 (1) 15-20, 2001.

Stauffer F., S. Attinger, S. Zimmermann, and W. Kinzelbach, Uncertainty estimation of well head protection zones: A Lagrangian approximation. Proc. Int. Groundwater Symp. "Bridging the gap between measurement and modeling in heterogeneous media", March 25-28, 2002, Lawrence Berkeley National Laboratory, Berkeley, California, Editor A.N. Findikakis, p. 63-66, 2002.

Hendricks Franssen H.-J., F. Stauffer, and W. Kinzelbach, Impact of spatio-temporally variable recharge on the characteristics of well capture zones. Proc. 4th Int. Conf. on "Calibration and Reliability in Groundwater Modelling", ModelCARE 2002, June 17-20 2002, Prague, Czech Republic, Editors K. Kovar and Z. Hrkal, p. 472-476, 2002.

Hendricks Franssen H.-J., F. Stauffer, and W. Kinzelbach, Reducing the uncertainty of well capture zones by inverse conditioning. Proc. XIV. Int. Conf. on "Computational Methods in

Water Resources", June 23-28, 2002, Delft, The Netherlands, Vol. 2, Editors, S.M. Hassanizadeh, R.J. Schotting, W.G. Gray, and G.F. Pinder; publ. in Series Developments in Water Science 47, Elsevier, Amsterdam, p. 1403-1410, 2002.

Stauffer F., S. Attinger, S. Zimmermann, and W. Kinzelbach, Uncertainty estimation of well catchments in heterogeneous aquifers. *Water Resour. Res.*, 38 (11) 1238-1247, 2002.

2.) Models and tracer methods for groundwater resource management

The research project "Models and tracer methods for groundwater resource management" is supported by the Swiss Science Foundation and is done jointly by three research groups (ETH Zürich/IHW, EAWAG, University of Bern). The task on groundwater modelling concerns the introduction of field observations into numerical-stochastic models using the Bayesian approach. The project addresses the following questions: How can we calibrate models in a more rigorous sense to minimise the misleading discrepancy between good calibration behaviour and erroneous prediction due to non-uniqueness of the calibration? How can tracer information on mixing and on ground water dynamics be included in transport models to check the correctness of models in a meaningful way and improve the robustness of predictions? How can we quantify the uncertainty and reliability of our model results?

The Bayesian approach is formulated in a way to make it applicable to the groundwater flow and transport equation. This method is compared with existing methods of conditional stochastic inverse modelling. The method of Hendricks-Franssen at the IHW is generalized to be applicable to transients of tracer concentrations at observation wells. By the time the methodology is developed using synthetic examples, the field studies by the project partners have advanced sufficiently to apply the methods to them too. All data collected in the field should be interpreted by a model giving not only a good fit but also yielding information on the uncertainty of this interpretation or alternatively on the space of model parameters, which within a certain precision lead to the same result.

Contacts:

Amsicora Onnis, IHW ETH Zürich; Harrie-Jan Hendricks Franssen, IHW ETH Zürich; Fritz Stauffer, IHW, ETH Zürich; Wolfgang Kinzelbach, IHW ETH Zürich.

3.) Reactive transport in heterogeneous porous media

Many solutes transported by groundwater are not inert but undergo chemical reactions. Most commonly, one encounters adsorption resulting in an exchange of solute between the mobile fluid and immobile regions of the solid matrix. In the case of nonlinear equilibrium adsorption the adsorbed concentration is presented by a nonlinear function of the dissolved concentration. As a result the retarded transport parameters, i.e. transport velocity and dispersion coefficients, become concentration-dependent. Thus, the mathematical treatment of such kind of nonlinear transport processes is not trivial even in the case of homogeneous media. Transport processes through heterogeneous porous media are usually investigated by means of stochastic models, which incorporate the heterogeneous structure of the medium. The stochastic theory is well established and linear transport phenomena have been studied

using analytical and numerical methods. In the framework of this project we focussed on transport with a nonlinear Freundlich isotherm in heterogeneous porous media. Using methods of statistical physics such as perturbation theory and homogenisation theory we investigated the large-scale transport behaviour and the corresponding effective transport parameters. While in the linear adsorption case it is possible to find effective parameters such as an effective constant retardation parameter and an effective dispersion parameter to characterize the transport on the large scale, this is no longer possible when the Freundlich exponent becomes a random variable. In that case it is shown that a new upscaled adsorption isotherm has to be used. The dispersion coefficient becomes concentration dependent. For heterogeneous media with very high contrasts or with more than one spatially fluctuating parameters, the analytical approach cannot be applied any more. In such cases extensive Monte Carlo simulations for determination of ensemble quantities are required. In the framework of the project the partners from Heidelberg University developed a fast computation code for simulating transport and reactions of a nuclear decay chain in groundwater. The project is funded by the Gesellschaft für Reaktorsicherheit, (Germany) and is carried out in collaboration with the Institute für Wissenschaftliches Rechnen in Heidelberg, the Institute of Mathematics of Bonn University and the Institute of Mathematics at the University of Freiburg. This code allows computing of ensembles on 3D heterogeneous media in a reasonable discretization. The results are of interest to nuclear waste repository planning.

Contacts:

Jiva Dimitrova Micha, IHW, ETH Zürich, Sabine Attinger, CoLab, ETH-Zürich, Wolfgang Kinzelbach, IHW, ETH Zürich

Publications:

P. Bauer, S. Attinger, W. Kinzelbach, 2001, Transport of a decay chain in homogenous porous media: analytical solutions. *J. Cont. Hydr.*, 49, 217-239, 2001.

S. Attinger, J. Dimitrova Micha, W. Kinzelbach, 2002, Multiscale Modeling of Nonlinearly Adsorbing Transport, *SIAM Multiscale Model. Simul.*, Vol. 1(3), 408-431, 2003

J. Dimitrova Micha, S. Attinger, W. Kinzelbach, Note on the transport of nonlinearly reactive transport in a single heterogeneous formation, submitted to *Nuclear Science and Engineering*, 2003

J. Dimitrova Micha, S. Attinger, W. Kinzelbach, Modeling of ensemble and real mixing in nonlinearly adsorbing transport, submitted to *Advances in Water Resources*, 2003

4.) A novel particle method for the solution of transport equations and its application to density-dependent groundwater flow problems

This contribution investigates a novel particle method for solute transport in groundwater using a Lagrangian scheme. The grid-free character of particle methods and the straightforward physical interpretation distinguishes them from established methods such as finite differences or finite elements. The interest in particle methods is big due to the fact that accurate solutions not suffering from numerical dispersion and spurious oscillations can be obtained at competitive computational expense. The numerical scheme used, originally

developed for viscous fluid flow carrying vorticity, is applied for 2D and 3D simulations of non-reactive solute transport in groundwater.

We treat the advection-dispersion-equation by means of the Particle Strength Exchange method (PSE) describing the diffusive-dispersive process. The key idea of the method is the approximation of the differential diffusion operator by an integral operator, which is discretized using as quadrature points the locations of the particles. The distorted particle field must occasionally be remeshed onto a new structured field in order to maintain stability and accuracy.

The goal of the work is to develop a particle code, which is capable to calculate the phenomena of density fingering with variable fluid density. For the validation of the method, exact solutions, standard benchmark problems and the application to a field study concerning density instabilities will be utilized. The work is embedded in a joint ETH project between the Institute of Computational Science (Prof. P. Koumoutsakos, ICOS), the Laboratory for Thermodynamics in Emerging Technologies (Prof. D. Poulikakos, LTNT), and the Institute of Hydromechanics and Water Resources Management (Prof. W. Kinzelbach, IHW). The aim of the joint effort is to develop a fast "billion particle code" that would be modular and useful for a number of applications.

Contacts:

Stephanie Zimmermann, IHW, ETH Zürich; Jens Walther, ICOS, ETH Zürich; Wolfgang Kinzelbach, IHW, ETH Zürich; Petros Koumoutsakos, ICOS, ETH Zürich

Publications:

S. Zimmermann, P. Koumoutsakos, W. Kinzelbach, Simulation of Pollutant Transport Using a Particle Method, *Journal of Computational Physics* **173**, 322-347, 2001

5.) Modelling of Density Driven Flows in Porous Media

Density driven flow is of interest in situations of seawater intrusion or up-coning of salt water from deep saline aquifers. The latter is the case in Brandenburg, Germany. In arid environments such as Botswana or Uzbekistan freshwater lenses form around ephemeral rivers and represent the only yearlong available drinking water resource, the surrounding groundwater being saline or brackish. In this situation the exploitation of the freshwater lens by pumping must be well planned in order to avoid the attraction of saline water into drinking water wells. When a salt-water layer forms on top of the aquifer, a phenomenon observed under saltpans or swamp islands in the arid tropics, fingering phenomena may develop and constitute an important mechanism of transporting salt water downward. We simulate density driven flow, which is quite demanding as far as discretization is concerned. Especially the unstable fingering situation is very sensitive to numerical artefacts. We start out to investigate the onset of instability by network models in 2D and 3D. Fingering simulations in comparison with experimental benchmarks are performed with d3f, a multigrid, finite volume simulation package. We also employ an algorithm based on the method of characteristics and a novel algorithm, which is developed in an ETH-project described above.

The work is embedded in the EU SALTRANS project involving the Weizmann Institute, Israel, the Politechnical University of Catalonia, Barcelona, the Institut de Physique du Globe, Paris, and the universities of Rennes, Edinburgh and Leeds. Further means are made available through the INTAS framework together with Moscow University and scientists in Uzbekistan.

Contacts:

Rudolf Held, IHW ETH Zürich; Wolfgang Kinzelbach, IHW,ETH Zürich

Publications:

K. Johannsen, W. Kinzelbach, S. Oswald, and G. Wittum, Numerical simulation of density driven flow in porous media, *Advances in Water Resources*, 25(3), 335-348, 2002.

S.E. Oswald and W. Kinzelbach, Three-dimensional physical benchmark experiments to test variable-density flow models, 2003, *J. of Hydology*, in press

R. Held, W. Kinzelbach, and M.A. Celia, Characterization of stable and unstable flow regimes via dynamic pore-scale network simulation. *Proceedings Int. Conf. Computational Methods in Water Resources XIV*, Hassanizadeh et al. (eds.), Delft, The Netherlands: 1059-1066 JUN 2002.

R. Held, K. Johannsen, and W. Kinzelbach, Modelling of unstable density-dependent solute transport: Macroscopic versus microscopic model applications and experimental benchmarks, *Geophysical Research Abstracts*, EGS-AGU-EUG Assembly, Volume 5, ISSN 1029-7006, 2003.

Title: Large-Eddy Simulation of Transitional and Turbulent Wall-bounded and Free Shear Flows

Researchers: Nikolaus A. Adams (TU Dresden), Andreas Jocksch, Leonhard Kleiser, Sebastian Müller, Benjamin Rembold, Philipp Schlatter, Steffen Stolz, Roland von Känel, Jörg Ziefle

Institute/ Institute of Fluid Dynamics
Group: Prof. L. Kleiser

Description:

Most engineering and geophysical flows occur at high Reynolds numbers. Due to their wide range of length and time scales such turbulent flows are not amenable to Direct Numerical Simulations (DNS). In Large-Eddy Simulations (LES) one only resolves the large scales, while their interaction with the non-resolved subgrid scales is modeled. Unlike solutions of the Reynolds-averaged Navier-Stokes equations (RANS), which are the workhorse for present-day industrial flow computations, LES are also able to provide information about the large-scale unsteady flow field that can be crucial for many problems such as fluid-structure interactions or noise generation. In addition, LES can be expected to yield much more reliable results for the mean flow and turbulence statistics than RANS for a number of more complex flow cases.

In our recently developed Approximate Deconvolution Model (ADM) for LES, the unclosed correlations are computed directly from the approximately unfiltered flow field, and the interaction between resolved and non-resolved scales is taken into account by a relaxation term. LES using ADM have been demonstrated to give excellent results for a range of flows including isotropic turbulence, incompressible channel flow, supersonic channel and compression ramp flows and compressible rectangular jet flow, all at a fraction (order one percent) of the cost that would be needed for a DNS of the same flows.

Applications of the model are being extended to physically more complex flow cases involving transition, massive separation and swirl. We have been able to demonstrate that it is well possible to simulate transitional wall-bounded and free shear flows on the basis of the ADM approach. Large-scale simulations have been started for supersonic compression ramp flows at higher Reynolds numbers for which experimental data are available for comparison. DNS and LES data for subsonic jet flow have been evaluated successfully with respect to computation of noise radiation. Moreover, a new promising approach using high-pass filtered eddy viscosity models has been developed. First tests have been very successful.

The ADM approach was also implemented in an industrial-type finite volume code. Following successful test computations for a compressible turbulent channel flow, the more challenging case of turbulent shock-boundary-layer interaction was tackled, and excellent results were again obtained. An extension to multiblock geometries is in progress.

References: See separate list.

Title: Simulation of Particle-laden Flows

Researchers: Thorsten Bosse
Carlos Härtel
Leonhard Kleiser
Anna Kubik
Eckart Meiburg*

**Institute/
Group:** Institute of Fluid Dynamics
Prof. L. Kleiser
*Dept. of Mechanical and Environmental Engineering,
University of California, Santa Barbara, CA, USA

Description:

This project is concerned with the simulation of disperse two-phase flows, in which a large number of small particles are suspended in a carrier fluid. We consider dilute suspensions, i. e. flows with small particle concentrations where the particle–fluid interaction is the predominant process while direct particle–particle interactions may be neglected (two-way coupling). The particles are assumed to be much smaller than the smallest relevant scales of the fluid motion. This allows us to model the particles as point–forces without resolving their finite size. Each particle is tracked along its trajectory (Lagrangian tracking), while the fluid equations are solved in an Eulerian framework.

In order to study fundamental properties of particle suspensions as well as effects of the numerical implementation and parameters, the settling and break–up of suspension drops has been considered. A suspension drop is an initially spherical cloud of particles suspended in initially still fluid. Under the influence of gravity such a suspension drop usually deforms into a torus, which eventually becomes unstable and breaks up into a number of secondary blobs. A systematic study of the influence of physical and numerical parameters has been performed, such as the Reynolds and Stokes numbers, the initial conditions, the grid resolution, and the number of particles inside the drop.

Particulate wall–bounded flows with separation were studied using the setup of a particle–laden flow over a backward–facing step. Models for wall–particle interaction have been refined and implemented. The various forces acting on the particle have been estimated for a range of different flows and aerodynamic types of particles. Following particle trajectories, all known forces acting on the particle were calculated for laminar and turbulent flow in a channel and over a backward–facing step. In addition, the study was conducted also for wall–near regions. For the majority of cases, the drag and gravity force terms were found to be of nearly the same magnitude and by far dominant, being much larger than all other forces.

In the future, turbulence modification by particles in a three-dimensional homogeneous, isotropic setting will be addressed. Initial steps towards this end have been undertaken.

References: See separate list.

Title: Planning with Virtual Alpine Landscapes and Autonomous Agents

Researchers: C. Gloor*, K. Nagel*, D. Cavens**, E. Lange**, W. Schmid**

Institute/ * Inst. for Computational Science, Dept. of Computer Science, ETHZ

Group: ** Inst. für Raum- und Landschaftsentwicklung, ETHZ

Description:

Autonomous agents modeling, which is based on concepts from artificial life and computer simulations, enables one to populate a virtual world with rule-driven agents which can act as surrogates for real humans. The NFP-48 project “Planning with Virtual Alpine Landscapes and Autonomous Agents” applies this method to the modelling of hikers in a tourist area. The project consists of a simulation of the “physical” system, in which the agents are moved through the virtual environment, and of a simulation of “strategies”, which models agents’ decision-making.

The simulation starts from a synthetic population, presumably consisting of tourists staying at hotels or visiting for a day. For each tourist, a daily or possibly weekly activity plan is generated. These activities include, say, to hike to a certain peak, to have a coffee at a mountain restaurant, or to go shopping in the village. These activities are then connected by routes. Routes are computed according to generalized cost functions, which depend, for example, on scenical beauty or on the number of other hikers that are encountered.

The mobility simulation takes care of the physical aspects of the system, such as interaction of the agents with each other and the environment. For our simulation, we need to model each pedestrian individually, since they need to be able to make decisions. The agents are able to follow arbitrarily complicated paths through variable terrain.

A learning algorithm on top of this makes the tourists adapt, for example in order to avoid other hikers.

Progress since last year includes:

- An improved mobility simulation, based on diploma work by Laurent Mauron;
- an improved and more robust messaging mechanism between the modules;
- the possibility to send arbitrary “events” from the mobility simulation;
- and a “lightweight” agent database that records agents’ strategies.

References:

[1] See www.inf.ethz.ch/~nagel/projects/alpsim.

[2] C. Gloor and K. Nagel. A pedestrian simulation for hiking in the alps. In *Swiss Transport Research Conference*, Monte Verita, Switzerland, March 2003. See www.strc.ch.

[3] L. Mauron. Pedestrians simulation methods. Diploma thesis, Swiss Federal Institute of Technology ETHZ, 2002.

Title: Large-scale Multi-agent Transportation Simulations

Researchers: N. Cetin,* B. Raney,* K. Nagel,* M. Vrtic,** K. Axhausen**

Institute/ * Institute for Computational Science, Dept. of Computer Science, ETHZ

Group: ** Institute for Transport Planning and Systems (IVT), ETHZ

Description:

Traffic modeling is a challenging subject since not only the flow of the traffic through the city needs to be modeled, but also what causes traffic in the first place, i.e. the human decisions leading to travel. Our approach is *agent-based*, which means that we resolve each traveler individually throughout all modules of the simulation package. In contrast to physics particles, agents have more internal complexity. Since a metropolitan area can have of the order of 10^7 travelers, this poses a considerable computing challenge.

Our overall approach consists of separating a physical simulation layer, where the agents have very limited capabilities such as collision avoidance and lane changing, from a tactical/strategic layer, in which the agents compute decisions such as route or destination choice. The physical simulation layer is represented by the traffic micro-simulation. We use parallel computing to achieve satisfactory computing speeds. The hardware is a 128-CPU Beowulf cluster with Ethernet communication; 64 CPUs are also connected via Myrinet. In the last year our top simulation speed has gone from about 300 times faster than real time to nearly 800 times faster for 10^6 particles in the simulation; this corresponds to doing a simulation of all car traffic in all of Switzerland during a full 24-hour day in less than 2 min of computing time. The tactical/strategic layer currently consists of a prototype module for activities generation (what do people do during a day and where?), and a module for route planning (how do people get to their destinations?).

Since these modules interact, it is necessary to iterate between them, meaning that the computing burden increases even further. We also use a so-called agent database where the agents keep track of their strategies and the scores of those strategies. In the case of traffic simulation, a strategy is a specific activity plan and an associated route plan, and a score is calculated via a utility function that factors in the starting time, ending time, and duration of each activity in the agent's plan, as well as how much time the agent spends traveling between activities. In the last year we have moved the agent database from a standard disk-based relational database implementation to a memory-based object-oriented implementation. This new implementation provides an interface for new modules to easily communicate new strategies to the agent database. This communication is file-based at present.

We have applied our simulation framework to a real-world scenario by simulating all of the car traffic in Switzerland during the morning rush hour. We compared the results to field data collected throughout the country, and showed it to be a closer match than the results of a more traditional traffic assignment model used by transportation planners.

Our future plans go in two directions: (1) Real-world case studies, specifically of a high-resolution Zurich network (2) A distributed plug-and-play implementation, where additional modules can be added on an arbitrary CPU of the cluster, and the framework will take care of using them for the simulation.

References:

- [1] B. Raney, M. Balmer, K. Axhausen, and K. Nagel. Agent-based activities planning for an iterative traffic simulation of Switzerland. In *Presented at the tri-annual meeting of the International Association for Travel Behavior Research (IATBR)*, Lucerne, Switzerland, August 2003. See <http://www.ivt.baum.ethz.ch/allgemein/iatbr2003.html>.
- [2] D. Charypar and K. Nagel. Generating complete all-day activity plans with genetic algorithms. In *Presented at the tri-annual meeting of the International Association for Travel Behavior Research (IATBR)*, Lucerne, Switzerland, August 2003. See <http://www.ivt.baum.ethz.ch/allgemein/iatbr2003.html>.
- [3] K. Nagel and B. Raney. Large scale multi-agent simulations for transportation applications. In *EC workshop "Behavioural responses to ITS"*, 1.-3. Apr 2003. Published on CD-ROM; see sim.inf.ethz.ch/papers.
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- [5] B. Raney, A. Voellmy, N. Cetin, M. Vrtic, and K. Nagel. Towards a microscopic traffic simulation of all of Switzerland. In P.M.A. Sloot, C.J.K. Tan, J.J. Dongarra, and A.G. Hoekstra, editors, *Computational Science – ICCS 2002, Part I*, number 2329 in Lecture Notes in Computer Science, pages 371–380. Springer, Heidelberg, Amsterdam, 2002.
- [6] B. Raney and K. Nagel. Iterative route planning for large-scale modular transportation simulations. *Future Generation Computer Systems*, submitted. See sim.inf.ethz.ch/papers.
- [7] B. Raney and K. Nagel. Truly agent-based strategy selection for transportation simulations. Paper 03-4258, Transportation Research Board Annual Meeting, Washington, D.C., 2003.
- [8] N. Cetin and K. Nagel. A large-scale agent-based traffic microsimulation based on queue model. In *Swiss Transport Research Conference*, Monte Verita, Switzerland, March 2003. See www.strc.ch. Earlier version, with inferior performance values: Transportation Research Board Annual Meeting 2003 paper number 03-4272.

