Molecular Science Computing Facility

The Molecular Science Computing Facility (MSCF) supports a wide range of computational activities in environmental molecular research, from benchmark calculations on small molecules to reliable calculations on large molecules, from solids to simulations of large biomolecules, and from reactive chemical transport modeling to regional cloud climate modeling. The MSCF provides an integrated production computing environment with links to external facilities and laboratories within the U.S. Department of Energy (DOE) system, collaborating universities, and industry.

Capabilities

MSCF provides computational resources for Computational Grand Challenges in environmental molecular science and basic and applied research areas that address the environmental problems and research needs facing DOE and the nation. Computational Grand Challenge projects typically involve multiple investigators from universities, national laboratories, and industry working collaboratively as teams. These projects are usually granted computer time allocations for three years. MSCF supported 15 three-year Grand Challenge projects during 2004. The average annual computer time allocation for Grand Challenge projects in 2004 was 739,080 CPU hours, an increase of nearly 320% over the previous year. This increase is attributed largely to the new MPP2 computing system that is now fully functional.

MSCF also supports smaller, shorter-term projects called MSCF Pilot Projects. Pilot Projects are limited to a maximum of 75,000 processor hours and a one-year duration, with short extensions occasionally granted for project completion. MSCF supported 44 Pilot Projects during 2004, with an average allocation of 40,000 CPU hours. Pilot Projects are typically directed at developing the capability to submit a Computational Grand Challenge proposal in the future (e.g., a combination of theory/method or code development activities, or calculations that provide the initial scientific basis of a Computational Grand Challenge proposal).

Instrumentation & Capabilities

- **MPP2**. Production cluster of 978 HP rx2600 nodes, 1956 1.5-gigahertz IA64 processors, 450 terabytes local disk, 6.8 terabytes memory, and 11.8 teraflops theoretical peak performance
- **Lustre**. Shared cluster filesystem, 53 terabytes
- **NWfs**. EMSL long-term data store, 85 terabytes
- **Network**. OC12 (600 MBit/sec) internet connection, Gigabit Ethernet MSCF backbone
- **NWVisus**. Visualization server, SGI Onyx 3400Graphics, 8 processors, 16 GB RAM, 2 Infinite Reality3 pipes, 144 GB disk, with a PanoramTech 3 screen monitor
- Digital video editing suite
- Access GRID internet node
- **Molecular Science Software Suite**. NWChem, Ecce, GA Tools

MSCF high-performance computing systems had 424 total users during 2004. Of this total, most of the users (i.e., 78%) were external users (not from Pacific Northwest National Laboratory [PNNL]), and the remainder (i.e., 22%) were PNNL staff, postdoctoral fellows, or students. The distribution of the users by type of institution was 60% from universities, 22% from PNNL, 10% from other DOE laboratories, 4% from industry, 1% from other agencies of the federal government, and 3% from other agencies (Figure 1).

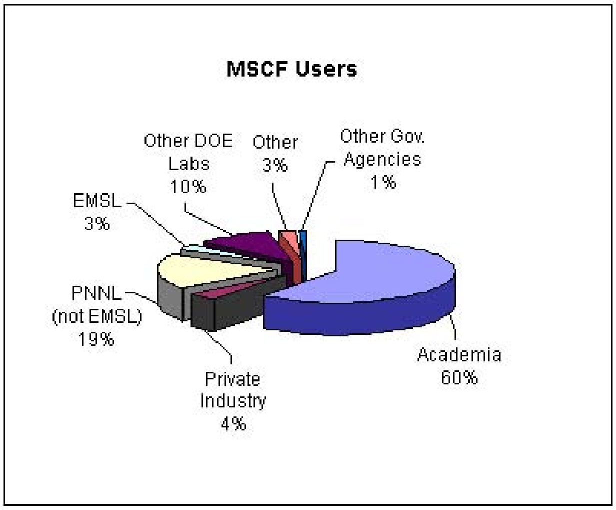

Figure 1. MSCF resource allocation by user affiliation.

User Computing in MSCF. To optimally address the complex environmental problems facing DOE and the nation and to best use limited staff resources, the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) follows the recommendation of the EMSL Science Advisory Committee to use a Computational Grand Challenge approach to providing large blocks of resources to the user community. A call for proposals is issued annually, and teams of computational scientists respond with peer-reviewable proposals for system time allocations. Access for the Grand Challenge teams is for periods of one to three years. The following criteria are used when reviewing proposals:

- scientific merit
- appropriateness of the proposed method or approach
- relevance to the environmental problems and research needs of DOE and the nation
- technical competence of the investigators
- reasonableness and appropriateness of the proposed computer resources.

The process used to review proposals and allocate MSCF computing resources is shown in Figure 2. The request for proposals is open to all researchers, regardless of their institution or source of funding. For reference, the recent request for Computational Grand Challenge proposals involved 22 external scientific reviewers from leading universities and research institutions from around the world. Proposals received two reviews on average, and three reviews in certain cases.

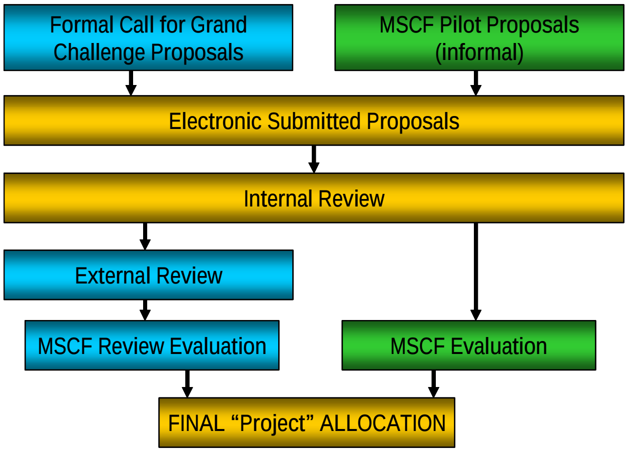

Figure 2. Review process and allocation proposal flow chart.

