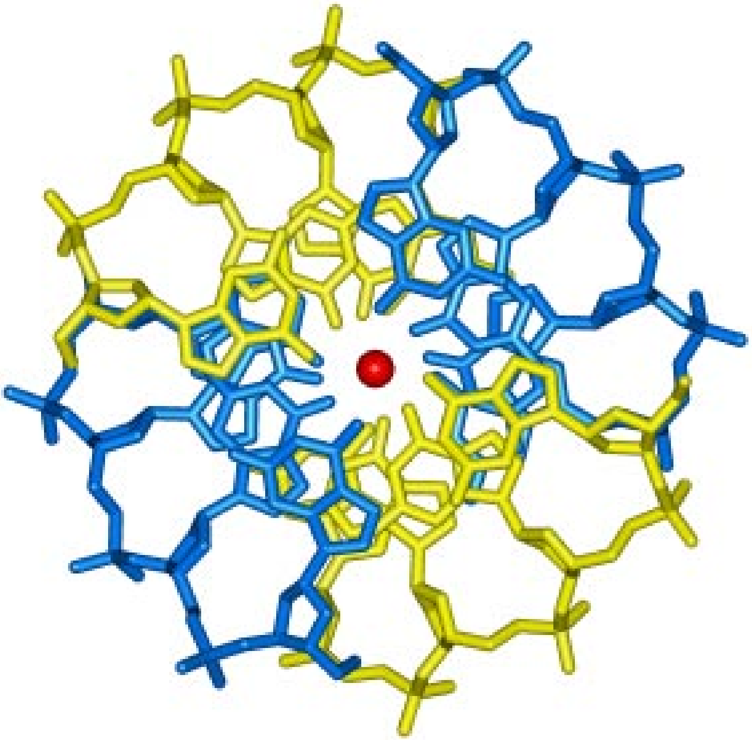
METACenter



Annual Report 1999

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Information about *METACenter*

Introduction

The first *Annual Report* of the *METACenter* got into your hands. It is the first written report about history, hardware and software of *METACenter*, but chiefly about research projects solved with the use of its computers, and the achieved results.

The whole field of high performance computing faces a new and important challenge initiated by high performance processors and high throughput networks: to use these new possibilities to further develop the field. Two answers to this challenge can be thought: one is the foundation of *computer clusters* (e.g. Beowulf like systems), the second is a creation of *computational grids* (or simply Grids). In both cases the high throughput network connects the computers and a qualitatively new phenomenon is emerging: *distributed metacomputer*, with individual computers as its computing nodes and the high throughput network as its bus (or, better, its interconnect). Clusters are usually built with the local area networks and its capabilities (Ethernet, Fast and even Gigabit Ethernet, ATM, Myrinet, SCI) and they connect usually *common* (one or two processor) computers, while computational grids connect very powerful parallel and vector supercomputers with the aid of wide area network (WAN) technologies. It is not uncommon, due to the state of current technology, to have the throughput (capacity) of the wide area networks orders of magnitude higher than the capacity of local area ones (e.g. OC-192 with the throughput of 9.6 Gb/s is not available for local networks) and this throughput is almost equal to throughput of the internal computer buses and other interconnects (32 bit PCI bus clocked at 33 MHz has a throughput of some 1 Gb/s, the first IBM SP2 used High Performance Switch with the throughput of mere 320 Mb/s). The only difference lies in the latency, which is several orders of magnitude higher in networks than within computer themselves.

High performance computers connected into a computing grid are not only capable to solve problems not tractable by individual nodes due to the lack of power, but the Grid helps to create new programming environment even for *ordinary* users, the environment which offers wider spectrum of available hardware and software while reducing the diversity of user interfaces (shared batch queues, same environment on different computers, same name space for users, files, and software packages, ...) and making the use much easier (increasing thus the total work efficiency). It came as no surprise that such a Grid is constructed since 1996 even in Czech Republic under the name *METACenter*.

Supercomputers without users have no justification for their existence. The main goal of this Annual Report is not to show the hardware and software, but to present main projects solved on *METACenter* computers. While the emphasis is on the last year results, lack of previous Reports led to the presentation of older, but still important results as well (some nodes already produced their own Annual Reports, e.g. the detailed presentation of West Bohemia Supercomputing Center is available in their *Annual Report 1998*, published by the West Bohemia University in May 1999; however, these Reports are usually in Czech only).

21 papers covering practically all the areas where high performance computers are used were selected. List of publications where results were obtained with the use of

METACenter computers accompanying individual papers are the best proof of not only interest in the high performance hardware, but also of its efficient use. Many results were published in the most renowned international journals or presented on important international conferences and together they helped to improve the position of the Czech science and technology in the international community.

History

METACenter was founded as a response to a particular situation in the academic community of the Czech Republic at the beginning of the year 1996. When, in 1994 under the auspices of the Universities' Development Fund of the Ministry of Education of the Czech Republic within its pilot project, first high performance computing centers were to be established, solution called *fragmentation* by many of its opponents had won. It was decided to support three and later five high performance centers at three (five) different universities of Czech Republic, instead of buying and installing just one large(r) high performance supercomputer.

Many good reasons supported this decision, the most important are listed bellow:

- While the raw computing power of individual computers can be easily shared through the computer network, this is not so easy for the knowledge how to efficiently use them. One center would without doubt concentrate the knowledge to one place (this is generally not bad), but in the same time it would reduce the chances of individual end users to understand the installed hardware and software in the direct proportion to their physical distance to the center.

- One center means there is no competition. End users are not able to compare services and the center has no partner to discuss new development plans. Together this means diminishing interest in external users (center is gradually able to *keep itself busy*), gradual stagnation, and loss of motivation — a sole center will either got all his funding or the supercomputing facilities will cease to exist within the Czech Republic.

- Supercomputing covers very broad and distinct scientific areas and nowhere in Czech Republic scientists from at least the major of these fields are concentrated at one place (within just one institution). Computers installed at different places will open a path to *specialization*, both in hardware (different computer architectures), development environments and especially application software (computational chemistry and physics, technical areas, like mechanics, fluid dynamics, symbolic and general numerical computational systems, and many others).

- "Natural" place for installation of the one supercomputer would be Prague, but this was strongly opposed by representatives from other country regions. High concentration of universities and other scientific and research facilities in Prague unfortunately leads to some belittling of out of Prague institutions and their requirements (even worse, it is easy to rationalize this *belittling*, at least to some extent); also, the support for remote (far away) access is reduced — everything is *near* in Prague when compared to the distance to other university and academic cities within Czech Republic.

- Budget for running costs was not available within the original pilot project and no one university within Czech Republic was able to finance really large supercomputing center on its own. And last but not least, the large universities themselves took the project as a long awaited opportunity to get some funding for medium and high performance computing facilities.

All this lead to the decision to buy three POWER Challenge computers from SGI and to install them at Institute of Computer Science of Charles University in Prague (ICS CU), in Center on computational and information services of Technical University in Brno (CCIS TU) and at Institute of Computer Science of Masaryk University in Brno (ICS MU). At the same time two additional places were selected to have new hardware installed in the following year (1995): the West Bohemia University in Pilsen (WBU) and Computer Center of the Czech Technical University in Prague (CC CTU).

At the beginning of 1996 five high performance computers from SGI, Digital (Pilsen) and IBM (Czech Technical University) were available at the above mentioned five Czech universities. Powerful scalar processors were used in all these computers (none used a vector processor) and they covered both main architectural designs: SGI and Digital systems were representatives of SMP (Symmetric Multiprocessing), this means that just a single copy of operating system runs on all processors and the memory is hardware shared among them, while the IBM SP2 computer with a typical representative of DM (Distributed Memory) system, i.e. a system where each processor runs its own copy of operating system and has its own memory (the total computer memory is thus *distributed* among the individual processors). The major application software packages differed, too: computational chemistry and physics got high priority at ICS MU and ICS CU, with some presence at CC CTU, while technically oriented packages were available at WBU, CC CTU, TU, and program Fluent was also available at ICS CU. Access to the Matlab system was available primarily at CTU, WBU and MU, and other differences existed, too. On the other hand, all these computers were made accessible to all users from the academic community of the Czech Republic, i.e. to all professors and scientists at universities and at Academy of Science and to large extent to all university students (not only to the mentioned five universities).

In 1996 Ministry of Education launched a new program called TEN-34 CZ to support high performance networks and their applications. This program opened the opportunity to further qualitative development of the high performance centers, founded and developed in previous years. A project *METACenter* was approved and financed, with then goal to create a computational Grid whose nodes will be the above mentioned computers.

METACenter Project

The original *METACenter* project, funded in years 1996–1998 had the following goals:

1. To unify end users' interfaces, both at the administrator and user levels. When a login is created on any *METACenter* computer, all other nodes are automatically made available, including access to the shared disk space. This also includes the unification of application software interfaces (user is not forced to change habits when moving from one node to another) and the user name space should be shared among the nodes (all users has the same `login` names on all nodes).

2. Establish a unified authentication mechanism on all *METACenter* nodes. It was decided to use the Kerberos 4 system with a cross-realm authentication between individual nodes. The base Kerberos system was enriched with new commands which allow practically transparent user movement between individual computers, authenticated access to resources without need to reauthenticate (and passwords should never be sent in open form through the network).

3. To create a shared disk space. AFS distributed filesystem implementation from Transarc Corporation (USA) was deployed, with Kerberos 4 as the authentication mechanism. AFS site licenses for the above mentioned five universities (WBU, CTU, CU, TU, and MU) together with the multilicense for the whole Academy of Science allows without additional cost to create AFS cells with required number of servers and they also allow unlimited access to AFS from any number of end user stations with vendor supported UNIX like operating system (practically all the commercial UNIXes are covered and starting from AFS version 3.5 Linux is also supported, but neither Windows NT nor any other non-commercial UNIX operating systems like NetBSD or FreeBSD are covered by these multilicenses; however, a source code license is available for Windows NT, which can be used to make Windows NT binaries which can be used practically as the UNIX binaries but without any vendor support). The project funding allowed to buy around 500 GB of disk space available in full to the *METACenter* users.

4. Open and unify the batch queueing system. While all the nodes are open for the interactive work, all long running jobs should be submitted via a batch queueing system. All nodes use the same batch queueing system (Load Sharing Facility, LSF, from Platform Computing, Canada) with the exception of IBM SP2, where the LoadLeveler is the primary batch queueing system (LSF licenses were installed on IBM SP2 with the goal to create a "gateway" between both batch queueing systems). In accord with the development of the LSF system the WAN extensions were planned, which allow to share one set of batch queues between all nodes (and to submit a work for remote computer locally).

5. Network connectivity. All the nodes are connected via ATM to the high speed national network backbone of the TEN-34 CZ complex project. The local throughput (between node computer and the backbone point of presence) is always at least as high as the backbone throughput itself.

   The use of managed bandwidth with defined quality of service parameters was planned to follow up the development of the high speed backbone.

6. Parallel and distributed computing support. Fortran 90 compilers were available on all nodes since the project startup. PVM (Parallel Virtual Machine) was a basic communication tool gradually replaced by MPI (Message Passing Interface). While the main advantage of the *METAComputer* for end users lied primarily in the establishment of the unified user interface and shared distributed filesystems, the environment to support large scale distributed application jobs is created and supported (parallel Fluent, which was itself a project within the TEN-34 CZ program, conformational analysis of large and complex biomolecules, surface quality assessed via numerical analysis of ellipsometry and reflectometry data, . . .).

Project *METACenter* was successful in all but the following two goals:

1. Connecting the LSF and LoadLeveler batch queueing systems and tight integration of the IBM SP2 into the *METAComputer*. Beside other reasons, the completely different architecture with respect to the SGI and Digital machines was the main cause of this failure. Almost incompatible base programming environment and relative lack of interest by end users, which have a distributed environment already available on the IBM SP2 and which are much less motivated to collaborate on the creation of the *METAComputer* were the main reasons for the lack of integration support.

2. Use of *METACenter* for a really large scale distributed jobs. While several test jobs were run with success, the available software is not yet fully developed to seamlessly support distributed tasks. End users, as seen even from results presented in this Annual Report, in general are not too motivated to use a computing power which surpasses a capacity of an individual node. On the other hand it should be noted that even in USA there is no more than 20 really large scale projects on a Grid, so, when taking into account the number of inhabitants of USA and of Czech Republic even one application would be a comparable interest (and, when comparing the scientific potential of USA and CR, even less than one application should suffice). As the *METAComputer* and its concepts will become well known within the scientific community it could be forethought that more interest in large scale distributed computing will emerge as more and more complex tasks should be solved.

Since 1999 further development of *METACenter* is covered by the research intention of the CESNET, z.s.p.o. enterprise[1]. The team was reduced to staff from WBU, CU, and MU, but the collaboration with other nodes is still active. The whole system is built in open way to allow join of new nodes at any moment.

Deployment of the Kerberos 5 system (with the use of the open source `heimdal` implementation from KTH, Stockholm, Sweden) was the main result of the year 1999 effort. Kerberos 5 is much better suited to support the requirements of secure and easy access to the *METACenter* nodes. Creation of the backup infrastructure, which with the access to a high capacity tape robot will allow backups and archiving of user data from all *METACenter* nodes, was a second major achievement.

Hardware

The following hardware directly related to the activities of *METACenter* is available at its individual nodes. High speed local network infrastructure, connection to the metropolitan area networks and through it to the high speed national TEN-155 CZ backbone is also supported by individual nodes. Detailed description together with information of other hardware (especially workstations and network active parts) is available on the *METACenter* and individual nodes web pages (`http://www.ics.muni.cz/scb/`, `http://zsc.zcu.cz`, `http://www.cuni.cz/supercomp/`, `http://www.civ.cvut.cz/`, `http://www.cis.vutbr.cz/supercomp/`).

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[1] CESNET, z.s.p.o. is a company founded and fully owned by Czech universities and Czech Academy of Science. Its main purpose is to develop and run the high speed national academic network, TEN-155 CZ (the successor of the TEN-34 CZ). CESNET also runs one of the largest commercial internets within Czech Republic and with the access to the academic high speed network is among the most important Czech ISPs.

ICS MU Brno

Computational servers
SGI POWER Challenge XL
12 processors MIPS R10000/195 MHz
Memory: 2 GB
Disk capacity: 100 GB
Network interfaces: 10 Mb/s Ethernet, 155 Mb/s ATM Fore (VME)
Hostname: `grond.ics.muni.cz`
Theoretical performance: 4.8 GFLOPS

SGI Origin 2000
32 processors MIPS R10000/195 MHz
Memory: 16 GB
Disk capacity: 365 GB
Network interfaces: 4×10/100 Mb/s Fast Ethernet, 4×155 Mb/s ATM (SGI/XIO)
Hostname: `eru.ics.muni.cz`
Theoretical performance: 12.8 GFLOPS

SGI Onyx^2
8 processors MIPS R10000/195 MHz
Special features: 2×graphical subsystem InfiniteReality2 with 128 MB texture memory at each subsystem (in two raster managers) and total of 10 output video channels
Memory: 2 GB RAM
Disk capacity: 30 GB
Network interfaces: 10/100 Mb/s Fast Ethernet, 155 Mb/s ATM Fore (PCI)
Hostname: `onyx.ics.muni.cz`
Theoretical performance: 3.2 GFLOPS

The following computer is used as a fileserver:
Sun Enterprise 450
2 processors UltraSparc/300 MHz
Memory: 512 MB
Disk capacity: 80 GB
Network interfaces: 10/100 Mb/s Fast Ethernet, 2×155 Mb/s ATM (Sun)
Hostname: `nimloth.ics.muni.cz`

Backup systems:

- TZ877 drive (DLT 2000) with a 7 tape magazine, tape capacity 10/20 GB without/with compression,
- since September 1999 tape robot Exabyte X200 with six Mammoth II drives and a magazine for 200 tapes, tape capacity 60/120 GB without/with compression, total on-line capacity 12/24 TB.

Power Supply:
Uninterruptible power supply SOCOMEC with 45 kVA, backed by a motor generator with a capacity of 100 kVA.

ICS CU Prague

Computational servers
SGI POWER Challenge XL
12 processors MIPS R10000/195 MHz
Memory: 2 GB
Disk capacity: 57 GB
Network interfaces: 10 Mb/s Ethernet, 155 Mb/s ATM Fore (VME)
Hostname: `hal.ruk.cuni.cz`
Theoretical performance: 4.8 GFLOPS

SGI Challenge S
1 processor MIPS R4400/150 MHz
Memory: 128 MB
Disk capacity: 1 GB
Network interfaces: 10 Mb/s Ethernet
Hostname: `halik.ruk.cuni.cz`

Digital AlphaServer 2100A
2 processors Alpha 21064/300 MHz
Memory: 512 MB
Disk capacity: 10 GB
Network interfaces: 155 Mb/s ATM Fore
Hostname: `asterix.ruk.cuni.cz`

Digital AlphaServer 2100A
2 processors Alpha 21064/300 MHz
Memory: 512 MB
Disk capacity: 10 GB
Network interfaces: 155 Mb/s ATM Fore
Hostname: `obelix.ruk.cuni.cz`

A disk array with 90 GB total capacity is connected to the POWER Challenge and both Digital computers.

Power Supply:
All computers are connected to an uninterruptible power supply.

WSC WBU Pilsen

Computational servers
Digital AlphaServer 8400 5/300
8 processors Alpha 21164 EV5/300 MHz
Memory: 2 GB
Disk capacity: 32 GB
Network interfaces: 2×10 Mb/s Ethernet, 100 Mb/s FDDI (PCI)
Hostname: `kirke.zcu.cz`
Theoretical performance: 4.8 GFLOPS

Compaq AlphaServer GS140
8 processors Alpha 21264 EV6/525 MHz
Memory: 8 GB RAM
Disk capacity: 13 GB
Network interfaces: 10/100 Mb/s Fast Ethernet, 155 Mb/s ATM (PCI)
Hostname: `pasifae.zcu.cz`
Theoretical performance: 8.0 GFLOPS

Digital AlphaServer 2100A/200, Digital AlphaServer 1000, Digital AlphaServer 1000A and Digital AlphaServer 800 with 130 GB disk serve as fileservers for West Bohemia Supercomputing Center and *METACenter*.

Backups:

- TZ877 drive (DLT 2000) with a 7 tape magazine, tape capacity 10/20 GB without/with compression,
- TZ887 drive (DLT 2400) with a 7 tape magazine, tape capacity 20/40 GB without/with compression,

Power Supply:
UPS Fiskars 9100C (10 kVA)
UPS IVM D15-33 (15 kVA)

Software

The unification of end user interface and environment to smooth any movement between individual nodes is one of the main *METACenter* ideas. This transparency is not an end in itself, the main reason is to increase efficiency of the software budget. Individual *METACenter* nodes are for many reasons specializing themselves to a particular especially application software. SCB MU may serve as a typical example, as this nodes specializes to the parallel and distributed application development support and also to the application software for computational chemistry and physics. This specialization is due to the requirements but also due to the particular knowledge of Masaryk University users. On the other hand, the application software at WBU in Pilsen reflects the more technical orientation of that university.

The following list of installed software is not overly detailed and therefore is not complete. Its main purpose is to serve as a quick reference for current and future end users.

Common software

AFS	distributed file system License conditions: university wide license
LSF	Load Sharing Facility, batch queueing system License conditions: individual computers are licensed, licenses for LSF-WAN are also available
SGI Varsity	full development environment for SGI computers, including parallel compilers and libraries, debugging tools, … License conditions: licenses for group of machines, each node has 25–50 individual licenses

PVM	Parallel Virtual Machine, environment for development of parallel and distributed programs using message passing paradigm License conditions: open source license
MPI	Message Passing Interface, standard in the area of parallel and distributed computing License conditions: proprietary vendor implementations are available together with open source implementations (under different licensing schemes), especially MPICH and LAM
MAPLE	system for symbolic and numerical computing License conditions: university wide license for MU and CU
MATLAB	system for technical computing, together with a lot of toolboxes License conditions: 150 floating licenses of Matlab and Simulink and 10–150 floating licenses for more than 10 toolboxes
GNU	development and other tools from the GNU project License conditions: General Public License

ICS MU Brno

NQE	batch queueing system on Origin 2000 computer License conditions: permanent license for this computer
KAI C++	C++ compiler from Kuck and Associates License conditions: permanent license with yearly maintenance fee
Paradise	environment for parallel computing which uses a shared blackboard (tuple space) from Scientific Computing Associates, USA License conditions: permanent license for 15 processes
NAG Fortran 77	numerical functions library License conditions: permanent license, yearly maintenance fee
Gaussian94 i 98	ab initio quantum chemical program License conditions: full license for supercomputing centers
AMBER 5.0	program for molecular modeling, molecular mechanics and dynamics plus many accompanying tools License conditions: permanent license without maintenance
MM3	program for molecular mechanics License conditions: permanent license
MSI/BIOSYM	set of programs for molecular mechanics, dynamics and ab initio computing including a set of visualisation tools License conditions: permanent license
CSDS	Cambridge Structural Database System License conditions: permanent license

Oracle	Oracle 8.0 database including Advanced Networking, Distributed Database, Parallel enhancements, PL/SQL, Pro*C precompiler and Developer/2000 client development environment License conditions: permanent license, obtained through Oracle universities support, limited to educational and research use

ICS CU Prague

Gaussian94 and 98	ab initio quantum chemical program License conditions: full license for supercomputing centers
AMBER 5.0	program for molecular modeling, molecular mechanics and dynamics plus many accompanying tools License conditions: permanent license without maintenance
MSI/BIOSYM	set of programs for molecular mechanics, dynamics and ab initio computing including a set of visualization tools License conditions: permanent license
Fluent	modeling of liquid flow, heat transfer and chemical reactions License conditions: 10 floating licenses with expiration at the end of the year 2000

WSC WBU Pilsen

DEC Campus	SGI Varsity analogue for Compaq/Digital computers License conditions: permanent license with yearly maintenance fee
KAP C	C compiler from Kuck and Associates License conditions: permanent license
KAP Fortran77	Fortran77 compiler from Kuck and Associates License conditions: permanent license
Fluent	modeling of liquid flow, heat transfer and chemical reactions License conditions: 20 permanent floating licenses with yearly maintenance fee
Forge 3	program for simulation of material forging with the finite element method (FEM) License conditions: full licence for West Bohemia University with yearly maintenance fee
ANSYS	program for solving electrical, magnetical, heating and dynamic problems (FEM)
MARC	general-purpose nonlinera finite element solver (FEM) program for advanced engineering problems License conditions: permanent license for `pasifae.zcu.cz` (solver) and `kirke.zcu.cz` (pre- and post-processing)

PAM	set of programs (Flow, Crash, Shock, Generis, View) for flows of liquids and gases, deformation problems, propagation of dynamic waves, strikes of 3D bodies and appropriate per- and post- processors License conditions: license for one year
LS-Dyna	program for problems of striking and wave propagation (FEM License conditions: license for one year
Hypermesh	general preprocessor for LS-Dyna, MARC, Ansys License conditions: license for 3 years with yearly maintenance fee

Other programs include many CAD/CAM systems for (powerful) graphical workstations.

Utilization statistics

At least base statistical data about the use of computers with respect to the CPU utilization are collected at all *METACenter* nodes. The utilization of Brno, Prague, and WBU nodes is presented in the following graphs. Consolidation of the basic statistical data within all *METACenter* nodes should supply more precise data for the next year Annual Report.

All the following graphs denote situation in the first 11 months of the year 1999. First two graphs depicts distribution of the consumed CPU time between individual academic institutions (based on end users affiliation to the institutions). The situation at ICS MU is presented in the first graph, the second depicts the situation at ICS CU and the third depicts the situation at WBU.

Comparing figures 1 and 2 we see that one of the base *METACenter* assumptions, the automatic reciprocity of individual nodes without any administrative formal support is fulfilled. Local utilization at both ICS CU and ICS MU is near 50 % of available CPU time; it is clear that users prefer local machines. On the other hand 15 % of the ICS MU computer performance is consumed by CU users and 17 % of the ICS CU computer performance is consumed by MU users.

METACenter node utilization by Academy of Science users demonstrates that the physical distance to the computer does not play too important role when a computer is selected. ICS MU node is used almost twice as much by Academy of Science users than the ICS CU node. On the other hand negligible presence of CTU users at the ICS MU node have probably a different cause, which is the ICS MU orientation to the computational chemistry and physics and a total lack of application software for technically oriented users. ICS CU `hal.ruk.cuni.cz` computer has a computational dynamics program `Fluent` installed, and this is the software mainly used by CTU users.

It can be also seen that WBU users are currently *saturated* by their own powerful computers and reflecting the fact that ICS CU and ICS MU computers does not have any technically oriented application software installed (with the noted exception of `Fluent`) the WBU users have no motivation to move to these nodes. Orientation to different application software thus evidently leads to the proper utilization of those nodes where the application software is available; potential migration to the appropriate application software is eased through the *METACenter* and its consistent unification of end user environment and interfaces.

Interesting information can be drawn from the figure 5, too. The dominant position of the ab initio quantum mechanics program Gaussian in version 94 and 98) is not challenged even by the second most used program, Amber for molecular dynamics and modeling. Commercial products like Turbomole and especially Discover have only minor position, despite their quality and efficiency.