See also <http://www.inf.ethz.ch/~nagel/projects/traffic>.

Title: A detailed finite element model of the kidney for use in trauma research.

Researchers: Jess Snedeker, Peter Niederer
Institute/ Institute of Biomedical Engineering
Group:

Description:

Blunt abdominal trauma (automotive accidents, sporting injury, etc.) leads mainly to injuries of the kidney, the liver and the spleen, all of which may result in death or disability of the injured person. The development of an accurate and realistic finite element model (FEM) of the abdominal region is critical to understanding the mechanisms of blunt impact abdominal injury. The specific goals of the present project can be summarized as follows: The development of a FE model of the human kidney which (i) is based on realistic anatomical and mechanical properties of the involved soft tissues and body fluids under dynamic loading conditions, (ii) reflects the particular location and surroundings of the kidney in the human body and (iii) is subjected to typical loading patterns derived from accidental impact situations.

References: Snedeker et al. 2002, in Journal of Visualization and Computer Animation.
Snedeker et al, 2003, in STAPP Car Crash Journal 47. In press.
Snedeker et al, 2003, in Journal of Biomechanics. In review.

Title: A Finite Element Model of the Uterus

Researchers: Stephan Weiss
Peter Niederer

**Institute/
Group:** Institute of Biomedical Engineering
Biomechanics

Description:

In order to facilitate a virtual-reality simulation of hysteroscopy for training purposes which is based on a realistic description of the interaction between the target tissues to be treated and the surgical instruments used for an operation, a computer model of the involved objects is needed which is capable of running in real time. For this purpose, a stable and explicit FE formulation for the integration of the time-dependent continuum-mechanical equations is being developed. This model will not run in real time, but it is intended to serve as a reference for simplified formulations to be used in a real-time simulator.

References: A paper is submitted to *Technology and Health Care*.

CSE research project description

Title: Polarized atomic orbitals for linear scaling methods

Researchers: G. Berghold*
J. Hutter**
M. Parrinello***

**Institute/
Group:** *Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany
**Institute of Organic Chemistry, University of Zurich, Switzerland
***Department of Physical Chemistry, Swiss Federal Institute of
Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss
Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

We present a modified version of the polarized atomic orbital (PAO) method [M. S. Lee and M. Head-Gordon, *J. Chem. Phys.* **107**, 9085 (1997)] to construct minimal basis sets optimized in the molecular environment. The minimal basis set derives its flexibility from the fact that it is formed as a linear combination of a larger set of atomic orbitals. This approach significantly reduces the number of independent variables to be determined during a calculation, while retaining most of the essential chemistry resulting from the admixture of higher angular momentum functions. Furthermore, we combine the PAO method with linear scaling algorithms. We use the Chebyshev polynomial expansion method, the conjugate gradient density matrix search, and the canonical purification of the density matrix. The combined scheme overcomes one of the major drawbacks of standard approaches for large nonorthogonal basis sets, namely numerical instabilities resulting from ill-conditioned overlap matrices. We find that the condition number of the PAO overlap matrix is independent from the condition number of the underlying extended basis set, and consequently no numerical instabilities are encountered. Various applications are shown to confirm this conclusion and to compare the performance of the PAO method with extended basis-set calculations.

References: *J. Chem. Phys.* **116** (2002) 1800

Title: Cesiumauride ammonia (1/1), CsAu·NH₃: a crystalline analogue to alkali metals dissolved in ammonia?

Researchers: A.V. Mudring*
M. Jansen*
J. Daniels**
S. Krämer***
M. Mehring***
J.P. Prates Ramalho****
A.H. Romero*****
M. Parrinello*****

Institute/ *Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany
Group: ** Anorganisch-Chemisches Institut, Friedrich-Wilhelms-Universität Bonn, Germany
***Physikalisches Institut, Universität Stuttgart, Germany
****Departamento de Quimica, Universidade de Evora, Portugal
*****Facultad de Fisica, Pontificia Universidad Catolica de Chile, Santiago, Chile
*****Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Treating CsAu with liquid NH₃ yields the deep blue ammoniate CsAu·NH₃. The unusual electronic structure, as well as the properties, indicate that this unique compound, which behaves like an alkali metal when dissolved in ammonia, may serve as a guide to a more thorough understanding of solvated electrons.

References: Angew. Chem. Int. Ed. **41** (2002) 120

Title: Car-Parrinello study of Ziegler-Natta heterogeneous catalysis: stability and destabilization problems of the active site models

Researchers: M. Boero*
M. Parrinello**
K. Terakura***
H. Weiss****

**Institute/
Group:** *Joint Research Center for Atom Technology, Angstrom Technology Partnership (JRCAT-ATP), Tsukuba, Ibaraki, Japan
** Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland
***Joint Research Center for Atom Technology, National Agency of Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
****BASF AG, Polymer Research Division, Ludwigshafen, Germany

Description:

Recent results on Car-Parrinello simulations of $MgCl_2/TiCl_4$ Ziegler-Natta heterogeneous catalytic systems are reviewed and the stability of Ti active site configurations on the various active surfaces are discussed. In particular, the focus is on the ability of an active center to carry out the polymerization process efficiently, achieved by monitoring geometrical changes and associated energetics during the reaction. The active site geometry is crucial in enhancing or decreasing the activation barrier, in selecting the olefin enantioface and in some cases in destabilizing the catalytic center. A key point in the binding/destabilization interplay is the matching of Ti with the substrate, an issue that represents a fundamental difference with respect to homogeneous systems.

References: Mol. Phys. **100** (2002) 2935

Title: Protonation state of the equatorial ligands and dynamics of the OH \cdots O units in a cobaloxime biomimetic

Researchers: C. Rovira*
K. Kunc**
M. Parrinello***

**Institute/
Group:** *Centre de Recerca en Química Teòrica, Parc Científic de Barcelona, Spain
**Laboratoire d'Optique des Solides, CNRS and University of P. and M. Curie, Paris, France
***Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

The protonation state of the dimethylglyoxime ligands in the B₁₂ coenzyme biomimetic [Co(CCl=CHCl)(dmgH)₂(py)]·CHCl₃ was investigated by using first-principles molecular dynamics. Our simulations at 173 and 300 K reveal that one of the oxime protons remains bonded to a nitroxyl group, while the proton of the second NO \cdots H-ON unit is essentially shared with similar probability between the two oxygen atoms. This reconciles the results of the experimental determination (Jones, P. G.; Yang, L.; Steinborn, D. *Acta Cryst.* **1996**, C52, 2399), showing all N-O distances as equivalent, with the commonly accepted rule that the protonation state of the dimethylglyoxime ligands can be identified by the different N-O distances. Further aspects of the dynamics of the OH \cdots O units, in relation to the occurrence of weak CH \cdots O intermolecular interactions, are analyzed.

References: Inorg. Chem. **41** (2002) 4810

Title: Pulling monatomic gold wires with single molecules: an ab initio simulation

Researchers: D. Krüger*
H. Fuchs*
R. Rousseau**
D. Marx***
M. Parrinello****

**Institute/
Group:** *Physikalisches Institut, Westfälische Wilhelms-Universität Münster,
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**Current address: International School for Advanced Studies
(SISSA/ISAS), Trieste, Italy
***Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum,
Germany
****Department of Physical Chemistry, Swiss Federal Institute of
Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss
Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Car-Parrinello molecular dynamics simulations demonstrate that pulling a single thiolate molecule anchored on a stepped gold surface does not preferentially break the sulfur-gold chemical bond. Instead, it is found that this process leads to the formation of a monoatomic gold nanowire, followed by breaking a gold-gold bond with a rupture force of about 1.2 nN. The simulations also indicate that previous single-molecule thiolate-gold and gold-gold rupture experiments both probe the same phenomenon, namely, the breaking of a gold-gold bond within a gold nanowire.

References: Phys. Rev. Lett. **89** (2002) 186402

Title: Electronic structure of wet DNA

Researchers: F.L. Gervasio*
P. Carloni**
M. Parrinello*

Institute/

Group: *Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland
**International School for Advanced Studies (SISSA/ISAS) and Istituto Nazionale di Fisica della Materia (INFN), Trieste, Italy

Description:

The electronic properties of a Z-DNA crystal synthesized in the laboratory are investigated by means of density-functional theory Car-Parrinello calculations. The electronic structure has a gap of only 1.28 eV. This separates a manifold of 12 occupied states which came from the π guanine orbitals from the lowest empty states in which the electron is transferred to the Na^+ from PO_4^- groups and water molecules. We have evaluated the anisotropic optical conductivity. At low frequency the conductivity is dominated by the $\pi \rightarrow \text{Na}^+$ transitions. Our calculation demonstrates that the cost of introducing electron holes in wet DNA strands could be lower than previously anticipated.

References: Phys. Rev. Lett. **89** (2002) 108102

Title: A field-theoretical approach to simulation in the classical canonical and grand canonical ensemble

Researchers: S.A. Baeurle*
R. Marto_àk**
M. Parrinello**

Institute/ *Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany
Group: **Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

In this paper we present a new approach to simulation methods for classical statistical mechanics relying on a field-theoretical formalism. It is based on applying the complex Hubbard–Stratonovich transformation to the canonical and grand-canonical partition function, which allows one to reexpress their particle representation in terms of a functional integral over a fluctuating auxiliary field. The thermodynamic averages from the resulting field representations can then be calculated with a conventional Monte Carlo algorithm. We explored the applicability of the auxiliary field methodology for both the canonical and grand-canonical ensemble using a system of particles interacting through a purely repulsive Gaussian pair potential in a broad range of external parameters. In the grand-canonical case this technique represents an alternative to standard grand-canonical Monte Carlo methods. Generally providing a framework for simulating classical particle systems within a continuum formalism can be useful for multiscale modeling where the field or continuum description naturally appears within quantum mechanics on smaller length scales and within classical mechanics on larger ones.

References: J. Chem. Phys. **117** (2002) 3027

Title: Pressure-induced structural transformations in a medium-sized silicon nanocrystal by tight-binding molecular dynamics

Researchers: R. Marto_ák*
L. Colombo**
C. Molteni***
M. Parrinello*

Institute/

Group: *Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland
**INFM and Dipartimento di Fisica, Università degli Studi di Cagliari, Monserrato (CA), Italy
***Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, Great Britain

Description:

We use a recently developed constant-pressure molecular dynamics method for nonperiodic systems to study pressure-induced structural transformations in medium-sized silicon nanocrystals, where the kinetics is experimentally known to be bulk rather than surface dominated, choosing Si₇₀₅ as a representative example. Pressure is applied and tuned through a liquid described by a classical potential, while the nanocrystal is treated within a tight-binding scheme. Upon pressurization the nanocrystal undergoes a structural transformation which starts at the surface and gradually propagates into the bulk core. The high-pressure structure is disordered and metallic, with an x-ray diffraction pattern compatible with both the ideal $\sqrt{3}$ -tin and simple hexagonal structures. Strong similarities with a recently calculated high-pressure phase of bulk amorphous silicon are evident. Upon pressure release, the original diamond structure is not recovered and a high degree of disorder persists.

References: J. Chem. Phys. **117** (2002) 11329

Title: NMR chemical shifts in periodic systems from first principles

Researchers: D. Sebastiani*
G. Goward*
I. Schnell*
M. Parrinello**

Institute/ *Max Planck Institute for Polymer Research, Mainz, Germany
Group: **Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

A recently developed *ab-initio* method for the calculation of NMR chemical shifts and magnetic susceptibilities in systems under periodic boundary conditions is presented and applied to a hydrogen-bonded molecular crystal. The calculations can unambiguously assign the chemical shifts to individual atoms in experimental spectra, and can further serve for the validation of simulated atomic trajectories and geometries. Apart from the example presented, the method can be applied to crystalline and amorphous insulators, as well as to isolated molecules using a supercell technique. The results are in good agreement with experiment.

References: Comp. Phys. Comm. **147** (2002) 707

Title: The role and perspective of ab initio molecular dynamics in the study of biological systems

Researchers: P. Carloni*
U. Rothlisberger**
M. Parrinello**

**Institute/
Group:**

*International School for Advanced Studies (SISSA/ISAS) and Istituto Nazionale per la Fisica della Materia (INFN), Trieste, Italy

**Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Ab initio molecular dynamics (MD) allows realistic simulations to be performed without adjustable parameters. In recent years, the technique has been used on an increasing number of applications to biochemical systems. Here we describe the principles on which ab initio MD is based. We focus on the most popular implementation, based on density functional theory and plane wave basis set. By a survey of recent applications, we show that despite the current limitations of size and time scale, ab initio MD (and hybrid ab initio MD/MM approaches) can play an important role for the modeling of biological systems. Finally, we provide a perspective for the advancement of methodological approaches which may further expand the scope of ab initio MD in biomolecular modeling.

References: Acc. Chem. Res. **35** (2002) 455

Title: Wave-function localization in reciprocal space

Researchers: M. Iannuzzi
M. Parrinello

**Institute/
Group:** Department of Physical Chemistry, Swiss Federal Institute of
Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss
Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

The localization of wave functions in real space is known to be extremely helpful in the investigation of the electronic properties and in the development of $O(N)$ methods. However, maximally localized wave functions in real space do not provide a good representation of the Bloch orbitals of a metallic system, where the localization procedure is very inefficient and of little use. On the other hand, in metals, it appears more natural to localize the wave functions in reciprocal space. In this work we propose a spread functional, which needs to be minimized in order to obtain maximally localized wave functions in reciprocal space and illustrate an efficient iterative minimization procedure. We also discuss the application of the method to some metallic systems and demonstrate that in this case the localized wave functions have features that can be useful for the analysis of electronic properties.

References: Phys. Rev. B **66** (2002) 155209

Title: Solvation structure and mobility mechanism of OH⁻: A Car-Parrinello molecular dynamics investigation of alkaline solutions

Researchers: B. Chen
I. Ivanov
J.M. Park
M. Parrinello
M.L. Klein

**Institute/
Group:** Center for Molecular Modeling and Department of Chemistry, University of Pennsylvania, Philadelphia, USA, Department of Chemistry, Division of Molecular and Life Science, Pohang University of Science and Technology, Korea, Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

The hydroxide ion (OH⁻) has an unusually high mobility in water, comparable to that of the proton. However, a consensus view of the OH⁻ mobility mechanism and its solvation structure has yet to emerge. In addition, X-ray and spectroscopic experiments reveal significant changes in the structural and dynamical properties of water in the presence of OH⁻. To gain insight into these questions, we have carried out Car-Parrinello molecular dynamics (CPMD) calculations for aqueous NaOH and KOH solutions under ambient conditions over a wide range of concentrations. These simulations are able to reproduce many puzzling phenomena, in particular, the loss of tetrahedral coordination of water (interpreted from a recent neutron diffraction with isotopic substitution experiment) and the appearance of new spectroscopic features at high concentrations. Furthermore, it is demonstrated that the observed behavior is a result of the formation of a variety of compact hydroxide-water complexes. The distribution of these complexes is dependent upon the concentration and the counterion. The present results reconcile conflicting structural interpretations from previous experimental and theoretical studies on hydroxide solutions. Analysis of the CPMD trajectories supports the view that the transport mechanism of the hydroxide ion is distinct from that of the proton.

References: J. Phys. Chem. B **106** (2002) 12006

Title: First-principles study of aqueous hydroxide solutions

Researchers: B. Chen
J.M. Park
I. Ivanov
G. Tabacchi
M.L. Klein
M. Parrinello

Institute/

Group: Center for Molecular Modeling and Department of Chemistry, University of Pennsylvania, Philadelphia, USA, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, Division of Molecular and Life Sciences, Pohang University of Science and Technology, Korea, Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Car-Parrinello molecular dynamics simulations have been carried out for aqueous NaOH and KOH solutions under ambient conditions over a wide range of concentrations. From these simulations, we have observed a continuous change of the water structure with added hydroxide, characterized by a significant shift of the second peak of the OO radial distribution functions to shorter distances. At the highest concentration investigated, the normal tetrahedral coordination of pure water is completely missing, a result that is consistent with a recent neutron diffraction experiment. The added hydroxide also gives rise to some unique spectroscopic features, including a "free" O-H stretch, a broadening of the normal water OH stretching band, and a large blue shift of both the librational band and the low-frequency translation. These results are in good agreement with the experimental data. Finally, it was demonstrated that the structural and dynamical behavior is inextricably linked to the formation of compact hydroxide-water complexes.

References: J. Am. Chem. Soc. **124** (2002) 8534

Title: First principles molecular dynamics study of catalysis for polyolefins: the Ziegler-Natta heterogeneous system

Researchers: M. Boero*and**
K. Terakura**
M. Parrinello***

**Institute/
Group:**

*Joint Research Center for Atom Technology, Angstrom Technology Partnership, Tsukuba, Ibaraki, Japan

**Joint Research Center for Atom Technology, Tsukuba, Ibaraki, Japan and Research Institute for Computational Science, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

***Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

We revise part of our recent *ab initio* molecular dynamics study on the Ti-based Ziegler-Natta supported heterogeneous catalysis of α -olefins. The results for the insertion of ethylene in the metal-carbon bond are discussed as a fundamental textbook example of polymerization processes. Comparison with the few experimental data available has shown that simulation can reproduce activation barriers and the overall energetics of the reaction with sufficient accuracy. This puts these quantum dynamical simulations in a new perspective as a virtual laboratory where the microscopic picture of the catalysis, which represents an important issue that still escapes experimental probes, can be observed and understood. These results are then discussed in comparison with a V-based catalyst in order to figure out analogies and differences with respect to the industrially more successful Ti based systems.

References: Int. J. Mol. Sci. **3** (2002) 395

Title: Escaping free energy minima

Researchers: A. Laio
M. Parrinello

**Institute/
Group:** Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

We introduce a powerful method for exploring the properties of the multidimensional free energy surfaces (FESs) of complex many-body systems by means of coarse-grained non-Markovian dynamics in the space defined by a few collective coordinates. A characteristic feature of these dynamics is the presence of a history-dependent potential term that, in time, fills the minima in the FES, allowing the efficient exploration and accurate determination of the FES as a function of the collective coordinates. We demonstrate the usefulness of this approach in the case of the dissociation of a NaCl molecule in water and in the study of the conformational changes of a dialanine in solution.

References: Proc. Natl. Acad. Sci. **99** (2002) 12562

Title: Ab *initio* molecular dynamics simulation of hydrogen fluoride at several thermodynamic states

Researchers: M. Kreitmeir*
H. Bertagnolli*
J.J. Mortensen**
M. Parrinello***

Institute/

Group: *Institut für Physikalische Chemie, Universität Stuttgart, Germany
**Department of Physics, Technical University of Denmark, Lyngby, Denmark
***Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Liquid hydrogen fluoride is a simple but interesting system for studies of the influence of hydrogen bonds on physical properties. We have performed *ab initio* molecular dynamics simulations of HF at several thermodynamic states, where we examine the microscopic structure of the liquid as well as its static and dynamic properties. The results obtained show good agreement with well established data, and, moreover, we were able to show significant changes within the structure depending on the system's temperature and density.

References: J. Chem. Phys. **118** (2003) 3639

Title: Predicting crystal structures: The Parrinello-Rahman method revisited

Researchers: R. Marto_àk
A. Laio
M. Parrinello

Institute/

Group: Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

By suitably adapting a recent approach [A. Laio and M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. **99**, 12 562 (2002)] we develop a powerful molecular dynamics method for the study of pressure-induced structural transformations. We use the edges of the simulation cell as collective variables and define a metadynamics that drives the system away from the local minimum towards a new crystal structure. In contrast to the Parrinello-Rahman method, our approach shows no hysteresis, and crystal structure transformations can occur at the equilibrium pressure. We illustrate the power of the method by studying the pressure-induced diamond to simple hexagonal phase transition in a model of silicon.