MSCF Resources

The MSCF provides a combination of production computing hardware and software resources and visualization tools to support the scientific research activities of the Computational Grand Challenge and EMSL Pilot Projects. The hardware and visualization resources are the High-Performance Computing System-2 (MPP2), NWfs, the Graphics and Visualization Laboratory (GVL), and the Molecular Science Software Suite (MS^3). These resources are discussed below.

MPP2. MPP2 provides a balanced supercomputer. Since becoming operational in July 2003 with a theoretical peak performance of 11.8 teraflops, 6.8 terabytes of RAM, and 450 terabytes of disk, the Hewlett-Packard (HP) supercomputer (Figure 3) has been tailored to meet the operational needs of EMSL users.

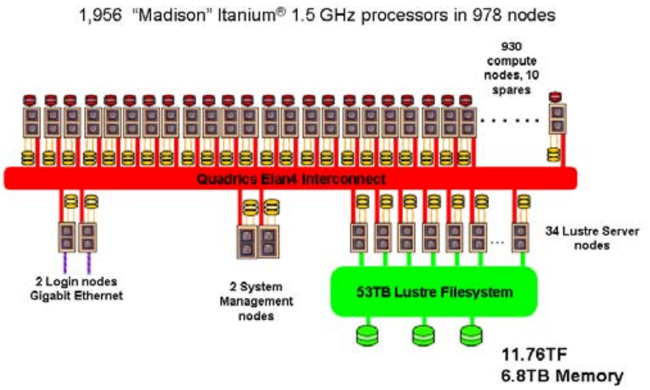

Figure 3. MPP2 Configuration.

NWfs. NWfs, which is the EMSL archive system located in MSCF, uses a groundbreaking approach to disk storage that clusters many low-cost commodity disks to provide fault-tolerant, high-performance storage. NWfs currently has more than 85 terabytes of storage available to users and the ability to grow to over a petabyte.

GVL. GVL provides production graphics and visualization facilities for the display and analysis of complex data sets from both experiments and simulations. GVL contains four high-performance graphics stations based on Silicon Graphics Incorporated (SGI) technologies with high-speed Gigabit Ethernet connections to the production supercomputers and to NWfs, a digital video system integrated with the workstations to facilitate the display and capture of scientific data, and digital video editing equipment for the preparation of scientific presentations. The video system also is connected to the EMSL auditorium and to the World Wide Web to facilitate internet conferencing. An IBM Scalable Graphics Engine is connected to the MSCF Dell Linux Cluster to provide the highest performance visualization capabilities.

MS^3. Software resources include MS^3, which is a comprehensive, integrated set of tools that enables scientists to understand complex chemical systems at the molecular level. MS^3 couples the power of advanced computational chemistry techniques with existing and rapidly evolving high-performance massively parallel computing systems with extensible problem-solving capabilities. The suite consists of three components: 1) the Northwest Computational Chemistry Software (NWChem), 2) the Extensible Computational Chemistry Environment (Ecce), and 3) the Global Array Tools (GA Tools). These three components are briefly described below.

- ***NWChem***. Version 4.6 of NWChem was released in June. Documentation and information are available on the NWChem website (http://www.emsl.pnl.gov/docs/nwchem). NWChem provides many methods for computing the properties of molecular and periodic systems using standard Gaussian and planewave-based quantum mechanical descriptions of the electronic wave function or density. In addition, NWChem can perform classical molecular-dynamics and free-energy simulations. These approaches may be combined to perform mixed quantum-mechanics and molecular-mechanics simulations.

  NWChem is available on almost all high-performance computing platforms, workstations, PCs, and clusters of desktop or workgroup servers. NWChem development provides maximum efficiency on massively parallel processors.
- ***Ecce***. Ecce, which is composed of a suite of client/server UNIX-based applications, is a domain-encompassing, problem-solving environment for computational chemistry. Applications for setting up, running, and analyzing the results of computational chemistry studies are built on top of a web-based data management and inter-application messaging server framework. A computational code registration capability supports several underlying chemistry codes and the ability to integrate new ones without reworking core Ecce applications. Running jobs through industry standard remote communications, like secure shell, and a batch queue management system registration capability allows transparent access to high-performance compute resources from users' desktop workstations. A simple installation procedure and extensive online help combine to make Ecce a preeminent user environment for computational chemistry. The current production release of Ecce is version 3.2.1. There are six major application components:
  - Calculation Manager aids in the organization and manipulation of computational chemistry studies. This tool allows an at-a-glance overview of the status of every calculation and easy access to key setup parameters and run statistics.
  - Molecule Builder is an intuitive point-and-click tool that enables the building, visualization, modification, and manipulation of three-dimensional visualizations of chemical systems.
  - Basis Set Tool enables the choice from over 245 predefined Gaussian basis sets or the ability to create new ones for use in *ab initio* electronic structure calculations.
  - Calculation Editor allows the user to choose input options using point-and-click interfaces for different chemistry codes, and then generates the code-specific input.
  - Job Launcher is used for submitting a calculation to a computer for processing. The user may submit a calculation to any computer that has been registered within Ecce and for which the user has an account.
  - Calculation Viewer provides convenient access to current information for a single calculation during execution or after completion. It has many features for viewing and visualizing chemical system properties.
- ***GA Tools***. GA Tools (also known as ParSoft) includes high-performance computing libraries and tools for applied parallel computing focused on inter-processor communications through the aggregate remote memory copy interface, high-performance input/output through the Parallel I/O tools, and programming models for hierarchical memory systems through the Global Arrays and Memory Allocator libraries. The development of these tools is driven by needs of real scientific application codes on the high end parallel systems.