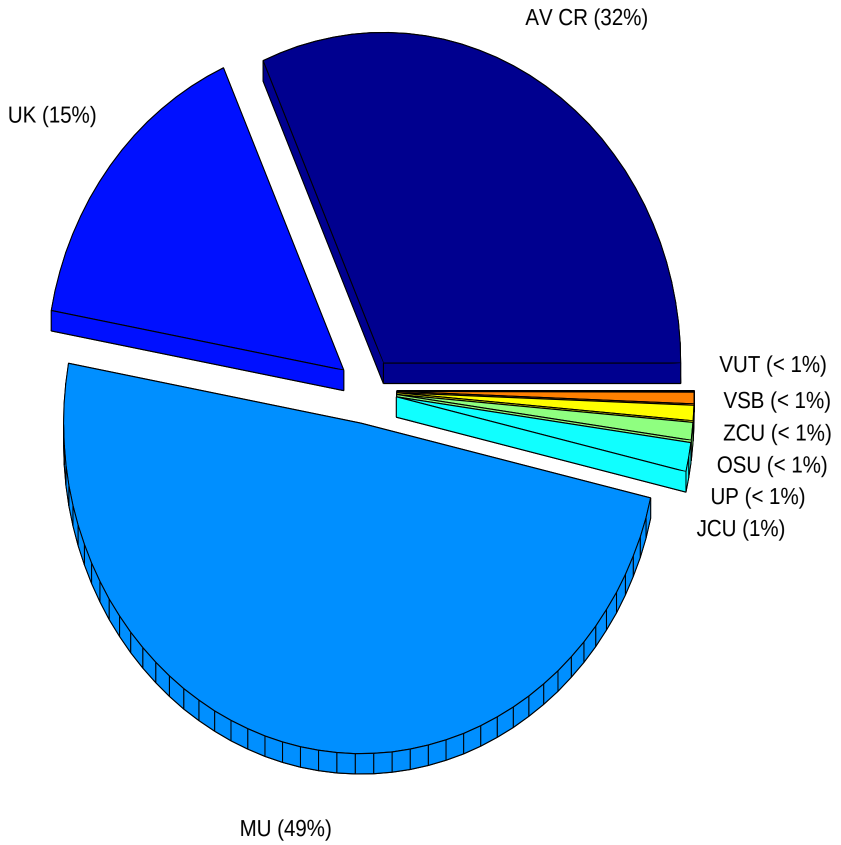

Fig. 1: CPU time distribution with respect to the end user affiliation to the academic institutions (SCB MU, `grond.ics.muni.cz`).

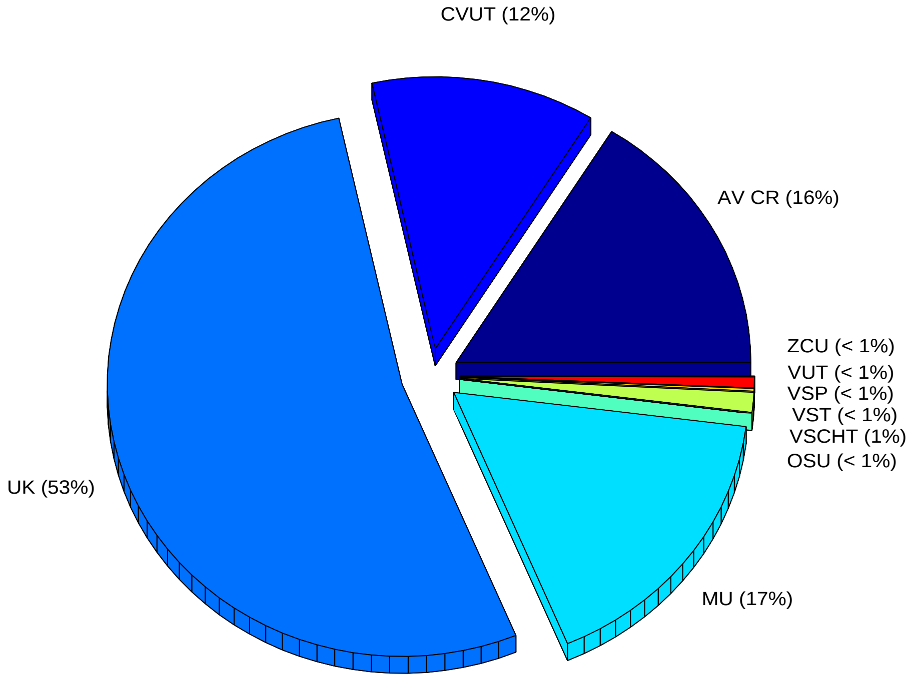

Fig. 2: CPU time distribution with respect to the end user affiliation to the academic institutions (ICS CU, `hal.ruk.cuni.cz`).

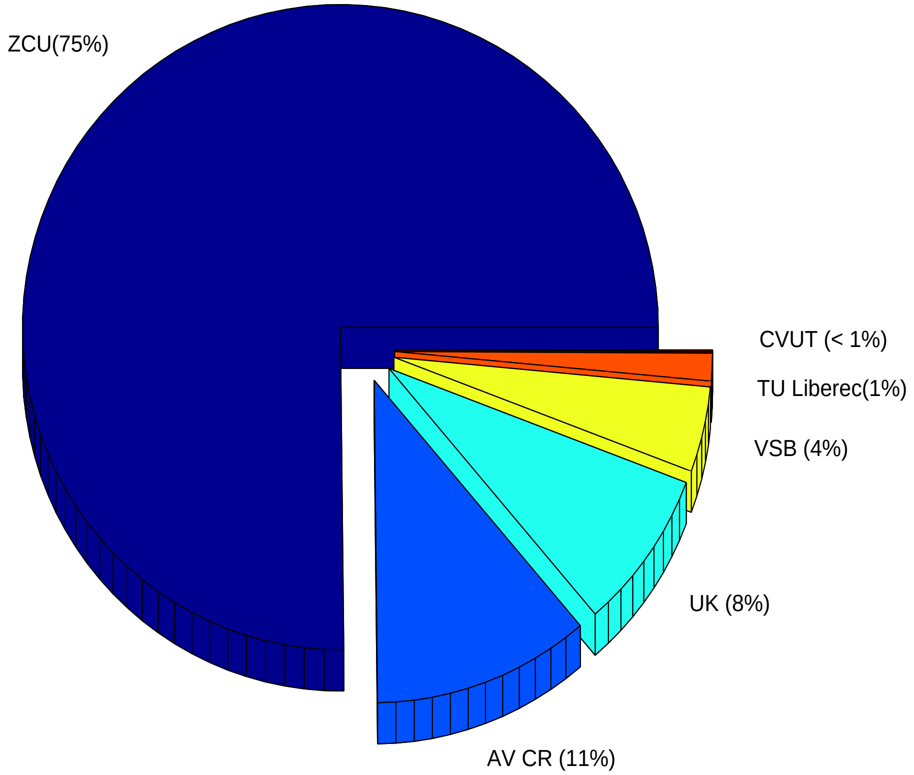

Fig. 3: CPU time distribution with respect to the end user affiliation to the academic institutions (WBU, `kirke.zcu.cz`).

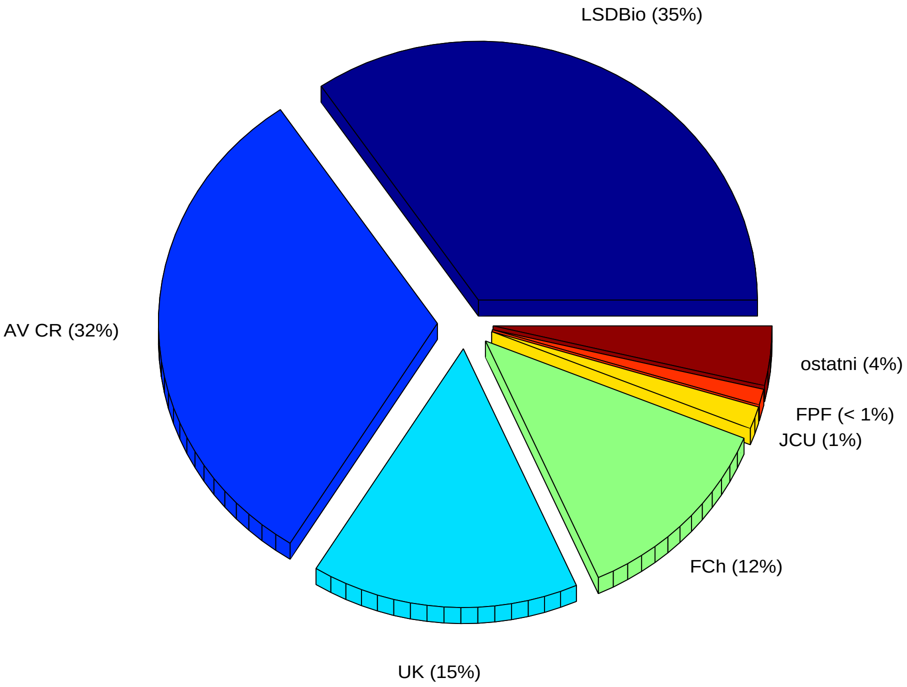

Fig. 4: CPU time distribution with respect to the end user groups/projects (SCB MU, `grond.ics.muni.cz`).

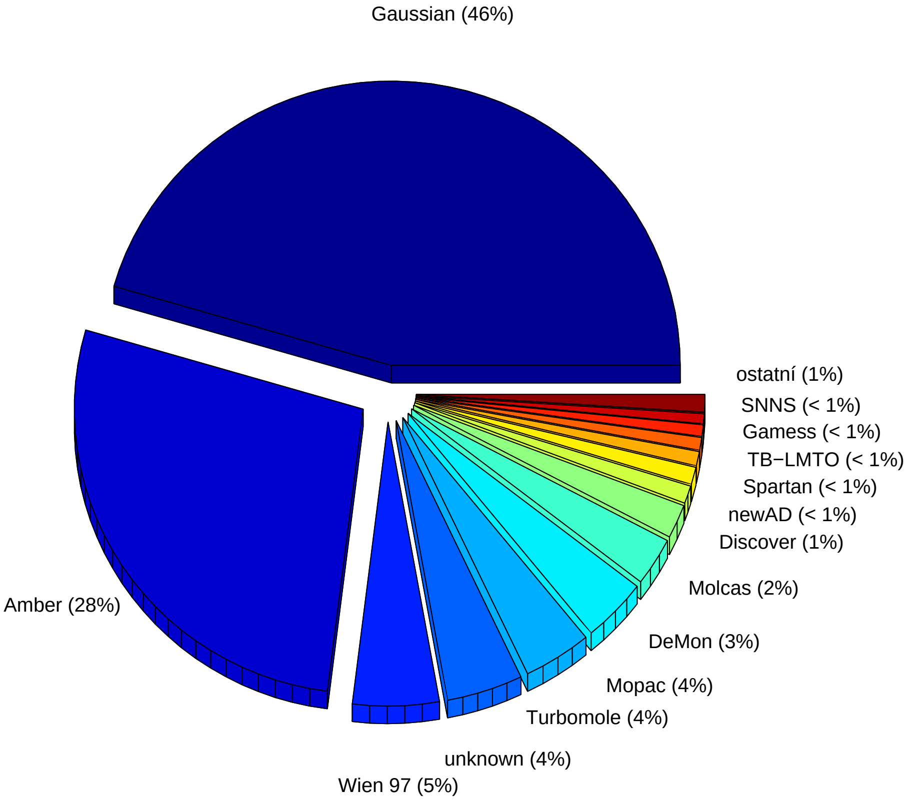

Fig. 5: CPU time distribution with respect to the used programs (SCB MU, `grond.ics.muni.cz`).

Reliability

Reliability, measured as a mean time between failures and also as a length of any individual failure, is very important quality and utilization feature. Base reliability data for `grond.ics.muni.cz` computer at SCB (ICS) MU are presented in the following table:

Mean time between downtimes	36 441 minutes (25 days, 7 hours, 21 mins)
Largest time between downtimes	150 369 mins (104 days, 10 hours, 9 mins)
Average length of downtime	255 mins (4 hours, 15 mins)
The largest downtime	1675 mins (1 day, 3 hours, 55 mins)

Very promising is especially the mean time between failures, which allows to use the `grond.ics.muni.cz` computer for very large and complex jobs which require weeks of computing time. Computer downtime may have different causes, including planned technical fixes and upgrades:

Downtime cause	Number	Total length (min)	Availability
Unscheduled	5	35	99,99 %
unknown reason (panic)	4	34	
reset	1	1	
Scheduled	11	3304	99,47 %
fix/replace hardware	4	240	
upgrade hardware	2	1848	
fix software	1	21	
other administrative	3	1154	
unknown reason	1	41	
Total	**16**	**3339**	**99,46 %**

As easily seen, the total availability was 99.46 %, i.e. from the 365 days per year the computer was out of commission for less than two days (precisely 1 day, 23 hours and 20 minutes[2]). With respect to the fact that unscheduled failures were responsible for a mere 35 minutes and that majority of all the scheduled events (and almost all the long lasting ones) has a common cause of the electrical installation upgrade (together with the installation of a new UPS and its connection to the backup motor generator) it is not unrealistic to require at least three nines reliability, i.e. to reduce the total downtime per year to less than 10 hours.

End user papers

Following pages represent the main purpose and contents of this Annual Report. They are dedicated to the presentation of individual end users, to the results which justify the existence of *METACenter* and its nodes. All papers of users with a project during the last two years are presented together with presentations of other users who achieved important results with the use of *METACenter* computing resources. In some cases the older results are not presented as some of the users left the *METACenter* (in many cases due to the move to abroad) and in the time of this Report preparation they were no more accessible.

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[2] 0.54 % of a year is 2 840 minutes; the 3 339 minutes presented in the table reflects a period of more than 14 months.

Energy Transfer and Relaxation in Bacterial Photosynthetic Units

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The structure of LH1 and subunits of purple bacterial photosynthetic units was solved only recently: they form rings of a large number of BChl molecules placed between protein α and β helices.

Exciton transfer regime is determined, generally and even in the circular subunits LH1 and LH2 of the antenna system of the purple bacterial photosynthetic units by

- symmetry, distances and interaction between chromophors,
- interaction with a bath (dynamical disorder),
- static disorder (in local energies and transfer integrals),
- temperature, and so on.

Our aim is to contribute by investigation of the time development of the exciton transfer and optical properties to the explanation of an influence of the static and dynamic disorders.

Our investigation of the influence of the static and dynamic disorder on the optical line shapes of linear and cyclic molecular aggregates in the framework of the colored (dichotomic) noise has included systems from dimer to the whole ring of 18 BCHl molecules in the LH2 subunit. Optical line shapes are obtained by solving of hundred thousands of differential equations for correlation functions, which are built up using the MAPLE package.

Obtained results have been presented on international conferences [1, 2, 3, 4] and published in international journals [5, 6, 7, 8, 9].

Exciton transfer takes place at the beginning inside the LH2 ring and between the LH2 rings. Exciton jumps also to the LH1 ring. At the end the exciton is trapped in the reaction center which is placed in the center of the LH1 ring. In presence of the bath, the exciton transfer is described by the time development of the matrix elements of the exciton density matrix. Equations of motion of the density matrix could be obtained by various methods. We are dealing with the dynamical equations which form an important generalization of the stochastic Liouville equations. Influence of the bath on the exciton transfer and relaxation is taken into account approximatively. Smallest system is built form the LH2 ring, the

LH1 ring and the reaction center. We are forced to describe the time development in the molecular aggregate of 52 molecules. Our method of the dynamical equations of motion for the diagonal and off-diagonal matrix elements of the exciton density matrix leads to the coupled system of the 2704 differential equations.

Exciton transfer the antenna system has two time scales. Excitation is very quickly distributed over the whole ring, from which it is further transferred to the another LH2 or LH1 ring, where it is trapped by the reaction center. For times much more longer then a transfer step inside one ring, the exciton transfer can be treated as hops between the rings.

As extension of our former simulations of the exciton transfer and relaxation in smaller molecular systems we have calculated the exciton transfer inside the rings and between incoherently coupled LH2 and LH1 rings. We have used a model Hamiltonian in which a local energy and transfer integral heterogeneity, interaction with the bath and influence of the static disorder has been taken into account. We have obtained, in the framework of the generalized Stochastic Liouville equations method, the time development of the site occupation probabilities of BChl molecules in the LH2, LH1 rings and in the reaction center

Obtained results have been presented on international conferences [10, 11, 12, 13, 14, 15, 16, 17, 18] and published in international journals [19, 20].

We have succeeded for a dimer in analytical calculation of the equations of motion for the exciton density matrix and for the correlation functions describing the optical line shapes in the framework of the colored (dichotomic) noise. The analytical solution of the time development of the site occupation probabilities (diagonal elements of the exciton density matrix), obtained by computer algebra, has been used to determine algebraically the memory functions.

Obtained results have been presented on international conferences [21, 22, 23] and published in international journals [24, 25].

Our investigation has been founded by contracts GAUK 105/1995, 345/1998 and GAČR 202/98/0499.

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Ab Initio Computations of Molecular Properties

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Computer simulations of molecular properties have become a vital part of spectroscopic experiments. Yet significant differences exist in the involvement of the theory in the data interpretation. For example, precision of available computational techniques is not sufficient for demands of the nuclear magnetic resonance, while the analysis of molecular vibrational circular dichroism is unthinkable without the support of ab initio calculations.

In the past we used available facilities of the Supercomputer Center namely for simulation of vibrational optical activity. This phenomenon can be measured either as vibrational circular dichroism or Raman optical activity and provides an interesting information about molecular structure, conformational behavior of peptides or nucleic acids. Because of the limitations of current quantum-chemical techniques, special procedures had to be developed allowing the interpretation of such experiments for bigger molecules and molecular systems.

The interpretation of optical activity provides also an important feedback to general procedures used in quantum chemistry. Particularly, our software was applied for prediction of the the nuclear spin-spin coupling and inelastic neutron scattering experiment.

Currently, our research includes namely modeling of complexes with nucleic acids and theory of the Raman optical activity.

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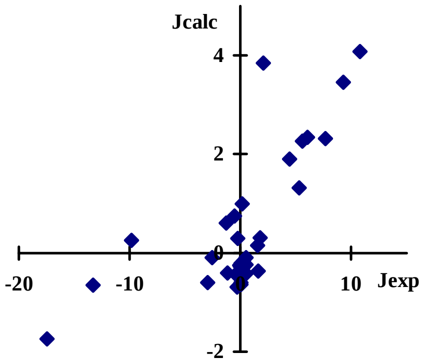

Figure 2: α-pinene, calculated and experimental spin-spin coupling constants.

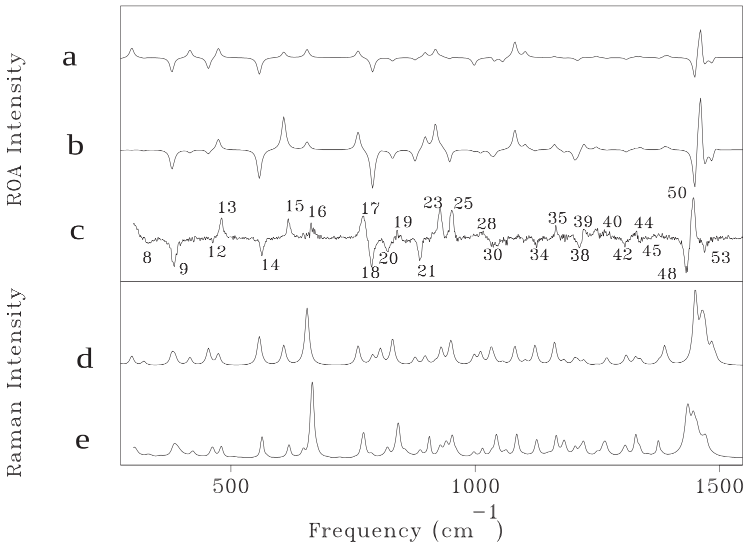

Figure 1: Experimental (c,e) and computed (a, b, d) Raman (bottom) and Raman optical activity (top) spectra of α-pinene.

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Quantum Chemical Ab Initio Studies of the Interactions of Metals with the Models of Biomolecules

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In the frame of Supercomputer centers of the both Charles University in Prague and Masaryk University in Brno, the computations of platinum complexes were performed. We treated the influence of tautomer equilibria of guanine and adenine with platinum adducts, hydration of square-planar platinum complexes. The influence of Pt species on the Watson-Crick base pairing, proton and charge transfer is explored at present. In the first step the influence of binding of square planar platinum complexes on tautomeric equilibria of the DNA bases guanine and adenine was investigated using a quantum chemical ab initio method based on the density functional method (hybrid exchange and correlation functional B3LYP). Neutral trans-dichloro-ammonia-, +1 charged chloro-diammonia-, and +2 charged triammonia-platinum(II) were chosen for coordination to bases. Only the N7 interaction site of the bases was considered since it is the most important binding site of cations to purine bases. The calculations demonstrate that the neutral platinum adduct does not change the tautomeric equilibria of the bases. Furthermore, N7 binding of the neutral Pt adduct moderately reduces the probability of protonation of the N1 position of adenine. Larger effects can be observed for +1 and mainly +2 adducts, but these can be rationalized by electrostatic effects. Since the electrostatic effects are expected to be efficiently compensated for by a charged backbone of DNA and counterions in polar solvent, no dramatic increase in mispair formation is predicted even for +2 Pt adducts which is in agreement with experiments. The interaction energies between Pt adducts and the nucleobases were also evaluated. These interaction energies range from ca. 210 kJ/mol for neutral Pt(II) adduct, interacting with both bases and their tautomers, up to 500 kJ/mol for the +2 charged Pt(II) adduct, interacting with the guanine keto tautomer and the adenine anti imino tautomer. The surprisingly large interaction energy for the latter structure is due to the strong H-bond between the NH_3 ligand group of the metal adduct and the N6 nitrogen atom of the base. The interaction energy between the amino tautomer of adenine and the Pt^{2+} adduct is around 410 kJ/mol. These results were submitted to *Journal of Biological Inorganic Chemistry*. In the Acknowledgement, the authors explicitly thank to the Supercomputer Centers in Brno and Prague for the generous allotment of computer time.

In the second step the influence of the platinum complexes on the charge and proton transfer between the hydrogen-bonded base pairs is computed. There calculations are still running.

The study devoted to the hydration of square-planar platinum complexes using the formalism of Gaussian-3 theory is in the final phase.

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Similarity-Based Image/Volume Registration of Biomedical Data*

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Our research is devoted to the following registration:

1. of stacks of serial optical slices captured by a confocal microscope from an oversized biological tissue specimen, and
2. of volumetric stacks of a human head (brain) captured by NMR (Nuclear Magnetic Resonance), CT (Computed Tomography) and SPECT (Single Photon Emission Computed Tomography).

The registration is a prerequisite for rendering and interactive visualization of the studied biological specimen. In case of 2 volumes captured by the various modalities are fused to provide more comprehensive information.

The registrations are based on similarity measures (the sum of absolute valued differences, normalized correlation coefficient, mutual information) and require optimization of the search for the global extreme of a similarity measure over a parametric space that consists of a set of rigid transformations (translation & rotation). Therefore, optimization strategies — full search or adaptive simulated annealing (ASA) — are used.

Full search scans the whole parametric space by a point-by-point manner; thus, it is an extremely time-consuming approach, especially in the case of volumes with 6 degrees of freedom (translations along x, y, z and rotations around x, y, z). However, the global extreme is found for sure in this case. On the other hand, finding the global extreme by using ASA has probability < 1, but the optimization process is much faster when compared with the full-search.

We implemented the registration procedures in C on SGI Power Challenge (`hal.ruk-.cuni.cz`) within Super-Computer Center of Charles University, and compared different similarity measures and optimization strategies concerning their speed and robustness.

Our experimental results confirm that as the most robust similarity measure can be considered mutual information. Robustness of the optimization by using ASA is very close to robustness of the full-search.

The chosen approaches are suitable for registration of biomedical data.