References: Phys. Rev. Lett. **90** (2003) 075503

Title: A concerted variational strategy for investigating rare events

Researchers: D. Passerone*
M. Ceccarelli**
M. Parrinello**

Institute/

Group: *Current address: Computational Laboratory (COLAB), Swiss Federal Institute of Technology (ETH), Zurich, Switzerland

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Description:

A strategy for finding transition paths connecting two stable basins is presented. The starting point is the Hamilton principle of stationary action; we show how it can be transformed into a minimum principle through the addition of suitable constraints like energy conservation. Methods for improving the quality of the paths are presented: for example, the Maupertuis principle can be used for determining the transition time of the trajectory and for coming closer to the desired dynamic path. A saddle point algorithm (conjugate residual method) is shown to be efficient for reaching a "true" solution of the original variational problem.

References: J. Chem. Phys. **118** (2003) 2025

Title: Water structure as a function of temperature from X-ray scattering experiments and *ab initio* molecular dynamics

Researchers: G. Hura*
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T. Head-Gordon* and**
M. Krack****
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Institute/

Group: *Graduate Group in Biophysics, University of California, Berkeley, USA
**Department of Bioengineering; University of California, Berkeley, USA
***Department of Molecular and Cell Biology, University of California, Berkeley, USA
****Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

We present high-quality X-ray scattering experiments on pure water taken over a temperature range of 2 to 77degreesC using a synchrotron beam line at the advanced light source (ALS) at Lawrence Berkeley National Laboratory. The ALS X-ray scattering intensities are qualitatively different in trend of maximum intensity over this temperature range compared to older X-ray experiments. While the common procedure is to report both the intensity curve and radial distribution function(s), the proper extraction of the real-space pair correlation functions from the experimental scattering is very difficult due to uncertainty introduced in the experimental corrections, the proper weighting of OO, OH, and HH contributions, and numerical problems of Fourier transforming truncated data in Q-space. Instead, we consider the direct calculation of X-ray scattering spectra using electron densities derived from density functional theory based on real-space configurations generated with classical water models. The simulation of the experimental intensity is therefore definitive for determining radial distribution functions over a smaller Q-range. We find that the TIP4P, TIP5P and polarizable TIP4P-Pol2 water models, with DFT-LDA densities, show very good agreement with the experimental intensities, and TIP4P-Pol2 in particular shows quantitative agreement over the full temperature range. The resulting radial distribution functions from TIP4P-Pol2 provide the current best benchmarks for real-space water structure over the biologically relevant temperature range studied here.

References: Phys. Chem. Chem. Phys. **5** (2003) 1981

Title: Efficient exploration of reactive potential energy surfaces using Car-Parrinello molecular dynamics

Researchers: M. Iannuzzi
A. Laio
M. Parrinello

**Institute/
Group:** Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

The possibility of observing chemical reactions in *ab initio* molecular dynamics runs is severely hindered by the short simulation time accessible. We propose a new method for accelerating the reaction process, based on the ideas of the extended Lagrangian and coarse-grained non-Markovian metadynamics. We demonstrate that by this method it is possible to simulate reactions involving complex atomic rearrangements and very large energy barriers in runs of a few picoseconds.

References: Phys. Rev. Lett. **90** (2003) 238302

Title: *Ab initio* simulation of H₂S adsorption on the (100) surface of pyrite

Researchers: A. Stirling*
M. Bernasconi**
M. Parrinello*

Institute/

Group: *Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland
**Dipartimento di Scienza dei Materiali and Istituto Nazionale per la Fisica della Materia, Università di Milano, Italy

Description:

The adsorption properties of H₂S on the (100) surface of pyrite have been studied by Car–Parrinello simulations. The predicted adsorption properties have been contrasted to those of water on the same surface. It was found that H₂S prefers molecular adsorption on the surface iron sites while the dissociative adsorption is highly unfavorable. The binding of the H₂S and HS⁻ species to the Fe sites results from a coordinative covalent bond from the ligand sulfur atom. The adsorption energy at full coverage is much lower than at partial coverage due to steric repulsion among the adsorbates. As opposed to water adsorption, hydrogen bonding plays a marginal role in H₂S adsorption.

References: J. Chem. Phys. **119** (2003) 4934

Title: Ab initio simulation of water interaction with the (100) surface of pyrite

Researchers: A. Stirling*
M. Bernasconi**
M. Parrinello*

Institute/

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Description:

Car–Parrinello simulations have been performed to study the interaction of water with pyrite (100) surface. The stability and the structural and electronic properties of both the molecular and dissociative adsorptions have been addressed. We found a very strong preference for molecular adsorption on the surface iron sites, in agreement with experiment. The dissociative chemisorption of water is energetically disfavored and is even locally unstable; the dissociated fragments transform back to the stable molecular form in a short molecular dynamics run. The calculations revealed that hydrogen bonding plays an important role in the stabilization of the adsorbed water for both the molecular and the dissociative states. We have shown that water forms a coordinative covalent bond with the surface iron atoms by donating electron to the empty iron d_z^2 orbitals which are the lowest empty states on the clean surface. At full coverage, the sulfur $3p$ states thus become the lowest available empty states and therefore the subject of possible electron-transfer reactions.

References: J. Chem. Phys. **118** (2003) 8917

Title: First-principles molecular-dynamics simulations of a hydrated electron in normal and supercritical water

Researchers: M. Boero*
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K. Terakura***
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C.C. Liew***

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Description:

A first principles study of a hydrated electron in water at ordinary and supercritical conditions is presented. In the first case, the electron cleaves a cavity in the hydrogen bond network in which six H₂O molecules form the solvation shell. The electron distribution assumes an ellipsoidal shape, and the agreement of the computed and the experimental optical absorption seems to support this picture. At supercritical conditions, instead, the H-bond network is not continuous and allows us to predict that the electron localizes in preexisting cavities in a more isotropic way. Four water molecules form the solvation shell but the localization time shortens significantly.

References: Phys. Rev. Lett. **90** (2003) 226403

Title: Influence of outer-shell metal ligands on the structural and electronic properties of horse liver alcohol dehydrogenase zinc active site

Researchers: F.L. Gervasio
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S. Mangani
M. Krack
P. Carloni
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**Institute/
Group:** Dip. di Chimica, Università di Firenze, Sesto Fiorentino, Italy, European Laboratory for Non linear Spectroscopy (LENS), Sesto Fiorentino, Italy, International School for Advanced Studies (SISSA/ISAS) and INFN-DEMOCRITOS Center for Numerical Simulation, Trieste, Italy, Dip. di Chimica, Università di Siena, Italy, Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

An analysis of the high resolution 3D structures of zinc enzymes shows that the Zn-His-carboxyl(ate)-HX (X = OH or NH) H-bond motif is common. We investigate here the influence of this motif in the active site of horse liver alcohol dehydrogenase, which features the Zn-His-Asp-H₂O motif. Density functional theory calculations are carried out on models of the active site complexed with the NAD⁺ cofactor, in which the metal ion binds either the alcohol substrate [Bahnson et al. *Proc. Natl. Acad. Sci. U.S.A* **1997**, *94*, 12797-12802]¹ or a water molecule [Meijers et al. *J. Biol. Chem.* **2001**, *276*, 9316-9321].² Our calculations suggest that in both complexes the presence of Asp49 significantly affects the structural and electronic properties of the metal site. Furthermore, they show that inclusion of the Asp bound water molecule is required to describe the energetics correctly. Finally, they suggest that the Asp49/water pattern could play a role in the enzymatic reaction.

References: J. Phys. Chem. B **107** (2003) 6886

Title: On the competition of the purine bases, functionalities of peptide side chains, and protecting agents for the coordination sites of dicationic cisplatin derivatives

Researchers: D.V. Deubel

Institute/

Group: Contribution of the Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland
c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland, University of Calgary, Alberta and Academia Sinica, Institute of Biomedical Sciences, Taipei, Taiwan, R.O.C.

Description:

The Pt-L bond energies of simple triammineplatinum(II) complexes, $[\text{Pt}(\text{NH}_3)_3\text{L}]^{2+}$, with oxygen-, nitrogen-, and sulfur-containing donor ligands L have been predicted and rationalized using density functional theory. The ligands L have been chosen as models for functionalities of peptide side chains, for sulfur-containing protecting agents, and for adenine and guanine sites of the DNA as the ultimate target of platinum anticancer drugs. Calculation of the Pt-L bond energy in $[\text{Pt}(\text{NH}_3)_3\text{L}]^{2+}$ reveals that the soft metal center of triammineplatinum(II) prefers N ligands over S ligands. This remarkable result has been discussed in light of several interpretations of the hard and soft acids and bases principle. The concept of orbital-symmetry-based energy decomposition has been employed for the determination of the contributions from σ and π orbital interactions, electrostatics, and intramolecular hydrogen bonding to the Pt-L bond energy. The calculations show that considerable differences in the bond energies of the triammineplatinum(II) complexes with N-heterocycles such as 1-methylimidazole, 9-methyladenine, and 9-methylguanine arise from electrostatics rather than from orbital interactions. Surprisingly, the net stabilization by hydrogen bonding between the (Pt)N-H group and the oxygen of 9-methylguanine is as weak as the intramolecular hydrogen bond in the aqua complex $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$, challenging the common hypothesis that DNA-active anticancer drugs require carrier ligands with N-H functionalities because of their hydrogen-bonding ability. The influence of a polarizable environment on the stability of the complexes has been investigated systematically with the dependence of the dielectric constant ϵ . With increasing ϵ , the complexes with S-containing ligands are more strongly stabilized than the complexes of the N-containing heterocycles. At $\epsilon = 78.4$, the dielectric constant of water, 9-methylguanine remains the only purine derivative investigated which is competitive to neutral sulfur ligands. These findings are particularly important for a rationalization of the results from recent experimental studies on the competition of biological donor ligands L for coordination with the metal center of $[\text{Pt}(\text{dien})\text{L}]^{2+}$ (dien = 1,5-diamino 3-azapentane).

References: J. Am. Chem. Soc. **124** (2002) 5834

Title: Stacking and T-shape competition in aromatic-aromatic amino acid interactions

Researchers: R. Chelli*
F.L. Gervasio**
P. Procacci*
V. Schettino*

Institute/

Group: *Università di Firenze, Dipartimento Chimico, Sesto Fiorentino, Italy
**Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

The potential of mean force of interacting aromatic amino acids is calculated using molecular dynamics simulations. The free energy surface is determined in order to study stacking and T-shape competition for phenylalanine-phenylalanine (Phe-Phe), phenylalanine-tyrosine (Phe-Tyr), and tyrosine-tyrosine (Tyr-Tyr) complexes in vacuo, water, carbon tetrachloride, and methanol. Stacked structures are favored in all solvents with the exception of the Tyr-Tyr complex in carbon tetrachloride, where T-shaped structures are also important. The effect of anchoring the two -carbons (C) at selected distances is investigated. We find that short and large C-C distances favor stacked and T-shaped structures, respectively. We analyze a set of 2396 protein structures resolved experimentally. Comparison of theoretical free energies for the complexes to the experimental analogue shows that Tyr-Tyr interaction occurs mainly at the protein surface, while Phe-Tyr and Phe-Phe interactions are more frequent in the hydrophobic protein core. This is confirmed by the Voronoi polyhedron analysis on the database protein structures. As found from the free energy calculation, analysis of the protein database has shown that proximal and distal interacting aromatic residues are predominantly stacked and T-shaped, respectively.

References: J. Am. Chem. Soc. **124** (2002) 6133

Title: Orbital symmetry as a tool for understanding the bonding in Krossing's cation

Researchers: D.V. Deubel

Institute/

Group: Contribution from the Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland, Academia Sinica, Institute of Biomedical Sciences, Taipei, Taiwan, R.O.C., and University of Calgary, Calgary, Alberta, Canada

Description:

The geometric and electronic structure of Krossing's cation, $\text{Ag}(\eta^2\text{-P}_4)_2^+$, which shows an unexpected planar coordination environment at the metal center and D_{2h} symmetry both in solution and in the solid state, have been investigated using density functional theory and orbital-symmetry-based energy decomposition. The analysis reveals that the contribution from electrostatic interactions to the bond energy is greater than that of orbital interactions. Partitioning of the latter term into the irreducible representations shows that, in addition to the 5s orbital, 5p orbitals of silver act as acceptor orbitals for electron donation from $\sigma(\text{P-P})$ orbitals (a_{1g} , b_{1u}) and $n(\text{P})$ orbitals (b_{3u}). Back-donation from the $4d^{10}$ closed shell of Ag into σ^* orbitals of the pnictogen cages (b_{2g}) is also important. However, this contribution is shown not to determine the D_{2h} structure, contradicting conclusions from the pioneering study of the title cation (*J. Am. Chem. Soc.* **2001**, *123*, 4603). The contributions from the irreducible representations to the stabilizing orbital interactions in the D_{2h} structure and in its D_{2d} -symmetric conformer are analogous, indicating that the planar coordination environment at the metal center in $\text{Ag}(\eta^2\text{-P}_4)_2^+$ is induced by intermolecular rather than by intramolecular interactions. Because ethylene coordination to a metal ion is an elementary reaction step in industrial processes, the bonding in $\text{Ag}(\text{C}_2\text{H}_4)_2^+$ has been analyzed as well and compared to that in Krossing's cation. Surprisingly, similar contributions to the bond energies and an involvement of metal 4d and 5p orbitals have been found, whereas a recent atoms in molecules analysis suggested that the metal-ligand interactions in silver(I) olefin complexes fundamentally differ from those in *tetrahedro* P_4 complexes. The only qualitative difference between the bonding patterns in $\text{Ag}(\eta^2\text{-P}_4)_2^+$ and $\text{Ag}(\text{C}_2\text{H}_4)_2^+$ is the negligible energy contribution from the b_{3u} irreducible representation in the ethylene complex because a respective symmetry-adapted linear combination of ligand orbitals is not available.

References: *J. Am. Chem. Soc.* **124** (2002) 12312

Title: Unified view of the interaction of tetrakis (carboxylato) dirhodium (II) with axial donor-acceptor ligands

Researchers: D.V. Deubel

**Institute/
Group** Institute of Biomedical Sciences, IBMS, Academia Sinica, Taipei, Taiwan, R.O.C. and Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland
c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Density functional calculations rationalize the bonding in $[\text{Rh}_2(\mu\text{-O}_2\text{CR})_4\text{L}]$ complexes with strong and very weak axial donor-acceptor ligands L such as "Arduengo" carbenes and aromatic hydrocarbons.

References: Organometallics **21** (2002) 4303

Title: Challenge of the copolymerization of olefins with n-containing polar monomers. Systematic screening of Nickel(II) and Palladium(II) catalysts with Brookhart and Grubbs ligands. 2. Chain-propagation barriers, intrinsic regioselectivity, and Curtin-Hammett reactivity

Researchers: D.V. Deubel
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Description:

The second level of a computational screening of late-transition-metal catalysts and nitrogen-containing polar monomers toward an incorporation of amines and nitriles in the polymer chain of polyolefins is reported. The structures and energies of the transition states for the insertion of the C=C bond of ethylene, propylene, acrylonitrile, and vinylamine into the metal-carbon bond of generic models for Ni(II) and Pd(II) complexes with diimine (Brookhart) and salicylaldiminato (Grubbs) ligands have been calculated using density functional theory. The calculations reveal the general trend that the activation energies for the ethylene, propylene, and acrylonitrile insertion in the Brookhart systems are similar, whereas the activation energies for the vinylamine insertion are much higher. The nickel systems show lower insertion barriers than do their palladium counterparts. For the chain propagation with the Grubbs catalysts, a Curtin-Hammett-type energy profile involving cis-trans isomerization and subsequent C-C insertion is predicted. The regioselectivity of the propylene, acrylonitrile, and vinylamine insertion is rationalized by the analysis of the frontier orbitals of the free monomers.

References: Organometallics **21** (2002) 4432

Title: Is the T-shaped toluene dimer a stable intermolecular complex?

Researchers: F.L. Gervasio*
R. Chelli**
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**Università di Firenze, Dipartimento Chimico, Sesto Fiorentino, Italy

Description:

By means of molecular mechanics and ab initio calculations, we show that toluene dimer can assume two different minimum energy structures. Both these arrangements are stacked with the methyl groups being parallel and anti-parallel to each other. Although our findings do not agree with the current opinion that one minimum energy structure is T-shaped, they appear to be consistent with available experiments on jet-cooled toluene.

References: J. Phys. Chem. A **106** (2002) 2945

Title: Quantum annealing by the path-integral Monte Carlo method: The two dimensional random Ising model

Researchers: R. Martoňák*
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Group: *Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zurich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland
**International School for Advanced Studies (SISSA) and INFN (Udr SISSA), Trieste, Italy
***International Center for Theoretical Physics (ICTP), Trieste, Italy

Description:

Quantum annealing was recently found experimentally in a disordered spin- $\frac{1}{2}$ magnet to be more effective than its classical, thermal counterpart. We use the random two-dimensional Ising model as a test example and perform on it both classical and quantum (path-integral) Monte Carlo annealing. A systematic study of the dependence of the final residual energy on the annealing Monte Carlo time quantitatively demonstrates the superiority of quantum relative to classical annealing in this system. In order to determine the parameter regime for optimal efficiency of the quantum annealing procedure we explore a range of values of Trotter slice number P and temperature T . This identifies two different regimes of freezing with respect to efficiency of the algorithm, and leads to useful guidelines for the optimal choice of quantum annealing parameters.

References: Phys. Rev. B **66** (2002) 094203

Title: First-principles modeling of paramagnetic Si dangling-bond defects in amorphous SiO₂

Researchers: A. Stirling*
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**Institut de Théorie de Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland et Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), Lausanne, Switzerland

Description:

We modeled paramagnetic Si dangling-bond defects in amorphous SiO₂ using a generalized-gradient density-functional approach. By creating single oxygen vacancies in a periodic model of amorphous SiO₂, we first generated several model structures in which the core of the defect consists of a threefold coordinated Si atom carrying a dangling bond. These model structures were then fully relaxed and the hyperfine parameters calculated. We found that the hyperfine parameters of such model defects, in both the neutral and positive charge states, reproduced those characteristic of the E^{\dagger} , in accord with experimental observations for amorphous SiO₂. By eliminating a second O atom in the nearest-neighbor shell of these defect centers, we then generated model defects in which the Si atom carrying the dangling bond forms bonds with two O atoms and one Si atom. In this defect, the spin density is found to delocalize over the Si-Si dimer bond, giving rise to two important hyperfine interactions. These properties match the characteristics of the hyperfine spectrum measured for the S center. Our results are complemented by the calculation of hyperfine interactions for small cluster models which serve the threefold purpose of comparing different electronic-structure schemes for the calculation of hyperfine interactions, estimating the size of core-polarization effects, and determining the reliability of cluster approximations used in the literature.

References: Phys. Rev. B **66** (2002) 245201

Title: The nature of intermolecular interactions between aromatic amino acid residues

Researchers: F.L. Gervasio*
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Description:

The nature of intermolecular interactions between aromatic amino acid residues has been investigated by a combination of molecular dynamics and ab initio methods. The potential energy surface of various interacting pairs, including tryptophan, phenylalanine, and tyrosine, was scanned for determining all the relevant local minima by a combined molecular dynamics and conjugate gradient methodology with the AMBER force field. For each of these minima, single-point correlated ab initio calculations of the binding energy were performed. The agreement between empirical force field and ab initio binding energies of the minimum energy structures is excellent. Aromatic-aromatic interactions can be rationalized on the basis of electrostatic and van der Waals interactions, whereas charge transfer or polarization phenomena are small for all intermolecular complexes and, particularly, for stacked structures.

References: PROTEINS: Struct. Func. and Genet. **48**, 117 (2002)

Title: Morphological and compositional evolution of the Ge/Si (001) surface during exposure to a Si Flux

Researchers: A. Rastelli*
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***INFM and L-NESS, Dipartimento di Scienza dei Materiali della Università degli Studi di Milano-Bicocca, Italy
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Description:

By using scanning tunneling microscopy we found that the surface reconstruction of Ge/Si(001) epilayers evolves from (M_N) to (2_N) , and eventually to (2_1) , during exposure to a Si flux. This sequence appears to be just the inverse of that observed during the growth of Ge or SiGe alloys on Si(001). However, molecular dynamics simulations supported by *ab initio* calculations allow us to interpret this morphological evolution in terms of Si migration through the epilayer and complex Si-Ge intermixing below the top Ge layer.