Development of Aggregate Remote Memory Copy (ARMCI) has been supported by EMSL operations and by the DOE Center for Programming Models for Scalable Parallel Computing.

MSCF Organization

MSCF is organized into three groups: the Visualization and User Services Group, the Molecular Science Software Group, and the Computer Operations Group.

Visualization and User Services Group (VisUS). This group provides an extremely diverse set of services for all users of the MSCF high-performance computers and GVL. Scientists who need access to high-end computing equipment frequently have difficulty getting started. The difficulties encountered range from logging in to getting user codes to run efficiently. VisUS handles user proposal applications, follows user progress during computational projects, manages proposal reviews for both Computational Grand Challenge projects and Pilot Projects, helps with user accounts, provides general consulting support for MSCF software packages, supports and maintains software, manages the GVL, conducts training and user workshops, develops visualization software and high-quality visualizations, and produces websites.

The group manages the Computational Grand Challenge and Pilot Project proposal process for the MSCF. This activity includes receiving the proposals, providing preliminary review for EMSL missions, preparing proposal packets for external peer review, evaluating peer reviews, granting project allocation, and managing the allocation by using the MSCF QBank, an open source dynamic-reservation-based allocations management system.

Consultants have various roles, including those of administrator, tutor, programmer, or research scientist, and field a variety of requests for support. During 2004, five scientific consultants responded to more than 700 email requests, and about 500 additional requests were handled over the telephone or during office visits. Consultants also work directly with MS^3 development teams to give customer feedback and to test functionality.

Information about the use and configuration of the MSCF computational resources is critical to the user base and is provided efficiently to users via the Internet through the MSCF home page. The MSCF website contains all necessary information about how to establish accounts and get started, and about computer configurations as well as documentation and web-based tutorials for MS^3. Scientists generate enormous amounts of data either from computational resources or from EMSL instruments. These data are usually complex and difficult to understand. The capabilities and expertise available in the GVL, including its high-performance graphics compute servers and state-of-the-art multimedia equipment, help scientists visualize these complex data. The real-time digital video capture capability from the graphics compute servers allows fast, yet high-quality, video production. Users can generate presentation media in any form—from video (including all international video standards) to web-based animations. The group also provides basic video production services.

Molecular Science Software Group. This group has the primary responsibility for developing and supporting MS^3. This effort includes developing high-performance versions of the software and new high-performance algorithms, responding to user requests for additional features, supporting and maintaining the software, diagnosing MS^3 problems associated with computer vendor hardware and software, consulting on specific MS^3 problems, distributing MS^3 to remote sites, porting software to new architectures, and conducting training and user workshops.

Staff of the MS^3 Group focus on developing next-generation molecular modeling software for newly evolving computer technologies, especially massively parallel computers. The group includes other PNNL matrixed staff and is composed of computational chemists and computer scientists (with external collaborations to mathematicians) who work together to develop the MS^3 software. This software is used by many of the MSCF Grand Challenge projects and has been distributed to almost 1000 sites worldwide. In addition to the development activities, this group is also responsible for training software users, conducting tutorial workshops, and providing user support. Toward this end, several resources have been developed to facilitate user interactions. These include MS^3 websites with user and reference manuals, download information, release notes, FAQs, a list of known bugs, tutorials, and benchmark information, as well as a support queue for answering direct user questions and user email lists. During 2004, the group responded to many queue requests, and ultimately the group moved the NWChem support mechanism to the user majordomo list to create a larger community of well-informed users.

Computer Operations Group. This group operates, maintains, and advances the capabilities of the MSCF scientific computing systems. The group is responsible for the operation and implementation of the various production supercomputers in the MSCF and has developed unique system management, monitoring, allocation management, and scheduling capabilities. The primary focus is on providing high-quality, reliable production computing cycles on the production computer in the MSCF to support very large parallel calculations for Computational Grand Challenge projects.

Upgrades

NWfs Hardware. In August, the MSCF received new hardware for the second-generation NWfs archive storage system. This hardware provides 380 terabytes for storage of data primarily generated by EMSL instruments and MPP2.

RAID5 and RAID6 Arrays. The MSCF contributed code to the Linux 2.6 kernel, enabling creation of Software RAID5 and RAID6 arrays that are larger than 2 terabytes. During testing of these changes, a 6-terabyte array was created. This array, which uses low-cost Serial ATA disk drives, is believed to be the largest Software Raid5/6 array created under Linux. This upgrade will enable low-cost, high-volume data storage that will support proteomics and other high-storage-volume projects.

Advanced Storage Technologies. EMSL benefits from a research alliance aimed at enabling a new generation of fast and efficient storage technologies for data-intensive computing. The long-term collaboration between PNNL and Silicon Graphics (SGI) will involve researching options for more than 2.5 petabytes of storage during the next two years. SGI delivered a single 380-terabyte file system to EMSL as part of the alliance's first phase. More information is available at http://www.pnl.gov/main/highlights/sgi.html.

MSCF Expansion and Elan4 Upgrade. Preliminary design work on facility expansion of the MSCF continued through January and into early February. Additionally, the parallel filesystem of the MPP2 supercomputer, which was upgraded to use Elan4, provides users with much faster access to the global filesystem. Early results of the upgrade demonstrated a sustained write rate of over 600 megabytes per second to the global filesystem by each client. Before the upgrade, the system demonstrated a write-rate of 200 megabytes per second. This threefold increase will profoundly impact the ability of the system's clusters to perform disk-intensive operations such as bioinformatics and indirect electron structure methods.

NWChem 4.6. With the change of the Elan3 network to Elan4 on the MSCF HP machine and significant efficiency improvements in NWChem, we have provided even more capability and higher capacity computing at the MSCF. Figure 4 shows a logarithmic plot of the wall clock time versus the number of processors used to execute the density-functional module of NWChem for the $Si_{75}O_{48}H_{66}$ molecule (3554 basis functions) on various platforms.