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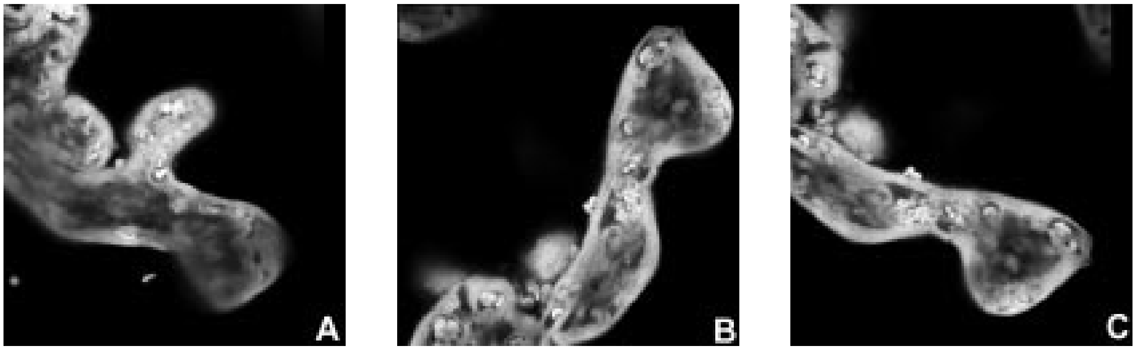

Figure 1: Example of registration of optical slices (512 × 512 pixels); A), B) are slices to be registered and C) is slice B) after registration; global extreme found in the position $x = -9,63$ (pixel), $y = -50,08$ (pixel), $\alpha = 97,03°$

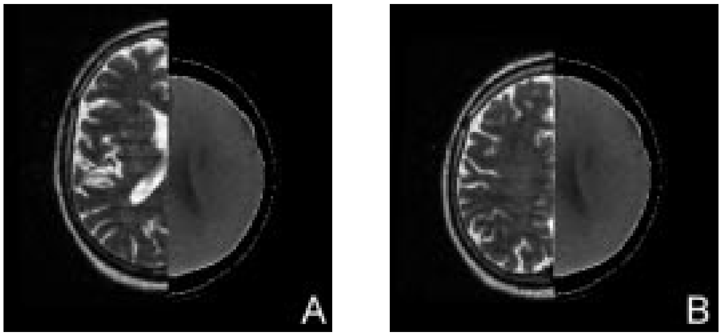

Figure 2: Example of volume registration (left part of images: NMR consisted of $256 \times 256 \times 200$ voxels, right part of images: CT consisted of $256 \times 256 \times 13$ voxels); A) is the fused 8th slice of volumes before and B) after registration; global extreme found in the position $x = 3.11$ (NMR voxel), $y = -10.10$ (NMR voxel), $z = 19.55$ (NMR voxel), $\alpha = -4.37°$, $\beta = 0.12°$, $\gamma = -2.14°$

Optics of Thin Films

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During the last five years problems concerning the construction of the models of thin film systems usable for studying the optical properties of these systems were solved. First of all the models of the system mentioned corresponding to real multilayer systems exhibiting various kinds of defects were studied. It was shown that the use of these models for interpreting experimental data was impossible without employing the modern numerical method. Therefore we developed the program enabling us the parallelization of these problems. For this purpose the package of PVM (parallel virtual machine) was used. By using several computers working simultaneously one could achieved a satisfactory velocity of computation. This fact allowed to solve the complicated analytical problems concerning the determination of the optical parameters of the multilayer systems with the defects in a suitable way.

The results obtained in this way are important from the point of view of the fundamental research concerning microelectronics, optoelectronics and nanotechnology. This importance is given by the fact that the optical methods used for analyzing the complicated multilayer systems are not destructive (the non-destructive method are very useful from the point of view of the modern technologies in the branches mentioned above). It should be noted that in our works we utilized the optical method based on interpreting the experimental data of ellipsometry and reflectometry.

The results published in the international journals:

Year 1996

The first results were published during the international conference ECASIA'95 (Montreux – Switzerland, October 9–13, 1995). These results corresponded to the studies of the influence of slight roughness on the ellipsometric parameter of very thin films. The results mentioned were also published in this proceedings of the conference [1].

Year 1997

In this year we dealt with the development of the optical method enabling us to determine the parameters of slight roughness of silicon substrate. The results concerning this problem were published in the international conference ECASIA'97 ((Göteborg – Sweden, June

16–20, 1997). The result were achieved using the optical method based on combining spectroscopic ellipsometry and spectroscopic reflectometry applied to several samples of the system studied. The results obtained within these combined optical method were confirmed using AFM (atomic force microscopy). The results were completed in the proceeding of this conference [2].

Year 1998

In this year several our papers were published. The first of them concerned the results achieved at our studies of very thin native oxide films taking place on gallium arsenide substrates. These results contained information about the optical parameters of these films together with the parameters characterizing slight roughness of their boundaries (the values of the parameters characterizing slight roughness of the boundaries were also confirmed by AFM). The results mentioned were presented in our poster presented in the international conference EMAS'97 (Torquay – UK, May 11–15, 1997) The article corresponding to this poster was published in the international journal Mikrochimica Acta [3].

Moreover, in this year we published two theoretical papers concerning the influence of slight roughness on the optical quantities characterizing thin films [4, 5]. Further, we solved the problem concerning the parameterization of the model of dispersion of the optical constants of amorphous solids. The results achieved were published in the journal Acta Physica Slovaca [6]. In the end of 1998 we presented a poster in the international workshop concerning Quantitative Microscopy (Lyngby – Denmark, November 5–6, 1998). The results presented in this poster concerned the comparison of AFM and the optical method at studying very slight roughness of solids. The results presented there were also published in the proceedings of this workshop [7].

Year 1999

In this year three papers concerning the utilization of our program have been published in the international journals [8, 9] so far. The first of them deals with the problem of the comparison of the measurements of surface roughness performed by the optical method on one hand and by non-optical method (AFM and profilometry) on the other hand. Note that the results contained in this paper were also presented in the form of a poster in the international conference on Wave and Quantum Aspects of Contemporary Optics (Stará Lesná – Slovak Republic, September 21–25, 1998). The latter of them was devoted to the characterization of hydrogenated amorphous silicon films employed for producing solar cells in practice. A part of the results comprised in this paper was also presented as a poster in the international conference 14th International Vacuum Congress (Birmingham – UK, August 31 – September 4, 1998). In this year it has been published our paper [10] too. This paper contains the results concerning the complete optical analysis of the system formed by the silicon substrate and silicon dioxide films (this system is often employed in semiconductor industry). It should be noted that some of the results of this paper were presented in the international conference Asia-Pacific Surface & Interface Analysis Conference (Singapore, November 30 – December 4, 1998).

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[10] Ohlídal, I., Franta, D., Pinčík, E., Ohlídal, M. *Complete Optical Characterization of the* SiO_2/Si *System by Spectroscopic Ellipsometry, Spectroscopic Reflectometry and Atomic Force Microscopy*. Surface and Interface Analysis, Chichester, England, UK: John Willey & Sons, 28, pp. 240–244. ISSN 0142-2421. 1999.

Ab Initio Study of Reactivity of Cisplatinum and of its Interaction with DNA Bases

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The project started in 1996. New information about parameters of the force field of cisplatinum bound to purine DNA bases- guanine and adenine was obtained,primarily for the out-of-plane bending parameter whose correct determination is of key importance for the subsequent molecular mechanics calculations of platinum-DNA adducts. The contribution of the deformation of the base plane was included which lead to a decrease of the values of the parameters of up to 50 % compared with previously published data . MM-calculations with our parameters should therefore result in smaller kink angles in modified DNA which will lead to a better accordance with experimental data.

Further goal of the project was theoretical study of the reactivity of cisplatinum and of its transformations within the cell. Results about cisplatinum hydrolysis, the first step of cisplatinum biotransformation in an organism, have been sent for publication. Results dealing with cisplatinum-guanine recognition and their mutual reactivity are being prepared for publication.

Publications prepared with the use of *METACenter*

[1] Z.Chval and M.Šíp: Force Field for Platinum Binding to Adenine and Guanine Taking into Account Flexibility of Nucleic Acid Bases, J.Phys.Chem. B 1998, 102, 1659.

[2] Z. Chval and M. Šíp: Pentacoordinated Transition States of Cisplatinum Hydrolysis, Inorg. Chem., submitted.

Used programs

- Gaussian94 (the *METACenter* version)
- Gamess (the self installed program)

Collision Processes of Rare Gas Atoms and Ions

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Results

Quasiclassical trajectory calculations [1] comprising collision processes in dilute noble gases were performed on the computers belonging to the joined $\mathcal{META}$*Center*. In particular, ternary recombination collisions [4]

$$\mathrm{A} + \mathrm{A} + \mathrm{A} \longrightarrow \mathrm{A}_2 + \mathrm{A}$$

and collision induced dissociation processes

$$\mathrm{A}_2 + \mathrm{A} \longrightarrow \mathrm{A} + \mathrm{A} + \mathrm{A}$$

were studied. The results obtained from those calculations were published in form of scientific papers [4, 5] and were surveyed in a PhD thesis [6]. At present, quasiclassical trajectory calculations of four-atom collisions [7]

$$\mathrm{A}_2 + \mathrm{A} + \mathrm{A} \longleftrightarrow \mathrm{A}_2 + \mathrm{A}_2$$

are running. Their results will be published soon. In addition, another paper [8] is being prepared at present in which computational data obtained using computers belonging to the $\mathcal{META}$*Center* are employed.

Plans

In the future, computational resources of the joined $\mathcal{META}$*Center* will be used in two principal directions:

1. Ab initio calculations of two- and three-body interaction potentials will be performed for heavier noble gases; and the calculated potentials will be employed in subsequent dynamical studies. This work will be done in co-operation with the Institute of Chemical Technology, Prague, Czech Republic, and the Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic. A grant application for the year 2000 was submitted to the Grant Agency of the Czech Republic.

2. Computational study of structure and dynamics of small ionic noble gas clusters will be performed using semiempirical methods — DIM [2] (diatomics-in-molecules) and HWD [3] (hemiquantal dynamics with the whole DIM basis). This project will be solved in co-operation with the Laboratoire de Physique Quantique, Université Paul Sabatier, Toulouse, France, the Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic, and the Institute of Mining and Metallurgy, Ostrava, Czech Republic. At present, the project is supported by the Internal Grant Agency of the University of Ostrava.

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[2] F. O. Ellison, J. Am. Chem. Soc. 85, 3540 (1963).

[3] F. X. Gadea and. P. J. Kuntz, Mol. Phys. 63, 27 (1988).

Publications prepared with the use of *METACenter*

[4] R. Kalus, J. Chem. Phys. 109, 8289 (1998).

[5] R. Kalus, J. Chem. Phys. 110, 3856 (1999).

[6] R. Kalus, Chemical Reactions of van der Waals Molecules, PhD thesis, Institute of Chemical Technology, Prague, Prague 1998 (in czech).

[7] will be submitted to Chem. Phys.

[8] will be submitted to Coll. Czech. Chem. Communications.

Research at the Laboratory of Biomolecular Structure and Dynamics

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Introduction

The research effort is concentrated to several areas. The main focus in the first one is organic quantum chemistry methodology. Current attention is paid to reaction paths and transition states elucidation. The second field involves conformational and dynamics studies on flexible molecules especially those with a biological interest (hydrocarbons and their derivatives, peptides, carbohydrates, oligonucleotides, nucleotide-sugars). The third direction is focused on computer study of interactions and reactions of large biological polymers, especially proteins, with small substrates, and also studies of structure and dynamics of supramolecules. The substantial part of the scientific orientation of the Laboratory in the field of Computational Chemistry and Molecular modeling is methodology development.

People involved in the projects:

Prof. RNDr. Jaroslav Koča, DrSc. (`jkoca`), head of the Laboratory
Bc. Michal Boháč (`bogey`)
Mgr. Jiří Czernek (`czernek`)
Mgr. Michal Čajan (`cajan`)
Mgr. Martin Černohorský, Ph.D. (`cerno`)
Mgr. Jiří Damborský, Dr. (`jiri`)
Mgr. Eva Fadrná, Ph.D. (`evaf`)
Mgr. Jan Grůza, Ph.D. (`samuel`)
Mgr. Sofiane Kettou (`kettou`)
Mgr. Zdeněk Kříž, Ph.D. (`zdenek`)
Mgr. Michal Kutý, Ph.D. (`michalk`)
Mgr. Martin Ludin (`ludin`)
Mgr. Pavla Petrová (`papetr`)
Mgr. Richard Štefl (`stefl`)

For further information see WWW pages

1. WWW page of the Laboratory of Biomolecular Structure and Dynamics
   `http://www.chemi.muni.cz/lbsd/lbsd.html`

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[1] `http://www.chemi.muni.cz/lsdb/lsdb.html`

2. WWW pages of individual members:
   `http://www.chemi.muni.cz/~jkoca/` — prof. RNDr. Jaroslav Koča, DrSc.
   `http://www.chemi.muni.cz/~jiri/` — Mgr. Jiří Damborský, PhD.
   `http://www.chemi.muni.cz/~zdenek/` — Mgr. Zdenek Kříž, PhD.
   `http://www.chemi.muni.cz/~evaf/` — Mgr. Eva Fadrná, PhD.

1. Quantum chemical calculations and computer studies of chemical reactions

Computer studies of chemical reactions using a quantum chemistry methodology are performed by the program VADER, developed in the Laboratory, which is intended for investigation of both conformational and reactional behavior of small and middle sized systems. It is built over an semi-empirical or ab-initio quantum mechanics.
In *METACenter*, programs enabling ab-initio calculations of NMR parameters are available. Our project focuses on magnetic properties of biologically relevant molecules — nucleic acids bases, base pairs, and nucleosides. We carry out calculations of nuclear magnetic shielding tensor and indirect nuclear spin-spin coupling tensor.

People involved: Czernek J., Černohorský M., Kettou S., Koča J., Kutý M.

Used programs

- *Application software installed in METACenter:* Gaussian92, Gaussian94, Gaussian98, Turbomole (Biosym/MSI)
- *Local software developed in LSDBio:* VADER
- *Software developed outside LSDBio:* deMon/NMR

Published papers in scientific journals and papers in press

[1] Czernek J., Sklenář V.: *Ab initio výpočty chemických posunů v biomolekulách.* Chem. Listy. (accepted), in Czech.

Review on the theory of *ab initio* computing of chemical shifts for the ^{1}H, ^{13}C, ^{15}N, and ^{19}F isotopes in the nuclear magnetic resonance spectres together with the most important applications in biologically important molecules studies. Paper is focused on the theoretical study of the influence of constitution and geometry on chemical shifts and the influence of hydratation interactions is also discussed.

[2] Czernek J., Sklenář V.: *Ab Initio Calculations of* ^{1}H *and* ^{13}C *Chemical Shifts in Anhydrodeoxythymidines.* J. Phys. Chem. A. **103** (in press).

For relatively large (containing 16 non-hydrogen atoms each) organic molecules, anhydrodeoxythymidines, ^{1}H and ^{13}C NMR chemical shifts were predicted using CPHF-GIAO, DFT-GIAO, and SOS-DFPT-IGLO methods. Both ab initio optimized and experimentally derived geometries of studied compounds were investigated. In the majority of cases, good agreement of theoretical and experimental chemical shifts was obtained with an average rmsd for SOS-DFPT-IGLO, DFT-GIAO, and CPHF-GIAO calculations of 5.5, 5.2, and 6.6 ppm for ^{13}C and 0.233, 0.269, and 0.297 ppm for

^1H, respectively. The best overall performance was found with the SOS-DFPT-IGLO technique.

[3] Černohorský M., Vaultier M., Koča J.: *Comparison of Conformational Behavior of the Short Alanine Peptides and Their Boron Analogues.* J. Mol. Struct. (Theochem) (in press).

Conformational behavior of short terminally blocked alanine peptides up to three residues has been analysed by means of a new computer program VADER. The program is based on Single-Coordinate-Driving method and it employs quantum chemistry energy calculation. The semiempirical AM1 method has been used in this study. Conformational behavior of alanine peptides has been compared with their boron analogues. It has been found that: 1. Semiempirical AM1 method creates an artifact in energy calculation of boron analogues for geometries where the dihedral angles are around zero value. In such a case, *ab-initio* methods have to be employed. 2. Boron analogues appear conformationally more flexible. They exhibit much higher number of energy minima along the PES. It has also been concluded that the program VADER is able to give quite a good estimation of stationary points. All stationary points found by VADER for monomers and those stationary points with relative energy less that 2.0 kcal/mol found for the dimers were subjected to frequency analysis of the Hessian matrix. In all cases they were confirmed as stationary points of the same category as predicted by VADER.

[4] Živný O., Czernek J.: *CCSD(T) Calculations of Vibrational Frequencies and Equilibrium Geometries for the Diatomics F_2, SF, and Their Ions.* Chem. Phys. Lett. (accepted).

For F_2, SF, and their monovalent ions, sophisticated CCSD(T)/aug-cc-pVQZ *ab initio* technique was employed to calculate accurate equilibrium geometries and harmonic vibrational frequencies. In cases when experimental values are unknown, the results obtained are indispensable for modeling of SF_6 thermal decomposition.

Papers submitted for publication in scientific journals

[1] Černohorský M., Kettou S., Koča J.: *VADER — New Software for Exploring Interconversions on Potential Energy Surfaces.* J. Chem. Inf. Comp. Sci. (in press).

A new computer program for investigating both reaction and conformational Potential Energy Surfaces (PES) based on the utilization of the extended Single Coordinate Driving technique is presented. The program is called *VADER* — advanced *VA*riation of Driv*ER*. It uses an external Quantum Mechanics program to calculate the energy of the studied system and also for the minimization procedure. On simple examples it is shown that the program is capable of studying the reactivity of small organic molecules and biomolecules. *VADER* is probably the first software which is able to generate the topology of reaction PES using quantum chemistry in an automated way. The program will be made available.

Contributions on scientific meetings

[1] Czernek J., Sklenář V.: *Ab Initio Calculations of the CSA for Biomolecules.* 13th

NMR Valtice. Meeting of the Central European NMR Discussion Groups, Valtice, April 27–29, 1998.

[2] Czernek J., Sklenář V.: *Calculations of NMR Parameters: Some Applications to Large Organic Systems.* Quantum Chemical Calculations of NMR and EPR Parameters, Smolenice, September 14–18, 1998.

[3] Czernek J., Sklenář V.: *On the Chemical Shift Anisotropy in Biomolecular Systems.* X^{th} Conference on Organic Chemistry and Biochemistry of Young Scientists, Liblice, June 15–20, 1998.

[4] Czernek J., Sklenář V.: *Ab Initio Calculations of Chemical Shielding and Coupling Constants in a Series of Nucleosides.* 12th NMR Valtice. Meeting of the Central European NMR Discussion Groups, Valtice, April 7–9, 1997.

[5] Czernek J., Sklenář V.: *Ab initio výpočty štěpících konstant v nukleosidech.* Pokroky v organické, bioorganické a farmaceutické chemii, Liblice, November 10–12, 1997. Abstrakt: Chemické listy 91, 1997, str. 1019.

[6] Czernek J., Sklenář V.: *Ab initio výpočty chemického stínění cytosinu.* Pokroky v organické a bioorganické chemii Liblice ’96, Liblice, November 4–6, 1996.

[7] Czernek J., Sklenář V.: *NMR Study of J-Coupling Network in* ^{13}C *and* ^{15}N *Labeled RNA Nucleotides.* 12th Symposium on Chemistry of Heterocyclic Compounds and 6th Blue Danube Symposium on Heterocyclic Chemistry, Brno, September 1–4, 1996.

2. Conformation behavior of biomolecules and molecular docking

The effort in the field of conformational, dynamics and molecular docking studies is to adopt search technologies described in the literature and to combine them with “in house developed” methodology to produce as much a complete picture of the conformational space as well as host-guest energy surface and its dynamics. An original methodology for exploring conformational space has been developed in the Laboratory during recent years. This methodology, called CICADA, has been tested on peptides, carbohydrates, oligonucleotides, nucleotide-sugars, and hydrocarbons and the results compared with available experimental data (especially NMR and X-ray). Potential as well as free energy are calculated together with population of single conformational families. Molecular dynamics simulations make it possible to include solvent molecules. It also allows us to study interactions of biomolecules with ions.

People involved: Fadrná E., Grůza J., Koča J., Kříž Z., Ludin M., Petrová P., Štefl R.

Used programs

- *Application software installed in $\mathcal{METACenter}$:* Gaussian94, AMBER-4.0, AMBER-4.1, AMBER-5.0, BIOSYM/MSI (InsightII, Discover, Turbomole), xmgr
- *Local software developed in LSDBio:* CICADA, PANIC, ANALYZE, COMBINE, AIDA, FAMILY

- *Software developed outside LSDBio:* Dials and Windows, Curves, JUMNA

Published papers in scientific journals and papers in press

[1] Petrová P., Koča J., Imberty A.: *Potential Energy Surfaces of Nucleotide-Sugars. Ab-Initio Calculations, Force-Field Parametrization and Exploration of the Flexibility.* J. Am. Chem. Soc. (in press).

Glycosyl esters of nucleoside di- or mono-phosphates, generally referred to as "sugar nucleotides", serve as a sugar donor during the biosynthesis of oligo- and polysaccharides. Therefore, they are of primary importance in carbohydrate metabolism in the living world. Not only the molecules themselves, but especially their complexes with proteins are of interest in structural glycobiology. For computational studies on these molecules, it is necessary to have access to empirical methods with appropriate force field parameterization. In this work, we propose a set of parameters, developed using ab-initio calculations with 6–31G* basis set at the SCF level on model compounds, for the commonly used AMBER force field. By implementation of the new parameter set together with the CICADA conformational search program, we have obtained a semi-quantitative description of conformational space, showing that nucleotide sugars can adopt several conformational families. The majority of them exhibit a "folded" rather than "extended" geometry due to frequent intramolecular hydrogen bonds and "stacking" interaction between the base and the six-membered sugar ring. For the seek of comparison, two molecular dynamics simulations were run in explicit water environment. The first simulation (3 ns) started with the semi-extended X-ray geometry and displayed major variations of all torsional angles, allowing for the visit of three conformational families. The second simulation (5 ns) started with the folded global minimum from the CICADA search. After about 3 s a transition for the ribose pucker yielded to the visit of a more extended conformational family. Experimental results show that in crystalline state, or in protein/carbohydrate complexes, extended conformations which are stabilized by interaction with surrounding molecules or with the protein surface, are more frequent.

[2] Štefl R., Fadrná, Koča J.: *Differences in Conformational Behavior of ATA and TAT Sequences in Single Strand DNA Trimers.* J. Biomol. Struct. Dyn. (in press).

The conformational behavior of single strand (ss) TAT and ATA trimers of DNA have been studied by computational chemistry tools including CICADA software interfaced with AMBER molecular mechanics and dynamics. The Single-Coordinate-Driving (SCD) method has been used in conjunction with molecular dynamics simulated annealing. It has been revealed that the conformational flexibility of each sequence differs substantially from the other one. Four common conformational families have been found for both trimers. These are: helical, reverse-stacked (base 3), half-stacked (base 3), reverse-stacked (base 1).However, the energies of conformers representing the families are different for both the studied systems. An additional conformational family, bulged, has been found for ss(ATA), while ss(TAT) has been found also in half-stacked (base 1) conformation. In general, ss(TAT) exhibits a higher number of low energy conformations while ss(ATA) shows one interesting low energy conformational interconversion between reverse-stacked (A3) family and half-stacked (A3) family. The high conformational variability of the trimers has been confirmed by flexibility analysis and by molecular dynamics simulations, which have also shown the conformational stability of single conformational families. It has been concluded that the methodology used is able to provide a very detailed picture of the conformational space of these molecules.

[3] Grůza J., Koča J., Pérez S., Imberty A.: *Comparison of Force-field Parametrizations as Applied to Conformational Analysis of Ribofuranosides.* J Mol. Struct (Theochem) **424**, 269–280 (1998).

The conformational behavior of Me-5-deoxy-α-D-ribofuranoside (1) and Me-5-deoxy-β-D-ribofuranoside (2) has been assessed through computations performed with the molecular mechanics programs MM3 using the flexible residue method and AMBER using the algorithm for conformational searches of the program CICADA. Both AMBER's native force field and all the known parameter sets for carbohydrates of the AMBER's force field were utilized. The results gained were completed and compared with ring shapes of D-ribofuranosides from ab initio calculations and from X–ray studies of D-ribofuranoside containing structures. While the production of apparently correct furanose models, which are thought to be even more flexible than pyranose rings, is a stringent test of the force fields in the modeling software, one can appreciate these results as a test of mean sugar parameter sets of program AMBER.

[4] Fadrná E., Koča J.: *A Combination of Driving Method with Simulated Annealing to Search Conformational Space.* J. Mol. Struct. (Theochem) **398–399**, 523-528 (1997).

A recently developed method to search conformational space has been tested on AUG trimer of RNA. The method is a combination of one coordinate driving approach with molecular dynamics simulated annealing. It is implemented in the new version of the program CICADA, which has been used in conjunction with the program AMBER, version 4.0. The results show, that all the combinatorially possible combinations of base orientations have been found (8 conformational families). Moreover, all basic interconversions have been detected except for one.

[5] Fadrná E., Koča J.: *Single-Coordinate-Driving Method Combined with Simulated Annealing. An Efficient Tool to Search Conformational Space.* J. Phys. Chem. B **101**, 7863–7868 (1997).

A single strand AUG RNA trimer has been studied by computational tools using a single internal coordinate driving method incorporated in the CICADA program interfaced with AMBER molecular mechanics. CICADA previously appearing a good tool for the global description of the small and middle–sized flexible organic molecules conformational space, failed in this particular case, giving a global minimum of 10 kcal/mol worse than molecular dynamics. We then combined the single–coordinate–driving method with simulated annealing, obtaining a global minimum substantially better than that from both CICADA and molecular dynamics. In addition, an interconversion path between both minima has been revealed. The new global minimum exhibits violation of stacking at the G terminal as reported in the experimental data. In comparison with the data obtained by other methods and reported in literature the new method yields more complete results. Additionally, the new method is able to find pathways of conformational interconversions connecting distant parts of the conformational space. The method is now implemented in the updated version of the CICADA program. The results have confirmed that even the PES of such a relatively small molecule exhibits a large amount of local minima, and that a clustering of the minima into conformational families appears necessary.