References: Phys. Rev. Lett. **90** (2003) 216104

Title: Insights into the electronic dynamics in chemical reactions

Researchers: D. Aktah*
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**Current address: Computational Laboratory (COLAB), Swiss Federal Institute of Technology (ETH), Zurich, Switzerland

Description:

We study with an ab-initio molecular dynamics method the bond-breaking, bond-forming process in chemical reactions. In order to obtain reactive trajectories we use a newly developed method based on the optimization of a suitably defined action. The Hellmann-Feynman forces, which are needed to optimize the action, are calculated within density-functional theory. We contrast a concerted [4+2] cycloaddition of cyclopentadiene and ethylene with the non-concerted [2+2] cycloaddition of two ethylene molecules.

We find that the duration of the bond-breaking, bond-forming processes due to the nuclear motion is about 100 fs. Moreover the electronic delocalization as well as the HOMO-LUMO energy gap during the two reactions allows us to distinguish clearly between the concerted and the non-concerted mechanism.

References: A manuscript has been submitted in *J. Phys. Chem.* 2003

Title: Mechanism of oxidative damage to DNA

Researchers: F.L. Gervasio
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Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

Oxidative damage of DNA via radical cation formation is a common cause of mutagenesis, and elaborate defense systems against its effects exist in almost all organisms. Based on state-of-the-art ab-initio molecular dynamics simulations, we show that there is evidence suggesting the existence of a steering mechanism that guides the first steps of this oxidation process towards a unique product. In the mechanism proposed here, guanine, which among the bases has the lowest oxidation potential, and the phosphate backbone play a crucial role. It has been recently shown that radical states can migrate along the DNA helix. We found that guanine, losing one of its protons to cytosine, acts as a radical sink, causing the localization and stabilization of an otherwise delocalized state. After this first step a subsequent chain of reactions, catalyzed by the phosphate backbone, leads to a specific radical precursor to the most common oxidation product found in DNA: 8-oxo-guanine.

References: A manuscript has been submitted in *Science* 2003

Title: Hydrogen bond driven chemical reactions: Beckmann rearrangement of cyclohexanone oxime into ϵ -caprolactam in supercritical water

Researchers: M. Boero*
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Description:

Recent experiments have shown that supercritical water (SCW) has the ability to accelerate and make selective synthetic organic reactions, thus replacing the common but environmentally harmful acid and basic catalysts. In an attempt to understand the intimate mechanism behind this observation, we analyze, via first principles molecular dynamics, the Beckmann rearrangement of cyclohexanone oxime into ϵ -caprolactam in supercritical water, for which accurate experimental evidence has been reported. The simulations show that differences in the wetting of the hydrophilic parts of the solute, enhanced by the particular thermal state, and the disrupted hydrogen bond network are crucial in triggering the reaction and in making it selective, thus offering a general *prescription* to tune a chemical reaction by tuning the thermodynamic state of the solvent. Furthermore, if the concentrations of H^+ and OH^- are enhanced with respect to the ordinary liquid, as expected by the higher K_w of SCW, they play separately an important role in two distinct stages of the reaction, accelerating the process and lowering significantly the activation barrier, leading to the formation of the product.

References: A manuscript has been submitted in *Science* 2003

Title: Hydrogen bonding water

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Description:

Computer simulations using density functional theory based ab initio path integral molecular dynamics have been carried out to investigate hydrogen bonding in water under ambient conditions. Structural predictions for both H₂O and D₂O, which include the effects of zero point energy, thermal motion, and many body polarization effects are contrasted with classical simulations that ignore nuclear quantum effects. The calculated effect of H/D isotope substitution on the water structure is much smaller than the difference between the classical and quantum path integral results, and is in excellent agreement with the measured H/D difference data from both neutron and x-ray scattering. The inclusion of zero point energy leads to an enhancement in the water dipole moment, and thus a shorter hydrogen bond in water compared to results based on purely classical nuclear dynamics. The calculated very small differences between the H₂O and D₂O structure factors provides support for the common practice of using H/D mixtures as a phase contrast in a wide range of neutron scattering experiments.

References: A manuscript has been submitted in *Nature* 2003

Title: Polyamorphism of ice at low temperatures from constant-pressure simulations

Researchers: R. Martoňák
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**Institute/
Group:** Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland

Description:

We report results of constant-pressure MD simulations of amorphous ice at low temperatures in the pressure range 0 - 15 kbar. By careful annealing of the high-pressure amorphous phase at each intermediate pressure we generate a fully relaxed state. We reproduce the experimentally observed phenomenology and confirm the existence of both recently observed phenomena, the VHDA phase and a continuum of highly compressible states between the HDA and LDA phases. The $V(p)$ dependence of these states defines an equation of state which connects the LDA ice at $p = 0$ with a compressed form of VHDA at $p > 7.5$ kbar. This curve has an unusual shape which could be experimentally investigated.

References: A manuscript has been submitted in *Phys. Rev. Lett.* 2003

Title: Ab initio calculations of the proton location in topaz-OH,
 $\text{Al}_2\text{SiO}_4(\text{OH})_2$

Researchers: S.V. Churakov*
U. Wunder**

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Group: *Department of Physical Chemistry, Swiss Federal Institute of
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Description:

The position of hydrogen in the structure of topaz-OH was determined by means of ab-initio quantum mechanic calculations. Static lattice energy calculations predict the existence of four non-equivalent positions of protons, which are characterised by O4-H1...O1, O4-H2...O2, O4-H3...O3 and O4-H4...O4 hydrogen bonds. The distribution of the protons between positions of local equilibrium is controlled by the proton-proton avoidance rule and the strength of the hydrogen bonds. The most favourable configuration of hydrogen atoms is achieved for adjacent protons, which form O4-H3...O3 and O4-H4...O4 hydrogen bonds, respectively. The thermal excitation of atoms at a temperature of 55 K is large enough that the hydrogen atoms occasionally change their positions to form O4-H1...O1 and O4-H2...O2 bonds. At ambient pressures and higher temperatures the protons are in a dynamic exchange between the allowed positions of local minima. As a consequence, for nearly room temperature conditions, the dynamic change between different structural configurations leads to the violation of all possible symmetry elements and with that to space group *P1*. The flipping of the protons between different sites is achieved by simple rotation of the OH-dipole and does not produce any significant distortion of the framework of topaz, which symmetry remains that of the space group *Pbnm*. Therefore, no reduction of symmetry has been observed in former X-ray studies on topaz-OH.

Calculated IR absorption spectra of topaz-OH were found to be in good agreement with measured spectra. According to the calculations, the two favourable configurations of protons might correspond to the measured peak splitting within the OH-stretching range. Experimentally observed low frequency band at 3520 cm^{-1} was assigned to the OH-stretching of the O4-H3...O3 bond, while the band at 3600 cm^{-1} was attributed to OH-stretching of the O4-H4...O4 hydrogen bond. Broad peak in FAR-IR frequency range at $100\text{-}150\text{ cm}^{-1}$ is attributed to the stretching of H3...O3 and H4...O4 contacts.

The rate of proton exchange at 670 K among different sites was estimated by ab-initio molecular dynamic simulations. The calculations predict that flipping of adjacent protons between O4-H3...O3 and O4-H4...O4 bonds at 670 K occur with a rate of about 1.96 THz.

References: A manuscript has been submitted in *Phys. Chem. Min.* 2003

Title: [3+2] versus [2+2] addition of metal oxides across C=C bonds.
Reconciliation of experiment and theory

Researchers: D.V. Deubel*
G. Frenking**

Institute/

Group: *Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland, and Academia Sinica, Taipei, Taiwan, R.O.C.

**Fachbereich Chemie, Philipps-Universität Marburg, Germany

Description:

The reaction of a metal oxide with a double bond is the initial step in the osmium-catalyzed *cis*-dihydroxylation of olefins. The mechanism of the addition of osmium tetroxide and rhenium(VII) oxides across C=C bonds was controversial. Early work indicated a [3+2] addition, and later kinetic studies suggested an initial [2+2] addition, whereas recent quantum-chemical calculations showed the [3+2] addition to be favored. Experiment and theory have now become reconciled. In this Account, we discuss recent contributions to the mechanistic debate as well as future challenges.

References: Acc. Chem. Res. **36** (2003) **Web Release Date:** May 21, 2003

Title: The Metal insertion route of the Ni + CO₂ → NiO + CO reaction

Researchers: Y. Hannachi*
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Chemical Research Center of HAS, Budapest, Hungary

Description:

The gas-phase reaction of the nickel atom with CO₂ molecule is investigated at the B3LYP and CCSD(T) levels of theory. The insertion-elimination route to NiO (³Σ⁻) + CO (¹Σ⁺) is found to be the most favorable mechanism. The insertion product on the ³A' surface is calculated to be about 15 kcal/mol higher in energy than the reactants. The insertion reaction is direct and needs to overcome an energy barrier of 34.6 kcal/mol. A second path, on the ³A' surface, is similar but the insertion product is less stable with respect to the corresponding ³A' species and the transition state is higher in energy. The ³A' insertion product can dissociate to NiO (³Σ⁻) + CO (¹Σ⁺) without exit barrier. This reaction is endothermic by 22 kcal/mol. The ³A' insertion product can also dissociate without exit barrier but leads to an excited state of nickel oxide (A ³Π). The Ni + CO₂ → NiO + CO reaction is found to be endothermic by 37.4 kcal/mol in good agreement with experiment (36.6 kcal/mol).

References: J. Phys. Chem. A (2003) **Web Release Date:** August 1, 2003

Title: Linear response and electron transfer in complex biomolecular systems and a reaction center protein

Researchers: F. Sterpone*
M. Ceccarelli**
M. Marchi*

Institute/

Group: *Commissariat à l’Energie Atomique, DSV-DBJC-SBFM, Centre d’Etudes, Saclay, Gif-sur-Yvette, France

**Department of Physical Chemistry, Swiss Federal Institute of Technology (ETH) Hönggerberg, HCI, Zürich, Switzerland c/o Swiss Center for Scientific Computing (CSCS/ETH), Manno, Switzerland, and Academia Sinica, Taipei, Taiwan, R.O.C.

Description:

This paper is focused on the dielectric linear response in the context of electron transfer reactions in complex biomolecules with and without explicit electronic polarization. Molecular dynamics simulation is used for a detailed investigation of two systems: A bacteriochlorophyll molecule in a homogeneous environment, liquid water; and a reaction center protein of bacterial photosynthesis in amphophilic solution. The limits of the linear approximation and the size of its deviation from results, in principle exact, obtained from thermodynamic integration are pinpointed. Our findings will be of crucial importance in further investigations of electron transfer in complex biomolecules making use of linear response – still the easiest and least time consuming approach.

References: J. Phys. Chem. B (2003)

Title: Numerics of Nematic Liquid Crystals

Researchers: Andreas Prohl*
Xiaobing Feng **
John W. Barrett ++

**Institute/
Group:** *Seminar for Applied Mathematics, ETHZ
**Department of Mathematics, The University of Tennessee, Knoxville, TN 37996, USA
++Department of Mathematics, Imperial College, London, SW7 2BZ, UK

Description:

Liquid crystals are certain low temperature phases that occur to some anisotropic molecules. In the practically relevant nematic phase, molecules of liquid crystals acquire orientational order but no positional order, i.e. on average they line up with each other locally but their positions are still random.

In the project, we consider the existing continuum models of Leslie-Ericksen (1973) and Ericksen (1991) which describe evolution of texture and overall fluid flow. Results range from analysis (i.e., existence, uniqueness, regularity of solutions) across numerical analysis of efficient space-time discretizations (i.e., implicit space-time discretizations, penalization and projection strategies), up to computational studies of evolving (point and line) defects.

References:

A. Prohl, “Computational Micromagnetism”, Teubner (2001)

J. W. Barrett, X. Feng, A. Prohl, “Convergence of a fully discrete finite element method for a degenerated parabolic system modeling nematic liquid crystals with variable degree of orientation”, in preparation (2003)

Title: How Important is Parity Violation for Molecular and Biomolecular Chirality?

Researchers: M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich

Description:

Parity violation leads to energy differences $\Delta_{\text{pv}}H_0^\ominus = N_A\Delta_{\text{pv}}E$ of enantiomers in the Femtojoule to Picojoule per mole range. Recently introduced methods of electroweak quantum chemistry predict such energy differences to be one to two orders of magnitude larger than previously accepted -- but still very small. How can such small energies be measured and what are the consequences for our understanding of molecular chirality, biomolecular homochirality, and perhaps fundamental physics? The essay gives some tentative answers to these questions. We discuss the current status of theory and some of the current experimental approaches. The extensive calculations on $\Delta_{\text{pv}}E$ carried out in our group are reviewed [1–12].

References:

- [1] M. Quack, *Angew. Chem.* **114**, 4812-4825 (2002)
- [2] A. Bakasov, T.K. Ha and M. Quack, in *Proc. of the 4th Trieste Conference (1995), Chemical Evolution: Physics of the Origin and Evolution of Life*, 287-296, J. Chela-Flores and F. Rolin eds, Kluwer Academic Publ. Dordrecht, 1996
- [3] A. Bakasov, T.K. Ha and M. Quack, *J. Chem. Phys.* **109**, 7263-7285 (1998), Erratum: *J. Chem. Phys.* **110**, 6081 (1999)
- [4] M. Quack, *Nova Acta Leopoldina* **81**, Neue Folge (No. 314) 137-173 (1999)
- [5] M. Quack and J. Stohner, *Phys. Rev. Lett.* **84**, 3807-3810 (2000)
- [6] M. Quack and J. Stohner, *Z. Physik. Chem.* **214**, 675-703 (2000)
- [7] R. Berger and M. Quack, *ChemPhysChem.* **1**, 57-60 (2000)
- [8] R. Berger and M. Quack, *J. Chem. Phys.* **112**, 3148-3158 (2000)
- [9] R. Berger, M. Quack and G. Tschumper, *Helv. Chim. Acta* **83**, 1919–1950 (2000)
- [10] R. Berger, M. Quack and J. Stohner, *Angew. Chemie* **113**, 1716–1719 (2001); *Angew. Chem. Intl. Ed. (Engl.)* **40**, 1667–1670 (2001)
- [11] M. Quack and J. Stohner, *Chirality*, **13**, 745–753 (2001)
- [12] M. Quack, *Angewandte Chemie* **101**, 588-604 (1989), *Angewandte Chemie (Intl.Ed.)* **28**, 571-586 (1989)

Title: Nonlinear intensity dependence in the infrared multiphoton excitation and dissociation of methanol pre-excited to different energies

Researchers: Boyarkin, O. V.**
Rizzo, T. R.**
Rueda, D.**
Quack, M.*
Seyfang, G.

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Laboratory of Physical Chemistry, EPF Lausanne

Description:

We report quantitative dissociation yields for the reaction $\text{CH}_3\text{OH}(v_{\text{OH}}) \xrightarrow{nh\nu} \text{CH}_3 + \text{OH}$ induced by infrared multiphoton excitation of methanol preexcited to various levels of the OH stretching vibration ($v_{\text{OH}} = 0, 1, 3, 5$) by detecting OH using laser induced fluorescence. It is demonstrated that for low levels of preexcitation ($v_{\text{OH}} = 0, 1, 3$) there is a substantial nonlinear intensity dependence, as a higher yield is found for self mode-locked CO_2 laser pulses (with higher peak intensity) as compared to single mode pulses of the same laser fluence, but lower peak intensity. In contrast, at high levels of preexcitation ($v_{\text{OH}} = 5$) this nonlinear intensity dependence is absent. Quantitative model calculations are carried out [1] using a case B/case C master equation approach [2] that takes nonlinear intensity dependence into account. The calculations are consistent with the experimental results and confirm the prediction that an important part of the selectivity of the CO_2 laser excitation step in IRLAPS (Infrared laser assisted photofragment spectroscopy) of CH_3OH is due to this nonlinear intensity dependence. We discuss further consequences of these experimental observations and theoretical predictions, which are also extended to IR multiphoton excitation of $\text{C}_2\text{H}_5\text{OH}$. Infrared (C–O) chromophore band strengths are reported for CH_3OH and $\text{C}_2\text{H}_5\text{OH}$.

References:

- [1] O. V. Boyarkin, T. R. Rizzo, D. Rueda, M. Quack, and G. Seyfang, *J. Chem. Phys.* **117** (21), 9793-9805 (2002).
- [2] M. Quack, *Multiphoton Excitation*, in "Encyclopedia of Computational Chemistry", Vol. 3, p. 1775-1791, P. von Ragué Schleyer, N. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III and P.R. Schreiner eds., John Wiley and Sons, 1998

Title: Tunneling Dynamics of the NH Chromophore in NHD₂ During and After Coherent Infrared Excitation

Researchers: R. Marquardt**
M. Quack*
I. Thanopoulos***
D. Luckhaus****

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Laboratoire de Chimie Théorique, Université de Marne-la-Vallée
*** Weizmann Institute of Science, Rehovot (present address)
**** Institut für Physikalische Chemie, Universität Göttingen (present address)

Description:

The time dependent quantum dynamics of the large amplitude motion of the NH stretching chromophore in NHD₂ is investigated during and after coherent multiphoton excitation by calculation of the wave packet evolution using global analytical potential energy and electric dipole hypersurfaces of ammonia derived from *ab initio* calculations. Intramolecular vibrational redistribution (IVR) between the NH stretching and bending motion and coupling to the radiation field induces a diffusion of probability density into the NH chromophore space, which includes the inversion coordinate. But inversion remains essentially dominated by a tunneling process, even at average energies well above the inversion barrier.

References:

R. Marquardt, M. Quack, I. Thanopoulos, and D. Luckhaus, J Chem Phys **118** (2), 643-658 (2003).

Title: Molecular spectra, reaction dynamics, symmetries and life

Researchers: M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich

Description:

We provide a short review of the work of the group for molecular kinetics and spectroscopy at the Laboratory for Physical Chemistry of ETH Zurich contributing to our understanding of the fundamental physical-chemical primary processes in chemical reactions. After a brief historical introduction, we present a selection of recent progress and thinking in three areas: 1. Experiments in high resolution molecular spectroscopy leading us from an elucidation and unraveling of molecular infrared spectra to the understanding of the molecular reaction dynamics and fast intramolecular processes from the nanosecond ($1 \text{ ns} = 10^{-9} \text{ s}$) to the femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) and even sub-fs or attosecond ($1 \text{ as} = 10^{-18} \text{ s}$) domain. 2. Theory of fundamental symmetries of physics and their violations in molecular spectra and dynamics of chiral molecules with a discussion of possible consequences for the role of chirality in the origin of life. 3. Speculative considerations on the relationship of spectra and dynamics of chiral molecules with the CPT theorem of physics and with the origin of matter and chiral life, and on the relationship of time reversal symmetry violation with the molecular origin of irreversibility and with the possible molecular origin of thought.

In the analysis of the experiments as well as in the theoretical part of our research extensive computations play an important role.

References:

M. Quack, *Chimia* **57** (4), 147-160 (2003).

Title: Theory of stereomutation dynamics and parity violation in hydrogen thioperoxide isotopomers $^{1,2,3}\text{HSO}^{1,2,3}\text{H}$

Researchers: M. Quack
M. Willeke

Institute/Group: Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich

Description:

We present quantitative calculations of the mode-selective stereomutation tunneling and parity violation in chiral hydrogen thioperoxide ('oxadisulfane') isotopomers XSOY with X, Y=H, D, and T. The torsional tunneling stereomutation dynamics are investigated with a quasi-adiabatic channel quasi-harmonic reaction path Hamiltonian approach, which treats the torsional motion anharmonically in detail and all remaining coordinates as harmonic (but anharmonically coupled to the reaction coordinate). We predict how stereomutation is catalyzed or inhibited by excitation of various vibrational modes compared to the corresponding stereomutation dynamics of the vibrational ground state. Parity-violating potentials were calculated with our recent multiconfiguration linear response (MC-LR) approach in the random phase approximation (RPA). We find that, in agreement with general scaling expectations, the parity-violating energy difference for the equilibrium structures of the two HSOH enantiomers (ca. $5 \times 10^{-12} \text{ J mol}^{-1}$) is situated intermediate between HOOH and HSSH. Our results on the stereomutation dynamics and the influence of parity violation on these are discussed in relation to investigations for the analogous molecules H_2O_2 , H_2S_2 , and Cl_2S_2 . As expected in XSOY (X, Y = H, D, and T), this influence is much larger than in the corresponding H_2O_2 isotopomers, but smaller than in H_2S_2 or Cl_2S_2 .