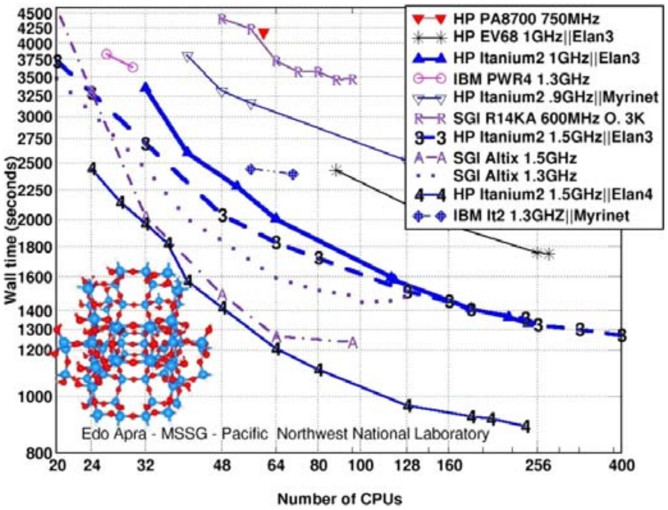

Figure 4. Wall clock time as a function of the number of processors used on various platforms for local density approximation calculations of 3554 basis functions.

Figure 4 illustrates that the Elan4 results achieved a significant improvement (25 to 45% on moderate numbers of processors) in time-to-solution by upgrading the network. These results also clearly show the excellent performance of the HP system. In addition to the hardware changes, significant changes were made in the grid partitioning of the density functional code and in pre-fetching in the molecular dynamics software to obtain better performance on the HP.

In addition to the changes made in the code to enable efficient, large scientific computations, the NWChem team has been adding additional capability. New many-body methods using the tensor contraction engine (TCE) have been added with the release of NWChem 4.6, CCSD(T) and CCSD[T] for closed- and open-shell systems with Abelian symmetry (contributed by Alex Auer, University of Waterloo), EOM-CCSD, EOM-CCSDT, EOM-CCSDTQ for excitation energies, transition moments, and excited-state dipole moments of closed- and open-shell systems, and CCSD, CCSDT, and CCSDTQ for dipole moments of closed- and open-shell systems.

TCE is a code developed in Python that produces a set of tensor equations from mathematical equations for many-body wave functions represented in normal-ordered second quantization. The tensor equations are further manipulated to produce a parallel implementation in software. In other words, TCE is an automated code-generating mechanism to produce highly scalable software in an expedited manner. The TCE effort is collaborative with other computational chemists and computer scientists located at Ohio State University, Oak Ridge National Laboratory, the University of Waterloo, and the University of Florida. The PNNL portion of the TCE effort is supported both through EMSL and through the Basic Energy Sciences Division of DOE’s Office of Science.

Significantly, large simulations were performed this year on the HP and changes were required in the software to enable these simulations to perform well. For example, using NWChem and the HP, we were able to compute a CCSD(T) energy of octane to get better computational thermodynamics of the system. The (T) part of the computation required 23 hours on 1400 processors and achieved 75% of the peak CPU capability. This efficiency improvement is very unusual for large simulations.

In addition, a capability development project was initiated to provide the EMSL and NWChem user community with a new property module that greatly enhances their ability to calculate experimentally observable properties. The properties that are now available to beta users are multipoles up to octupoles, electron and spin density, electrostatic potential, electric field, electric field gradient, spin-dipolar and Fermi-contact for hyperfine splitting, nuclear magnetic resonance shielding, indirect spin-spin coupling, and Mulliken population analysis.

Ecce. Two production releases of Ecce were made during 2004. The first was version 3.2, which was released in May, and the second was version 3.2.1, which was released in July.

The total number of sites that downloaded Ecce version 3.2 was 122 during the three months it was available, and 185 sites downloaded version 3.2.1 from July until the end of the year. Since version 3.1 was released in mid-August 2003, more than 440 different sites have downloaded Ecce production releases. Featured highlights of Ecce version 3.2 are shown in Figure 5 and include:

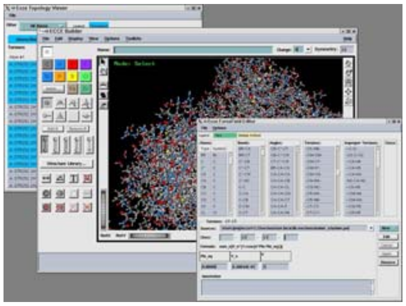

Figure 5. Snapshots of the Ecce ForceField Editor, Builder, and Topology Viewer (foreground to background, respectively)

- completion of the Builder molecular-dynamics toolkit Force Field Editor, which allows users to edit and combine files that use the NWChem force-field format
- completion of the Builder molecular-dynamics toolkit Topology Viewer, which allows users to assess whether available force fields are sufficient to cover systems being developed for molecular-dynamics simulations
- Builder DNA toolkit for creating segments of double-stranded DNA
- Gaussian 03 support (Gaussian 98 also remains supported)
- packaging of NWChem binary distribution with Ecce
- support for sharing calculation data by allowing users to grant per-user read-write or read-only access to project folders
- a simplified and more robust Ecce installation procedure.

Highlights of Ecce version 3.2.1 include:

- Builder Constraint/Restraint toolkit to freeze the value of bonds, angles, and torsions at specified values during geometry optimizations
- Builder isotope mass editing through the geometry table for overriding the default most-abundant isotope
- Builder QM/MM toolkit for setting up electronic structure calculations in a field of fixed-point charges
- NWChem 4.6 support
- Gaussian cube file support for the automatic detection and analysis of files created as part of a calculation run
- Macintosh OS X compute server support for running Ecce jobs
- on-line help updated with all new version 3.2 and version 3.2.1 features.