[6] Fadrná E., Koča J.: *CICADA Interface with AMBER. An Application on Oligonucleotides and their Fragments.* J. Biomol. Struct. Dynam. **14**, 137–152 (1996).

The potential energy hypersurfaces (PES) of several nucleotide fragments were analysed by the conformational search algorithm CICADA interfaced with the molecular mechanics program AMBER, version 4.0. The low energy conformers for dimethylphosphate,dinucleoside monophosphate fragments, and deoxyadenosine are described. Calculated relative and absolute flexibilities of single conformers, molecular fragments as well as entire molecules are introduced. The comparison of the results with the literature data shows good ability of the CICADA-AMBER combination to describe conformational space. It is revealed that the number of low energy conformers as well as flexibility decreases as the size of the molecule increases. The conformational behavior of freely rotatable single bonds, specially those within a sugar ring, is more “sharp” in larger structures.

[7] Kříž Z., Koča J., Carlsen P.H.J.: *Conformational behavior and flexibility of terminally blocked cysteine and cystine.* J. Mol. Mod. **2**, 51–61 (1996).

Conformational potential energy hypersurface, PES, for the terminally blocked L-Cysteine, L,L-Cystine and D,L-Cystine have been analyzed by means of molecular mechanics method in combination with the programs ROSE, CICADA, PANIC and COMBINE. Low energy conformations and conformational transitions, conformational channels, have been located. Global and fragmental flexibility and conformational softness have been calculated for each conformer as well as the entire molecule. The PES analyses were used for simulation of conformational movement based on Boltzmann probability of the obtained points on the PES. The Boltzmann travelling revealed interesting correlated conformational movement where three or even more dihedral angles changed simultaneously. It was shown that conformational behavior and flexibility were strongly influenced by the absolute configurations of amino acids in the peptides.

[8] Koča J.: *Computer Simulation of Conformational Movement Based on Interconversion Phenomena.* J. Mol. Struct. **343**, 125–132 (1995).

A computer method has been developed which is an alternative to molecular dynamics in the sense that it pictures conformational motion. It simulates propagation in conformational movement based on conformational interconversion phenomena. The method starts with the knowledge of the topology of the conformational potential energy hyper-surface, which is described by the minima and the transition states. The topology is obtained by the recently described software CICADA. The simulation of conformational motion is based on the Boltzmann statistics of movement between the minima and the transition states at a given temperature. The method is illustrated for methyl-α-glucopyranoside and α-D-gal$N$Ac(1–3)[α-L-Fuc(1-2)]Gal-O-Me molecules. Conformational transitions of hydroxyl groups as well as glycosidic linkages are discussed.

Papers submitted for publication in scientific journals

[1] Koča J., Ludin M., Pérez A., Imberty A.: *Single-Coordinate-Driving Method in Molecular Docking.* J. Comput. Chem. (submitted).

An extension of the computer program CICADA has been developed which allows us to use the Single-Coordinate-Driving (SCD) method in flexible molecular docking. The docking procedure is a composition of three independent space rotations, three independent translations and all the torsions which are selected by the user. One of the above parameters is driven and all the remaining coordinates are relaxed. Such a procedure follows low energy wells on the potential energy surface of the entire system. The program allows us to dock more than one ligand molecule into the receptor. We have run two test examples, docking the N,N-dimethylformamide into the alpha-cyclodextrin and docking the R-phenoxypropionic acid into the beta-cyclodextrin. The test examples show that the SCD approach is able to overcome high energy barriers and to cover the entire box within which the search is performed. The limitations of molecular dynamics docking in comparison with our approach are also shown in the paper. The philosophy of the newly developed approach is not only to find the best dock for the receptor-ligand(s) system, but rather to describe all the important binding modes and give a good starting point for studying the dynamics within the cavity during the docking process.

[2] Kříž Z., Carlsen P.H.J., Koča J.: *Conformational Features of Linear and Cyclic Enkephalins. A Computational Study.* J. Comp-Aided Mol. Design (submitted).

A theoretical conformational study using the CICADA program package (J. Mol. Struct. (Theochem), 1995, 337, 17–24) was performed for two linear enkephalins, Leu-enkephalin and Met-enkephalin, and two cyclic analogues, DLFE and DPDPE. The conformational flexibilities of whole molecules and selected torsions were calculated.
The low energy conformers obtained were compared with structures obtained by spectroscopic methods. The mutual space positions of key elements for receptor recognition were analysed. Conformations were clustered using RMS deviation computed for selected atoms. The different conformational behavior of aromatic rings in cyclic analogues of enkephalins was observed. While aromatic rings of cyclic analogues exhibit different conformational behavior, the linear enkephalins show similar behavior in these key parts.
Hydrogen bonds predicted by spectroscopic measurements were confirmed by our calculations. Also very specific conformational features, like concerted conformational movement, were analysed.

[3] Petrová P., Koča J., Imberty A.: *Effect of Cation Concentration on Molecular Dynamics Simulations of UDP-glucose.* Mol. Simul. (submitted).

Glycosyl esters of nucleoside di or mono-phosphates, generally referred to as “sugar nucleotides”, serve as a sugar donors during the biosynthesis of oligo- and polysaccharides; they are therefore of a primary importance in carbohydrate metabolism in the living world. Molecular dynamics simulations were used to explore the conformational flexibility of one nucleotide sugar, UDP-glucose (UDP-Glc). The AMBER program package was used with some new parameters especially developed for nucleotide sugars. Several simulations on this molecule in aqueous solution, each of 2 ns duration, were carried out for increasing concentrations of monovalent K+ and divalent Mg2+ ions. For the monovalent ion, it is revealed that its presence and concentration is crucial for the conformational behavior, resulting in the stabilization of the extended conformation. The preferred location of K+ is in close proximity to the negatively charged phosphate oxygens, but the ion moves freely and can occupy other sites. Since the size of this cation is close to the one of the water molecules, the hydration scheme is not perturbed. Completely different results are obtained when the divalent Mg2+ cation is introduced in the simulation. A very strong interaction is established between the phosphate group and the cation; as a result the UDP-Glc molecule is locked in a rigid extended geometry. The analyses of the trajectories provide new insight on the role of the metal ion in the catalytic mechanism of glycosyltransferases.

[4] Štefl R., Koča J.: *Unrestrained Molecular Dynamics Simulations of* $d(AT_5)_2$ *Duplex in Aqueous Solution: Hydration and Sodium Ions Binding in the Minor Groove* (submitted).

This paper describes the results of unrestrained molecular dynamics simulations of the [d(AT)5]2 duplex decamer in aqueous solution, with a sufficient number of sodium ions to provide electroneutrality to the system. Two 5ns trajectories starting from the A and B canonical forms were carried out using the Cornell et al. force field and the particle mesh-Ewald technique for electrostatic interactions. Both trajectories converged within about 500ps and produced stable and similar conformational ensembles, which exhibit qualitative features of B-DNA, as judged by root mean square deviations and helicoidal analysis. We also focused on the analysis of the structure and dynamics of the "spine molecules" (sodium ions and water molecules interact in specific sites of the minor groove). We observed that different parts of the primary and secondary layers of the "spine of hydration" were distinctly occupied by sodium ions and by water molecules. The occupancy by the sodium ions in the primary spine is exclusively observed in the ApT steps (with the residence times about 1–2 ns). The sodium ions are coordinated by the electronegative potential of O2 atoms from thymines, which induces strong decreasing of the propeller twist to very low negative values. This decrease is supported also by the repulsion between the sodium ion and H2 atoms of adenines. The uniquely low electrostatic potential of ApT steps is confirmed by additional calculations described here, based on continuum electrostatics and ab initio calculations. It was observed in our simulations that neither sodium ions nor sequence induce bending of the studied non-A-tract. We also find no evidence for the significant narrowing of the minor groove.

Contributions on scientific meetings

[1] Fadrná E., Koča J.: *Konformační chování krátkých oligonukleotidů – počítačové studium.* XXIII. Konference organických chemiků. Litomyšl, 1998

[2] Grůza J., Koča J., Imberty A.: *Conformational Analysis of Protein-Carbohydrate Interactions in Lathyrus Ochrus Isolectin II Complexed with a Fucosylated Bianten-*

nary N-glycan. The Second Electronic Molecular Graphics and Modelling Conference (MGM EC-2).

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[4] Fadrná E., Koča J.: *A Detailed Analysis of Conformational Behavior of AAA RNA Trimer Using Computational Chemistry Tools.* The 3-rd Canadian Computational Chemistry Conference, July 19–23, 1997. Edmonton, Alberta, Canada.

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[7] Koča J., Fadrná E.: *Single-coordinate-driving approach combined with simulated annealing: Tool to describe conformational behavior of flexible molecules.* 214$^{\text{th}}$ ACS Natl. Meeting, Sept 7–11, 1997, Las Vegas, Nevada, USA.

[8] Fadrná E., Koča J.: *A Combination of Driving Method with Simulated Annealing to Search Conformational Space.* Fourth World Congress of Theoretically Oriented Chemists-WATOC '96, Jerusalem 1996.

[9] Fadrná E., Koča J.: *Computer Study of Conformational Behavior of RNA Trimers.* Advances in Organic and Bioorganic Chemistry, Liblice 1996 in Czech.

[10] Grůza J., Koča J., Pérez S., Imberty A.: *A Comparison of Various Parametrizations of Carbohydrates of AMBER Molecular Mechanics. A Test of Ribofuranoside Conformations.* Fourth World Congress of Theoretically Oriented Chemists-WATOC '96, Jerusalem 1996.

[11] Koča J., Fadrná E.: *Traveling Through Conformational Space of Biomolecules Using Simulated Annealing.* Advances in Organic and Bioorganic Chemistry, Liblice 1996 in Czech.

[12] Kříž Z., Koča J., Carlsen P.H.J.: *A Detailed Description of Conformational Space of Mative Enkephalines and Their Cyclic Analogues.* Fourth World Congress of Theoretically Oriented Chemists-WATOC '96, Jerusalem 1996.

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[17] Kříž Z., Koča J., Carlsen P.H.J.: *Comparison of conformational behavior of open chain and cyclic enkephalines.* Conference on Molecular Structural Biology, Vienna, Sep 17–20, 1995.

3. Structure and dynamics study of supramolecular complexes

Structure and dynamics of supramolecules are solved by combining theoretical and modeling techniques. Properties of experimentally prepared amides and calix[n]arenes and their complexes with anions are studied by molecular modeling methods. The aim of this project is to design ligands with defined specifity to include anions.

People involved: Čajan M., Koča J.

Used programs

- *Application software installed in METACenter:* Gaussian94, Spartan4.0.0, Biosym/MSI (InsightII, Discover 2.9.8/96.0/4.0.0, Turbomole 95.0/3.0.0)

Published papers in scientific journals and papers in press

[1] Čajan M., Stibor I., Koča J.: *Computational Studies on the Stability of* [Amide]Br^- *Complexes.* J. Phys. Chem. (in press).

Theoretical studies on supramolecules have provided insight into their structure as well as their electronic distribution. While a number of such studies are found in the literature for neutral or cationic receptors, much less is known about anionic systems. Recently we have published (Stibor, I.; Haffed, D. S. M.; Lhoták, P.; Hodačová, J.; Koča, J.; Čajan M. Gazz. Chim. Ital. 1997, 127, 673) a study of amide bond activation for anion complexation where association constants were measured. In this paper, we present the results of calculations on single amides substituted on both sides of the amidic bond by an aromatic group with different substituents, as well as their complexes with anions using different methods of energy calculations. It is revealed, that: i) Only DFT methods give realistic results while neither semiempirical quantum chemistry nor molecular mechanics CVFF force field give a realistic insight; ii) The ligands (amides) themselves exhibit a different scale of non-planarity which is caused by the repulsion between the ortho-substituents of the aromatic moieties and oxygen atom of the amidic group; iii) The stability of the complexes is mainly correlated to three factors: the length of the hydrogen bond between the anion and amidic hydrogen, the interaction energy for the calculated complex, and the charge on the bromine atom within the complex.

Contributions on scientific meetings

[1] Čajan M., Damborský J., Koča J., Stibor I.: *QSPR modelování stability komplexů* [Amid]Br^-, 33. Konference “Pokroky v organické chemii a biochemii” Liblice, Česká Republika, 16.–18.11. 1998. Abstrakt: Chemické listy 92, 1998, str. 948.

[2] Čajan M, Stibor I., Koča J.: *Computational Studies on* [Amide]Br^- *Complexes,* X. Conference of Young Scientists on Organic Chemistry and Biochemistry, Liblice, Czech Republic,15.–20. 6. 1998. Abstract 18, p. 59.

[3] Hodačová J., Hafeed D.S.M., Dvořáková H., Koča J., Čajan M., Stibor I.: *Fluorinated amides: A novel class of neutral anion receptors.* 214th ACS Natl. Meeting, Sept 7–11, 1997, Las Vegas, Nevada, USA.

4. Protein engineering of enzymes involved in biodegradation reactions

A project of the application of molecular modeling techniques to proteins and protein engineering is focused on understanding of a catalytic mechanism and a rational re-design of haloalkane dehalogenases enzymes. The molecular modeling methods may assist in design and planning of the directed-mutagenesis experiments leading towards construction of the enzymes with enhanced catalytic activity or broadened substrate specificity.

The primary targets of our interests are the enzymes involved in detoxification of xenobiotic compounds, in particular the enzymes catalyzing dehalogenation reactions. These enzymes have a potential application for the treatment of waste water and a soil contaminated with halogenated aliphatic compounds. In addition, evolutionary events occurring in the enzymes during the adaptation to the new substrates at a molecular level are being investigated.

Hydrolytic dehalogenation of unsaturated halogenated aliphatic hydrocarbons has been studied in the project focused on Quantitative Structure-Biodegradability Relationships. Kinetic constants were determined experimentally for 21 substrates and molecular descriptors were derived using quantum-chemical calculations. Statistically significant QSBR model was constructed using Partial Least-Squares Projection to Latent Structures (PLS) method. Structural parameters determining the degradation rates were determined. Quantum-chemical study of dehalogenation reaction catalysed by haloalkane dehalogenase was completed. Semi-empirical AM1 method was used to map the reaction co-ordinate of the 2nd and the 3rd reaction step. Determination of the activation barriers for all the three reaction steps enabled us to identify the rate-limiting step of the dehalogenation reaction. The project focused on protein engineering of haloalkane dehalogenases was initiated. The 3D model of the haloalkane dehalogenase LinB was constructed. The location of the catalytic residues was predicted using this model. Mutant proteins carrying substitutions in the catalytic triad were constructed, purified and tested in collaboration with the University of Tokyo. Reaction mechanism of the haloalkane dehalogenase LinB was established from the results of mutagenesis.

People involved: Boháč M., Damborský J., Hynková K., Koča J., Kutý M., Prokop M.,

Used programs

- *Application software installed in METACenter:* MOPAC, Biosym/MSI (InsightII, Discover, Turbomole)
- *Local software developed in LSDBio:* Triton
- *Software developed outside LSDBio:* Simca-S, Modeller

Published papers in scientific journals and papers in press

[1] Hynková, K., Nagata, Y., Takagi, M., Damborský, J.: *Identification of the Catalytic Triad in the Haloalkane Dehalogenase from Sphingomonas paucimobilis UT26.* FEBS Letters **446**, 177–181 (1999).

The haloalkane dehalogenase from Sphingomonas paucimobilis UT26 (LinB) is the enzyme involved in the gamma-hexachlorocyclohexane degradation. This enzyme hydrolyses a broad range of halogenated aliphatic compounds, ia an alkyl-enzyme intermediate. LinB is believed to belong to the family of alpha/beta-hydrolases which employ a catalytic triad, i.e. nucleophile-histidine-acid, during the catalytic reaction, The position of the catalytic triad within the sequence of LinB was probed by a site-directed mutagenesis. The catalytic triad residues of the haloalkane dehalogenase LinB are proposed to be D108, H272 and E132. The topological location of the catalytic acid (E132) is after the beta-strand six which corresponds to the location of catalytic acid in the pancreatic lipase, but not in the haloalkane dehalogenase of Xanthobacter autotrophicus GJ10 which contains the catalytic acid after the beta-strand seven.

[2] Damborský, J.: *Computer Modelling of Microbial Hydrolytic Dehalogenation.* Pure and Applied Chemistry **70**, 1375–1383 (1998).

The biodegradation of organic compounds by microorganisms is an intrinsically complex process. A large number of sub-processes, like penetration of the compounds to the cells, biochemical catalysis and the release of products are taking place during the biodegradation. The separation of these sub-processes from each other and their detailed study is needed for a better understanding of the basic mechanisms of microbial degradation and for the improvement of bioremediation technologies by means of the construction of a new efficient biocatalyst. This contribution attempts to view the biodegradation reaction — hydrolytic dehalogenation — at the level of catalysing biomolecules. Computer modeling is used to extend the knowledge obtained from X–ray analysis, kinetic measurements and site-directed mutagenesis experiments. Among the issues discussed in this article are the determination of the rate–limiting step of the biodegradation reaction, the identification of the active–site amino acids involved in the reaction mechanism, the prediction of proteins' modifications leading to higher activity and the molecular mechanisms of the adaptation of bacteria for the degradation of xenobiotic compounds.

[3] Damborský, J.: *Quantitative Structure-Function and Structure-Stability Relationships of Purposely Modified Proteins.* Protein Engineering **11**, 21–30 (1998).

Quantitative structure-function relationships (QSFR) and quantitative structure-stability relationships (QSSR) analyses are described here. The objective of these analyses is to investigate and quantitatively describe the effect of the changes in structure of protein on its function or stability. During the analysis, the structural and physico-chemical properties of the amino acid residues are related to activity or stability data derived for the group of proteins containing systematic substitutions at certain positions. Four examples of the application of these analyses on the data obtained with proteins modified by site-directed mutagenesis experiments are provided. Structure-function relationships were studied for 15 mutants in position 172 of the haloalkane dehalogenase and 19 mutants in position 222 of the subtilisin, while the structure-stability relationships were investigated for 13 mutants in position 157 of phage T4 lysozyme and 18 mutants in position 49 of alpha-submits tryptophan synthase. A total of 402 molecular descriptors derived from AAindex database were used to quantify amino acid properties and the multivariate statistical technique–partial least squares projections to latent structures–was used to identify those of them which are important for explanation of the activity and stability data. Quantitative models were developed and internally validated for every data set. The possibilities for further development of both analyses and their application for predictive and analytical purposes in protein engineering research are discussed.

[4] Damborský, J., Berglund, A., Kutý, M., Ansorgová, A., Nagata, Y. and Sjöström, M.: *Mechanism-based Quantitative Structure-biodegradability Relationships for Hydrolytic Dehalogenation of Chloro- and Bromoalkenes.* Quantitative Structure-Activity Relationships **17**, 450–458 (1998).

Quantitative Structure-Biodegradability Relationships (QSBRs) have been developed for microbial hydrolytic dehalogenation of small chlorinated and brominated alkenes. Two different reaction mechanisms, S(N)2 and S(N)2', were considered for the dehalogenation of small haloalkenes by hydrolytic dehalogenases. Multivariate QSBRs based on quantum-chemically calculated descriptors were used to distinguish between these dehalogenation mechanisms. A QSBR based on atom valence and partial atomic charge on electrophilic site, together with the energy of the lowest unoccupied molecular orbital, molecular weight and dipole moment were able to explain 92% (81% cross-validated) of the quantitative variance in the dehalogenation rates. This QSBR supported a S(N)2 reaction mechanism. This reaction mechanism was also confirmed by GC-MS identification of the reaction products for the compounds which should give discriminating reaction products depending on mechanism. The substrate specificity of hydrolytic dehalogenases for unsaturated halogenated; substrates is discussed in the light of chemical structure and properties of the substrate molecules.

[5] Damborský, J., Lynam, M. and Kutý, M.: *Structure-Biodegradability Relationships for Chlorinated Dibenzo-p-dioxins and Dibenzofurans.* In. R.-M. Wittich (Ed.), Biodegradation of Dioxins and Furans, R.G. Landes Bioscience Publishers, Austin, pp. 165–228 (1998).

Biotransformation and biodegradation of chemical compounds are the major processes which determine the fate of organic compounds in aquatic and terrestrial environments. An understanding of biodegradation mechanisms and identification of factors which limit the biodegradation rates is desirable for the development of bioremediation technologies suitable for clean-up of contaminated soil and water. Practical examples from statistical design of optimal testing sets of compounds, and structure–biodegradability analysis of aerobic and anaerobic degradation of chlorinated dibenzo-p-dioxins and dibenzofurans will be provided.

[6] Damborský J., Boháč M., Prokop M., Kutý M, Koča J.: *Computational Site-directed Mutagenesis of Haloalkane Dehalogenase in Position 172.* Protein. Eng. **11**, 901–907 (1998).

The application of molecular modeling and quantum-chemistry calculations for the computational site-directed mutagenesis of haloalkane dehalogenase is described in this contribution. The exhaustive set of single point mutants of haloalkane dehalogenase in position 172 was constructed by homology modeling. The ability of substituting residues to stabilize the halide ion formed during the dehalogenation reaction in the enzyme active site was probed by quantum-chemical calculations. A simplified modeling procedure was adopted to obtain informative results on the potential activity of mutant proteins in a sufficiently short period of time, which could be in the future applicable for making bona fide predictions of mutants' activity prior to their preparation in the laboratory. The reaction pathways for the carbon-halide bond cleavage were calculated using microscopic models of wild type and mutant proteins. The theoretical parameters derived from the calculation, i.e. relative energies and selected atomic charges of educt, product and transition state structures, were statistically correlated with experimentally determined activities. The charge difference of educt and product on the halide-stabilizing hydrogen atom of residue 172 was the best parameter to distinguish protein variants with a high activity from mutant proteins displaying a low activity. All mutants with significant activity in the experiment were found to have this parameter one order of magnitude higher than mutants with low activity. The results obtained are discussed in the light of the practical application of this methodology for the prediction of potentially active protein variants. Further automation of the modeling procedure is suggested for combinatorial screening of the large number of protein variants. Coupling of the dehalogenation reaction with hydrogenation of the halide ion formed during the reaction in the enzyme active site was proposed as a possible way to improve the catalytic activity of the haloalkane dehalogenase of Xanthobacter autotrophicus GJ10.

[7] Kutý M., Damborský J., Prokop M., Koča J.: *A Molecular Modeling Study of the Catalytic Mechanism of Haloalkane Dehalogenase: 2. Quantum Chemical Study of Complete Reaction Mechanism.* J. Chem. Inf. Comp. Sci. **38**, 736–741 (1998).

Haloalkane dehalogenase is a bacterial enzyme, which catalyses hydrolytic cleavage of the carbon-halogen bond of haloalkanes. Quantum mechanical calculations at the semi-empirical level using the MOPAC/DRIVER methodology were applied to study the enzymatic hydrolysis of 1,2-dichloroethane to 2-chloroethanol. In our previous study, the first SN2 step of dehalogenation reaction was investigated (Damborský, J.; Kutý, M.; Němec, M.; Koča, J. A Molecular Modeling Study of the Catalytic Mechanism of Haloalkane Dehalogenase: 1. Quantum Chemical Study of the First Reaction Step. J. Chem. Inf. Comput. Sci. 1997, 37, 562–568). The present contribution explores the complete three-step reaction to determine the rate-limiting reaction step and to investigate the importance of active site residues for the kinetics and thermodynamics of the hydrolysis. The nucleophilic addition (AdN) step has the highest energy barrier, which is in qualitative agreement with experimental rates, assigning the second hydrolytic step as the rate-limiting one. In order to establish the catalytically important active-site residues, Mulliken charges of selected active-site atoms were monitored along the reaction pathway. A significant change in charges on the hydrogen atoms of Trp125, Trp175 and Phe172 active-site residues was observed. These residues interact with the halide ion released during the SN2 step. Changes in charges on the hydrogen atoms of Trp125 and Glu56 prove the significance of those residues in the stabilization of the partial charge developed on the oxygen atom of the nucleophilic aspartate (Asp124). The same methodology confirmed the importance of the charge relay system (Asp124, His289 and Asp260 residues) in the base-hydrolysis reaction (AdN step).

[8] Lynam M.M., Kutý M., Damborský J., Koča J., Adriaens P.: *Molecular Orbital Calculations to Probe Mechanism of Reductive Dechlorination of Polychlorinated Dioxins.* Environ. Toxicol. Chem. **17**, 988–997 (1998).