References:

M. Quack and M. Willeke, *Helv. Chim. Acta* **86** (5), 1641-1652 (2003)

Title: Ab initio calculation of mode selective tunneling dynamics in $^{12}\text{CH}_3\text{OH}$ and $^{13}\text{CH}_3\text{OH}$

Researchers: B. Fehrensen*
D. Luckhaus**
M. Quack*
M. Willeke*
T. R. Rizzo***

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Institut für Physikalische Chemie, Universität Göttingen (present address)
*** Laboratory of Physical Chemistry, EPF Lausanne

Description:

A simplified formulation of the harmonic reaction path Hamiltonian (RPH) approach is used to calculate mode specific tunneling splittings and stereomutation times in $^{12}\text{CH}_3\text{OH}$ and $^{13}\text{CH}_3\text{OH}$. The experimental torsional spectrum is very well reproduced, as well as the few known isotope shifts. The mode specific changes in tunneling splitting are investigated for the excitation of fundamentals and OH stretching overtone modes. Good agreement between experiment and the RPH model is obtained, except for excitations of modes, which are perturbed by anharmonic resonances. The inverted tunneling splittings (E level below A) experimentally observed for the fundamental transitions of the CH-stretching modes ν_2 and ν_9 and of the CH-rocking mode ν_{11} are shown to result from a pure symmetry effect and not from a breakdown of vibrational adiabaticity. Introducing a proper geometrical phase factor but retaining the adiabatic separation of the torsional dynamics yields calculated values of $\Delta\tilde{\nu}_2 = -3.6 \text{ cm}^{-1}$, $\Delta\tilde{\nu}_9 = -3.2 \text{ cm}^{-1}$ and $\Delta\tilde{\nu}_{11} = -8.2 \text{ cm}^{-1}$ that are in satisfactory agreement with experimental data. Negative tunneling splittings are also predicted for the asymmetric CH-bending modes ν_4 and ν_{10} and the CH_3 -rocking mode ν_7 . A smooth decrease of the tunneling splitting is calculated for increasing OH stretching excitation [$\Delta\tilde{\nu}(\nu_1) = 6.2 \text{ cm}^{-1}$, ..., $\Delta\tilde{\nu}(6\nu_1) = 1.5 \text{ cm}^{-1}$] in quantitative agreement with experiment [$\Delta\tilde{\nu}(\nu_1) = 6.3 \text{ cm}^{-1}$, ..., $\Delta\tilde{\nu}(6\nu_1) = 1.6 \text{ cm}^{-1}$]. The effect is shown to result in about equal parts from the increase of the effective torsional barrier and the effective lengthening of the OH bond.

References:

B. Fehrensen, D. Luckhaus, M. Quack, M. Willeke, and T. R. Rizzo, J. Chem. Phys. **119**, 5534 – 5544 (2003)

Title: The NH and ND stretching fundamentals of $^{14}\text{ND}_2\text{H}$

Researchers: M. Snels**
H. Hollenstein*
M. Quack*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Istituto di Fisica dell' Atmosfera, Area di Ricerca di Roma Tor Vergata

Description:

High resolution (0.004 cm^{-1} instrumental bandwidth) interferometric Fourier transform infrared spectra (FTIR) of $^{14}\text{ND}_2\text{H}$ were obtained on a BOMEM DA002 spectrometer under essentially Doppler limited conditions. We report the analysis of the ND and NH stretching fundamentals of $^{14}\text{ND}_2\text{H}$ with term values for the symmetric (*s*) and antisymmetric(*a*) sublevels with respect to the inversion plane of the planar geometry $T_v(s) = 2430.7990(7)\text{ cm}^{-1}$ and $T_v(a) = 2434.6222(8)\text{ cm}^{-1}$ for the ν_{3a} fundamental, $T_v(s) = 2559.8069(8)\text{ cm}^{-1}$ and $T_v(a) = 2559.9630(9)\text{ cm}^{-1}$ for the ν_{3b} fundamental and $T_v(s) = 3404.238(5)\text{ cm}^{-1}$ and $T_v(a) = 3404.316(5)\text{ cm}^{-1}$ for the ν_1 fundamental. The two modes ν_3 which are degenerate in ND_3 and whose degeneracy is lifted in ND_2H , are distinguished by the subscripts *3a* or *3b*, being symmetric (*3a*) or antisymmetric (*3b*) with respect to the C_s plane of symmetry of the equilibrium geometry of ND_2H . Up to 20 molecular parameters of the effective S-reduced Hamiltonian could be determined accurately for each fundamental. In particular, the inversion-rotation interaction parameter could be determined for the two ND-stretching modes. Assignments were established with certainty by means of ground state combination differences. The results are important for the mode selective inhibition or catalysis of inversion at the nitrogen atom by exciting ND and NH stretching vibrations, for treatments of isotope effects on inversion of ammonia by means of effective Hamiltonians as well as true molecular Hamiltonians on high dimensional potential hypersurfaces. Extensive numerical calculations are carried out in the analysis of the experiments.

References:

M. Snels, H. Hollenstein, M. Quack, J. Chem. Phys. in press (2003)

Title: Ab initio calculation of parity violating potential energy hypersurfaces of chiral molecules

Researchers: A. Bakasov*
R. Berger**
T. K. Ha*
M. Quack*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Chemistry Department, Technical University Berlin

Description:

We introduce the explicit concept of parity violating potential energy hypersurfaces, which govern the rotation-vibration tunneling dynamics as well as the time dependent parity violation in chiral molecules. Calculations are reported for sections of the hypersurfaces of H_2O_2 and H_2S_2 at various levels of electroweak quantum chemistry, including CIS-RHF, CIS-LR, and CASSCF-LR [1]. Important findings concern the observed increase of the parity violating potentials (E_{pv}) with increasing bond lengths r_{OO} and r_{SS} , the confirmation of lines and surfaces of "accidentally" zero E_{pv} at chiral geometries and the absence of a precise, simple scaling law for observables such as the measurable parity violating energy difference between enantiomers ΔE_{pv} . The latter is due to the complicated geometry dependent E_{pv} , although a rough scaling on the order of $Z^{(5\pm 1)}$ with nuclear charges of the two heavy centers can be confirmed. The results are discussed in relation to possible experiments on molecular parity violation and in relation to earlier results using various theoretical techniques [2–5].

References:

- [1] A. Bakasov, R. Berger, T. K. Ha, M. Quack, *Int. J. Quantum Chem.* in press (2003)
- [2] A. Bakasov, T. K. Ha, and M. Quack, in *Chemical Evolution, Physics of the Origin and Evolution of Life*, Proc. of the 4th Trieste Conference (1995), edited by J. Chela-Flores and F. Raulin (Kluwer Academic Publishers, Dordrecht, 1996), pp. 287-296.
- [3] A. Bakasov, T. K. Ha, and M. Quack, *J. Chem. Phys.* **109** (17), 7263-7285 (1998).
- [4] A. Bakasov and M. Quack, *Chem. Phys. Lett.* **303** (5-6), 547-557 (1999).
- [5] R. Berger and M. Quack, *J. Chem. Phys.* **112** (7), 3148-3158 (2000).

Title: Isotopomer-selective overtone spectroscopy of jet-cooled benzene by ionization detected IR + UV double resonance: The $N = 2$ CH-chromophore absorption of $^{12}\text{C}_6\text{H}_6$ and $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ near 6000 cm^{-1} .

Researchers: M. Hippler*
R. Pfab**
M. Quack*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Physical Chemistry, ETH Zürich

Description:

Employing our recently introduced IR+UV double-resonance scheme for obtaining mass-resolved infrared spectra, the isotopomer selected $N=2$ CH-chromophore absorption of $^{12}\text{C}_6\text{H}_6$ and $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ near 6000 cm^{-1} has been recorded in a supersonic jet expansion of the benzene isotopomer mixture at natural abundance. The $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ spectra are the first of this kind reported in the literature. The $^{12}\text{C}_6\text{H}_6$ spectrum is compatible with a proposed model of intramolecular vibrational redistribution with a distinct hierarchy of time scales: the CH-stretching state is the IR chromophore state coupled to the IR field. With a decay time of $\tau \approx 100\text{ fs}$, vibrational excitation is redistributed to a first tier of vibrational states, probably CH-stretching/bending combination bands coupled by strong Fermi resonances. Vibrational excitation is then further redistributed with $\tau \approx 0.35\text{ ps}$ to a second tier of states, possibly by weaker higher order anharmonic resonances. The observed line widths give a lower bound for the decay time into the dense background manifold, $\tau > 1.3\text{ ps}$. Although the experimental jet spectra are in qualitative agreement with previously published calculated spectra, they clearly disagree in finer details.

References:

M. Hippler, R. Pfab, and M. Quack, Proc. 18th Coll. High Resol. Mol. Spectroscopy, Dijon 2003, paper D14, p. 118
M. Hippler, R. Pfab, and M. Quack, to be published (2003)

Title: Combined Multidimensional Anharmonic and Parity Violating Effects in CDBrClF

Researchers: Martin Quack*
Jürgen Stohner*, **

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
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** Zürich University of Applied Sciences (ZHAW), Institute of Chemistry
and Biotechnology ICB, Winterthur

Description:

Parity violation causes rovibrational frequency shifts in infrared and microwave spectra between the corresponding lines of enantiomers of chiral molecules. In previous theoretical treatments of this effect simple harmonic and anharmonic adiabatic approximations were used which assumed that the vibrational potential as well as the parity violating potential are separable in normal (or local) coordinates. In the present work we investigate in detail the influence of nonseparable anharmonic couplings on vibrational frequency shifts caused by the parity violating potential in CDBrClF. We use the strongly coupled four dimensional CD- and CF-chromophore subspaces and discuss how relative frequency shifts are influenced by coupling in the pure vibrational potential as well as in the parity violating potential. A four dimensional parity violating potential energy hypersurface has been determined ab initio and fitted to a polynomial expansion. We analyse the nonseparable multidimensional representation of the parity violating potential in a chiral molecule. The effects of the multidimensional anharmonic couplings provide the dominant corrections. They are found to be about 20 % for the expectation value of J the parity violating energy difference ΔE_{pv} between enantiomers (coupled $\Delta_{\text{pv}} E/hc \approx 1.76 \times 10^{-12} \text{ cm}^{-1}$ compared to $1.96 \times 10^{-12} \text{ cm}^{-1}$ uncoupled). The corrections due to anharmonic multidimensional coupling can be more than a factor of two for vibrational frequency shifts, depending on the mode considered.

References:

J. Stohner, M. Quack, Proc. 18th Coll. High Resol. Mol. Spectroscopy, Dijon 2003, paper J13, p. 287
M. Quack, J. Stohner, J. Chem. Phys. in press (2003)

Title: Isotopic chirality and molecular parity violation

Researchers: R. Berger**
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A. Sieben*
M. Willeke*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Institut für Chemie, TU Berlin

Description:

We investigate parity violating energy differences in molecules, which are chiral by isotopic substitution [1, 2] (see also ref. [3] for an early discussion).

References:

- [1] R. Berger, M. Quack, A. Sieben and M. Willeke, to be published
- [2] R. Berger, M. Quack, A. Sieben and M. Willeke, Proc. 18th Coll. High Resol. Mol. Spectroscopy, Dijon 2003, paper F4, p.161
- [3] M. Quack, Angew. Chem.-Int. Edit. Engl. 28 (5), 571-586 (1989).

Title: Von den "unmessbar schnellen" chemischen Reaktionen zur Bestimmung ultrakurzer Zeiten für chemische Primärprozesse

Researchers: M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich

Description:

This paper reviews the development of ideas for the experimental investigation of chemical reactions leading from early formulation of rate laws, via relaxation techniques and pump-probe kinetic spectroscopy to "quantum chemical kinetics" with an important computational contribution in the analysis. We have developed a conceptually new approach to derive the fundamental physical-chemical primary processes of chemical reactions on time scales leading into the femtosecond and subfemtosecond domain on the basis of infrared spectroscopy with high frequency resolution but without short-time resolution. Selected applications include intramolecular wavepacket dynamics of chemical functional groups of isolated, individual molecules and IR-laser chemistry of molecules under infrared multiphoton excitation, hydrogen bond tunneling dynamics in hydrogen fluoride clusters (HF)₂ and the tunneling stereomutation of prototypical chiral molecules. One of the greatest current challenges is the elucidation of the influence of the parity violating weak interaction mediated by the Z-Boson of high energy physics on the dynamics of chiral molecules. Finally the possible relation between the properties of intramolecular kinetics – classical versus quantum delocalization in vibrational redistribution – to a speculative formulation of a "molecular psychology" is discussed.

References:

- [1] M. Quack, Akademie-Journal der Union der deutschen Akademien der Wissenschaften (Themenschwerpunkt Chemie) **1**, 38 – 44 (2003)
- [2] M. Quack, *Chimia* **55**, 753–758 (2001)
- [3] M. Quack, chapter 27 in: "Femtosecond Chemistry", J. Manz and L. Woeste eds., Proc. Berlin Conf. Femtosecond Chemistry, Berlin (March 1993), Verlag Chemie, Weinheim (1994), p. 781-818

Title: A global electric dipole function of ammonia and its isotopomers in the electronic ground state

Researchers: R. Marquardt**
M. Quack*
I. Thanopoulos***
D. Luckhaus****

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Laboratoire de Chimie Théorique, Université de Marne-la-Vallée
*** University of British Columbia, Vancouver (present address)
**** Institut für Physikalische Chemie, Universität Göttingen (present address)

Description:

A global analytical representation of the electric dipole hypersurface for ammonia and isotopomers is developed as a function of bond lengths and bond angles. Its simple and general form allows for the simultaneous description of all three dipole moment components using a small number of parameters. The parameter values are determined by adjustment to dipole moment values obtained from *ab initio* calculations at the MP2 and MCSCF level of theory. The dipole function is used to calculate six dimensional transition moments for NH₃, using wave functions obtained from a variational calculation and a global analytical representation of the potential hypersurface. The comparison with experiment demonstrates a fairly reliable description of the electric dipole hypersurface for molecular structures with potential energy equivalent to up to 10000 cm⁻¹. At higher excitations a qualitatively correct asymptotic behavior of the dipole function is assured by construction.

References:

R. Marquardt, M. Quack, I. Thanopoulos, D. Luckhaus, J. Chem. Phys. in press (2003)

Title: High resolution Fourier transform spectroscopy of CH₂D₂ in the region 2350 – 2650 cm⁻¹: The bands $\nu_5 + \nu_7$, $2\nu_9$, $\nu_3 + \nu_4$, $\nu_3 + \nu_7$, and $\nu_5 + \nu_9$.

Researchers: O. N. Ulenikov**
E. S. Bekhtereva**
S. V. Grebneva**
H. Hollenstein*
M. Quack*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Laboratory of Molecular Spectroscopy, Physics Department,
Tomsk State University

Description:

The infrared spectrum of the CH₂D₂ molecule has been measured in the region of 2350 – 2650 cm⁻¹ on a Bomem DA002 Fourier transform spectrometer with a resolution of 0.004 cm⁻¹ (FWHM, apodized) and analyzed with a Hamiltonian model which takes into account resonance interactions between all vibrational states in that region. More than 3000 transitions have been assigned to the band $2\nu_9$, $\nu_3 + \nu_4$, $\nu_5 + \nu_9$, $\nu_5 + \nu_7$, and $\nu_3 + \nu_7$ using ground state combination differences from the known ground state parameters. A set of 115 spectroscopic parameters for the excited vibrational states is obtained from a least squares adjustment. This reproduces the 646 initial upper ro-vibrational energies used in the fit with an $d_{rms} = 0.0036$ cm⁻¹. Extensive numerical calculations are carried out in the analyses of these experiments.

References:

O. N. Ulenikov, E. S. Bekhtereva, S. V. Grebneva, H. Hollenstein, and M. Quack, to be published
O. N. Ulenikov, E. S. Bekhtereva, S. V. Grebneva, H. Hollenstein, and M. Quack, Proc. 18th Coll. High Resol. Mol. Spectroscopy, Dijon 2003, paper H38, p. 261

Title: Mode-selective stereomutation tunneling as compared to parity violation in hydrogen diselenide isotopomers $^{1,2,3}\text{H}_2^{80}\text{Se}_2$

Researchers: M. Gottselig
M. Quack
M. Willeke

Institute/Group: Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich

Description:

We present quantitative calculations of the mode selective stereomutation tunneling in the chiral hydrogen diselenide isotopomers X_2Se_2 with $\text{X} = \text{H}, \text{D},$ and T [1]. The torsional tunneling stereomutation dynamics were investigated with a quasi-adiabatic channel quasi-harmonic reaction path Hamiltonian approach which treats the torsional motion anharmonically in detail and all remaining coordinates as harmonic (but anharmonically coupled to the reaction coordinate). We also investigated the influence of the excitation of fundamental modes on the stereomutation dynamics and predict which modes should be promoting or inhibiting. Our stereomutation dynamics results and the influence of parity violation on these are discussed in relation to our recent investigations for the analogous molecules H_2O_2 , HSOH , H_2S_2 and Cl_2S_2 . The electronic potential energy barrier heights for the torsional motion of hydrogen diselenide are similar to those of HSOH , whereas the torsional tunneling splittings are similar to the corresponding values of HSSH . The evaluated ground state values for the torsional tunneling splittings for D_2Se_2 are of the same order as the parity-violating energy difference reported in a recent paper of Laerdahl and Schwerdtfeger, whereas for T_2Se_2 the corresponding tunneling splitting is about three orders of magnitude smaller (see also a recent review [2]).

References:

[1] M. Gottselig, M. Quack, and M. Willeke, to be published (2003)

[2] M. Quack, *Chimia* 57 (4), 147-160 (2003).

Title: Parity violating potentials for the torsional motion of methanol and its isotopomers (CH₃OH, CD₃OH, ¹³CD₃OH, CH₃OD, CH₃OT, CHD₂OH and CHD₂OH)

Researchers: R. Berger**
M. Quack*
A. Sieben*
M. Willeke*

Institute/Group: * Group for Molecular Kinetics and Spectroscopy
Physical Chemistry, ETH Zürich
** Institut für Chemie, TU Berlin

Description:

We present calculations on the parity conserving, and the parity violating potentials in several methanol isotopomers for the torsional motion by the newly developed methods of electroweak quantum chemistry from our group. The absolute magnitudes of the parity violating potentials for methanol are small [1] compared to H₂O₂ and C₂H₄ [2, 3], but similar to C₂H₆, which is explained by the high (threefold) symmetry of the torsional top in CH₃OH [1] and C₂H₆ [2]. Chiral and achiral isotopic substitution in methanol leads to small changes only, but vibrational averaging is discussed to be important in all these cases. Simple isotopic sum rules are derived to explain and predict the relationships between parity violating potentials in various conformations and configurations of the several investigated isotopomers. The parity violating energy difference $\Delta_{pv}E = E_{pv}(R) - E_{pv}(L)$ between the enantiomers of the chiral methanol CHD₂OH first synthesized by Arigoni and coworkers [4] is for two conformers about $-3.66 \cdot 10^{-17} (hc) \text{ cm}^{-1}$ and for the third one $+7.32 \cdot 10^{-17} (hc) \text{ cm}^{-1}$. Thus for $\Delta_{pv}E$ the conformation is more important than the configuration (at the equilibrium geometries without vibrational averaging). Averaging over torsional tunneling may lead to further cancellation and even smaller values.

References:

- [1] R. Berger, M. Quack, A. Sieben, and M. Willeke, to be published (2003)
- [2] A. Bakasov, T. K. Ha, and M. Quack, *J. Chem. Phys.* **109** (17), 7263-7285 (1998).
- [3] R. Berger and M. Quack, *J. Chem. Phys.* **112** (7), 3148-3158 (2000).
- [4] D. Arigoni, *Topics in Stereochemistry*, **221**, 1213 (1969); J. Lüthy, J. Retey, and D. Arigoni, *Nature* **221** (5187), 1213 (1969).

Title: Modelling Weather and Climate on European and Alpine scales

Researchers: Christoph Schär, Olivier Fuhrer, Jan Kleinn, Daniel Leuenberger, Daniel Lüthi, Jürg Schmidli, Pier Luigi Vidale, Andre Walser

Institute/Group: Group of Prof. C. Schär, Institute for Atmospheric and Climate Science ETH, Zürich, Switzerland

Description:

Our research revolves around the study of continental and Alpine-scale weather and climate, with special focus on the water cycle, over a continuum of spatial and temporal scales. Regional climate processes are investigated with the help of our Regional Climate Model (RCM), the Climate High Resolution Model (CHRM). The dynamics of dry and moist atmospheric flow past complex topography are investigated with the help of a hierarchy of atmospheric models, including some non-hydrostatic ones (e.g. MC2, ARPS, LM). Hydrological processes in intermediate and major catchments in the Alpine region are investigated with the help of hydrological models (e.g. WASIM).