General information concerning Ecce can be found on the Ecce homepage, http://ecce.emsl.pnl.gov, while specific details about versions 3.2 and 3.2.1 are available at http://ecce.emsl.pnl.gov/docs/release/2864B-RV-32.pdf .

In August, Ecce was employed for the first time ever in an undergraduate classroom. Matthew Asplund at Brigham Young University incorporated Ecce and NWChem into the lab curriculum of his physical chemistry class. This milestone is significant in the development history of Ecce; the software has reached such a high level of robustness, reliability, and ease of use that it was chosen to replace an established commercial product. A number of the new features introduced in Ecce version 3.2.1 were developed in collaboration with Asplund. More details about these upgrades to Ecce can be accessed at http://www.emsl.pnl.gov/docs/inbriefs/ecce20040618.pdf.

Global Array Tools. Much of the EMSL work on the GA toolkit has concentrated on porting, tuning, and performance issues for the MSCF machine and on new algorithms that are required for improved performance. Additional efforts were directed toward bringing prototyped research capabilities into a production code.

Version 3.3 of the GA Tools was released in May 2004 and was made available for download from the GA Tools webpage. Additionally, in July, a beta version of GA 3.4 was created that includes support for processor groups. Processor groups will provide an opportunity for exploiting multilevel parallelism in applications and improving overall scaling on large processor configurations. In addition to maintenance, testing, and user support, specific new capabilities developed for Ecce include:

- non-blocking, one-sided operations on the Linux/Elan-4 systems (MPP2)
- optimized matrix multiplication (SRUMMA), which supports rectangular and transposed matrices (Figure 6)
- re-implementation of the ARMCI protocol stack for Elan4 to improve handling of noncontiguous data types and maximize overlap of communication with computations
- optimized port for the Mellanox Infiniband Network.

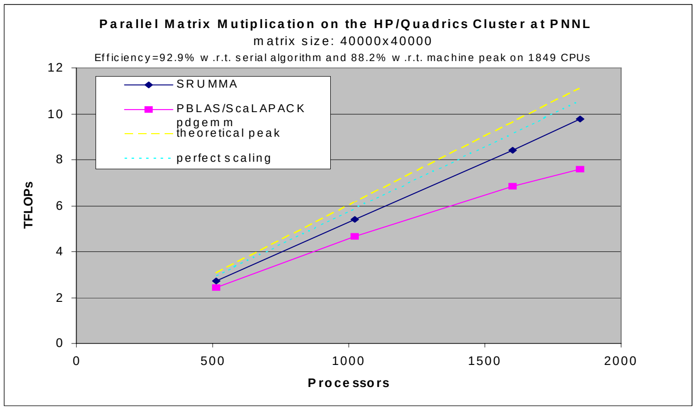

Figure 6. Optimized matrix multiplication (SRUMMA) performance.

Future Directions

During 2005, MSCF will be a stable production facility focused on accomplishing large, impactful science, including support for MSCF Computational Grand Challenges and Pilot Projects, as well as EMSL Grand Challenges and continuing support and development of the MS^3 software capabilities.

MSCF staff will be engaged in many different activities, and through these activities, the staff will continue to build advocacy and awareness of the capabilities available to the scientific user community in the MSCF and EMSL. These activities will include:

- creating information products (e.g., animations of user's research, brochures, fliers, etc.)
- presentations at national meetings
- organization of symposia in national meetings
- developing tutorials
- establishing an EMSL Distinguished Fellow position, associated initially with the MSCF.

Computational Investigation of the Fixed-Charge Derivative Tris(2,4,6-trimethoxyphenyl) Phosphonium Electrostatic Potential and the Charge-Remote Aspartic Acid Cleavage Mechanism

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Investigation of the charge-remote peptide fragmentation mechanism is important because the identification of peptides and proteins via tandem mass spectrometry is improved when peptide fragmentation patterns can be accurately predicted. Peptides are the building blocks for proteins, and understanding their structure and function can reveal new strategies for bioremediation techniques.

Mass spectrometry is one way to identify proteins in a complex sample. Typically this process begins with protein digestion, and the resulting peptide fragments are separated by liquid chromography and then analyzed with tandem mass spectrometry. The large volume of data collected from this process is then sorted and analyzed by a sequencing algorithm. This method is currently being used successfully in a high-throughput manner. However, because prediction of the fragmentation pattern is an important part of the sequencing algorithm, the algorithm can be improved with a better fundamental understanding of why proteins tend to fragment in certain ways.

The presence of aspartic acid in a peptide causes preferential fragmentation patterns, which reduces the probability of peptide identification by existing sequencing algorithms. Aspartic acid tends to cleave preferentially on its carbon-terminal side. This selective cleavage is more prominent when the number of ionizing protons does not exceed the number of arginines present in the peptide. This observation is significant because the enzyme trypsin is commonly used to digest proteins and leads to a significant number of arginine-containing peptides that are analyzed for identification by tandem mass spectrometry.

Selective cleavage data suggest that aspartic acid cleaves by means of a charge-remote mechanism because when the proton is sequestered at the basic arginine side-chain, preferential cleavage at aspartic acid is observed. When a mobile proton is available, cleavage is randomized, and many cleaves along the peptide backbone are observed. This phenomenon was further investigated by attaching the fixed-charge derivative Tris(2,4,6-trimethoxyphenyl) phosphonium (TMPP) to the nitrogen terminus of aspartic acid-containing peptides. Presumably, the peptide backbone will cleave by means of a charge-remote mechanism because of the absence of a mobile ionizing proton. Selective cleavage at aspartic acid is observed when the fixed-charge derivative is present, but when an additional proton is added, charge-directed cleavages along the peptide backbone also are prominent.