Ab initio Restricted Hartree Fock (RHF) and Density Functional Theory (DFT) as well as semiempirical Austin Model 1 (AM1) and Parametrization Method 3 (PM3) molecular orbital calculations were carried out for a range of chlorinated dioxin molecules to obtain molecular descriptors such as HOMO-LUMO gaps (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) and partial atomic charges. The HOMO-LUMO gap is an indicator of stability in a molecule: the larger the gap the greater the stability of the molecule toward further reaction. These calculations indicate that with increasing extent of chlorination, the gap decreases . The observed charge pattern shows that carbon atoms in the peri (1,4,6,9) ring positions have a partial negative charge while those in the lateral (2,3,7,8) position have a partial positive or small partial negative charge. The descriptors, from the more precise Density Functional Theory (DFT) Method, were used to rationalize experimental observations of dechlorination of dioxins. Reductive dechlorination pathways from two different experimental studies were examined using partial charges and estimated Gibbs free energy of dechlorination. For both sets of data, highly thermodynamically favorable and less thermodynamically favorable pathways were observed. It was observed for a given chlorinated dioxin, when more than one degradation pathway was possible, that dechlorination in the most thermodynamically favored pathway occurs at the most positively charged carbon atom in the ring which was usually a lateral carbon atom. These results are discussed in light of a possible mechanism for reductive dechlorination.

[9] Damborský J., Kutý M., Němec M., Koča J.: *A Molecular Modeling Study of the Catalytic Mechanism of Haloalkane Dehalogenase: Quantum Chemical Study of the First Reaction Step.* J.Chem.Inf.Comp.Sci. **37**, 562–568 (1997).

The haloalkane dehalogenase of soil bacteria Xanthobacter autotrophicus is an enzyme, which catalyses the environmentally important detoxification process, namely

- the hydrolytic cleavage of the carbon-halogen bond. A molecular modeling study has been conducted with the structures of the wild type enzyme and its mutants in order to investigate the mechanisms of the dehalogenation reaction at molecular level. Semi-empirical quantum chemical calculations have been applied to elucidate the importance of the active site residues for kinetic and thermodynamic characteristics in the first step of dehalogenation reaction. The results obtained from these calculations have been compared with previously published experimental results. The strength of the application of molecular modeling method for the study of the evolutionary aspects of biodegradation of organic pollutants is discussed.

Contributions on scientific meetings

[1] Damborský, J., Koča, J.: *Computer-Assisted Re-Design of Enzymes for Degradation of Xenobiotic Compounds.* Biosorption and Bioremediation II. July 12–17, 1998; Prague, Czech Republic.

[2] Damborský J., Kutý M., Boháč M., Koča J.: *Can we Improve Degradation of 1,2-dichlorethane by the Methods of Protein Engineering?.* Minisymposium about Biosorptions and Microbial Degradations (in Czech). Prague, Nov 24–28, 1997.

[3] Damborský, J., Kutý, M., Koča, J., Němec, M., Holoubek, I.: *How do microbes degrade chemicals?.* 7th Annual Meeting of SETAC-Europe, Amsterdam, The Netherlands, April 6–10 (1997).

[4] Damborský J., Kutý M., Koča J., Němec M., Holoubek I.: *Molecular Modeling: A Tool for Studying Mechanisms of Microbial Degradation and Development of QSBRs.* 7th International Workshop on QSARs in Environmental Science, Copenhagen, June 24–28, 1996.

[5] Kutý M., Damborský J., Koča J.: *A Contribution to Study the Mechanism of Enzymatic Dehalogenation by Molecular Modeling.* Advances in Organic and Bioorganic Chemistry, Liblice 1996 in Czech.

[6] Kutý M., Damborský J., Koča J.: *Quantum Chemical Study of the First Reaction Step of the Dehalogenation Enzymatic Reaction.* Fourth World Congress of Theoretically Oriented Chemists-WATOC '96, Jerusalem 1996.

[7] Damborský J., Kutý M., Němec M., Koča J., Holoubek I.: *Modelování vztahu mezi strukturou a degradabilitou halogenovaných alkanů.* Tomáškovy dny '95, červen 1995.

[8] Damborský J., Manová K., Kutý M., Němec M., Koča J.: *Mikrobiální degradace cizorodých látek v prostředí.* 20. kongres Československé spol. mikrobiologické, 18–21.9.1995, Ostrava.

[9] Damborský J., Manová K., Kutý M., Němec M., Koča J., Holoubek I.: *Modelování a predikce biodegradability organických látek.* Toxicita a biodegradabilita odpadů a látek významných ve vodním prostředí. Milenovice 1995.

Determination of Parameters of K Giants Atmosphere

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Abstract. The determination of the atmosphere parameters of stars is one of important problems of modern astrophysics. One of the most accurate methods is model atmosphere method, i.e. the computation of the theoretical (synthetic) spectrum using suitable model atmosphere.

The synthetic spectrum is computed using the model atmosphere, i.e. the dependence of the important physical parameters (density, temperature, electron density, eventually occupation of the most important energy levels of atoms and ions) on the atmosphere depth. The most appropriate program for the calculation of model atmosphere of late type K giants is Kurucz's program ATLAS9 [2, 3]. One of its advantages is involving of large number of opacity sources, more than 58 million line transitions, which is important for cool stars.

The program SYNSPEC36 [1] computes the synthetic spectrum from the model atmosphere in the given wavelength interval. Accurate values of constants describing each line (mainly wavelengths, oscillator strengths, energy levels and damping parameters) are necessary to obtain a good fit of the observed spectrum. That is why we utilized the VALD database [4].

The computation of atmosphere parameters of stars (i.e. effective temperature, surface gravity and chemical composition) is minimization of the differences between observed and synthetic spectrum by changing of the atmosphere parameters. For an example of the minimization results for star α Ari see fig. 1.

The method was discussed and first results for four K giants were given in the proceedings of the Czech and Slovak conference [5] and in the European journal in the paper [7]. These results were included in the diploma thesis [6] too. Moreover, we have calculated atmosphere parameters of more than 100 K giants and paper is now prepared [8].

The all computation are computer time consuming task. Consequently, an minimization used to match the observed spectra is highly exacting also. Moreover, a huge amount of the dates (characterising atomic and molecular lines) for such a computation are necessary. We acknowledge the Brno Supercomputing Center for kindly provided computer time and disk space, which enabled such an extensive computation.

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[1] `http://www.physics.muni.cz/~krticka`

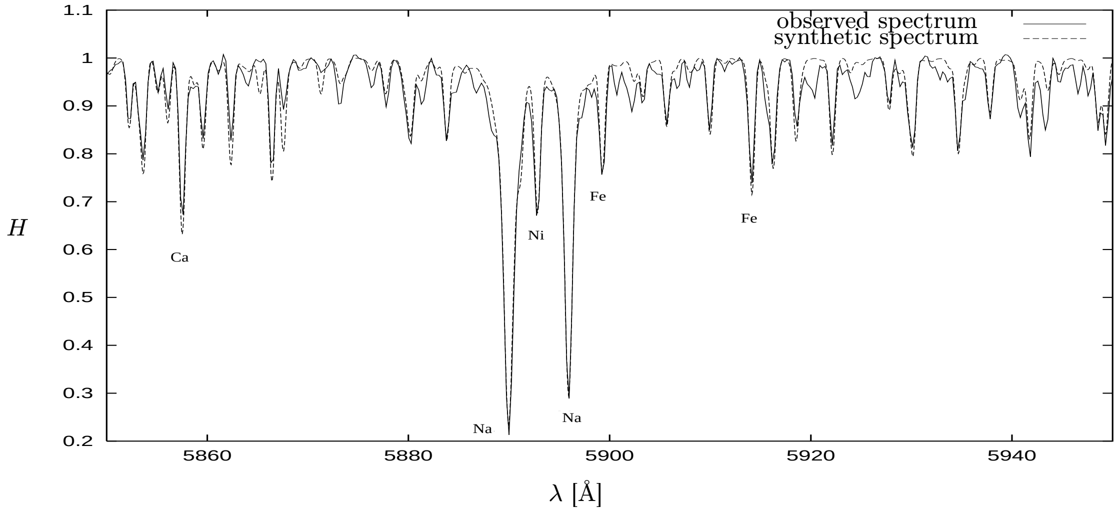

Figure 1: Comparison of the observed (solid line) an synthetic (dashed line) spectra of α Ari in the region of well-known sodium doublet. The graph shows the dependence of the relative flux H (y-axis) on the wavelength (x-axis). Selected lines are identified. From [7].

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[2] Kurucz R. L., The Stellar Populations of Galaxies, IAU symp. 149, Kluwer Acad. Press 1992.

[3] Kurucz R. L., 1993, CD-ROM No. 18:ATLAS9 Stellar Atmosphere Programs and 2 km/s Grid.

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Publications prepared with the use of *METACenter*

[5] Krtička J., Proceedings of Czech and Slovak Conference on Stellar Astronomy, p. 73, Brno 1998.

[6] Krtička J., Diploma thesis, Faculty of Science, Masaryk University, Brno 1998.

[7] Krtička J., Štefl V., 1999, A&AS 138, p. 47.

[8] Krtička J., Štefl V., 1999, in preparation.

Bromo- and Imidosubstituted Benzosemiquinones

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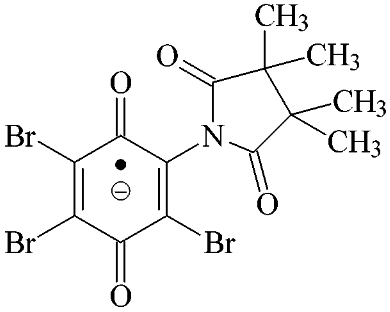
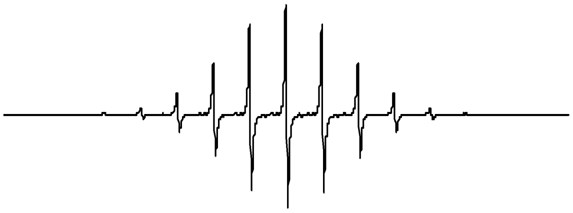
The problems connected with both *p*-benzosemiquinone derivatives and non-substituted *p*-benzoquinone have been of particular interest in the last decade due to importance of these compounds in the electron transport in biological systems. Quinones are dicarbonyle compounds derived from aromatic hydrocarbons having an unsaturated conjugated chinoidic structure. These compounds are suitable for being studied with density functional theory (DFT) methods of quantum chemistry whose applications are objects of increasing interest. Quinones are not typical carbonyle compounds due to conjugation of C=O bond with C=C bond.



The goal of this work was to describe the redox behavior of chosen *p*-benzoquinone derivatives by cyclic voltammetry and measure the electron paramagnetic resonance spectra (EPR) hyperfine structure (HFS) of electrolytically generated semiquinones. The hyperfine structure of experimentally measured EPR spectra was compared to calculated values of hyperfine structure splitting constants obtained from spin densities calculation using DFT-based quantum chemical methods. The calculation also provides electron affinity values of given quinones.The methods described above were applied to all brominated and methylated derivatives of *p*-benzoquinone. Moreover synthetic techniques applied led to some new derivatives where the bromine atom was substituted by tetramethylsuccinimidyle and to other ones that were partially methylated and partially brominated.

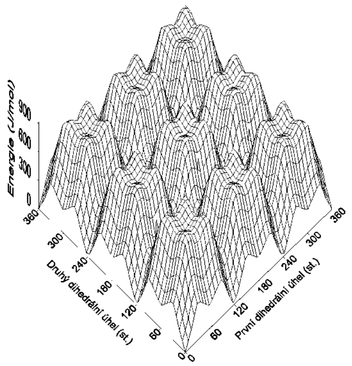
The basic process for EPR study of radical elements is the reduction of quinone, that proceeds via two single electron transfer steps in an alcaline and an aprotic environment. The first step led to the formation of semiquinone, a relatively stable and intensively colored π-electron radical anion. It is possible to study semiquinones electrochemically by cyclic voltammetry. Moreover, since semiquinones are paramagnetic compounds, they can also be studied by EPR spectroscopy. Successively the semiquinone is transformed into an arenediole dianion by receiving another electron in the second step of the reduction.

In the quantum chemical part of my diploma work, DFT methods were applied in order to find parameters that can be compared to experimental features. The Gaussian 94 software package was used for this purpose. B3LYP, B3P86 and B3PW91 methods



were chosen for the calculation of the electron affinities and the splitting constants of EPR spectra HFS of particular derivatives. All these methods belong to hybrid methods which are characterized by better convergence and better description of HOMO-LUMO orbitals with respect to pure DFT methods.

Electron affinity is defined as the energy released when an electron is added to a neutral molecule and it is calculated as the energy difference between the neutral and radical anion form of the same molecule. It is also possible to use a second calculation method based on Koopman's theorem. According to this theorem the LUMO orbital energy in neutral molecule is the same as the electron affinity. The calculation of splitting constants of EPR spectra hyperfine structure is based on the possibility of obtaining spin density values for particular atoms as a result of geometric optimization of anion radical structures. The methyl group rotation in mono- and dimethyl-*p*-benzoquinone was investigated from the energy point of view together with its influence on spin density values and consequently on hydrogen atom splitting constants.



The result of this work is a theoretical description of redox and spectral characteristics of *p*-benzoquinone derivates, that is consistent with the experimental description.

- The following compounds were synthetised:
  - 2-methyl-1,4-benzoquinone,
  - 2,3,5-trimethyl-1,4-benzoquinone,
  - 2,3-dibrom-5,6-dimethyl-1,4-benzoquinone,
  - 2,3,5,6-tetramethyl-1,4-benzoquinone,
  - 2,3,5-tribrom-6-tetramethylsukcinimidyl-1,4-benzoquinone,
  - 2,5-dimethyl-3,6-dibrom-1,4-benzoquinone,
  - 2,5-dibrom-3,6-ditetramethylsukcinimidyl-1,4-benzoquinone
- The cyclic voltammetry curves for all compounds and the EPR spectra for their radical anions were measured. The EPR spectra were interpreted by means of computer simulations and their hyperfine structure was compared to the calculated splitting constants.
- The calculated electron affinities and splitting constants are consistent with the experimental data.
- The changes in molecular geometry after the reduction correlate well with the available literature data.

- The splitting constants of bromine atoms is not detectable in the hyperfine structure of EPR spectra.
- The redox potential of particular derivatives correlate well with the values of electron affinities.
- The attested theoretical dependence of the change in β-protons spin density values from an angle in the plane of the ring allows to calculate the hydrogen atom splitting constant in the methyl group as an average of three values obtained from a unique optimization of molecular geometry with neglecting weighting by energy.
- It is possible to determine that a certain method is suitable for a certain kind of problem from the following findings

$$\begin{array}{ccc} \text{B3LYP, B3PW91} & \Leftrightarrow & \text{EA} \\ \text{B3PW91} & \Leftrightarrow & \text{HJS EPR} \end{array}$$

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X-ray Structure Analysis of LinB — Haloalkane Hydrolytic Dehalogenase from *Sphingomonas paucimobilis* UT26

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Haloalkane hydrolytic dehalogenase LinB from *Sphingomonas paucimobilis* UT26 — one of enzymes involving in dechlorination of γ-hexachlorocyclohexane, a potent but also toxic halogenated organic insecticide — is the enzyme that is extensively studied by many different experimental and theoretical techniques at LBSD, Masaryk University Brno. The one of the methods is diffraction of X-ray by single crystals — the method with requirements not only for advanced experimental equipment but for powerful computers and fast graphic too.

The crystals of LinB belong to space group P21212 with unit-cell parameters $a = 50.29$, $b = 71.70$, $c = 72.73$ Å. We collected cryogenic ($T = 100.0$ K) data to 1.58 Å with wavelength $\lambda = 0.9420$ Åat the beam-line BL711, MAXII synchrotron in Lund [1].

The structure was solved by molecular replacement (AmoRe). Refinement of the structure was carried of consecutively by:

1. weighted automated refinement procedure (wARP),
2. maximum-likelihood method (REFMAC),
3. restrained weighted conjugate-gradient refinement on basis of F2 (SHELXL-97) in conjunction with interactive computer graphic (program O), to crystallographic R-factors R and Rfree of 15.2 % and 21.3 % for all experimental data and 14.8 % and 20.6 % for observed (F $> 4\ \sigma$(F)) reflections [2, 3].

The monomeric enzyme is a spherical molecule and is composed, alike as the other members of the protein superfamily of the α/β-hydrolases, to two domains. Domain I has α/β-type structure with central eight-stranded twisted β-sheet, domain II lies like a cap on top of domain I and consists mainly of α-helices.

The knowledge of the 3-D crystal structure of LinB — as we know, the first new protein structure determined by diffraction of X-ray in Czech Republic — will be used as input for consecutive molecular modeling with aim to understand and to modify or to improve catalytic properties of our enzyme. For purpose of detail location of LinB active site we performed another data collection, before it the LinB single crystal was soaked for four hours in reservoir liquor with 25 mM 1,3-dibromopropane (DBP) at 278 K. Soaking of the crystal in DBP solution had negligible effect on the cell parameters. We collected data synchrotron data at the beam-line BL711, MAXII (it was usable to 2.0 Å resolution) and we solved the structure. The results were surprising. Despite of short time of soaking, both Br atoms were released from DBP and we found in electron density only the final products of dehalogenation of DBP: one Br ion and OH-$(CH_2)_3$-OH chain close to the active site of the enzyme and the second Br ion, that was bounded at boundary of the protein.

Acknowledgment

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Theoretical Study of the Electronic Structure of Ordered Phases of Semiconductor Alloy $Ga_{0.5}In_{0.5}P$[*]

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The semiconductor alloy $Ga_{0.5}In_{0.5}P$ is used in optoelectronic devices operating in the visible spectral range. It is usually prepared in the form of a thin film grown on GaAs substrate. Since 1988, it is known that for some conditions of the epitaxial growth the films exhibit long range order: one set of atomic planes is predominantly occupied by In atoms, and the complementary set is predominantly occupied by Ga atoms. The above mentioned atomic planes can have one of the two crystallographic orientations $(\bar{1}11)$ and $(1\bar{1}1)$. Results of recent experiments indicate that for some growth conditions even more complex atomic arrangements appear: the structure can consist of alternating layers of the two orientations. In some layers the $(\bar{1}11)$ orientation prevails whereas the other layers exhibit the $(1\bar{1}1)$ type of ordering. The ordering results in another interesting phenomenon. The ordered alloy has a narrower excitation gap than the disordered one. It means that for a certain range of wavelengths the light is absorbed in the ordered phase whereas it penetrates the disordered one. Obviously, this phenomenon can have practical applications. However, the experimentally observed value of the band gap narrowing is much lower than that predicted in many theoretical studies.

We have investigated the stability of selected ordered phases using a semiempirical model and we have performed *ab initio* calculations of their band structure (excitation energies). For this purpose we have used the relativistic version of the linear muffin-tin orbital method. We have explained the reasons for the deviations from the simplest possible ordering. We have also shown that even a very low concentration of the defects—so called antiphase boundaries, i.e., boundaries between the regions exhibiting the $(\bar{1}11)$ orientation of the atomic planes and regions exhibiting the $(1\bar{1}1)$ ordering—causes a substantial widening of the fundamental band gap (excitation gap). The existence of antiphase boundaries has been proved in several experiments and the results of our study thus explain the discrepancy between the predicted (for perfectly ordered structure) and measured value of the band gap narrowing. The results of our study have been published in [1]. The band-structure computations were carried out at the Supercomputer centre in Brno.

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[*] Part of the research project “First-principles studies of the electronic structure of solids”

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Calculation of Electron Structure in Solid State Systems

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With the development of new computer technologies, extensive systems have become the subject of growing interest of computational physicists and chemists. Among them the solid state systems with translation periodicity are of special interest. Two distinct approaches based on the Hartree-Fock Hamiltonian are used in the calculations of the electron properties of solids: i) Crystal Orbital (CO) method and ii) methods based on a cluster model.

Crystal orbital method is formulated in the reciprocal crystal lattice that allows the use of the Bloch functions providing periodicity of an infinite crystal. The disadvantage of this approach is that, due to its numerical complexity, simplified types of Hamiltonian (e.g. Hubbard-type Hamiltonians, EHT Hamiltonian, the method of nearly free electrons, and similar types) are often used. Application of a complete Hartree-Fock Hamiltonian leads to further restriction limiting the number of atoms considered. This, in effect, causes the neglect of long-range order interactions that are, for many systems, important. Due to the aforementioned reasons, application of the ab initio method is restricted to relatively small bases as well as to limited spatial range of interactions and rather small number of **k**-points. These limitations, in general, may be too restrictive and do not allow proper description of the physical and chemical properties of more complex solid state materials.

The cluster model-based treatment represents the second approach to the electron structure calculations of solids. Within this approach, the solid state system is replaced by s cluster containing a finite number of atoms. In general, the bigger cluster considered in the calculations, the closer to the real values the calculated results are. However, due to numerical reasons, the calculations must be restricted to small clusters that, in turn, causes significant errors linked to the boundary effects (unsaturated bonds on the cluster boundaries). Our calculations show that the influence of the boundary effects are at unacceptable level even for clusters containing several hundreds of atoms.

An interesting approach for band structure calculations based on the cyclic — cluster model was formulated recently. This rather simple approach has been used for evaluation of chemisorption on boron nitride and graphite on the level of EHT and CNDO/2. We extended cyclic cluster method for general three dimensional problems and elaborate the program SOLID98 in the UNIX version as well as PC version.

The calculation procedure is formulated in a general way and leads to the use of complete Hartree-Fock Hamiltonian (with electron-electron interactions included) applicable on different levels such as ab initio, semiempirical, or DFT method. On the bases of quasi-relativistic INDO Hamiltonian, clusters containing many thousands of atoms have been studied.

Cluster Crystal Orbital Method

Cluster Crystal Orbital method uses the finite clusters containing tens of thousands of atoms. The use of extremely large clusters leads to automatic inclusion of the long-range interactions that may have important influence on the electron properties of solid state systems. Within this method the modulo-periodic boundary conditions ensure the periodicity of the wave function, eliminate the so-called boundary effects, and allow the use of transformation in to the Bloch orbital basis. The calculation of electron density in several thousands of **k**-points regularly distributed within the first Brillouin zone ensures the physically correct calculation of density matrix for band structure calculations.

Denoting the unit cell vectors as $\mathbf{a}_i$ $(i = 1, 2, 3)$ a finite cluster is built-up translationally replicating the elementary unit cell in the respective lattice vector directions N_i $(i = 1, 2, 3)$ times. Then $N = N_1N_2N_3$, is the total number of unit cells considered in the cluster. M-atomic orbital basis functions $|\rho^{\mathbf{R}}\rangle$ are associated with each elementary unit cell. Atomic orbital basis functions are described by a pair of indices ρ and $\mathbf{R}$ in which ρ refers to the index of atomic orbital (ρ ranges from 1 to M) within a given cell and $\mathbf{R}$ covers the range of all possible lattice translations

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{1}$$

where n_i $(i = 1, 2, 3)$ indicates one of the possible N_i translations in the direction $\mathbf{a}_i$. The reciprocal space vector $\mathbf{k}$ is defined in a standard way,

$$\mathbf{k} = \frac{m_1}{N_1}\mathbf{b}_1 + \frac{m_2}{N_2}\mathbf{b}_2 + \frac{m_3}{N_3}\mathbf{b}_3 \tag{2}$$

where the reciprocal lattice vectors $\mathbf{b}_i$ fulfil the condition $\mathbf{a}_i\mathbf{b}_j = 2\pi\delta_{ij}$. The idea behind the cyclic cluster approach is to impose the same surrounding on all unit cells of the cluster. The interactions of the central unit cell are imposed to the rest of the cells. For a finite cluster, a "ring periodicity" is imposed by adopting the following identity

$$\mathbf{R} + \mathbf{R}' = \sum_{i=1}^{3} \left\{ n_i + n_i' - N_i \operatorname{int}\left(\frac{2(n_i + n_i')}{N_i} \right) \right\} \mathbf{a}_i \tag{3}$$

where int() is the integer part function. For a cluster constructed in a way described above, the translation symmetry is guaranteed [1, 2]. Hence, for all integrals over any one-particle ($\hat{h}$) and two-particle ($\hat{g}$) operator (and of course for many-particle operators) the translation periodicity (Born-Karman periodic conditions) within the considered cluster mathematically described by

$$\langle p^{\mathbf{R}+\mathbf{R}}|\hat{h}|q^{\mathbf{R}}\rangle = \langle p^{\mathbf{R}}|\hat{h}|q^{\mathbf{O}}\rangle = h_{pq}^{\mathbf{RO}} \tag{4}$$

$$\langle p^{\mathbf{R}_i+\mathbf{R}'} q^{\mathbf{R}_2+\mathbf{R}'}|\hat{g}|r^{\mathbf{R}'} s^{\mathbf{R}_1+\mathbf{R}'}\rangle = \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2}|\hat{g}|r^{\mathbf{O}} s^{\mathbf{R}_1}\rangle \tag{5}$$

has to be fulfilled for all lattice translations $\mathbf{R}$. The physical interpretation of Eqs. (4,5) is such that each unit cell of the cluster "feels" such an environment as if it was in the centre of the cluster. This assumption would be valid for an infinite cluster, but even in such case the requirements of Eq. (4) are not applicable in general and ambiguities may arise also with multicenter two electron integrals. Hence, in ab initio treatments one need some sort of averaging manipulations with integrals. However, due to the partial ZDO (Zero Differential Overlap) approximation in the used INDO method, the requirements of Eqs. (4,5) are automatically fulfilled for all integrals considered. Therefore, transformation to Bloch orbital basis is uniquely given by the following finite summations

$$|p^{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}}^{N} \exp(i\mathbf{k}.\mathbf{R}) |p^{\mathbf{R}}\rangle \tag{6}$$

After performing this Fourier transformation, the Fock matrix factorises into N blocks of the size $M \times M$, where M is the number of atomic orbitals in the elementary unit cell, i.e.

$$F_{pq}^{\mathbf{kk}'} = F_{pq}^{\mathbf{kk}} \delta_{\mathbf{kk}'} = \sum_{\mathbf{R}}^{N} F_{pq}^{\mathbf{RO}} \exp(i\mathbf{k}.\mathbf{R}) \tag{7}$$

The cluster choice determines exactly all the $N_{\mathbf{k}} = (N_1 N_2 N_3 + 1)/2$ independent values of the wave vector $\mathbf{k}$. The necessary Fock-matrix elements of the closed-shell systems in INDO Hamiltonian approximation are

$$F_{pq}^{\mathbf{RO}} = h_{pq}^{\mathbf{RO}} + \sum_{\substack{\mathbf{R}_1,\mathbf{R}_2 \\ \overline{(\mathbf{R}_3=\mathbf{R}_1-\mathbf{R}_2)}}}^{N} \sum_{r,s}^{\text{cell}} P^{\mathbf{R}_3\mathbf{O}} (2\langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | q^{\mathbf{O}} s^{\mathbf{R}_2} \rangle - \langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | q^{\mathbf{R}_2} s^{\mathbf{O}} \rangle) \tag{8}$$

$$P_{pq}^{\mathbf{RO}} = \frac{1}{N} \sum_{\mathbf{k}}^{N} P_{pq}^{\mathbf{k}} \exp(i\mathbf{k}.\mathbf{R}) \tag{9}$$

$$P_{pq}^{\mathbf{k}} = \sum_{m}^{\text{occ}} (c_{pm}^{\mathbf{k}})^{\star} c_{qm}^{\mathbf{k}} \tag{10}$$

Having formed the $\mathbf{F}$ matrix, one performs its diagonalization, calculates the new density matrix and returns back to the Fock matrix till self-consistency is achieved. With an increasing value of N the bulk limit is approached

$$E_{HF/\text{cell}}^{\text{bulk}} = \lim_{N \to \infty} \left(\frac{E_{HF}(N)}{N} \right) \tag{11}$$

It has been shown, that this limit can in fact be accomplished in a rather short computing time. Since for the converged results the density matrix can be safely treated as the one corresponding to the bulk, *a posteriori* calculations for characteristic paths in the **k**-space for any point within the first Brillouin zone are fully justified.