For the simulation of European regional climate, multiple state of the art, general circulation models (GCMs) are currently run at high resolution (grid spacing equivalent down to 100 km) by the European climate community in the context of two major research projects which will be active for the next few years, one funded by the Swiss SNF (NCCR Climate), the other by the European Commission (PRUDENCE). These current and future (scenario) simulations, together with the re-analyses provided by the European Center for Middle-Range Weather Forecasts (ECMWF, ERA-15 and ERA-40) are used to drive RCMs, which serve as dynamical downscaling tools. Our own CHRM, which we have extensively applied and verified in the past (using ERA-15 forcing data), is forced at the boundaries (nudged) with global data provided by the Hadley Center (HadAM3h) and the Max Planck Institut (ECHAM) GCMs. These simulations, with Δx of 56 and 14 km, use a nested grid approach and cover a 30 year period under current climate conditions in addition to a 2071-2100 period, driven by climate change scenarios (e.g. SRES A2, B2). Results of the 56 Km simulations stored at our Institute are accessed by many European PRUDENCE partners, through OpenDAP technology, and used for impacts modeling. The 14 km simulations are used to drive the WASIM hydrological model, also for impacts studies.

The principal focus of the PRUDENCE project is the production of regional climate change information, and the assessment of its reliability (as related to climate) but also of the dependence on different model formulations. Estimate of local impacts and risks are also produced in this context. The NCCR Climate project has broader scientific focus, but also covers continental climate processes, such as the moisture cycle (and relative feedbacks) within the soil, the land surface and the atmosphere. Our contribution to the NCCR Climate project also concurrently addresses research topics related to the debate on the ability of the GCMs to credibly represent tropospheric moisture dynamics and thermodynamics within different scenarios, together with consequences for precipitation estimation over the North Atlantic-European domain.

The purpose of the Mesoscale Alpine Project (MAP) is to improve the understanding of orographically influenced precipitation events and related flooding episodes involving deep convection, frontal precipitation and runoff. This includes the numerical prediction of moist processes over and in the vicinity of complex topography; the understanding and forecasting of the life-cycle of Foehn-related phenomena; the study of three-dimensional gravity wave breaking and associated wave drag; and the production of data sets for the validation and improvement of high-resolution numerical weather prediction, hydrological and coupled models in mountainous terrain. These research goals are pursued by exercising a hierarchy of numerical models, also applied in weather forecasting, and applying them at very high resolution to case studied of relevant weather events, which were amply documented by the MAP datasets.

Title: Domain decomposition preconditioners for hp finite elements on anisotropically stretched meshes

Researchers: Dr. Andrea Toselli (Project Leader)
Dr. Xavier Vasseur

Institute: Seminar for Applied Mathematics
Group: Department of Mathematics

Description:

It is well-known that solutions of elliptic boundary value problems in polyhedral domains have corner and edge singularities. In addition, boundary layers may also arise in laminar, viscous, incompressible flows with moderate Reynolds numbers at faces, edges, and corners. Suitably graded meshes, geometrically refined towards corners, edges, and/or faces, are required in order to achieve a fast rate of convergence of hp finite element approximations.

In order to make the iterative solution of very large algebraic systems of finite element equations possible and efficient on parallel architectures, domain decomposition techniques (DD) have been used extensively in recent years. These methods are by now well-understood for standard equations (e.g., simple diffusion or viscous flow problems at moderate Reynolds number in regular 2-d or 3-d domains), with subdomains and meshes of regular shape. In this case, optimal or nearly optimal convergence of iterative solution techniques based on domain decomposition is by now well-established. This pertains to low order standard finite element discretizations as well as to high-order p -version or spectral element discretizations. However, their performance in general degrades drastically whenever anisotropic meshes or very thin subdomains are employed.

The purpose of this project is to extend some of the most popular and powerful DD methods to finite element approximations on anisotropic meshes of a wide class of equations. It consists of a theoretical part, where efficient methods are devised and analyzed, and a programming part, where these novel methods are implemented and tested on some real life problems.

Extensive numerical tests showing the performance and robustness of domain decomposition preconditioners for the solution of algebraic linear systems arising from hp finite element approximations of scalar elliptic problems on geometrically refined boundary layer meshes in two and three dimensions have been performed.

This project is sponsored by the Swiss National Fund under Grant 20-63397.00.

Title: Generalized *hp*-FEM for Lattice Structures

Researchers: A. W. Rüegg, A.-M. Matache, Ch. Schwab

Institute/Group: Seminar for Applied Mathematics

Description:

Progress in manufacturing techniques allows the production of *lattice materials* of increasing complexity that are of growing importance in mechanical engineering, optoelectronics, etc.

Typically, when trying to characterize the physical properties of such materials, one has to take into account *three different length scales*: the macroscopic size l of the material block, the microscopic scale of the heterogeneities ε and finally the thickness of the bars δ . Taking the limit $\delta \rightarrow 0$, the remaining dimensionally reduced structures can be modeled by *networks* consisting of one-dimensional curves periodically arranged in a higher dimensional space.

A high order *generalized Finite Element Method* (gFEM) is developed to solve numerically elliptic *partial differential equations* (PDE's) on periodic lattice structures (see [3]). The standard polynomial spaces are replaced by conforming function spaces that are adapted to the micro-scale dependent coefficients of the differential operator, i.e. information much smaller than the macro mesh size $H \gg \varepsilon$ is built into the shape functions. These two-scale FE-spaces are obtained by augmenting the standard piecewise polynomial FE spaces with non-polynomial, periodic micro shape functions that are solutions of suitable unit cell problems on the reference network.

Taking into consideration the periodicity of the micro shape functions, the computation of the stiffness matrices to solve the discrete two scale problem can be realized with *work independent of the micro scale length* ε .

This method is implemented in C++ within the programming framework described in [2].

This Research is supported under the project "Homogenization and multiple scales" HMS2000 of the EC (HPRN-CT-1999-00109), by the Swiss Federal Government under Grant BBW 01.0025-01 and by the Swiss National Science Foundation under Project "Hierarchic FE-Models for periodic lattice and honeycomb materials" with Number SNF 21-58754.99.

References:

- [1] A.-M. Matache, *Sparse Two-Scale FEM for Homogenization Problems*, Journal of Scientific Computing, (2002) **17**, 659–669
- [2] A.W. Rüegg, *Implementation of Generalized Finite Element Methods for Homogenization Problems*, Journal of Scientific Computing, (2002) **17**, 671–681
- [3] A.W. Rüegg, A. Schneebeli, R. Lauper, *Generalized hp-FEM for Lattice Structures*, SAM-Research Report 2002-23

Title: Design of an *hp*-adaptive FE code for general elliptic problems in 3D

Researchers: Philipp Frauenfelder
Kersten Schmidt
Christoph Schwab

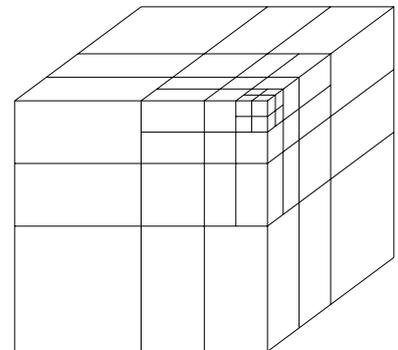
**Institute/
Group:** Seminar for Applied Mathematics
Departement of Mathematics

Description:

Many problems of engineering interest cannot be solved by applying a FEM based upon uniform meshes. To resolve boundary layer effects by a uniform mesh in a shell problem would make the numerical method prohibitively expensive and it would not be possible to obtain any solution of good quality. It is also advantageous if the meshsize as well as the polynomial degree can be adapted to account for boundary layer effects.

The project is design of a 3D *hp* FEM code that incorporates tetrahedral as well as hexahedral, prismatic and pyramidal elements. Based upon an existing C++ class library for fully *hp*-adaptive 2D FEM, 3-d classes in the library are developed.

On hexahedral meshes, the code is able to deal with non-conforming meshes resulting from element subdivisions. Anisotropic subdivisions are possible: into two, four or eight new elements. This allows for anisotropic refinements (see figure) and scale resolution. The mesh in the figure is non-conforming, ie. there are so-called *hanging nodes* which have to be treated carefully. Hanging nodes are eliminated by constraining the associated degrees of freedom by the degrees of freedom of the parent element (recursively if necessary). The approximation order (polynomial degree of the shape functions) can be chosen anisotropically and element by element.



Using the code, we are solving Maxwell equations in the frequency domain using weighted regularization (Costabel, Dauge). Other problem classes will follow.

References:

P. Frauenfelder, C. Lage. *Concepts—An Object Oriented Software Package for Partial Differential Equations*, Vol. 36, Nr. 5 (2002), 937–951.

Title: FEM for Elliptic Problems with Stochastic Data

Researchers: Christoph Schwab
Radu Alexandru Todor

**Institute/
Group:** Seminar for Applied Mathematics
Department of Mathematics

Description:

Often the data (load vector) of a PDE is either incompletely known or uncertain to some extent which makes its description as a random field more realistic. The problem itself becomes then a stochastic differential equation (SDE), whose solution is, in general, a random field taking values in a suitable function space. Complete description of this random field requires knowledge of its joint probability densities, so that in applications one is often only interested in the first (expectation), second (correlation) and sometimes even higher order moments of the random solution. Deterministic PDEs for the moments of the random solution can be derived, but solving them proves difficult due to their high-dimensional character. The project aims at reducing the apparent huge numerical complexity of such problems. More precisely,

- a) for the problem with deterministic coefficients, but stochastic right hand side, we develop efficient FEM for the numerical solution of the deterministic boundary value problems in high-dimensional, tensorized domains. The goal is here to achieve essentially the same scalability of the solution algorithm for the second (and higher) order moments as for the solution of the deterministic problem.
- b) for the problem with stochastic coefficients, the stochastic Galerkin method will be used, which discretizes the stochastic PDE simultaneously in physical and probability space. Since the latter is infinite-dimensional, this strategy will lead to potentially extremely high dimensional deterministic problems to be solved; also here we will develop strategies for complexity reduction in the presence of high dimensions by *sparse interpolands* and by *adaptive approaches*.

References:

- C. Schwab, R.A. Todor, *Sparse finite elements for stochastic elliptic problems with Stochastic Data*, SAM Report 2002-05 (to appear in Numerische Mathematik).
- C. Schwab, R.A. Todor, *Sparse finite elements for stochastic elliptic problems - higher order moments*, SAM Report 2003-04 (to appear in Computing).

Title: Fast deterministic pricing of options for Lévy driven assets and stochastic volatility models

Researchers: Ana-Maria Matache*
Christoph Schwab**

Institute/ *Seminar for Applied Mathematics and RiskLab
Group: Department of Mathematics
**Seminar for Applied Mathematics
Department of Mathematics

Description:

The fast numerical valuation of financial derivatives for Lévy driven assets and stochastic volatility models is addressed.

Lévy processes offer more flexibility than Brownian motion and appear superior e.g. for modelling short-term asset returns whose distributions are heavy-tailed. Lévy models lead to parabolic integro-differential equations with non-local Dynkin operators which, in general, cannot be solved in closed form. Standard discretizations lead to ill-conditioned and densely populated matrices which must be inverted in each implicit time-step. Wavelet based Galerkin discretizations allow to "compress" these matrices to sparse and well-conditioned ones. The resulting algorithm has log-linear complexity comparable to that of the best finite-difference schemes for the usual Black-Scholes type models, and can also accommodate local and stochastic volatility models. This technology was extended to pricing American contracts on Lévy driven assets where we use the wavelet basis to precondition the iterative solver of the corresponding linear complementarity problem in each time-step.

As part of this project we also addressed the problem of pricing of options within stochastic volatility models. We developed a wavelet based method which allows to handle the resulting degenerate parabolic partial differential equation in an optimal fashion.

We also plan to assess model risk and perform sensitivity studies, including deterministic evaluation of the model's "greeks" and model parameter fitting to given market data.

This research is supported by RiskLab, Switzerland under the RiskLab project *Fast Deterministic Valuations for Assets Driven by Lévy Processes*.

References:

A.-M. Matache, T. von Petersdorff and C. Schwab, *Fast deterministic pricing of options on Lévy driven assets*, submitted, available also as Research Report 2002-11, Seminar for Applied Mathematics, ETH Zürich

<http://www.sam.math.ethz.ch/reports/details/include.shtml?2002/2002-11.html>

A.-M. Matache, P.-A. Nitsche and C. Schwab, *Wavelet Galerkin pricing of American options on Lévy driven assets*, submitted, available also as Research Report 2003-06, Seminar for Applied Mathematics, ETH Zürich

<http://www.sam.math.ethz.ch/reports/details/include.shtml?2003/2003-06.html>

Title: Rigorous numerical modeling and design of high-efficiency photodetectors for modern optical communication systems

Researchers: Damir Pasalic,
Rüdiger Vahldieck

Institute: Laboratory for Electromagnetic Fields and Microwave Electronics (IFH)

Group: Field Theory Group

Description:

High-speed photodetectors are key components of modern optical communication systems. As optical amplification becomes more widely employed in such systems, the photodetectors capable of maintaining high efficiency and broad bandwidth under high optical illumination are of special interest. As complexity of the photodetectors increases, the standard means of their analysis, such as the equivalent circuit model, are not adequate any more. Therefore, there is an increased interest for a more general, numerical approach to their analysis. In this project, we are developing a new, hybrid method for rigorous analysis of photodetectors of general geometry. The method is a combination of a 2D drift-diffusion semiconductor analysis and a full-wave EM simulator. As a result of the semiconductor analysis, currents at the device's cross-section are obtained. Then, they are used as the source currents in a full-wave EM simulation of the structure to obtain microwave parameters of interest, such as microwave phase velocity and S-parameters at the interface with the embedding microwave circuit. For full-wave EM simulations, the frequency-domain TLM method is employed.

Title: Application of model order reduction in the optimization of microwave filters and diplexers

Researchers: Klaus Krohne,
Rüdiger Vahldieck

Institute: Laboratory for Electromagnetic Fields and Microwave Electronics (IFH)
Group: Field Theory Group

Description:

The application of general purpose electromagnetic field solvers in the optimization of microwave filters and diplexers is often impeded by an excessive computational effort despite the progress made in the performance of computer hardware over the last years. The limiting factors are the high number of necessary simulation runs as well as the deteriorated efficiency of those solvers when applied to highly resonant structures, such as filters.

With the help of the Model Order Reduction (MORE) Technique, the system's poles and zeros as well as their sensitivity can be computed in a very efficient manner, which makes MORE extremely suitable for resonant structures. At the same time, it significantly reduces the number of solver runs while maintaining a high level of generality.

Commercial electromagnetic modelers are used to generate a discrete state-space model of the system, the poles and zeros of which as well as their sensitivities are then extracted with the help of MORE. This yields a linearized relation of the system parameters and the designable geometry parameters which can be used in a fast computation of an objective function. This objective function can be minimized easily using commercially available optimizers.

This process has been applied to and tested successfully on several examples. It has also shown a surprisingly low level of sensitivity to the initial parameter choice, which is very critical to most optimization techniques.

Title: Reverberation chamber simulation, measurement, and optimization

Researchers: Christian Bruns,
Pascal Leuchtmann
Rüdiger Vahldieck

Institute: Laboratory for Electromagnetic Fields and Microwave Electronics (IFH)
Group: Field Theory Group

Description:

Reverberation chambers offer a new method for electromagnetic compatibility (EMC) tests, usable for radiated emissions and immunity testing of electronic products. The testing principle is based on the idea to have “isotropic” electromagnetic fields within the volume of the equipment under test (EUT). This is achieved by using one or more so-called mode tuning stirrers which rotate inside an overmoded, metallic cavity.

A numerical model was developed in the IFH field theory group to understand the complex electromagnetic fields inside the reverberation chamber. The model consists of the chamber itself, several mode stirrers, various excitations (dipole, biconical, logarithmic-periodic antennas) and a canonical EUT. Our simulation uses a hybrid method of moments (MoM) / physical optics (PO) / multi-level fast multipole method (MLFMM) approach to compute and visualize the currents, electric and magnetic near and far fields. Simulating such a realistic, finitely conducting chamber with irregular stirrers over a 80 MHz...2 GHz frequency range is computationally very challenging and therefore carried out on a distributed machine cluster with up to 8 processors and 32 GByte RAM. The simulation results are benchmarked against measurements, parameters such as the field covariance and anisotropy coefficients are extracted for different stirrer positions and statistically analyzed. This study allows us to propose guidelines for the design and optimization of reverberation chambers.

Title: Electromagnetic simulations of complex structures with the Finite-Volume Time-Domain method.

Reseachers: Christophe Fumeaux
Dirk Baumann
Pascal Leuchtmann
Rüdiger Vahldieck

Institute: Laboratory for Electromagnetic Fields and Microwave Electronics (IFH)
Group: Field Theory Group

Description:

The Finite-Volume Time-Domain (FVTD) method has been applied to the numerical solution of Maxwell's equations since the end of the 1980's. The essential characteristic of the method is its applicability in unstructured meshes (e.g. made of tetrahedrons) that permit conformal meshing of complex structures. Therefore, the FVTD method constitutes a powerful alternative to the popular Finite-Difference Time-Domain method (FDTD) which makes use of Cartesian meshes. Conformal meshing has significant advantages for the modeling of small details within larger structures, for curved surfaces and also in connection with different materials: Small cells are required only in restricted areas of the computational domain.

In this project, the FVTD algorithm is further developed and applied to the numerical solution of challenging electromagnetic problems. The implemented numerical scheme is of second-order accuracy both in time and in space. A generalized local time stepping scheme has been developed to increase the efficiency of the computation in inhomogeneous meshes.

The presently implemented code offers (1) a preprocessor that refines and checks the geometrical data delivered by a commercial mesh generator and formulates the electromagnetic problem (initial boundary conditions, sources etc.), (2) a kernel for the field computations able to handle hard and soft sources, transmission line ports, different types of absorbing boundary conditions (ABC's) as well as electric and magnetic conducting surfaces and (3) a postprocessor including a near-to-far field transformer, graphics representation and S-parameter extraction.

The code is successfully applied to the computation of antennas such as dielectric lens antennas, horns and cavity-backed spirals. The FVTD method permits to resolve precisely the fine structural details near the feed structures and results in very accurate simulations.

Title: Numerical modeling, design and optimization of guiding structures for modern telecommunication systems

Researchers: Erdem Ofli
Rüdiger Vahldieck

Institute: Laboratory for Electromagnetic Fields and Microwave Electronics (IFH)
Group: Field Theory Group

Description:

Modern communication systems consist of a large number of components operating at microwave and millimeter wave frequencies. The demand for accurate modeling and design has resulted in a large variety of CAD tools based on numerical simulation of electromagnetic fields. In this project, highly specialized and thus numerically efficient and accurate simulation tools are developed for the design of guiding structures such as waveguide sections, waveguide bends, junctions, power dividers, transformers and for components such as directional couplers, filters. The numerical techniques employed in this project are the Mode Matching technique (MMT) and the newly developed Coupled Integral Equation Technique (CIET). In conjunction with novel optimization strategies utilizing surrogate models, new and vastly improved CAD tools for waveguide structures have been established.

Title: Validation of the GROMOS Force-field Parameter Set 45A3 against Nuclear Magnetic Resonance Data of Hen Egg Lysozyme

Researchers: T.A. Soares
L.J. Smith*
X. Daura**
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie
*OCMS, University of Oxford, Oxford, UK
**Universitat Autònoma de Barcelona, Spain

Description:

The quality of molecular dynamics (MD) simulations of proteins depends critically on the biomolecular force field that is used. Such force fields are defined by force-field parameter sets, which are generally determined and improved through calibration of properties of small molecules against experimental or theoretical data. By application to large molecules such as proteins, a new force-field parameter set can be validated. We report two 3.5 ns molecular dynamics simulations of hen egg white lysozyme in water applying the widely used GROMOS force-field parameter set 43A1 and the new set 45A3. The two MD ensembles are evaluated against NMR spectroscopic data: NOE atom-atom distance bounds, $^3J_{NH}$ and $^3J_{\alpha\text{-beta}}$ coupling constants, and ^{15}N relaxation data. It is shown that the two sets reproduce structural properties about equally well. The 45A3 ensemble fulfills the atom-atom distance bounds derived from NMR spectroscopy slightly less well than the 43A1 ensemble, with most of the NOE distance violations in both ensembles involving residues located in loops or flexible regions of the protein. Convergence patterns are very similar in both simulations: atom-positional root-mean-square differences (RMSD) with respect to the X-ray and NMR model structures and NOE inter-proton distances converge within 1.0-1.5 ns while backbone $^3J_{HN}$ -coupling constants and 1H - ^{15}N order parameters take slightly longer, 1.0-2.0 ns. As expected, side-chain 3J -coupling constants and 1H - ^{15}N order parameters do not reach full convergence for all residues in the time period simulated. This is particularly noticeable for side chains, which display rare structural transitions. When comparing each simulation trajectory with an older and a newer set of experimental NOE data on lysozyme, it is found that the newer, even larger, set of experimental data agrees better with each of the simulations. The experiment converges towards the theoretical result.