Computational modeling was recently undertaken at the W.R. Wiley Environmental Molecular Sciences Laboratory to rule out direct interaction between the charge-carrying

TMPP group and aspartic acid. Initially, the optimized structure and electrostatic potential of TMPP with a methyl group terminal was calculated. Results obtained from simulations using this model verify that most of the positive charge is buried within the TMPP derivative near the charged phosphorus atom. Therefore, it is presumed that this positive charge will not be able to influence the cleavage of an aspartic acid on an attached peptide in a charge-directed manner.

In addition, the structure of TMPP attached to a small peptide, alanine-aspartic acid, was computationally investigated (Figure 1). The carbon-terminal hydroxyl of the alanine-aspartic acid peptide was replaced with methyl to simulate a continuing peptide chain. Results demonstrate that the fixed-charge derivative does not interact via hydrogen bonding with the nucleophilic oxygen of the aspartic acid residue and, therefore, does not influence cleavage at that site. Results also show the aspartic acid nucleophilic oxygen lies approximately 3.5 Å from the electrophilic carbon, a reasonable distance for nucleophilic attack. Currently, calculations are under way to locate the transition state for the charge-remote aspartic acid cleavage mechanism.

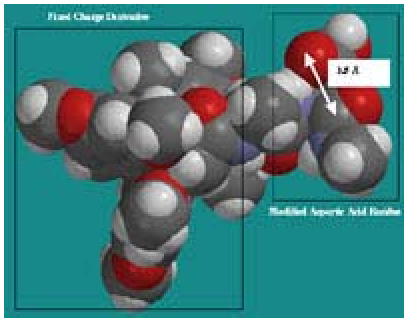

Figure 1. Computational model demonstrating the lack of hydrogen bonding between the fixed-charge derivative and the modified aspartic acid residue, and the proximity (3.5 Å) of the nucleophilic oxygen to the electrophilic carbon.

Computational Study of Polycyclic Aromatic Hydrocarbons and Their Derivatives

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Commonly formed by the incomplete combustion of coal, oil, wood, tobacco, and organic materials, polycyclic aromatic hydrocarbons and their ions are key molecular species in many branches of chemistry, such as combustion, environmental, and materials chemistry, and they play a role in environmental contamination. The existence of these species in interstellar media also is strongly suspected.

Polycyclic aromatic hydrocarbons (PAHs) are strong candidates for the carriers of interstellar infrared emission features and diffuse interstellar visible absorption bands, and are thought to be a major carbon reservoir in the interstellar medium. They also are primary intermediate species that form in combustion processes and are the most ubiquitous environmental contaminants from natural and manmade sources with varied mutagenic and carcinogenic activities. It has been proposed that PAHs are the precursors of flame-produced soot and fullerenes.

The goal of this work is to elucidate the spectroscopic properties and reaction dynamics of PAH radicals using a combination of theoretical and experimental techniques. Two approaches are employed. In the first approach, we performed an assortment of experimental and theoretical techniques to thoroughly characterize the properties and reactions of a variety of individual PAH ions. In the second approach, we studied a large number of PAH ions at once using a single experimental or theoretical technique with wide applicability and high throughput. From the computational perspective, the greatest challenge was developing an efficient and accurate theoretical tool applicable to sizable open-shell species that notoriously pose difficult electronic structure calculations.

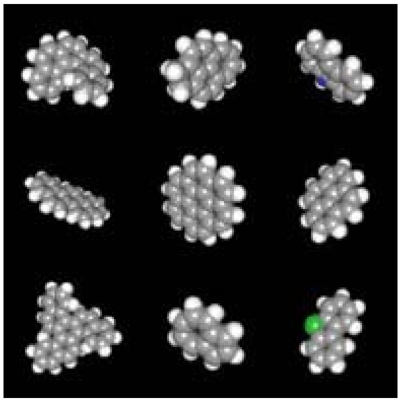

Figure 1. Some of the polycyclic aromatic hydrocarbons studied.

In previous studies, we demonstrated that time-dependent density functional theory (TDDFT) performed remarkably well for the interpretation of the spectroscopic properties of some PAH radicals. In FY 2002, we implemented a TDDFT method in NWChem for execution on massively parallel supercomputers. In fiscal year 2003, we performed TDDFT calculations for 51 radical cations and 7 radical anions of PAH (Figure 1) and presented a uniform, comprehensive interpretation of the spectroscopic data (Hirata et al. 2003a). We have shown that TDDFT is indeed capable of predicting the transition energies to the low-lying excited states of PAH ions to within an average of 0.3 eV. This accuracy is hardly affected by the sizes of PAH ions, the types of transitions, the types of orbitals involved, or other perturbations. Also addressed has been the well-known weakness of TDDFT in dealing with Rydberg excited states, for which we have developed a correction scheme that overcomes such a deficiency (Hirata et al. 2003b).

Concurrently, we combined various experimental techniques, including matrix-isolation Fourier transform infrared, ultraviolet-visible light spectroscopies, and Fourier transform ion cyclotron resonance mass spectroscopy with TDDFT, to describe the structures and reaction of the PAH 2,3-benzofluorene and its derivatives in detail (Banisaukas et al. 2004). Apart from the spectral assignment and structural determination made by theory and experiment, the study revealed a fascinating tendency of benzofluorene (also observed with other PAHs) to lose hydrogen and acetylene units successively and to eventually become pure carbon clusters. Our understanding of the mechanism of this hydrogen-loss process was advanced by theory and mass spectroscopy. We believe that this mechanism has significant implications in the fate of PAHs in interstellar media and in hydrocarbon combustion processes.

This research was performed in part using the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory.