The program SOLID98 was used for calculation of structure and electron structure of wide scale of model systems including insulators, semiconductors, as well as metals, semimetals and superconductors.

From our first results some important features and application perspectives of the presented method can be summed as follows:

1. The method presented offers an effective tool for a fast calculation and acceptable description of the electronic and structural properties of systems with periodic structure.

2. The CPU time requirements are relatively low and the results are obtained within a short time. Therefore the application of the method for the standard calculations in the area of solid-state physics and chemistry, chemical synthesis, crystallography, seems to be very promising.

3. The method might play an important role in the area of education — it can bridge the field of physics and chemistry and help in the education of chemists solving the problems of solid state chemistry, and, on the other hand, it can help the solid state physicists to acquire a "feeling" of the chemical aspects of the problem considered.

4. The method can serve as a valuable tool for calculations of very complex crystalline materials, which cannot be dealt with using current methods of solid state physics.

5. Due to the possibility of working with a considerable large unit cell, the calculations of defects in materials appears to be feasible.

6. The applied quasi-relativistic INDO method is parametrized for all atoms of the periodic table and includes dominant relativistic effects. This allows calculations of a number of interesting systems containing heavy atoms.

We are, of course, aware of some of the weak points of the method presented. Above all is the fact that the method is, by its nature, approximative. However, performing the quantum chemical calculations a correct balance between the physical relevancy of the model considered and the rigorousness of the method applied needs to be achieved. In view of this, even the most extensive ab initio calculations with insufficient scope of the long range-order interactions and not large enough number of **k**-points, and/or limited wave function basis set, do not yield sufficiently correct results. It is namely the above mentioned model-method balance reached within our approach that we consider crucial and which makes the approach useful.

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Mathematical Modeling of Nonlinear Dynamics of Chemical, Biological and Electrical Systems

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Introduction

Nonlinear dynamics is a new branch of science that studies nonlinear phenomena which occur in mathematical models and which are observed in experiments. It profits both from a general knowledge of the theory of dynamical systems and bifurcations, and from the experience accumulated in interpretation of specific examples.

We study mathematical models of nonlinear systems in the form of difference equations (DE) or ordinary differential equations (ODE). The techniques we use include: numerical integration, map iteration, computation of dynamical invariants (generalized dimension, Lyapunov exponents), of invariant sets (stable and unstable manifolds), of bifurcation points (limit points, Hopf bifurcation), continuation (computation of curves of solutions in dependence on a selected parameter and bifurcation curves in the parameter space).

We use our own software for both numerical computation (`easynum`) and for 2-dim graphical presentation (`xpplot`). The software is written in C and is free and available on our web page. For symbolic computation and for 3-dim presentation we use the commercial software *Mathematica* by Wolfram Research.

Ferroresonance — nonlinear phenomenon in electrical power system

We investigate dynamic behavior of a three-phase power system represented typically by the circuit in fig 1.

Magnetic saturation of the iron core in the power transformer causes nonlinear inductance that can be described by the equation

$$I_{\mathrm{nlin}} = k_A\ \varphi + k_B\ \varphi^n$$

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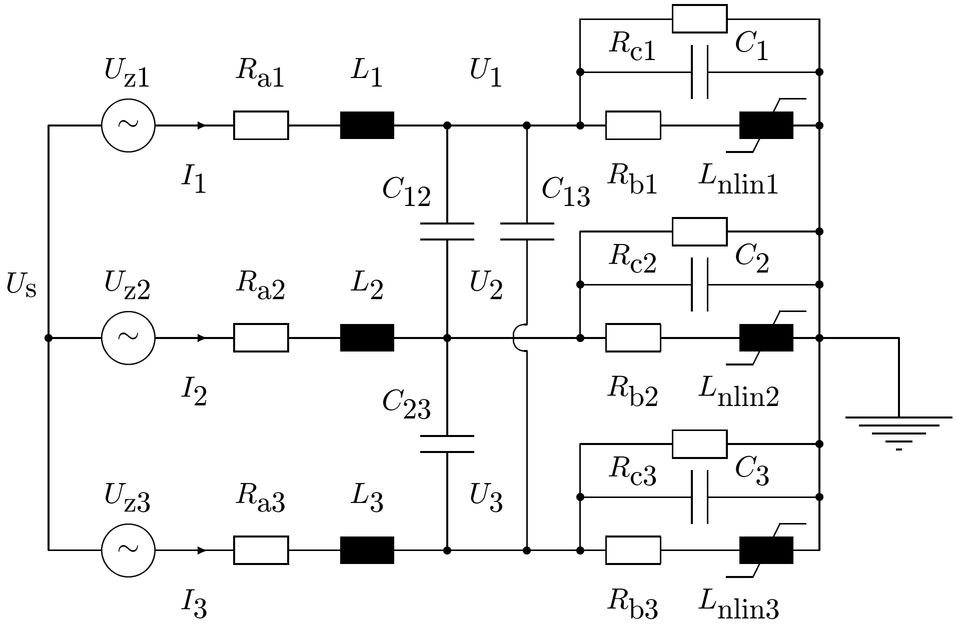

Figure 1:

where typically $k_A = 1.9 \times 10^{-3}$, $k_B = 1.2 \times 10^{-20}$, $n = 11$. This gives rise to a wide variety of nonlinear phenomena, including amplitude resonance (when the output voltage is a non-monotonic function of the input voltage), bending of resonance peaks (which are almost symmetrical for linear circuits), multistability (co-existence of more stable attractors), asymmetric oscillation, multi-peak oscillations, quasi-periodicity and chaotic behavior.

These manifestations are dangerous not just because of overvoltage but they can threaten the safety circuits resulting in unnecessary switching off.

Dynamical Systems Generated by Two Alternating Vector Fields and the Baker-Campbell-Hausdorff formula

Adiabatic fixed-bed reactors with periodic flow reversal are used industrially for SO_2 oxidation and for the catalytic combustion of traces of hydrocarbons in exhaust air, because their energy efficiency exceeds that of autothermal reactors with recuperative heat exchange considerably.

To achieve safe and environment-friendly operation of these reactors, understanding of the dynamics is necessary. Complete mathematical models involve a large number of nonlinear partial differential equations with a huge number of parameters hard to measure.

To understand the basic dynamics we use models in the form of a set of n ordinary differential equations, where n is small. The periodic flow reversal is modeled by alternating two vector fields $u, v \colon R^n \to R^n$, that operate on the state space R^n for a fixed time interval each. These non-autonomous piece-wise continuous dynamical systems (called "dynamical systems with blinking" or "zig-zag dynamical systems") are investigated both analytically and numerically. The geometrical symmetry of the chemical reactor can be generalized to a case when the two vector fields u, v are G-related, where G is an involution (i.e. $G^2 = \text{identity}$).

Detailed numerical study of both conservative ("blinking vortex") and dissipative ("blinking nodes", "blinking cycles" and "blinking Lorenz") systems shows that the technique of blinking can be used to initiate and to control chaos.

For low switching period the dynamics can be approximated by "averaged" system. Consideration of higher order terms leads to the famous Baker-Campbell-Hausdorff (BCH) formula

$$w = u + v + \frac{1}{2}[u,v] + \frac{1}{12}([u,[u,v]] - [v,[u,v]]) - \frac{1}{24}[u,[v,[u,v]]] + \cdots$$

containing Lie brackets of the two vector fields

$$[u,v] = Du.v - Dv.u$$

where Du stands for the matrix of partial derivatives and dot stands for dot product of a matrix and a vector. We can come to this result by different ways. One of them is the Taylor expansion, or using the mathematical theory of Lie groups and Lie algebras. To use the latter approach associativity is necessary. To assure associativity we first generalise a vector field $\vec{u}$ into a differential operator $\hat{u}$ operating on a suitable set of smooth functions $\varphi\colon R^n \to R^n$ such that

$$\hat{u}(\varphi) = D\varphi.\vec{u}\,.$$

We use the BCH formula for operators and then we come back to vector fields using the observation that

$$\vec{u} = \hat{u}\ (\text{identity}).$$

Analytical results are supported and illustrated by numerical examples.

Excitable Dynamical Systems

The key property of neural and muscle cells in living organisms is the excitability — the ability to produce a large amplitude response to a superthreshold input signal, while remaining almost insensitive to small (sub-threshold) input perturbation. After the excitation the cell goes through a short refractory state — a state of suppressed sensitivity to further perturbation. Mathematical models of biological excitable cells are convenient tools to study dynamic behavior under single-pulse, periodic or quasi-periodic perturbation. Important quantity for signal processing is the firing ratio, the ratio of the number of output spikes over the number of input perturbations during a long time interval. The dependence the firing ratio versus the perturbation amplitude and the perturbation period forms an interesting mathematical function — the "devil staircase".

Results in this field help to understand dynamic behavior of both individual cells and entire organs and enable construction of efficient cardio-stimulators.

Continuation

Many problems in the numerical study of dynamical systems lead to the system of n algebraic equations for $n+1$ unknowns, written as

$$f(x) = 0$$

where $x \in R^{n+1}$ and $f \in R^n$.

Continuation is a numerical method to find the solution of this equation in the form of a 1-dim curve in R^{n+1}.

One simple example is to find a stationary point y_0 (that may be either stable or unstable) of ODE with 1 real parameter p.

$$\frac{dy}{dt} = f(y, p)$$

The stationary point y_0 is the solution of the equation

$$f(y_0, p) = 0.$$

The brute-force attack is to solve this equation for various values of p independently.

The points $x = (y_0, p)$ will (under general conditions on f) form a 1-dim curve in R^{n+1}. This curve may form a S-shaped meander giving more than one y for certain p. Continuation is a good method to follow this curve. Continuation is a predictor-corrector method. Given one point x_0 on the curve we may predict the next point $x_1 = x_0 + h * u$ where h is the step size and u is a unit vector in the desired direction. One simple prediction may be the (vector) difference of the last 2 points. Then the corrector is used to locate the next point x on the curve precisely. One simple corrector may be to solve the set of equations

$$\begin{aligned} f(x) &= 0 \\ (x - x_1).(x_1 - x_0) &= 0 \end{aligned}$$

where the dot "." is the dot product of two vectors in R^{n+1}. The second equation means that we want the correction $(x - x_1)$ to be perpendicular to the prediction $(x_1 - x_0)$. These corrector equations can be solved numerically using the Newton method.

It is a good practice to adjust the step size according to how complicated the solution is. A simple step size controller may be based on the number of Newton iterations necessary to achieve a prescribed precision. If the number of iterations is too small, meaning the solution is easy, then enlarge the step size; if the number of iterations is too large, then shorten the step size.

Conclusion

We have shown several examples where numerical computation is an important part of solving problems with direct technological application. Availability of massive computational resources is necessary for further progress. In this context the supercomputer in the *METACenter* Brno-Praha-Plzeň is a remarkable achievement in the support of scientific research in the Czech Republic.

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Predicting Molecular Properties with Electronic Structure Methods

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Regular polyhedral molecules. P_{20} and its inclusion compounds

Based upon the geometrical properties of regular polyhedrons, the possibility of existence of certain polyhedral molecules composed of only one element is investigated. Very promising candidate — regular dodecahedron — is selected as the convenient polyhedral structural pattern and phosphorus as the appropriate element. A series of high-level ab initio calculations is performed on dodecahedral P_{20} molecule, including the predictions of its thermodynamic and kinetic stability, natural bond orbital analysis, vibrational analysis and inclusion of some elements into the molecular skeleton. Due to the potential stabilising agents that may eventually form stable inclusion compounds and the estimated high kinetic stability, the question of the possible existence of P_{20} is answered in the positive.

A study of interactions of biologically important functional groups with transition metal ions

Both of the above studies belong to a longer term project oriented towards the interactions of biomolecules with transition metals. The aim of the project is the molecular design of shorter peptide structures, specifically binding selected transition metals.

In the former study, two sources of experimental data were exploited (Protein Data Bank and Cambridge Structural Database) in order to determine preferred coordination geometries of six divalent cations (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}). Metal-binding sites of approximately 100 metalloproteins and 3000 smaller transition metal complexes were analysed and classified. The correlation between the geometries of small-molecule crystal structures and the metal-binding sites in metalloproteins was investigated. The abundance of amino acid residues participating in coordination metal-protein bonds of metalloproteins was evaluated. From the performed analysis it follows that the octahedral arrangement is preferred by Co^{2+} and Ni^{2+}, tetrahedral by Zn^{2+}, square planar by Cu^{2+}, and linear by Hg^{2+}. Cadmium (II) cation tends to bind in both tetrahedral and octahedral arrangements and single coordination geometry cannot be unambiguously ascribed to it.

In the latter one, model complexes of hydrated zinc(II) and nickel(II) cations with one water substituted for methanol, methanethiol, and ammonia were studied. An accuracy of various computational methods, influence of the basis set, and a role of the coordination geometry were investigated. It has been shown that Density Functional Theory calculations (B3LYP functional) yield very accurate results, but the basis set of at least triple-zeta quality with polarization and diffuse functions should be used. The calculated mean absolute difference between DFT and QCISD(T) reaction energies for the substitution reactions on the central metal ion was less than $0.5\,\mathrm{kcal.mol}^{-1}$. It has been also observed that the metal-ligand distances and the reaction energies of monosubstituted hydrated complexes of metal ions are strongly dependent on the number of ligands in the first coordination sphere and the coordination geometry. The implications of having reliable, accurate and relatively fast method for the calculation of transition metal complexes were discussed. Several applications oriented towards the interactions of transition metals with the amino acid residues has been mentioned.

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The Gas Circuit-Breaker Interrupting Process Modeling

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The project description

The project is oriented on HV circuit-breaker modeling. The interruption process of circuit-breaker is based on interaction between high pressure, high temperature plasma (electric arc with maximal power about 50 MW), gas flow (subsonic and transonic) and electric field (non homogeneous field with surface and free space charges). Due the extreme task difficulties only parts of interruption process are usually modeled (simplified models). The complex model with energy source (electric arc integration) is prepared. Those models are mainly based on gas flow calculations, which are performed with software FLUENT using. The West Bohemia Supercomputer Center resources (software and hardware) play the main role in those calculations.

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Electronic Structure and Atomic Configuration of Extended Defects in Metallic Materials

(COST Action P3 "Simulation of physical phenomena in technological applications")

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Introduction

Extended defects play a significant role in metallic materials as they control many physical and chemical properties of technological importance such as mechanical properties, recrystallization, electronic conductivity, diffusion, corrosion resistance, etc.

Under extended defects we usually mean such perturbations in the three-dimensional periodic arrangement of ideal structures which are, at least in principle, infinite in one or two dimensions, e.g. dislocations, cracks, antiphase boundaries, grain boundaries, interphase interfaces, etc. A common characteristic of extended defects is that the ideal periodicity of the crystal is perturbed in a relatively large region and the symmetry of that region is considerably reduced. Investigations of the properties and structure of extended defects constitutes one of very important directions in contemporary materials science.

Most common extended defects in crystalline materials are grain boundaries (GB). They may be defined as interfacial transition regions between two crystals (or grains) in a single-phase material, which are in contact with each other but differ in crystallographic orientation. They may be considered as planar imperfections which, in contrast to dislocations, are not accompanied by long-range strain and stress fields. Their atomic configuration differs substantially from that of the bulk only in a narrow region, usually spanning not more than several lattice spacings, and most of significant interfacial phenomena occur in this region.

It was found in recent studies that atomic configurations in the GB region or at other interfaces may contain certain metastable structures, different from the ground-state structures. For example, the 9R (α-Sm) structure was theoretically predicted and verified by high-resolution electron microscopy (HREM) at GB's in silver and copper. Similarly, the bcc structure was found at certain grain boundaries in copper. Occurrence of such phases at interfaces is even more likely in more complex non-cubic alloys such as TiAl. Indeed, new structural features of this alloy have been discovered very recently. A B19-type hcp-based structure was found in a Ti-48 at. %Al alloy quenched from the disordered phase and a series of structural transitions in the form of changes in the stacking sequence of the close-packed atomic planes was observed in the Ti and Al layers in Ti/Al multilayered thin films.

Consequently, to explore adequately extended defects both in pure metals and in intermetallics or alloys, a detailed information about possible metastable structures as well as lattice transformations connecting them is needed. Armed with this knowledge one can predict whether an interface may be associated with a metastable structure and assess thus its stability and ability to transform to other structures (for example during deformation or due to changes in stoichiometry).

The subject of our project are metastable structures arising at high deformations. These deformations transform the ground structure of the material to some other structures with a different symmetry. In most cases, they may be described as one-parameter transformation paths.

Results and discussion

The computers of the *METACenter* were employed mostly for electronic structure calculations and total energy of elemental metals and intermetallic compounds along such transformation paths. We have performed calculations of total energy of titanium along the tetragonal (bcc → fcc), trigonal (bcc → simple cubic structure → fcc) a hexagonal (bcc → hcp) transformation path using three different approaches: (i) first-principles full-potential linear augmented plane waves method (FLAPW), (ii) recently developed “bond-order” potentials (BOP), and (iii) central interatomic potentials of the Finnis-Sinclair (FS) type. The first-principles FLAPW method is based on fundamental quantum mechanics (we solve the Schrödinger equation for a solid) and its results serve as “benchmarks” in assessing the applicability of treatments (ii) and (iii), which are by far not so computationally intensive and, therefore, we can use them for computer simulations of atomic configurations of extended defects in materials.

Our calculations show that BOP reproduce very well the behavior of total energies along all three transformation paths. Consequently, they include correctly the influence of angular forces and directional bonds mediated by d-electrons. Central interatomic potentials reproduce the total energies along the tetragonal and trigonal deformation paths, but they are not able to resolve the fcc and hcp structures, which exhibit the same number of atoms in the first and second coordination spheres and the structural energy difference is due to directional bonds. The results are prepared for publication.

For the same purpose, we studied the change of total energies along the above mentioned transformation paths in intermetallic compounds NiAl and TiAl, which constitute a basis of a new class of advanced materials for high-temperature applications. In case of two-component intermetallics the tetragonal deformation path may be considered as a transition from the B2 (CsCl) structure to the $L1_0$ structures, the trigonal path from the B2 structure to the $L1_1$ structures (here also the B1 (NaCl) structure is included) and the hexagonal path from the B2 structure to the B19 structures. Here we performed calculations only by means of first-principles FLAPW method and of central interatomic

FS potentials, as bond-order potentials were not constructed yet. It turns out that the FS potentials reproduce the first-principles results in NiAl very well and, therefore, they may be used for atomistic modeling of structure of extended defects with a high degree of confidence. The influence of directional bonds in NiAl may be considered as not very important. In TiAl, the FS potentials qualitatively reproduce the result of first-principles calculations, but, again, they are not able to distinguish the structures with the same number of atoms in the first and second coordination spheres (this is the case of the structures $L1_0$, which is analogous to the fcc structure, and B19, which is analogous to the hcp structure). Consequently, in TiAl we can use the FS potentials only for modeling of such defects where the distances of the first and second neighbours (the radii of coordination spheres) differ essentially from those in the ground-state structure $L1_0$. The results were recently published [1].

The behavior of total energy along transformation paths is very closely related to anisotropy of theoretical (ideal) tensile strength. We have studied this anisotropy in tungsten, copper and intermetallic compound NiAl, using the first-principles FLAPW method [2]. It turns out that the existence or absence of symmetry-dictated extrema of total energy has a decisive role for the values of theoretical strength. A very nice example is the intermetallic compound NiAl. At the tetragonal deformation path (corresponding to uniaxial loading along the [001] direction, which is known as the hard single-crystal orientation), the only high-symmetry structure is the ground-state B2-structure, and the total energy along this path is strongly increasing. At the trigonal deformation path (corresponding to uniaxial loading in the [111] direction), a symmetry-dictated maximum in total energy appears, which is due to occurrence of the high-symmetry B1 structure. As a result, the total energy along this deformation path does not increase so steeply and the strength of the material for this orientation is lower. All these aspects are discussed in detail in paper [3].

Most of the results presented above, together with some more general aspects of electronic structure and atomic configuration of lattice defects in metallic materials were also presented in the invited talks [6] and [7] at the 9th Int. Conf. on Intergranular and Interphase Boundaries in Materials in Prague and at the 1998 Conference on Computational Physics: Modeling Collective Phenomena in Complex Systems in Granada (the invited talk [6] is published in the Proceedings of the Conference [3]), and in other presentations [5, 8, 9].

Used programs

- **User installed programs:** The first-principles FLAPW electronic structure calculations were performed using the code WIEN97 which was written at the Vienna University of Technology. The exact bibliographical reference is

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Interactions of Nucleic Acid Bases and the Structure of DNA

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The DNA molecule is one of the most important biomolecules. The DNA exhibits enormous conformational variability which is essential for its biological roles. The most important class of three dimensional DNA structures are the double-helical architectures. The DNA double helix can adopt a number of distinguished structures (B-DNA, A-DNA, Z-DNA) and have a pronounced local base sequence-dependent variability which is essential for molecular recognition processes. DNA molecules can adopt also many other architectures such as triple and quadruple helices, hairpins, zippers etc. All of these forms are believed to perform some specific biological and biochemical functions.

Among the most important contributions determining the DNA structure and dynamics are hydrogen bonding and stacking interactions of nucleic acid bases. Recent advances in computational chemistry allowed for the first time to achieve a physically correct description of interactions of nucleic acid bases. High-level ab initio quantum chemical calculations carried out since 1994 mainly in our laboratory (J. Heyrovský Institute of Physical Chemistry, Prague) provided a reliable description of H- bonding and stacking interactions of nucleic acid bases (for reviews see [1, 2]). Subsequent studies characterized complexes between base pairs and metal cations and provided the first insight into the nonadditivity of molecular interactions in these systems [3]. Quality and reliability of ab initio calculations with inclusion of electron correlation effects can be compared to gas phase experiments but the ab initio calculations allow to study a much broader range of molecules and interactions. One of the most important outcomes of our studies was a verification of empirical potentials used for molecular modeling. We have shown [4] that the recently introduced Cornell et al. force field [5] currently utilized by the AMBER molecular modeling package provides quite consistent and realistic description of interactions of nucleic acid bases (except of interactions between bases and metal cations). This finding justifies the use of molecular dynamics simulations and other empirical-potential based methods in studies of the role of interactions of nucleic acid bases in the structure and dynamics of nucleic acids. Reliable empirical potential studies are very important since quantum chemical calculations are quite limited in studies of DNA structure; quantum chemical methods do not allow to study realistic systems. In order to directly address issues of biological relevance large systems must be consider and solvent must be properly included.