References: submitted to Proteins: Struc.Func. Gen. (2003)

Title: Molecular Dynamics Simulations of Peptides Containing an Unnatural Amino Acid: Dimerization, Folding and Protein Binding

Researchers: H.B. Yu
X. Daura*
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie
*Universitat Autònoma de Barcelona, Spain

Description:

Molecular dynamics simulations have been performed to study the dimerization, folding and binding to a protein of peptides containing an unnatural amino acid. NMR studies have shown that the substitution of one residue in a tripeptide beta-strand by the unnatural amino acid Hao (5-HO₂CCONH-2-MeO-C₆H₃-CO-NHNH₂) modifies the conformational flexibility of the beta-strand and the hydrogen-bonding properties of its two edges: the number of hydrogen-bond donors and acceptors increases at one edge while at the other they are sterically hindered. In simulations in chloroform, the Hao containing peptide 9 (i-PrCO-Phe-Hao-Val-NHBu) forms a beta-sheet-like hydrogen-bonded dimer, in good agreement with the available experimental data. Addition of methanol to the solution induces instability of this beta-sheet as confirmed by the experiments. Molecular dynamics simulations also reproduce the folding of the synthetic peptide 1a (i-PrCO-Hao-Ut-Phe-Ile-Leu-NHMe) into a beta-hairpin-like structure in chloroform. Finally, the Hao-containing peptide Ac-Ala-Hao-Ala-NHMe is shown to form a stable complex with the Ras analogue Rap1A in water at room temperature. Together with the available experimental data, these simulation studies indicate that Hao-containing peptides may serve as inhibitors of beta-sheet interactions between proteins.

References: submitted to Proteins (2003)

Title: Free energies of binding of polychlorinated biphenyls to the estrogen receptor from a single simulation

Researchers: C. Oostenbrink
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

Relative free energies of binding to the ligand binding domain of the estrogen receptor have been calculated for a series of 17 hydroxylated polychlorinated biphenyls. Since traditional thermodynamic integration or perturbation approaches are hardly feasible for these numbers of compounds, the one step-perturbation approach is applied and is shown to yield accurate results based on only two 2ns molecular dynamics simulations of an unphysical, judiciously chosen, reference state. The mean absolute difference between the calculated and experimental binding free energies for the 17 compounds is 3.4 kJ/mol, which illustrates the accuracy of the GROMOS biomolecular force field used. Excluding the three largest ligands from the comparison reduces the deviation to 2.0 kJ/mol, i.e. less than $k_B T$. Apart from the relative free energy, structural information about the binding mode and binding orientation for every compound can also be extracted from the simulation, showing that a ligand bound to its receptor cannot be represented by a single conformation, but samples an ensemble of different orientations.

References: Proteins (2003) in press

Title: Energy-Entropy Compensation in the Transfer of Nonpolar Solutes from Water to Co-Solvent/Water Mixtures

Researchers: N.F.A. van der Vegt
D. Trzesniak
B. Kasumaj
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

Co-solvent binding to solute molecules dissolved in co-solvent/water mixtures greatly affects solute properties such as its solubility and structural stability. Denaturation of proteins by the co-solvents urea and guanidinium chloride as well as the effects of co-solvents on aqueous solution properties relevant to the characteristics of hydrophobic solvation are topics of ongoing discussion in the literature and warrant a detailed description of the nature of the binding interactions. In this communication we discuss how energetic and entropic contributions may favour or oppose the co-solvent interaction with a series of nonpolar molecules in the limit of infinite solute dilution. We report thermodynamic quantities pertaining to the transfer process of noble gases and aliphatic hydrocarbons from neat water to co-solvent/water binary solvent mixtures. All quantities are calculated by means of molecular dynamics (MD) simulations. Dependent on how strongly the co-solvent is hydrated, we show that entropy changes favour or oppose the transfer process in such a way that they may either compensate or reinforce the change in energy.

References: submitted to ChemPhysChem (2003)

Title: Entropic Contributions in co-Solvent Binding to Hydrophobic Solutes in Water

Researchers: N.F.A. van der Vegt
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

Gas solubility in liquids is driven by favorable solute-solvent interactions while being opposed by the entropic cost of creating a molecular sized cavity of suitable size. We have investigated these contributions to the solvation free energy of small, hydrophobic solutes and studied the dependence of the entropy cost of solute insertion on solvent-solvent interactions in co-solvent/water mixtures by means of molecular dynamics simulations. The co-solvents acetone, dimethyl sulfoxide, and sodium chloride were studied. Acetone, which weakly interacts with water relative to hydrogen bonding interactions in neat water, preferentially binds to hydrophobic solutes thereby raising their solubility. We find that this process is driven by a reduced entropic expense of opening up molecular-sized cavities close to the acetone methyl moieties. Sodium chloride and dimethyl sulfoxide are strongly hydrated, causing entropy to oppose hydrophobic solute insertion even stronger than in neat water. In sodium chloride/water the solute is preferentially "wetted" causing it to be "salted-out". Dimethyl sulfoxide methyl moieties bind to the hydrophobic solute. This process, occurring at the expense of entropy, is driven by a favorable solute-solvent energy and causes "salting-in" of the hydrophobic solute.

References: submitted to J. Phys. Chem. B (2003)

Title: An Effective Force Field for Molecular Dynamics Simulations of Dimethyl Sulfoxide and Dimethyl Sulfoxide-Water Mixtures

Researchers: D.P. Geerke
C. Oostenbrink
N.F.A. van der Vegt
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

An improved model for molecular dynamics simulations of liquid dimethyl sulfoxide (DMSO), compatible with the GROMOS96 force field, has been developed. The new model was parameterized to reproduce the density and heat of vaporization, and showed good agreement with experimental values for a variety of other properties of the liquid. Together with the SPC and SPC/L models for water, the new parameter set was used for the simulation of DMSO-water mixtures. In accordance with experiment, strong non-ideal behaviour was observed for the thermodynamic and dynamic properties of the mixtures over the range of compositions. For most of these properties, both the DMSO-SPC and DMSO-SPC/L model produced values in agreement with experiment. For all properties studied, slightly better results were obtained using the SPC/L model for water. Compared to other DMSO and DMSO-water models tested in the literature, our parameter sets were found to perform similarly or slightly better. Finally, we studied the solvation of two lipophilic probes (neopentane and *tert*-butanol) in the DMSO-water mixtures. As expected, the solubility of the probes was found to increase with the mole fraction DMSO.

References: J. Phys. Chem. B (2003) in press

Title: Computer Simulation of Urea-Water Mixtures: A Test of Force Field Parameters for Use in Biomolecular Simulation

Researchers: L.J. Smith*
H.J.C. Berendsen**
W.F. van Gunsteren

Institute/Group: *OCMS, University of Oxford, Oxford, UK
**University of Groningen, The Netherlands
Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

A molecular model for urea to be used in conjunction with the simple point charge (SPC) model for liquid water in protein denaturation studies is validated by comparison of molecular dynamics (MD) simulation results to experimental data at 298 K as a function of urea mole fraction. The density, enthalpy of mixing, free enthalpy of urea hydration and urea diffusion show very good agreement with the experimental values. The experimental error in the free enthalpy of hydration, which is dominated by the inaccuracy of the vapour pressure of solid urea, is larger than the simulation error. This limited accuracy does not allow a check of the non-ideality of the solution. Free enthalpies have been obtained by thermodynamic integration. The importance of a correct use of the combinatorial factor in the partition function when interpreting simulation results obtained by thermodynamic integration is discussed. The tested, GROMOS96 compatible, force field parameters form a good basis for biomolecular simulations using urea-water mixtures.

References: submitted to J. Phys. Chem. A (2003)

Title: Molecular dynamics simulations of small peptides: Can one derive conformational preferences from ROESY spectra?

Researchers: C. Peter
M. Rüping*
H. Wörner
B. Jaun*
D. Seebach*
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie
*Laboratory of Organic Chemistry

Description:

Folding properties of β -peptides were investigated by means of NMR experiments and MD simulations of β -dipeptides, which serve as small test systems to study the influence of stereocenters and sidechains on hydrogen-bond and consequently on secondary-structure formation. Two stereoisomers, SR and SS, of a Val-Phe dipeptide, and of the corresponding Ala-Ala dipeptide, and a Gly-Gly dipeptide were simulated in methanol for 40 ns. In agreement with experiment, at 298 K the isomers of the Val-Phe dipeptide adopt quite different conformers, the differences being reduced at 340 K. Interestingly, the SR isomer shows enhanced hydrogen bonding at the higher temperature. The adopted conformations are primarily determined by the R or S sidechain substitution, and less by the type of sidechain. Back-calculation of ^1H ROESY spectra and ^3J coupling constants from the MD simulations and comparison with the experimental data for the Val-Phe dipeptides shows good agreement between simulation and experiment, and reveals possible problems and pitfalls, when deriving structural properties of a small and extremely flexible molecule from NMR data only. Inclusion of all aspects of internal dynamics is essential to the correct prediction of the NMR spectra of these small molecules. Cross comparison of calculated with experimental spectra for both isomers shows that only a few out of many ROESY peaks reflect the sizeable conformational differences between the isomers at 298 K.

References: Chem. Eur. J. (2003) in press

Title: Single-step perturbations to calculate free energy differences from unphysical reference states: limits on size, flexibility and character

Researchers: C. Oostenbrink
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

Relative free energies for a series of not too different compounds can be estimated accurately from a single simulation of an unphysical reference state that encompasses the characteristic molecular features of the compounds. Previously, this method has been applied to the calculation of free energies of solvation and of ligand binding for small molecules. In the present study we investigate the limits to the accuracy of the method by applying it to a realistic model of the binding of a set of rather large ligands to the protein factor Xa, a key protein to current efforts to design anti-coagulation drugs. The evaluation of the binding free energies and conformations of nine derivatives of a biphenylamidino inhibitor leads to insights regarding the effect of the size, flexibility and character of the unphysical part of the ligand in the reference state on the accuracy of the predicted binding free energies.

References: J. Comput. Chem. (2003) in press

Title: Circular dichroism spectra of β -peptides: Sensitivity to molecular structure and effects of motional averaging

Researchers: X. Daura
D. Bakowies
D. Seebach*
J. Fleischhauer**
W.F. van Gunsteren
P. Krüger**

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie
*Laboratory of Organic Chemistry
**Institute of Organic Chemistry, RWTH Aachen, Germany

Description:

Circular dichroism spectra of two β -peptides, i.e. peptides composed of α -amino acids, calculated using ensembles of configurations obtained by molecular dynamics simulation are presented. The calculations were based on 200 ns simulations of a β -heptapeptide in methanol at 298 K and 340 K and a 50 ns simulation of a β -hexapeptide in methanol at 340 K. In the simulations the peptides sampled both folded (helical) and unfolded structures. Trajectory structures with common backbone conformations were identified and grouped into clusters. The CD spectra were calculated for individual structures, based on peptide-group dipole transition moments obtained from semi-empirical molecular orbital theory and using the so-called matrix method. The single-structure spectra were then averaged over entire trajectories and over clusters of structures. Although certain features of the experimental CD spectra of the β -peptides are reproduced by the trajectory-average spectra, there exist clear differences between the two sets of spectra in both wave-length and peak intensities. The analysis of individual contributions to the average spectra shows that, in general, the interpretation of a CD signal in terms of a single structure is not possible. Moreover, there is a large variation in the CD spectra calculated for a set of individual structures that belong to the same cluster, even when a structurally tight clustering criterion is used. This indicates that the CD spectra of these peptides are very sensitive to small local structural differences.

References: Eur. Biophys. J. (2003) in press

Title: The Charge Distribution at the sn2 Ester Group of Dipalmitoylphosphatidylcholine Affects the Phase Behaviour of the Hydrated Bilayer

Researchers: I. Chandrasekhar
W.F. van Gunsteren

Institute/Group: Laboratory of Physical Chemistry, Switzerland,
Gruppe für Informatikgestützte Chemie

Description:

The dependence of molecular dynamics simulations of lamellar systems consisting of amphipathic lipids in the liquid-crystalline phase on the polarity of the hydrophilic head-group is examined. The charge on the glycerol ester group of the sn2 group has a remarkable effect on the square area per lipid in contrast to simulations of non-polar, neutral lipids where it has been found to have little effect. The magnitude of the charge assigned to the pendant ester oxygens significantly influences the distribution of water around the ester moieties. The enhanced solvation of the pendant ester oxygen on the sn2 chain with increased charge has a direct influence on the phase behaviour of the system.

References: submitted to J. Membr. Sci. (2003)

Title: Simulation of Global Climate and Climate Change with General Circulation Models

Researchers: Martin Wild
Andreas Roesch
Peter Tschuck
Christian Schneeberger
Martin Schraner
Atsumu Ohmura

Institute/ Institute for Atmospheric and Climate Sciences ETH
Group: Global Climate Modeling Group

Description:

Human induced climate change is, by its nature, a problem of global dimensions. The most powerful tools to investigate the potential impact of human activities on the Earth's climate are three dimensional numerical models of the global climate system. Such models are used in our projects to investigate the response of the Earth's climate to natural and human induced perturbations. The emphasis is on the simulation of present and future climate, using the latest model version of the global climate model developed at the Max Planck Institute for Meteorology in Hamburg (ECHAM5). With this institution, the ETH group has been collaborating in the field of global climate modeling over more than a decade. Due to the generous computational resources allocated to this by the National Center for Scientific Computing (CSCS) in Manno, scenario runs with a very high global resolution of 1.1° can be carried out. This allows an improved representation particularly of orographic effects such as terrain induced precipitation. Scenarios for the late 21th century are currently underway at CSCS, with increased levels of atmospheric greenhouse gases as given in the Special Report on Emission Scenarios (SRES) A2 and B2 provided by IPCC (Intergovernmental Panel on Climate Change).

The focus of the ETH group in this context is on the near surface climate, from global down to European and Alpine scales. Particular emphasis is placed on the surface energy and water exchange processes, and their potential changes under increased greenhouse forcing. Of interest in this context is, for example, the change in the atmospheric thermal emission downwelling to the surface, which is the most direct effect felt at the surface from a change in atmospheric greenhouse gas composition. GCM estimated changes of this greenhouse forcing can be related to worldwide surface measurements, which are collected at ETH within the Baseline Surface Radiation Network (BSRN). This allows an early detection of the greenhouse effect from a surface perspective.

A further focus is on the impact of greenhouse warming on the cryosphere (snow, mountain glaciers, polar ice sheets and their effects on sea level). The high spatial resolution of the scenarios allows unprecedented estimates of the cryospheric contribution to sea level changes, resulting in interesting new outcomes for the future contribution of Greenland to sea level.

References:

See separate list in Publications

Title: Protein NMR structure determination with automated NOE cross peak identification in NOESY spectra and NOE assignment using the software packages ATNOS and CANDID.

Researchers: Torsten Herrmann*^{***}
Francesco Fiorito*
Kurt Wüthrich*^{***}

Institute: Institut für Molekularbiologie und Biophysik, ETH Zürich
The Scripps Research Institute, La Jolla, CA, USA

Description:

The software package ATNOS/CANDID performs automated peak picking and NOE identification in 2D homonuclear and 3D heteronuclear-resolved NOESY spectra, automated NOE assignment of NOESY cross peaks and 3D protein structure calculation in conjunction with the torsion angle dynamics algorithm of DYANA. The ATNOS/CANDID approach for automated NOESY spectral analysis significantly accelerates the process of protein 3D structure determination by NMR. In 2002/2003, the software Atnos/CANDID was used for *de novo* structure determinations of more than 10 proteins (see the following project descriptions).

References: Herrmann, T., Güntert, P. and Wüthrich, K.
J. Mol. Biol. **319** (2002), 209–227

Herrmann, T., Güntert, P. and Wüthrich, K.
J. Biomol. NMR. **24** (2002), 171–189.

Title: NMR structure determination of prion proteins

Researchers: Sophie Bonjour
Daniel Perez
Dominikus A. Lysek
Ralph Zahn
Peter Güntert
Thorsten Lühns
Christine von Schroetter
Kurt Wüthrich

Institute: Institut für Molekularbiologie und Biophysik, ETH Zürich

Description:

The prion protein (PrP) is an indispensable factor in the development of transmissible spongiform encephalopathies (TSEs), such as Creutzfeldt-Jakob disease in humans, BSE ("mad cow disease") in cattle, and scrapie in sheep. PrP is a highly conserved glycoprotein in mammals, where it is predominantly expressed in neuronal tissue, which has also been found in birds and reptiles. We have solved a number of 3-dimensional structures of recombinant mammalian prion proteins, and are analyzing similarities and differences that might bear on the species barrier for infectious transmission of TSEs. Further, we are extending these studies to birds and reptiles in search of new insight into the physiological role of PrP in healthy organisms.

References: Lühns, T., Riek, R., Güntert, P. and Wüthrich, K.
J. Mol. Biol. **326** (2003), 1549-1557.

Zahn, R., Güntert, P., von Schroetter, C. and Wüthrich, K.
J. Mol. Biol. **326** (2003), 225-234.

Title: NMR structure of the apoptosis- and inflammation-related NALP1 pyrin domain.

Researchers: Sebastian Hiller*
Andreas Kohl**
Francesco Fiorito*
Torsten Herrmann*
Gerhard Wider*
Jürg Tschopp***
Markus G. Grütter**
Kurt Wüthrich*

Institute: *Institut für Molekularbiologie und Biophysik, ETH Zürich, Switzerland
**Biochemisches Institut der Universität Zürich, Switzerland
***Institut de Biochimie, Université de Lausanne, Epalinges, Switzerland

Description:

Signalling in apoptosis and inflammation is often mediated by proteins of the death domain superfamily in the Fas/FADD/Caspase-8 or the Apaf-1/Caspase-9 pathways. This superfamily currently comprises the death domain (DD), the death effector domain (DED), the caspase recruitment domain (CARD), and the pyrin domain (PYD) subfamilies. The PYD subfamily is most abundant, but three-dimensional structures have so far only been available for the subfamilies DD, DED and CARD, which have an antiparallel arrangement of six helices as a common fold. We have now solved the NMR structure of PYD of NALP1, which is involved in the innate immune response and is a component of the inflammasome. The structure of NALP1 PYD differs from all other known death domain superfamily structures in that the third helix is replaced by a flexibly disordered loop. This unique feature appears to be related to the molecular basis of familial Mediterranean fever (FMF), a genetic disease caused by single point mutations.

Reference: Hiller, S., Kohl, A., Fiorito, F., Herrmann, T., Wider, G., Tschopp, J., Grütter, M. G., and Wüthrich, K.
Structure (2003), in press.

Title: NMR structure of crotamine, a myotoxin from the *Crotalus durissus terrificus* venom.

Researchers: Valmir Fadal*, **
Pascal Bettendorff*
Torsten Herrmann*
Walter F. de Azevedo Jr**
Eduardo B. Oliveira***
Tetsuo Yamane****
Kurt Wüthrich*

Institute: *Institut für Molekularbiologie und Biophysik, ETH Zürich
**Departamento de Física, Universidade Estadual Paulista-UNESP, Sao Jose do Rio Preto-SP-Brazil
***Departamento de Bioquímica e Imunologia, Universidade de Sao Paulo, Ribeirao, SP, Brazil
****Centro de Biotecnologia, Instituto Butantan, Sao Paulo, Brazil.

Description:

Crotamine is one of four major components of the venom of the South American rattlesnake *Crotalus durissus terrificus*. Like its counterparts in the family of the myotoxins, it induces myonecrosis of skeletal muscle cells. The NMR structure of crotamine was determined, which may be representative also for other members of the myotoxin family.

Reference: Manuscript in preparation.

High-performance Hardware

6.1 Competence Center for Computational Chemistry

The following resources are available:

- a cluster of 40 dual-processor PC's;
- two Compaq AlphaServers with 6 and 8 EV6/525 processors.

The research activities of the Competence Center for Computational Chemistry C⁴, its members and the operation of the C⁴ hardware are described in the C⁴ Annual Report 2002/2003, which is published in November 2003.