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Seasonal Coupled Meteorology-Chemistry Simulations for the Great Lakes Region

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In addition to the effect of ozone on human health, it is well known that high-surface ozone concentrations can adversely affect many types of vegetation. Developing models to predict ozone concentrations is critical to future policy decisions.

The software code PEGASUS was developed as part of a study to advance atmospheric chemistry modeling capabilities and distinguish between ozone generated in urban environments and the ozone coming from the stratosphere to the lower atmosphere. The acronym identifies the research organization that developed the code (Pacific Northwest National Laboratory), the mathematical framework (Eulerian), the multiple chemical phase capability (Gas and Aerosols), the software's Scalability, and the Unified System it provides to describe both chemical and meteorological processes.

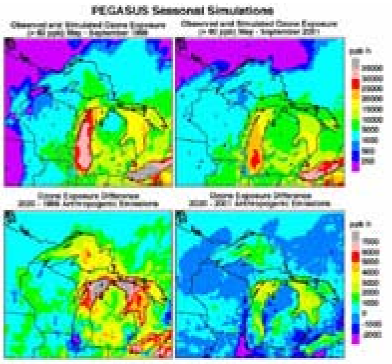

Figure 1. PEGASUS seasonal simulations.

PEGASUS was used to determine ozone exposure over the Great Lakes Region for two time periods: from May to September 1999 and from May to September 2001 (Figure 1). These two time periods were selected because ozone levels over the Great Lakes Region were higher and lower than normal during the summers of 1999 and 2001, respectively. PEGASUS was also used to examine the effect of future anthropogenic emission projections on ozone exposure. The modeling system was run in a nested grid configuration, with an outer grid that encompassed eastern North America with a horizontal grid spacing of 36 kilometers and an inner grid over the Great Lakes Region with a horizontal grid spacing of 12 kilometers. The number of nodes used on the inner and outer grids was 89 x 89 x 50 and 125 x 92 x 50, respectively. The meteorological driver for PEGASUS was run first to generate the synoptic, mesoscale, and boundary layer atmospheric conditions from May to September in both 1999 and 2001. The atmospheric conditions at hourly intervals were used to drive the gas-phase chemistry in PEGASUS along with time-varying background lateral boundary conditions for ozone and mobile, area, and point-source emissions of ozone precursors. About 55,000 node hours were required to run the modeling system for the two time periods, and an additional 7000 node hours were needed for emission projection simulations.

The predicted spatial and temporal variations in ozone concentrations over the Great Lakes Region were often consistent with measurements obtained from the U.S. Environmental Protection Agency's monitoring stations; however, uncertainties in the emissions estimates and predicted cloudiness likely contributed to model errors at specific times and places. The model also captured the overall month-to-month variability. Ozone exposures, determined as the sum of the hourly ozone concentrations higher than 80 parts per billion (ppb), over the two time periods are shown in Figure 1. Ozone levels greater than 80 ppb impact human health, while ozone levels greater than 60 ppb have been shown to be detrimental to the health of many types of vegetation. The simulated ozone exposure was found to be higher during the 1999 time period than during the 2001 time period, a finding that is consistent with the measured ozone levels in most locations. The largest differences between observed and simulated ozone exposure occurred south of Lake Erie.

An advantage of this model is that it predicts ozone exposure in remote regions where no measurements were made. A fraction of the predicted ozone originating from large urban and industrial sources was transported northeast to Canada where it impacted the remote forested regions surrounding the Great Lakes. The two simulations were repeated with anthropogenic emission projections for the year 2020 to estimate how ozone exposure will change given the same meteorological conditions. Figure 1 indicates that the meteorological conditions during the 1999 time period led to lower ozone concentrations in the immediate vicinity of large metropolitan areas, while higher concentrations were produced downwind in remote locations along the shores of the Great Lakes. The meteorological conditions during the 2001 time period resulted in lesser increases of ozone given the same emission projections.

This research was supported by the U.S. Department of Agriculture Forest Service and the U.S. Department of Energy's Atmospheric Sciences Program. Development of PEGASUS was supported by the Laboratory Directed Research and Development program of Pacific Northwest National Laboratory. This research was performed in part using the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory.

NWPerf

RW Mooney,$^{(a)}$ ***KP Schmidt,***$^{(a)}$ ***SS Studham,***$^{(a)}$ ***and J Nieplocha***$^{(b)}$

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(b) Pacific Northwest National Laboratory, Richland, Washington

Understanding software performance and use of large supercomputers is a complicated task. Recently, software developers at the W.R. Wiley Environmental Molecular Sciences Laboratory created a tool to gather pertinent information and present it in a user-friendly display.

NWPerf, a new system for analyzing fine granularity performance metric data on large-scale supercomputing clusters, is able to measure application efficiency on a system-wide basis from a global system perspective and to provide a detailed view of individual applications. NWPerf provides these capabilities while minimizing the impact on the performance of user applications. The system may be used to detect and eliminate application performance problems, resulting in vastly improved performance. The NWPerf architecture has proved to be a stable and scalable platform for gathering performance data on the 1960-CPU production Linux cluster in the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL).

Computing jobs are showing a general trend toward improved performance on the EMSL MPP2 supercomputer, shown by the percentage of peak flops from October 2003 through March 2004 (Figure 1).