MD simulations of hydrated oligonucleotides represent a very promising tool to investigate many aspects of nucleobase interactions in real environments. Until very recently the reliability of MD simulations of nucleic acids was quite limited due to low performance of computers, and inaccuracies in the force fields and simulation techniques. However, in recent years quality of MD simulations improved qualitatively and MD simulations now represent an important and successful tool to study structure and dynamics of nucleic acids at the atomic resolution level. Advance of fast computers and implementation of the particle mesh Ewald (PME) method for treatment of long range interactions into DNA simulations in 1995–1996 is one of the most revolutionary achievements in computational molecular biology in the last decade [6]. We have successfully implemented the PME MD technique in our laboratory and we have used it for a thorough analysis of structural and dynamical properties of unusual four-stranded nucleic acid forms, namely the four-stranded hemiprotonated intercalated i-DNA and the parallel and antiparallel guanine quadruplex structures [7, 19].

Since 1995 a significant portion of our quantum-chemical and later molecular dynamics studies have been carried out on the SGI supercomputer in the Supercomputer Center, Brno. Although we have had an access to very good computer facilities abroad in the course of our project, we have greatly appreciated excellent possibilities in Supercomputer Center Brno, and its support for real supercomputing. In most cases we have carried out in Brno unique calculations which we were unable to run on any other machine available to us.

In Brno, we have performed reference quantum-chemical calculations for H-bonding and stacking interactions and nonplanarity of exocyclic amino groups. These calculations have been done using the Coupled Cluster method with noniterative triple electron excitations — CCSD(T) [8, 10]. The exceptionally demanding CCSD(T) method belongs to the most accurate ab initio techniques. One of the most important results of these studies is that the economical second order Moeller-Plesset method (MP2) tends to overestimate the aromatic stacking interactions, while for all other interactions studied the MP2 and CCSD(T) methods provide essentially identical results.

In Brno, we have also carried out the first MP2 gradient optimizations on stacked nucleobase dimers [14]. We have also made an thorough analysis of base stacking interactions and the reliable quantum chemical data have been used for an extensive comparison with empirical potentials [12, 13, 18].

We have also utilized the SGI supercomputer to large-scale ab initio studies of interactions between metal cations and DNA base pairs [11, 16, 17, 20]. Quantum chemical studies of metal-cation containing complexes are very important since metal-cation containing clusters cannot be properly described by empirical potentials. The calculations allowed us, among other things, to rationalise systematic differences between zinc and magnesium groups of cations and to understand the influence of cation binding on the stability of standard and mismatch nucleic acid base pairs.

Besides the quantum chemical calculations, we have carried out in Brno large-scale molecular dynamics simulations. We have done the first PME MD simulations on four-stranded DNA motifs i-DNA [15] and G-DNA [19]. Our studies belong to the most extensive MD studies performed on hydrated nucleic acids so far and revealed a number of new aspects of molecular interactions in unusual DNA forms. For example, we have demonstrated that DNA is capable to form stable three-dimensional structures with repulsive base stacking interactions, we have thoroughly characterized the integral role of cations in guanine quadruplex molecules and we have proposed an alternative topology for the guanine quadruplex stem.

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Study of Conformational and Electronic Properties of Linear Conjugated Polymers

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Introduction

Unlike the other polymers, the conjugated polymers possess interesting optical and electrical properties following from their chemical structure.

According to the conjugation, two types of conjugated polymers are distinguished. In π-conjugated polymers, sp_2 p_z hybridization of four carbon valence electrons in covalent bonds leads formally to one unpaired electron per carbon atom. This polymers can be recognized through the alternation of single and double bonds along the chain. This arrangement gives delocalization of bonding and antibonding molecular orbitals along the chain. The semiconducting properties arise from the overlap of electron orbitals along the chain, forming the valence and conduction bands.

In polysilanes, the overlap of the sp_3 orbitals of the neighbouring silicon atoms leads to the formation of the σ-bonds. However, the hybridized orbitals localized on the same atom also overlap. Delocalization of molecular orbitals along the chain (σ-conjugation) is given by the ratio of the overlap integrals between the hybridized orbitals localized on the same atom and those localized on the neighbouring atoms. If this ratio is close to one the delocalization is ideal.

Poly(phenylenevinylene)

The scientific interest in poly(p-phenylenevinylene) (PPV) is connected above all with the research of electroluminiscence. The aim is to develop and improve polymer light emitting diodes (LED) and other modern optoelectronical devices. The model of the electroluminiscence in polymers is based on quasiparticle conformational defects – polarons, excitons and bipolarons.

The above mentioned conformational defects in the phenylene vinylene oligomers (PVOs) consisting of 4 to 12 repeating units are investigated by means of the quantum mechanical methods. The conformations are determined by means of the minimization of the total Hartree-Fock (HF) energy calculated at 3–21G level. The HF calculations of the excited states are followed by the CI-Singles calculation. All conformational degrees of freedom (atomic coordinates) are optimized.

Aromatic and quinoidal character of PVO structure

The defect-free PVO chain possesses aromatic structure. In the presence of a defect (polaron, bipolaron, exciton) the PVO chain has quinoidal character. For describing the character of the chain structure, the bond length alternation parameter Δ is defined as a function of the bond lengths between the atoms of the repeating unit (see Fig. 1). The positive value of the parameter Δ (0.235 Å at HF/3–21G level) means aromatic character of the structure, the negative one means quinoidal character.

The calculated values of the parameter Δ for the defect-free PVO and PVOs with exciton, positive polaron and positive bipolaron, all containing 8 repeating units, are shown in Fig. 2. The exciton and bipolaron are extended along the whole oligomer. In contrast, the extent of the polaron is only about 4 monomer units and the rest of the chain remains aromatic.

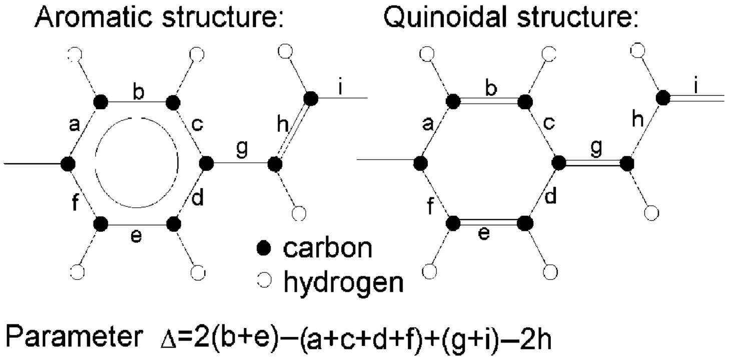

Figure 1: Two structures of the PPV monomer unit and the definition of the parameter Δ by means of the bond lengths a to i.

Infra-red vibrational spectra of PVOs

The equilibrium conformations of the PVOs make possible to calculate the vibrational transitions. All presented HF and CI-Singles vibrational frequencies are multiplied by the uniform scaling factor 0.89 .

The infra-red (IR) frequencies of the defect-free oligomer were calculated also by means of B3LYP/3-21G method. In this case, the scaling factor 0.96 was used.

The comparison of the theoretical spectrum of the defect-free PVO (4 repeating units) with the experimental spectrum of PPV is in Table 1. The types of the vibrations of the phenylene rings are denoted by means of the Wilson notation for *para*-derivatives of benzene.

The theoretical HF frequencies of the transitions No. 1, 7, 8 and 9 (see Table 1) are in good agreement with the experimental ones. The HF frequencies of the out of plane bend transitions No. 3, 5 and 6 are about 30–40 cm^{-1} higher than the experimental ones. On the

No.	HF f [cm^{-1}]	B3LYP f [cm^{-1}]	Exper. (polymer) f [cm^{-1}]	Assignment	Notation by Wilson
1	561	538	557	phenylene out of plane ring bend	16b
2	710	693	–	out of plane ring bend of the phenylene at the chain end	–
3	876	828	837	phenylene C–H out of plane bend	11
4	980	915	–	C–H out of plane bend of the vinylene at the chain end	–
5	994	952	965	both vinylene and phenylene C–H out of plane bend	10b
6	998	959	965	both vinylene and phenylene C–H out of plane bend	10b
7	1308	1324	1334	both vinylene and phenylene C–H in plane bend	mixed
8	1415	1417	1423	C–C ring stretch	19b
9	1507	1501	1517	C–C ring stretch	19a
10	2975	3040	3024	vinylene C–H stretch	–
11	2979	3055	3047	phenylene C–H stretch	13
12	2981	3055	3047	phenylene C–H stretch	13
13	3012	3080	3076	phenylene C–H stretch	20b

Table 1: Theoretical frequencies of the IR transitions of the defect-free phenylene vinylene oligomer (4 repeating units) in comparison with the experimental values for PPV.

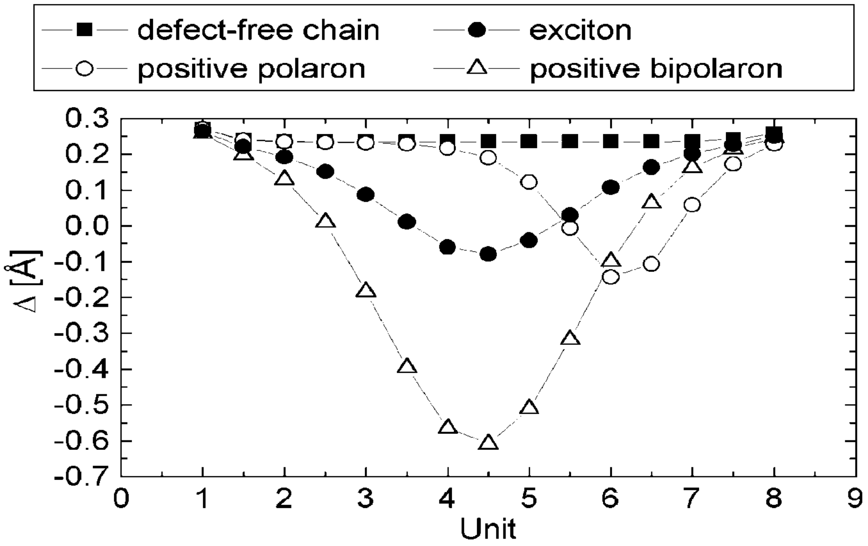

Figure 2: Change of the structure in the region of the defect for PVOs containing 8 repeating units. Parameter Δ is calculated by means of the HF/3–21G method (and CI–Singles for exciton, ROHF method for polaron).

contrary, the calculated C–H stretch transitions No. 10, 11, 12 and 13 are shifted to lower frequencies. All the B3LYP frequencies are in very good agreement with the experiment.

The theoretical IR spectrum of the PVO (4 repeating units) containing the exciton consists of similar transitions as the spectrum of the defect-free PVO but the frequencies of some transitions are slightly shifted and the IR intensities are different. The out of plane bends No. 3, 5 and 6 (see Table 1) are shifted up to 40 cm^{-1} lower. The C–C ring stretches and the phenylene C–H stretches have almost the same frequencies as the ones calculated for the defect-free PVO. A significant C–C ring stretch (8a by Wilson notation) occurs at 1569 cm^{-1}. Its experimental frequency is 1594 cm^{-1}. The vinylene C–H stretch No. 10 is significantly lower in the exciton spectrum.

In the theoretical vibrational spectra of PVOs containing polaron and bipolaron, numerous very strong in plane transitions are observed between 500 cm^{-1} and 1500 cm^{-1}. Most of them correspond to the in plane C–H bends mixed with the complex in plane ring vibrations.

Poly(organosilanes)

In σ-conjugated polymers, the quasiparticle conformational defects play similar role in the transport of charges and the luminiscence as in the case of the π-conjugated polymers. However, there is much less theoretical as well as experimental results for σ-conjugated polymers and many features of the quasiparticles in polysilanes are not known yet.

Defect	Polysilane	Si–Si bond length [Å]	Bond angle [^{0}]	Method
defect-free	unsubst.	2.334 2.336 2.334	111.8	B3LYP
	subst.	2.356 2.350 2.356	113.2	B3LYP
positive polaron	unsubst.	2.413 2.383 2.413	95.7	B3LYP
	subst.	2.429 2.382 2.429	103.8	B3LYP
negative polaron	unsubst.	2.400 2.478 2.400	137.8	B3LYP
	subst.	2.351 2.405 2.351	110.7	B3LYP
defect-free	unsubst.	2.344 2.348 2.344	111.7	HF
	subst.	2.366 2.363 2.366	113.9	HF
exciton	unsubst.	2.371 2.642 2.371	148.7	CIS
	subst.	2.447 2.502 2.447	91.2	CIS

Table 2: Comparison of the Si–Si bond lengths and Si–Si–Si bond angles in substituted (oligo(methyl-phenylsilane)) and unsubstituted oligosilanes for the different quasiparticles.

Unsubstituted oligosilanes

The conformations of the oligomers containing positive and negative polarons (four, six and eight monomer units) were optimized by means of ROHF, UHF and B3LYP methods at 3-21G$^{(*)}$ level. The conformations of the oligomers containing exciton were optimized by means of ab initio CIS method at the same level.

It was found that the negative polaron conformation is in comparison with the defect-free conformation stretched. On the other hand, the conformation of the positive polaron is shrunk. The middle Si–Si bonds of the conformations calculated by means of ROHF and UHF methods are very long. Because such bonds can be easily split these conformations are unstable. The B3LYP conformations are more stable and probably more realistic.

Quasiparticles in oligo(methyl-phenylsilane)

The conformations of the defect-free tetramer and the tetramers containing positive and negative polarons and exciton were optimized by means of B3LYP/3-21G$^{(*)}$ method.

In Table 2, there are the Si–Si bond lengths and Si–Si–Si bond angles in substituted (oligo(methyl-phenylsilane)) and unsubstituted oligosilanes compared for the different quasiparticles. There is very strong influence of the substituents on the conformations of the negative polaron and exciton. In both cases the middle Si–Si bond is much shorter for the substituted polymer and the bond angles are smaller. On the other hand, the influence of the substituents on the conformation of the positive polaron is small.

Conclusions

Using the *METACenter* supercomputers the following main results were achieved:

1. **Poly(phenylenevinylene)**
    - The conformations of the quasiparticle conformational defects (polaron, bipolaron and exciton) of poly(phenylenevinylene) were determined at HF/3-21G level. They were described by means of the bond length alternation parameter.

  - Infra-red vibrational spectra were computed by HF/3-21G method for the different conformational defects and lengths of the oligomers. For the defect-free oligomer, the results were corrected by the B3LYP/3-21G method. These results are in very good agreement with the experiment. The types of vibration were assigned on the basis of normal modes.

2. **Polysilanes**
   - Conformations of the quasiparticle defects (positive and negative polarons and exciton) of polysilane were determined. The polaron results computed by the methods ROHF, UHF and B3LYP were compared.
   - Conformations of the positive and negative polarons in the tetramer of methyl-phenylsilane were determined by means of the B3LYP method. Conformation of the exciton in the same oligomer was determined by means of the ab initio CIS method. The results were compared with the results for the unsubstituted polysilane.
   - Infra-red vibrational spectra of oligo(methyl-phenylsilane) and several other poly(organosilane) were determined.

Current research and plans

1. **Oligo(methyl-phenylsilanes)**
   The conformational defects of the oligomers consisted of 6–10 repeating units are studied. These oligomers should be long enough to model the conformational defects of the polymer. The study of the IR spectra is going on. The larger basis sets are used to obtain more accurate results. There will be studied the changes of the band structure of the one-electron energy levels connected with the creation of the quasiparticle defects. The electrical and optical properties of the poly(organosilanes), such as high quantum generation efficiency, high charge-carrier mobility, efficient luminiscence, and optical non-linearity, can be utilized in new optoelectronic devices.

2. **Phthalocyanines**
   In addition to the conjugated oligomers the phthalocyanines are also investigated. The conformations of the phthalocyanines (both the metal-free and with the central metal) are calculated by means of the DFT methods using non-standard basis sets. The changes of the IR spectra arising upon phthalocyanine oxidation are calculated and compared with the experimental results. This problem is interesting from point of the new type of the proposed superconductivity based on π–d electron interactions. Here a new conduction band (polaronic) near the Fermi level must be formed.

Acknowledgment

In addition to the *METACenter* project, the research is supported by the projects “Sigma and pi conjugated polymers: electron structure, molecular morphology, quasiparticle chain defects, charge injection. Theory and experiment.” No. 203/99/P009 of the Grant Agency of the Czech Republic, “Current modulator based on molecular wire with attached photochromic groups” No. A1050901 of the Grant Agency of the Academy of Sciences of the

Czech Republic and "Molecular sciences: Processes of electron, and proton transfer and energy exchange in gasses and condensed phase. Part (C): Electronic Processes in molecular materials." No. ME 270 of the Ministry of Education of the Czech Republic.

Publications prepared with the use of *METACenter*

[1] J. Pospíšil, J. Honskus, J. Fähnrich, P. Hlídek, P. Toman: Optical and electrical properties of poly(p-phenylene vinylene) light emitting diodes *J. Lumin.* **72-74,** 522-523 (1997).

[2] P. Toman, L. Skála, J. Pospíšil: Conformational properties of poly(p-phenylene vinylene) *Czech. J. Phys.* **48(4),** 507-511 (1998).

[3] P. Toman, L. Skála, J. Pospíšil: Quantum mechanical calculations of electronic-conformational defects in phenylene vinylene oligomers *Vacuum* **50(1-2),** 223-226 (1998).

[4] P. Toman, L. Skála, J. Pospíšil: Conformational properties of quasiparticles in poly(p-phenylene vinylene) *Adv. Mater. Opt. Electron.* **8,** 111-119 (1998).

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[6] P. Toman: Quasiparticles in σ-conjugated polymers *Synth. Metals* (in print).

Quantum Chemical Calculations of the NMR Parameters

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This work is done in cooperation with the Laboratory of Biomolecular Structure and Dynamics (LBSD) and the Faculty of Medicine, MU Brno. We are interesting mainly with the properties of quaternary benzo[c]phenanthridine alkaloids occurring in a number of species of the Papaveraceae, Fumariaceae and Rutaceae families. These compounds display some biological activities, especially antimicrobial, antiparasitic and antitumor properties.

The aim of this work is to obtain theoretical values of chemical shielding constants and coupling constants of the studied compounds. Calculated values are than compared with experimental values and help us to interpret experimental data. In most cases studied compound can achieve several conformations. Therefore, as a part of these calculations, conformational analysis must be performed.

Because studied molecules are relatively big (approximately 40 heavy atoms), conformational analysis is performed using semiempirical quantum chemical methods (mostly AM1) implemented in Gaussian 94 program. Chemical shifts and coupling constants are calculated using DFT approach and GIAO or IGLO methods. Gaussian 94 program is used for the calculations of chemical shifts by the GIAO method, deMon software is used for the calculation of chemical shifts and coupling constants by IGLO method.

Publications prepared with the use of *METACenter*

[1] R. Marek, J. Toušek, L. Králík, J. Dostál and V. Sklenář: Conformational Study of C2 Symmetrical Benzo[c]phenanthridine Alkaloid Derivatives. Chem. Lett. 1997, 369.

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[3] J. Dostál, J. Slavík, M. Potáček, R. Marek, O. Humpa, V. Sklenář, J. Toušek, E. de Hoffman, and R. Rozenberg: Structural Studies of Chelirubine and Chelilutine Free Bases. Collect. Czech. Chem. Commun. 63, 1045–1055 (1998).

[4] R. Marek, J. Toušek, J. Dostál, J. Slavík, R. Dommisse and V. Sklenář: 1H and 13C NMR Study of Quaternary Benzo[c]phenanthridine Alkaloids. Magn. Reson. Chem. in press.

Use of Computer Facilities of the *METACenter* by the Department of Physical and Macromolecular Chemistry of the Faculty of Science, Charles University, Prague

Karel Procházka, Zuzana Limpouchová, Marta Pacovská, Tereza Vrbová, David Viduna, Karel Jelínek, Jiří Fišer and Filip Uhlík[1]

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Research and pedagogical staff members of the Department of Physical and Macromolecular Chemistry of the Faculty of Science, Charles University in Prague have been using extensively computing facilities of the *METACenter*. Time-consuming computations at the supercomputers in the *METACenter* represent important scientific tool especially for two research groups studying physical chemistry of polymers and theoretical and quantum chemistry.

Physical Chemistry of Polymers Group

prof. RNDr. Karel Procházka, DrSc.

The research group of Prof. Karel Procházka, that includes members of the department (Z. Limpouchová, M. Pacovská, D. Viduna, and K. Jelínek) and also members of the Laboratory of Specialty Polymers, School of Science (T. Vrbová), has a long tradition and experiences in experimental and theoretical studies of association processes in polymer systems. Theoretical studies of chain conformations and the structure of polymeric associates are based on extensive computer simulations. This research activity has been supported by approx. ten grants. Almost all computer simulations were performed on supercomputers in the *METACentrum*.

During the last five years, i. e., since the foundation of the *METACentrum*, computer simulations have been used for studies of conformations of polymer chains in dense and geometrically constrained systems (e. g., in cores of the block copolymer micelles). The results of Monte Carlo simulations, which contribute for understanding the thermodynamic stability of micellar systems, have been published in prestigious international journals J. Phys. Chem., Macromolecules, etc. (See the list in the appendix.) Other simulations were

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[1] `http://sals.natur.cuni.cz/metacentrum.html`

aimed to interpret various experimental results, especially the time resolved fluorometric measurements. A series of simulations of the non-radiative energy transfer and migration between fluorophores tagged to the ends of chains in micellar cores has been performed in order to explain the time resolved fluorescence quenching and the time resolved fluorescence depolarisation. The results have been presented at international conferences and published in scientific journals Macromolecules, J. Fluorescence, etc. (See the list in the appendix.)

Recently, the solubilization of the homopolymer in micellar cores has been also studied. The solubilization processes play important role in the formation of so called "anomalous micelles". The studies concern conformations of the core-forming blocks and conformations of chains solubilized in cores. Results of the performed simulations show which factors play the key role in solubilization processes of the homopolymer in micelles. Our preliminary results indicate that these systems are thermodynamically stable and their experimentally observed instability is caused by kinetic barriers during the formation of micelles. Results of these computer studies have been prepared for publication.

The newest project is the study of polymer chains in the middle layer of multilayer micelles. These nanoparticles (so called "onion skin micelles") were prepared experimentally in our research group. Their structure and properties have not yet been studied in detail. Several recognized laboratories have shown interest in cooperation in this research topic (e. g., Oak Ridge National Laboratory, US Dept. of Energy, Dept. of Physical Chemistry, University of Uppsala). The first results of Monte Carlo simulations of chain conformations of the middle layer were summarized in the diploma theses (K. Jelínek: Monte Carlo simulations of polymer chains conformations in the middle layer of the multilayer micelles, Dept. of Phys. and Macromol. Chemistry, Charles University, Prague 1999). The latest results will be published soon.

List of grants that have been using computer facilities of the *METACenter*

1. Laboratory of Specialty Polymers, Ministry of Education of the Czech Republic VS 97103 (K. Procházka).
2. Association processes in polyelectrolyte systems, Ministry of Education of the Czech Republic FR VŠ G4/1714/1999 (K. Procházka).
3. Multi-Layered Polymeric Colloid Structures: Model Systems for Studies of Photoinduced Processes in Organized Media, Grant Agency of the Czech Republic 203/97/-0249 (K. Procházka, Z. Tuzar).
4. Energy Migration in Polymeric Systems, Ministry of Education of the Czech Republic FR VŠ G4/1220/1997 (K. Procházka).
5. Complexes of Low-Molar-Mass Surfactants with Organized Polymeric Structures, Grant Agency of the Charles University 1197/1997 (K. Procházka, Z. Tuzar).
6. New Polymeric Particles Prepared in Block Copolymer Micelles, Grant Agency of the Czech Republic 203/96/381 (Z. Tuzar, K. Procházka).
7. Novel Colloid Objects: Polyelectrolyte Micelles, Grant Agency of the Czech Republic 203/94/0693 (K. Procházka, Z. Tuzar).

8. Study of Ultrafast Photophysical and Photoinduced Processes in Organized Polymeric Systems, Grant Agency of the Charles University 144/1994 (K. Procházka, Z. Tuzar).
9. Solubilization Properties of Water Soluble Block Copolymer Micelles, Grant Agency of the Czech Republic 203/93/1063 (Z. Tuzar, K. Procházka).

List of results obtained in the *METACentrum*

Publications in scientific journals

[1] T. Vrbová, Z. Limpouchová, K. Procházka: A Monte Carlo Study of Copolymer Chain Conformations in Dilute Solutions in Good and in Selective Solvents. Collect. Czech. Chem. Commun. **60**, 736–750 (1995).

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[3] D. Viduna, Z. Limpouchová, K. Procházka: Conformations of Self-Avoiding Tethered Chains and Nonradiative Energy Transfer in Dense and Constrained Systems. A Model for Cores of Polymeric Micelles. Macromolecules **30**, 7263–7272 (1997).

Contributions at international conferences

[1] K. Procházka, Z. Limpouchová, D. Viduna: Nonradiative Energy Transfer in Cores of Block Copolymer Micelles, NATO ASI Meeting “Solvents and Polymer Organization”, Antalya, Turky, August 1–12, 1995.