Information: <http://www.igc.ethz.ch/C4>

6.2 Swiss Centre for Scientific Computing (CSCS, url: <http://www.cscs.ch>)

A. Introduction

The mission of the Swiss Centre for Scientific Computing is to enable top-class computational science in Switzerland and to promote scientific computing by collaborative research and development. As science and technology centre, the CSCS provides leading-edge expertise in computational modelling, graphics and visualization, information processing and software engineering together with high-end computing, storage, archiving and visualization resources. The complementary expertise in enabling technologies and advanced computing resources make CSCS an attractive partner for academia and industry

B. Computing resources

In 2002-2003, CSCS has offered HPC services on two architectures:

- a) Parallel Vector Processing, with a NEC SX5 of 16 CPUs, totalling a peak performance of 128 GFlops and 64 Gbytes shared memory, running under Super-UX R11.1 with NQS scheduler. The network connection is provided via GigabitEthernet, HiPPI and FastEthernet,
- b) Massively Parallel Processing, with 8 IBM Regatta p-690 SMP for a total of 256 CPUs, 768 GBytes of main memory, totalling a peak performance of 1.38 TFlops. The SP frame is switched by a Double Colony system in order to have a Parallel Environment with a Global Parallel File System of 4 TB. The overall system runs on AIX 5.1 with LoadLeveler job management system. The system is complemented by 2 Nighthawks (Power-3 nodes, total of 32 CPUs and 32 GBytes main memory) with a peak performance of 48 GFlops.

The list of software and scientific applications running on these systems is given extensively under www.cscs.ch.

C. Archive facility

Archival services are provided to Users by a SUN E6000 file and archive server, which transparently handles data movement between the fast StorageTek 9176 raid disk cache of 2 TB and two high-capacity StorageTek Powderhorn tape silos with mixed SCSI / FiberChannel technology providing a data volume currently in excess of 150 TB; this data management is done by the SAM-FS Hierarchical Storage Management software.

D. User community

The user community computing on these two HPC systems is widely distributed over the two Swiss Institutes of Technology and the Cantonal Universities. The group of Prof. M. Parrinello (Computational Science, ETH Chemistry Department) is the major user of the MPP system. The CSCS Research Committee reviews Large User (LU) projects and grants access to the computing resources. A list of the LU for 2002/3 projects is given under section F of this chapter.

The CSCS has an on going collaboration with MeteoSwiss and the national *Forschungsschwerpunkt Klima*, one of major users of the NEC SX5.

E. Highlights in support and development in 2002/2003

HPC Application Support

One of the major successes of 2002 has been the finalization of the installation and the starting of the full production (Jan. 2003) of the IBM Massively Parallel Processing supercomputing facility, as a complement to the of the existing NEC SX-5 Parallel Vector Processing architecture. Particular focus was put on porting/tuning user applications, providing both emerging and latest versions of commercial applications, and in general the overall programming/execution environment.

Targeting an efficient and effective use of the overall HPC facilities, the support team consolidated and completed the Computational Chemistry Framework as well as the Mathematical and Numerical Libraries. The available portfolio now covers a wide algorithms/methods spectrum as of:

- Libraries and Tools; Vampir, MathKeisan, ASL, GPFA, NAG, NetCDF, FISHPACK, Zufall, ESSL, FFTW, LAPACK, MASS, P-ESSL, ScaLAPACK, WSMP, GA Toolkit, TurboMP, hpmcount, NAGWare, MLIB, VECLIB, Mathematica, Matlab and Maple.
- Chemistry Applications: ADF (v2002.03), CPMD (v3.7.2), Gamess-US (v3 JUL 2003R1), Gaussian03 (G03-rev-B.04), Gaussian98 (G98RevA.11.3), Amber (v7), Dalton (v1.2.1), GROMACS (v3.1.4), JAGUAR (v5.0), MPQC (v2.1.4), NWCHEM (v4.5), TURBOMOLE(v5.6), WIEN2K (v2k_02), MolPro (v2002.6), Molcas (v5.4.111), MELDF-X and PRDDO/M (v5.1).
- Engineering Applications: STAR-CD, CFX and FLUENT.

In the frame of the collaboration between CSCS and MeteoSwiss, further optimization and vectorization of the latest developments of the aLMo code (the Alpine Local Model) were performed by tuning the code on the vector architecture with the valuable help of the NEC specialists. In addition, a real-time meteorological observational database was set: this data base is being employed operationally to better define the initial conditions for the simulations and is now also being used for climatology research and analysis of past extreme events.

Finally, passable effort has been provided to process incoming day-by-day users support requests as well as the consolidation and regular update of the overall technical documentation available under the CSCS user web portal (<http://www-users.cscs.ch>).

HPC Benchmarking and development

The EUROGRID project aims to build a European Grid infrastructure that gives users a seamless, secure access to High Performance Computing resources and that advances computational science in Europe. The CSCS is directly involved in the "HPC Research GRID" and in the "Meteo-GRID" work packages of this project. The first work package consists of establishing a European GRID network of leading High Performance Computing centres from different European countries, while the second work package's goal is to exploit the power of the established grid in order to support on-demand weather forecasts. For this purpose, the CSCS developed the LM plug-in application that extends the basic functionality of the standard EUROGRID software. This application allows performing high-resolution short-range weather forecasts with the relocatable non-hydrostatic "Lokal-Modell" (LM) of the Deutscher Wetterdienst (DWD) in the EUROGRID environment.

The ENACTS (European Network for Advanced Computing Technology for Science) project aims at evaluating future trends in the way that computational science will be performed and the pan-European implications. As outcome of the first year activities, the reports "Grid Service Requirements" and "HPC Technology Roadmap" are currently available for download. The CSCS contributed to those activities with the "Grid Enabling Technology" report written together with the Foundation for Research and Technology-Hellas (FORTH) in Greece.

In January 2003, Sun announced the code release for JAM, the Job & Application Manager prototype developed by Sun and the CSCS, under open source as part of the Sun Grid Engine project. JAM is a proof-of-concept, Jini technology based, graphical interface to Grid Engine. It provides a framework for selecting from a set of registered applications, and selecting a Grid Engine queue to which the job is submitted, with support for filtering on various queue attributes. Once the job is submitted, it can be monitored and controlled via JAM. In particular, JAM exploits the dynamic nature of the Java technology environment together with the concepts of leases, distributed events and transactions, introduced by the Jini programming model to build a spontaneous network of collaborative resources

Since performance information on single processor such as Power-4 can hardly be obtained, the CSCS developed a so called Performance Environment able to transparently measure runtime performance of system, processes and jobs, consisting of client and server daemons that permanently monitor system activity. Users can automatically and easily get job information and statistics, including performance, during execution and after completion. If needed, the server can generate very compact process accounting files, e.g. on an heavily loaded 256 CPU system a file of 1.5 MB size can track more than 95% of system activity per day. To our knowledge, CSCS is the only site to date able to globally monitor system, processes and job performance of IBM Power4 Clusters.

In conjunction with the development of the Performance Environment, a Java based tool has been developed in order to easily generate, via GUI or in batch mode, resource usage reports of the CSCS HPC platforms. Accounting data can be retrieved from databases (Oracle or MySQL) using JDBC API. Unlike other existing products, the tool allows the generation of global system usage statistics, as well as detailed performance analysis of user codes.

Scientific visualization

The Scientific Visualization activities in 2002 were concentrated on two main projects: first, the development based on AVS/Express of a Molecular Visualization toolkit which allows the rapid prototyping of visualization scenarios and visualization methods for molecular sciences. The toolkit is used internally to support the activities of Prof. Parrinello and was distributed in source code to MPI Dresden, U. of Dortmund, INRIA, and ETH Zürich. Secondly, a completely automatic chain of visualization outputs was created for the daily runs of Swiss Meteorology. The development consisted in including a Lagrangian Eulerian Advection algorithm in AVS/Express to provide spatially and temporally correlated animation sequences of wind data.

Support for CFD in general remained a priority. The group continued its efforts in generic development of tools and environments, with the evaluation of the AMIRA software, a study of Direct Manipulators User Interface widgets in VTK, a major effort at understanding and

applying Volume Rendering techniques, and a strong effort at using SMP and MPI for parallel visualization and rendering.

Finally, the group contributed to the international research community with reviews for IEEE Transactions on Computer Graphics and Visualization and IEEE Computer Graphics and Animation; and with committee duties for the 2002 European Visualization and Simulation conference, and the 2002 Eurographics Workshop on Parallel Graphics and Visualization.

F. Large users projects

During the second half of 2002 and the first half of 2003, the CSCS Research Committee has granted time for using the two systems for the following projects:

Avellan F. (EPFL)	Unsteady Flow Analysis in Hydraulic Turbomachinery
Beniston M. (UniFr)	Global and Regional Climate Modelling
Bürgi Th. (ETHZ)	Enantioselective Hydrogenation of activated Carbonyl compounds over chirally modified Platinum
Burkhart H. (UniBa)	Algebraic Multilevel Methods for the Solution of Large Sparse Linear Systems of Equations from Sheet Metal Forming Process Simulations
Chapuis G. (UniLA)	Modelling of incommensurate Structures
Cooper A. (EPFL)	Computation of Stellarator Coils, Equilibrium and Stability
Huw Davies (ETHZ)	The ERA40 climatological project
Daul C. (UniFR)	Computational Chemistry of Molecules and Solids Containing Metal Atoms
Fäh D. (ETHZ)	Site Effects assessment using Ambient Excitation
Fichtner W. (ETHZ)	Computational Science and Engineering in Microelectronics and Optoelectronics
Gerhard O. (UniBA)	Formation and Evolution of the Milky Way
Hasenfratz P. (UniBE)	Chiral symmetric Dirac Operator in lattice QCD
Hutter J. (UniZH)	Development and Application of Time-Dependent Density Functional Theory
Klein Ch. (ETHZ)	Ab Initio MD Study of Methionyl Aminopeptidases and their Inhibitors
Kleiser L. (ETHZ)	Numerical Simulation of Transitional, Turbulent and Multiphase Flows
Koumoutsakos P. (ETHZ)	Machine Learning Algorithms for Flow Modelling and Control
	Simulations using Particle Methods: Towards the Development of Multiscale Computations for Biosensors
Leriche E. (EPFL)	Direct Numerical Simulation of the Buoyancy-Driven Turbulence in a Cavity: the DNSBDTC project
Leutwyler S. (UniBE)	Proton Transfer and Hydrogen Bonding in Microsolvent Clusters and Nucleic Acid Base Pairs: Theory and Dynamics
Mareda J. (UniGE)	Quantum Chemical Investigations of Cyclization Reactions Involving Cationic Species
Meuwly M. (UniBA)	Electronic Structure Calculations for Molecular Dynamics Simulations of Iron-containing, reactive Centers of Biomolecules
Oganov A. (ETHZ)	Minerals and Planetary Materials
Ohmura A. (ETHZ)	Global Climate Change: Modelling Atmosphere/Ocean Variability on decadal time scales
Parlow E. (UniBA)	Experimental High Resolution Weather Forecast to predict near Surface Conditions and Fog
Pasquarello A. (EPFL)	Disordered Network-Forming Materials
Posternak M. (EPFL)	Structural and Electronic Properties of Solids and Surfaces
Quack M. (ETHZ)	Quantum mechanical Simulation of Molecules and Molecular Clusters
Röthlisberger U. (EPFL)	Computer Modelling of the Molecular mechanisms Involved in Light Detection
	Ab initio hybrid Simulations of Electron Transfer Reactions
	Simulation of Copper Binding Sites in Mouse Prion Protein

<i>Röthlisberger U. (EPFL)</i> <i>(cont'd)</i>	First-Principles Characterization and Design of Radiopharmaceuticals
	Car Parrinello Study of Catalytic Mechanisms of DNA Repair Enzymes
Schär Ch. (ETHZ)	Modelling Weather and Climate on European and Alpine scales
Schmutz W. (WRC/PMOD)	Variability of the Sun and Global Climate
Stocker Th. (UniBE)	MONALISA: Modelling and Reconstruction of North Atlantic Climate System Variability
Troyer M. (ETHZ)	Quantum Phase Transitions and Strongly Correlated Systems
Vogel P. (EPFL)	New Organic Chemistry based on Sulfur Dioxide
Weber J. (UniGE)	Computational Quantum Chemistry of Increasingly Complex Systems
Wesolowski T. (UniGE)	Modelling Complex Molecular Systems using embedded Cluster Approach
Yadigaroglu G. (ETHZ)	Numerical Simulation of Direct Contact Condensation for Nuclear Reactor Safety Systems
	Direct Numerical Simulation of Condensation in Air-Water Stratified Flows
	Large Eddy Simulation of Turbulence for Interface Tracking Based Simulation of Multi-Phase Flows

6.3 The Beowulf Cluster “Asgard”

Beowulf clusters are massively parallel supercomputers built from commodity components, standard PCs running Linux and Ethernet networks. They profit from the low cost of the building blocks and offer the best price/performance ratio for many applications that are not limited by network bandwidth or latency. Most applications in physics are perfectly parallelizable and run with optimal speedup on a cluster – no fast network is needed except for access to the file server. These applications include embarrassingly parallel applications such as parameter studies, where a single program has to be run thousands of times with different input parameters. Other methods that are well suited to a cluster are Monte Carlo simulations, where independent samples can be created on different CPUs with minimal communication needs. Since the majority of applications in physics are of these types, the cluster provides an ideal platform, complementary to the traditional supercomputers at ETH.

The Asgard Beowulf cluster, which was installed early in the year 2000 still works very well but an updated cluster is required to satisfy growing demand for CPU time. With available startup funds of Prof. Matthias Troyer (D-PHYS) and Prof. Ralf Hiptmair (D-MATH) and additional funding to be obtained from the Schulleitung, the procurement process for an Asgard successor was started in May 2003. Currently evaluations of the tenders are performed and a preliminary study suggests that we will be able to obtain a six times faster machine with slightly more processors at lower cost than the original cluster.

The users were very satisfied with the performance of the machine, which was to be expected for the majority of CPU-intense but not network-demanding applications. Surprisingly, besides these perfectly parallelizing applications the network bandwidth and latency turned out to be good enough not only for the development and testing of nontrivial parallel applications, but also for many production runs of problems such as beam dynamics, relativistic stellar plasmas and strongly correlated quantum systems.

As regards the operating mode, the cluster is split into two main queues, one for parallel jobs with up to 256 CPUs, and one for a large number of serial applications. In addition, processes with low memory demands are run as low-priority background jobs, using up the remaining idle time. We can thus achieve near-optimal usage of more than 95% - a very high number compared to traditional supercomputers.

For further details about the hardware, software, operating mode, account applications and user projects we refer to the Asgard web page at <http://www.asgard.ethz.ch>.

Asgard research projects

Since not all of the projects on Asgard are included in this annual report we list the main user projects here. For details we refer to the description of these projects on the Asgard web page at <http://www.asgard.ethz.ch>.

Theoretical Physics

Soliton's Dissipation Through Emission Of Radiation

by G. Interlandi, W. Aschbacher, J. Fröhlich and M. Troyer

Vortex Collisions: Crossing or Recombination?

by M. Bou-Diab and G. Blatter

Quantum Phase Transitions in the 2D Hardcore Bosonic Hubbard Model

by G. Schmid and M. Troyer

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by Adrian Biland

Backtracing of Cosmic Ray Particles

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by Haitao Liu

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Parallelization of Low-Communication Processes

by Jörg Waldvogel and Peter Leikauf

Solving of Boundary Integral Equations

by Gregor Schmidlin and C. Schwab

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by Wesley P. Petersen and Rolf Jeltsch

Multi-dimensional FFT algorithms on Asgard

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Parallel Smoothing for Multigrid via Sparse Approximate Inverses

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A new Field Solver for Space Charge dominated Beams

by Andreas Adelman, Stefan Adam, Rolf Jeltsch and Ralph Eichler

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Crystallization in Polymer Melts under Elongational Flow

Nonequilibrium dynamics computer simulation of polymer fluids

Computer Science

Development and Application of Biologically Inspired Optimization Algorithms
by Sibylle Müller and Petros Koumoutsakos

Traffic simulations
by Kai Nagel and Res Voellmy

Macro-economic modeling, computational economics and statistics
by E.J. Kontoghiorges and P. Arbenz

6.4 Information Technology Services

The following resources are available:

Cray SV1 Cluster consisting of

- 1 Cray SV1-B/16-8 (Athos): 16 Vector CPUs (300 MHz), 8 MB Memory
- 1 Cray SV1-B/8-4 (Porthos): 8 Vector CPUs (300MHz), 4 GB Memory
- 320 Gigabyte Disk, shared through Gigaring among the cluster
- Unicos Operating System

The clusters major usage is highly vectorized, moderately (up to 8 processors) parallel code in the fields of climate modeling, theoretical physics and astronomy.

The following compilers, libraries and applications are installed on the cluster:

ANSI II C: Compiler

C++: Compiler

FORTRAN-90: Compiler

MPGS: graphical library and viewer

GROMOS: biomolecular simulation

UniChem 5.0 (Cadpac, DGauss, MNDO): chemistry

MOPAC, DISCO, ACES2: chemistry

AMBER 5: chemistry

Gaussian-94 (for educational purposes only): chemistry

PAM: finite elements

CFX-F3D: fluid dynamics

NAG Mk 19, IMSL 10: numerical libraries

Maple 4.3: symbolic calculus

ranq, zufall: random number libraries

mfft: multitasked fast forier transforms

egm: graphical library

The Cray SV1 service will be terminated by the end of 2003.

Hewlett Packard Superdome Cluster consisting of

- 1 HP Superdome (Stardust): 64 PA8600 CPUs (550 MHz), 64 GB Memory, 400 GB Disk, HP/UX Operating System
- 1 HP Superdome (Pegasus): 32 PA8600 CPUs (550 MHz), 32 GB Memory, 400 GB Disk, HP/UX Operating System

The cluster is used for parallel code taking advantage of the shared memory programming model offered by the cc-numa architecture of these systems. Many standard applications (finite element modeling, mathematics, simulations, etc.) are in this category.

The systems major usage is in the fields of thermodynamics, fluid dynamics, virtual production (FEM) and theoretical physics.

The following software is available on the Superdome cluster:

HP Fortran: Compiler and associated products

HP Fortran 90: Compiler and associated products

HP C/ansi: C Developer's Bundle for HP-UX 11.00

HP C++: Compiler
KAI Guide C++: Open MP
Abaqus 5.8: General-purpose finite element analysis
ACSL: Advanced continuous simulation language
Ampl 9.5.13: Modeling language for Mathematical Programming
ANSYS 5.5: Finite element analysis
AVS: Advanced visual system
CPLEX 65: Linear optimization solver
CFX Tascflow: CFD analysis and design tool
Diana 7.2: Finite element analysis
Gaussian 98: semi empirical and ab initio molecular orbital (MO) calculations.
MARC/MENTAT K7.3: Nonlinear finite element program
Matlab 11.1: Language for technical computing
Molcas 5: Quantum chemistry software
NAG F95: Fortran library
IMSL: Fortran Numerical Libraries
Para Phoenix 32: CFD
Patran 9.0: Finite element (Modeling, Analysis, Results evaluation)
Tecplot 8.0: Tool for visualizing a wide range of technical data
PV-Wave: Signal Processing Toolkit

7

Outlook

This report documents the strength, scope and dynamics of CSE at the ETH. The fact that CSE is defined to be a "Strategische Erfolgs-Position", SEP, guarantees that the board of the ETH is fostering the field of CSE and of Computing in general, in almost all departments.

Computational research is stimulated in two directions, by creating the organization and means to foster interdisciplinary research on an ETH wide basis, and by strengthening in each field the research which uses computation as a major tool. In both directions we expect to see further development.

In the various departments of the ETH researchers in various fields of computation have been hired and we expect this trend to continue in the future. Unfortunately, the current financial problems of the ETH slow down this process.

In the coming year, we shall learn a lot about the practical implementation of our new Bachelor program in CSE. Clearly some fine tuning will have to be done. We plan to organize a workshop in 2006 on our experiences of this new curriculum. We hope that some of the first group of students will be able to participate as well as the ones who will have started the first time in the Master program. In addition this workshop should give the possibilities to exchange experiences with representatives from other institutions with similar programs and to learn about recent developments in research.

On the hardware side a process to enlarge the existing Beowulf has been started and we hope that in the near future this machine will be available.

Overall, we look optimistically into the future and are already looking forward to see the next annual report to find out about new exciting research happening at the ETH.

Zürich, October 31, 2003
Rolf Jeltsch

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