[2] D. Viduna, Z. Limpouchová, K. Procházka: Simulation of Energy Migration in Blocks of Block Copolymer Micelles, Liquid Matter Workshop 96, Strážné 26.–29. 9. 1996.

[3] D. Viduna, Z. Limpouchová, K. Procházka: Excitation Energy Migration in Polymeric Micelles, The 3rd International Conference on Fluorescence Techniques and Fluorescent Probes, Prague, Czech Republic, April 1997.

[4] K. Procházka, D. Viduna, Z. Limpouchová: Monte Carlo Study of Chain Conformations in Polymeric Micelles, American Chemical Society Meeting, San Francisco, USA, April 1997.

[5] D. Viduna, Z. Limpouchová, K. Procházka: Monte Carlo Simulations of Chain Conformations and Processes of Nonradiative Energy Transfer in Polymeric Micelles, International Workshop on Computer Simulations of Liquids. Orlík, Czech Republic, May 1997.

[6] D. Viduna, Z. Limpouchová, K. Procházka: Conformations of Chains Solubilized in Cores of Block Copolymer Micelles. MC Study, Microsymposium on Polymers at Interfaces, Prague, Czech Republic, July 1997.

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[8] K. Procházka, M. Štěpánek, Z. Limpouchová, Y. Teng, S. E. Webber, P. Munk: Block Copolymer Micelles in Aqueous Media, International Conference on Associating Macromolecules. Fontenvraud, France, November 1997.

[9] K. Jelínek, Z. Limpouchová, K. Procházka: MC Study of Chain Conformations in Block Copolymer Micelles, The 4th Liblice Conference on Statistical Thermodynamics of Fluids, Železná Ruda, ČR, 4. 6.–8. 6. 1998.

Diploma theses

[1] David Viduna: Simulation of Nonradiative Energy Transfer in Micellar Cores of Block Copolymers, Praha 1996.

[2] Karel Jelínek: Monte Carlo simulace konformací řetězců v micelách blokových kopolymerů, Praha 1999.

RNDr. Tereza Vrbová, PhD.

Monte Carlo methods are very useful tools for investigation of conformational and thermodynamic properties of polymer molecules in dilute solution, and many research groups around the word focus on Monte Carlo simulations of such systems. *Self-avoiding walks* are often used as a model of polymer molecules.

Linear polymer molecules in dilute solution in the vicinity of an impenetrable wall represent a very interesting problem, one that is very demanding on computer time. During the last 10 months we have performed numerous computer runs, taking advantage of the *METACentrum* facilities and our effort resulted in an article accepted at an internationally renowned journal (Vrbova and Prochazka: Adsorption of self-avoiding walks at an impenetrable plane in the expanded phase: A Monte Carlo study, accepted at *Journal of Physics A: Mathematical and General*).

Currently we are finishing another Monte Carlo study, in which we use *neighbour-avoiding walks* attached to an impenetrable surface, where we want to learn something about the conformational properties of polymer molecules in dilute solution in a very good solvent, and we hope to publish the results soon. Also, a very thorough study of a model of a polymer molecule near a liquid-liquid interface is in progress.

None of the above mentioned projects would have been possible to do without the use of the *METACentrum* computer facilities. We presented our results at the *Workshop on Monte Carlo Methods* at the Fields Institute, Toronto, October 1998, and a poster on the Monte Carlo study of a polymer molecule near a liquid-liquid interface was accepted at the *4th Liquid Matter Conference* at Granada, July 1999. We also expect to publish several articles in international scientific journals.

The projects described above are financially supported by GAČR, grant # 203/99/P017 under the name "Monte Carlo simulation of phase transitions of polymer molecules in dilute solution near surfaces and interfaces".

Theoretical and Quantum Chemistry

doc. RNDr. Jiří Fišer, CSc.

1. J. Fišer (principal investigator), J. Vojtík (co-investigator): Ab initio calculations of hyperfine structure of nuclear quadrupole coupling of diatomic anions (GA UK, 1994–5). The aim of the project was to test the method of calculating nuclear quadrupole coupling constants for a complete range of vibration-rotation states of some selected diatomic anions. Comparison of the obtained results with those for the corresponding neutral molecules revealed the main factors responsible for the basic features of quadrupole hyperfine patterns in diatomic systems.

   Publication: [1].

2. R. Polák (principal investigator), J. Fišer (principal co-investigator): Theoretical Investigation of Collision Systems and Dynamics of Internal Motion (GACR, 1995–7). The goal of the project was to provide and rationalize information necessary for interpretation of hyperfine nuclear quadrupole and spin-rotation structure of low-lying rovibronic states of di- and triatomic systems at the level of sophistication corresponding to the laser induced fluorescence and saturation spectroscopy measurements.

   Publication: [2].

3. J. Vojtík (principal investigator), J. Fišer (principal co-investigator): Theoretical Study of Dynamics of Penning ionization in the $He(2^3S)-D_2$ system (GACR, 1995–7). A theoretical picture of the dynamics of the autoionization event was obtained for collision energies ranging from 20 to 150 meV. The treatment of the dynamics consisted in 2D classical trajectory calculations based on static characteristics which include quantum mechanical treatment of the perturbed $D_2\,(v'')$ and $D_2^+(v')$ vibrational motion. The effect of the collision energy on the total cross section of the autoionization process and corresponding PIES spectra was discussed.

   Publication: [3].

4. R. Polák (principal investigator), J. Fišer (principal co-investigator): Fine Structure of Quantum States and Reactivity of Small Systems (GACR, 1996–8). Information on hyperfine structure caused by nuclear quadrupole, spin-rotation and spin-spin interactions was obtained for some diatomic systems. The rovibrational dependence of the corresponding hyperfine parameters was calculated by averaging of the property curve over radial wave functions. The radial Schrödinger equation was solved numerically by the Colley-Numerov technique, the potential being a cubic spline fit to the accurate MRSD-CI potential.

   Publications: [4, 5].

Publications prepared with the use of *METACenter*

[1] J. Vojtík, J. Fišer: Ab initio calculation of the nuclear quadrupole coupling constants of rovibrational levels in the $X^2\Sigma^+$ state of all isotopic variants of LiH^-. Chem. Phys. **193** (1995) 47.

[2] J. Fišer, J. Vojtík: Theoretical Study of Nuclear Quadrupole Coupling Constants of Rovibrational Levels in the $X^3\Sigma^-$ State of OH^+. Int. J. Quantum Chem. **57** (1996) 441.

[3] J. Vojtík, R. Kotal, J. Fišer: Classical trajectory picture of the autoionization event in $He(2^3S)-D_2$ Penning ionization: collision energy dependence. Chem. Phys. **229** (1998) 165.

[4] J. Fišer and J. Vojtík: Nuclear Quadrupole Coupling Constants of BeH, BeH^+ and BeH^-: Ab initio Study of their Rovibrational Dependence. Chem. Phys. **205** (1996) 351.

[5] J. Vojtík and J. Fišer: Rovibrational Dependence of the Nuclear Quadrupole Coupling Constants of HF, OH^- and NeH^+. Chem. Phys. **218** (1997) 13.

Filip Uhlík

In 1996, only 11 years after their discovery, R. F. Curl, H. W. Kroto and R. E. Smalley were awarded the Nobel Prize for the discovery of fullerenes. Their discovery has founded probably the most dynamically developing branch of chemistry today. Fullerenes were used for preparation of high temperature superconductors, magnetic plastics, drugs against HIV and many other interesting substances and materials. Despite the successes in these studies of fullerenes plenty of problems remain unsolved and their solutions will require much work of both experimentalists and theoreticians.

One of these problems is a question of the number of fullerene isomers and their relative stability. Even an approximate theoretical solution requires computer hardware of *METACenter* or better, because localization of stationary points on potential energy hypersurface, calculation of second derivatives and the following construction of partition functions and calculation of weights of isomers in thermodynamic equilibrium as a function of temperature for system of fullerene size is on a border of today's computational chemistry capabilities.

Publications: [1, 2, 3, 4, 5].

Another interesting problem is a prediction of properties of new potential materials, for example complexes of fullerenes with noble gases, metals and fullerenes covered with metals.

Publications: [6, 7, 8, 9].

Population analyses, whose goal is to give a description of electronic structure near to classical chemical terms as partial charge on atom or order of chemical bond, is the last field of interest. Testing newly developed methods requires calculations of wave functions for many systems and basis sets. This was allowed by computer hardware in *METACenter*.

Publications: [10, 11, 12, 13].

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The Differences in Numerical Solutions of Planar Impinging Jet as Resulted from Turbulence Model Choice

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Introduction

Impinging jet results when a fluid issues from a nozzle, which is arranged against the target surface. The jet strikes into the surface, then it changes its direction and the fluid flows along the surface away. Present investigation is focused on the submerged jet, when the jet itself and a surrounding fluid both have practically the same density and viscosity, and their mixing occurs. The target surface is planar, immovable and non-porous. This case has been measured recently thus present computed results can be compared to the primary experimental data. The measurement of flow velocity was made using Pitot-Prandtl probe with a diameter 2 mm, further the pressure on the target surface and mass transfer there were measured — see [2, 3]. The evaluation of the mass transfer coefficient was made by the naphthalene sublimation technique. The governing equations are solved by a finite-volume method using FLUENT solver — see [1]. Three turbulence models were used, namely the standard k-ε model, the Renormalization Groups model (or “RNG model” in short) and the Reynolds stress model (or “RSM” in short). The computation was performed using multiprocessor Silicon Graphic computer of Charles University in Prague.

Primary experimental parameters

Experiment has been performed in air.
Kinematics viscosity: $\nu = 1.62 \times 10^{-5}\,\mathrm{m^2 s^{-1}}$;
Density: $\rho = 1.143\,\mathrm{kg.m^{-3}}$;
Thermal conductivity $\lambda = 2.77.10^{-2}\,\mathrm{W.m^{-1}.K^{-1}}$;
Specific heat: $1011\,\mathrm{J.kg^{-1}.K^{-1}}$;
Pressure of the ambient $p_{\mathrm{op}} = 99334\,\mathrm{Pa}$;
Nozzle width: $b = 10\,\mathrm{mm}$;

Nozzle-to-plate spacing: $s = 100\,\mathrm{mm}$;
Jet average velocity $w_{cntr} = 28.6\,\mathrm{ms}^{-1}$;
Reynolds number: $\mathrm{Re_b} = 17\ 875$;
Euler number: $\mathrm{Eu} = \frac{p_{UK}}{\rho w_{\mathrm{cntr}}^2/2} = 1.09$, where $p_{UK} = 508\,\mathrm{Pa}$ is an overpressure at the inlet, i.e. in the chamber located upstream nozzle.

Numerical results

The series of cases was solved; present paper deals with following seven typical examples.

Example No.	Turbulence model	Grid	Heat transfer
5	RNG	157×128	No
6	k-ε	157×128	No
7	RSM	157×128	No
11	RSM	157×128	Yes
12	k-ε	314×256	Yes
13	RNG	314×256	Yes
14	RSM	314×256	Yes

Table 1:

The other data were identical for all examples. An overpressure at the inlet and the pressure at the outlet were prescribed 508 Pa and 0 Pa, respectively.Turbulence intensity at the inlet, a characteristic domain length scales at the inlet and at the outlet were prescribed 1 %, 0.6 m and 0.22 m, respectively. The presumption of the turbulence intensity at the outlet was 10 %. Thermal boundary condition for the heat transfer computation was prescribed as uniform heat flux from the target plate into the fluid; the value was $1000\,\mathrm{W.m}^{-2}$.

Discussion

First, the Euler number was evaluated like a criterion of a pressure drops. Computed values are showed in Table 2, experimental value Eu=1.09 was given in paragraph 2. The differences between the computed and experimental values are rather big; worthy note, the Euler number is very strict criterion, because of the square of the velocity at the slot-jet exit plane in the Eu definition.

Further, the relationships plotted on the following figures are discussed.

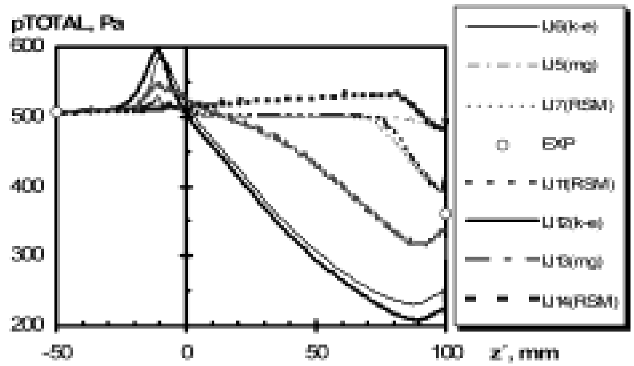

Figure 1:

Figure 1 shows total pressure along the jet axis; plotted pTOTAL — value means the overpressure against the ambient; z'-coordinate has an orientation from the slot nozzle exit plane ($z' = 0$) to the target surface ($z' = 100\,\mathrm{mm}$). Good agreement between the experiment and computation with RNG model and finer grid is evident (see EXP- points and IJ13-curve). On the other hand, the behavior of RSM is dependent on the grid, and finer grid gives not acceptable result (see IJ14- curve, when the pTOTAL increases along the jet). The explanation of this point needs next work; the RSM demands finite-difference scheme with higher order, which has bigger tendency to be numerical unsteady. (Unstable tendency like a result of higher precision of finite-difference scheme is a typical trend, independent on the turbulent model, but the case with the RSM behaves more sensitive.) According to our expectation, standard k-ε model gives the worse result.

Figure 2 shows a velocity magnitude along the jet axis. The RNG model gives the best result, i.e. very good agreement of the computation and experiment (see IJ 13- and EXP-curves).

Example No.	w_{cntr}, m/s	$q = \rho\frac{w_{cntr}^2}{2}$	$\mathrm{Eu} = \frac{508}{q}$
5	25.0	357	1.42
6	23.8	324	1.57
7	24.2	335	1.52
11	25.2	363	1.40
12	24.0	329	1.54
13	26.1	389	1.30
14	25.8	380	1.33
experiment	28.6	467	1.09

Table 2:

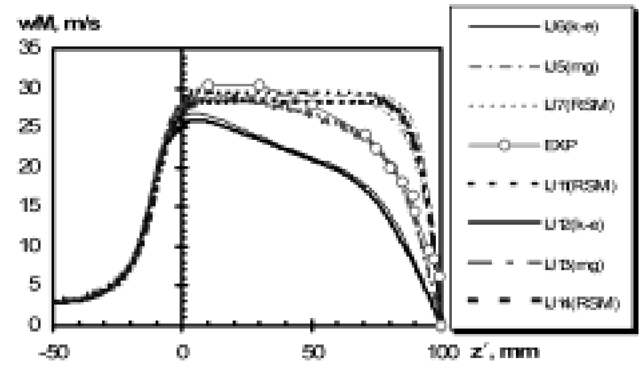

Figure 2:

Figure 3 shows the pressure on the target surface; y-coordinate has an origin on the nozzle axis ($y = 0$). The RNG model again gives the best result, i.e. good agreement of the computation and experiment, see IJ 13- and EXP- curves, respectively.

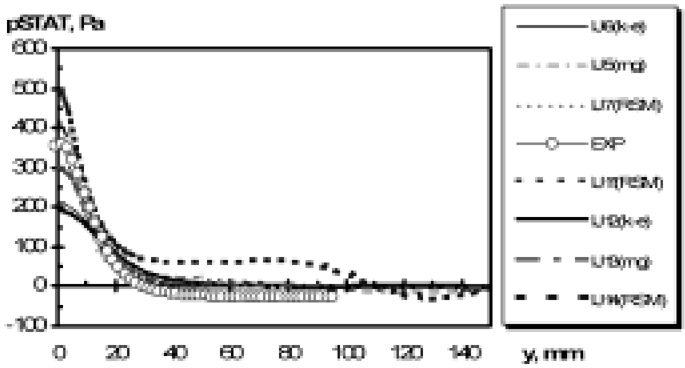

Figure 3:

Figure 4 shows velocity magnitude profiles in the nozzle exit plane. According to our expectation, the RNG model and the RSM one yield better results at finer grids.

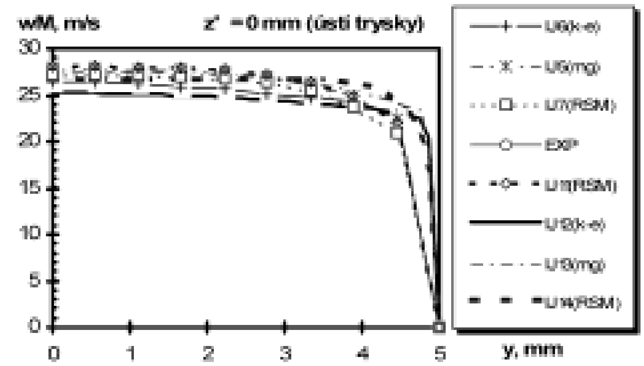

Figure 4:

Figures 5–8 show velocity magnitude profiles computed/measured 10 mm, 30 mm, 50 mm and 81 mm downstream the nozzle exit, respectively. The RNG model gives good agreement of the computation and experiment again, see IJ 13- and EXP- curves; the RSM model gives good results as well.

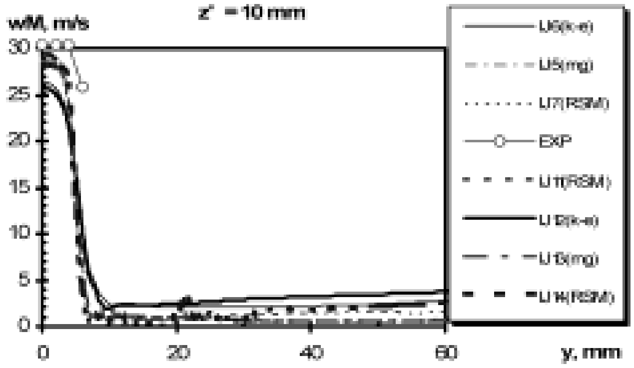

Figure 5:

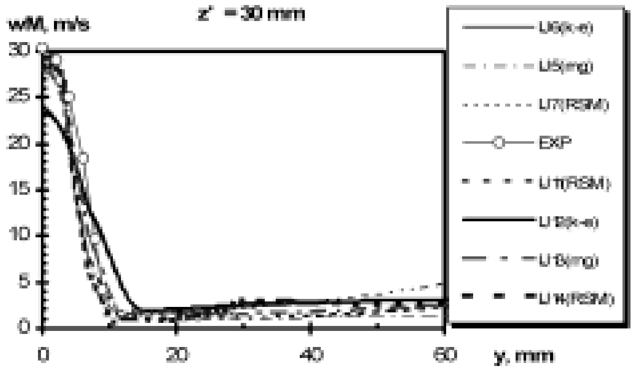

Figure 6:

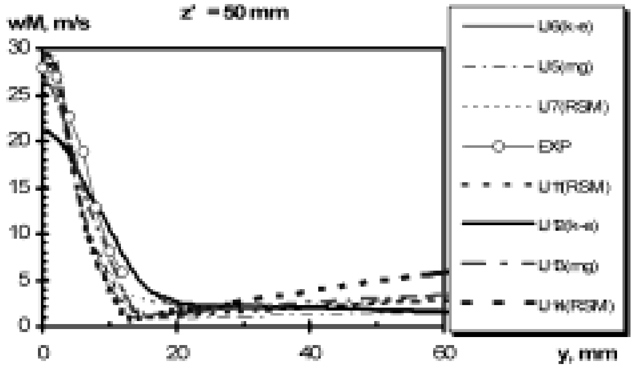

Figure 7:

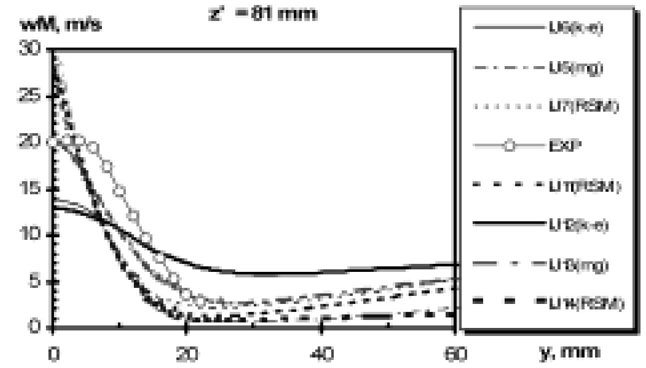

Figure 8:

Figures 9, 10 and 11 show velocity magnitude profiles computed/measured 10 mm, 30 mm, 48 mm from the nozzle axis, respectively; z-coordinate has an orientation perpendicular to the target surface ($z = 0$ is on this surface). The RNG model and the RSM one both give quite good results, like at the foregoing figures 5–8.

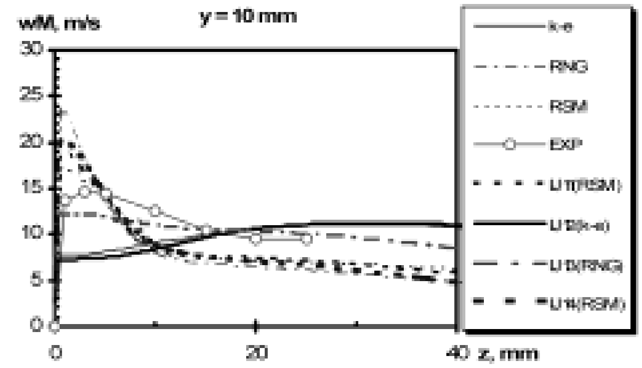

Figure 9:

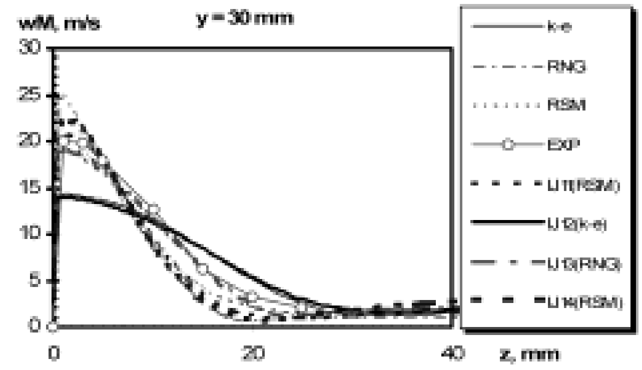

Figure 10:

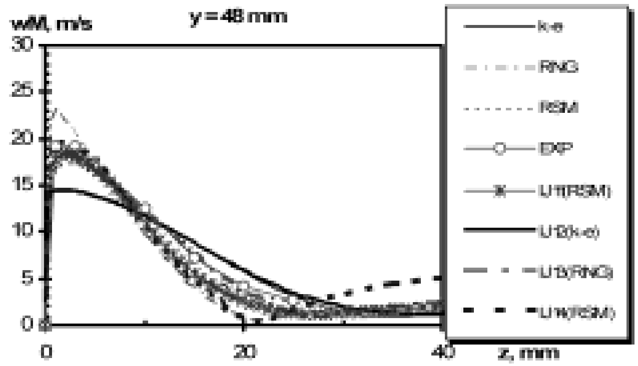

Figure 11:

Figure 12 shows computed/measured heat transfer coefficient on the target surface; the experimental value was evaluated using heat-mass transfer analogy from the mass transfer coefficient, which was measured by the naphthalene sublimation technique [2, 3].

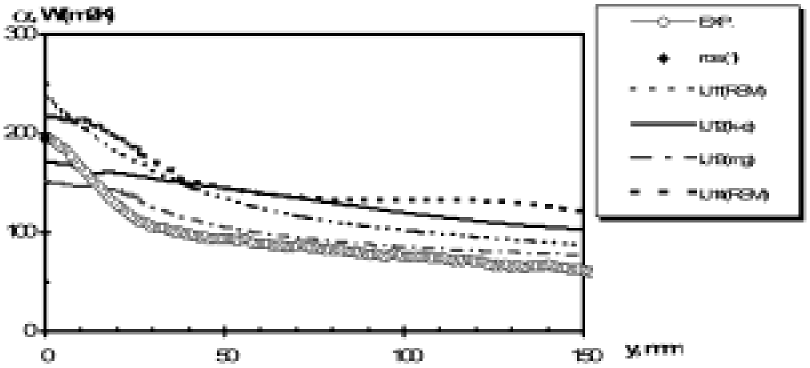

Figure 12:

Conclusion

The present results indicate that the numerical simulation of turbulent impinging jet should be based mainly on the RNG model turbulence. The RNG model seems to be advisable (for present jet case) despite its exact explanation is rather vague The RSM is very robust model, moreover it gives a velocity fluctuation, but it demands more CPU time as well as the higher precision of the finite-difference scheme. The RNG model demands the higher precision of the finite-difference scheme, too. A doubtless result is the impropriety of the standard k-ε model (in the form implemented in FLUENT solver) for an impinging jet computation. It is planned to perform additional experimental/numerical study of impinging jet with smaller nozzle-to-plate spacing the computation will be made mainly with RNG model. The other basic case of impinging jet is generated when a fluid issues from a round nozzle; it will be study in the future using two- and three- dimensional computations.

Acknowledgment

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