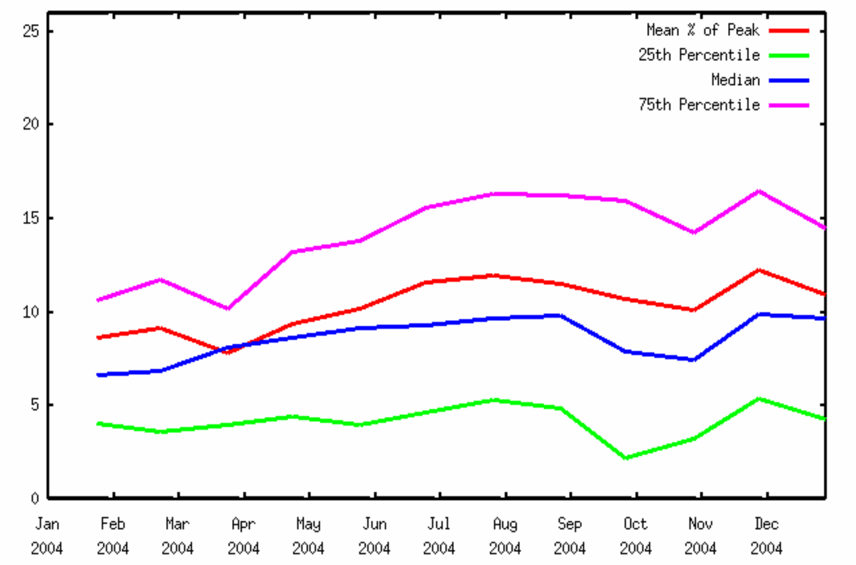

Figure 1. Trend toward improved performance on the EMSL MPP2 supercomputer after implementation of NWPerf.

MPP2 statistics for peak flops show a correlation between NWPerf performance and job size. Near the 256-node size, the mean and median deviate (Figure 2). This performance improvement over the general trend is directly attributable to two Computational Grand Challenge users running larger jobs.

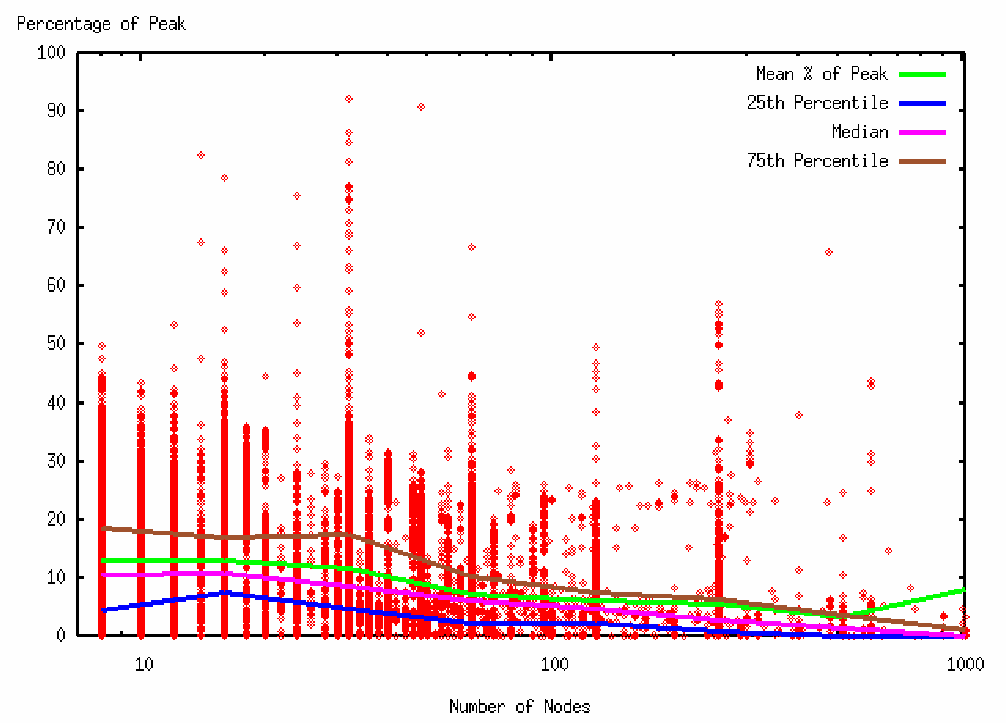

Figure 2. Job size has a direct correlation to performance of NWPerf.

Finally, NWPerf was used to search for a problem in a mass spectrometry analysis code that had a performance problem; use of NWPerf and analysis of bottlenecks led to an improvement of the code's performance by about four hundredfold. NWPerf was then used to search for other jobs with similar characteristics and to help resolve problems encountered by the associated users. As a result, one biogeochemistry code reported improvements of more than 50% by changing a few compiler flags.

The Growth Morphology of the {100} Surface of KDP (Archerite) on the Molecular Scale

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(b) Lawrence Livermore National Laboratory, Livermore, California

Potassium dihydrogen phosphate is used as a frequency doubler in lasers and has become a standard experimental material for crystal growth studies with a large body of information. This allows computational results to be easily applied to this body of research.

First-principle calculations were conducted to examine the surface morphology of the {100} face growth hillock of potassium dihydrogen phosphate ($[KNH_4]H_2PO_4$) (Figure 1), also known as KDP or archerite (Stack et al. 2004). KDP is a crystal structure used extensively in industrial applications (e.g., the National Ignition Facility at Lawrence Livermore National Laboratory) (Stack et al. 2004). To perform the calculations, the plane-wave pseudopotential density-functional theory (PWPP-DFT) and Car-Parrinello *ab initio* molecular dynamics functions of the NWChem software package were used. The PWPP-DFT function provides a good economy of calculation time, especially for non-transition metal systems as large as this one, yet provides accurate energy predictions. Step energies also were calculated using the difference between a step and a slab, with the same number of atoms and cell dimensions. The {100} surface energy was calculated by subtracting the total PWPP energy of a bulk phase from the energy of the same cell, but with space added in the [100] direction, so that the area of the calculation and the number of atoms were the same. Detachment energies of KH_2PO_4 growth units adsorbed to steps were calculated by subtracting the energy of the step with the growth unit adsorbed from the energy of a step and the energy of the isolated growth unit. Typical simulations were run for approximately 2000 iterations at 5 atomic units per time step (1.2×10^{-16} seconds per time step) with steady-state reached after approximately 1000 iterations.

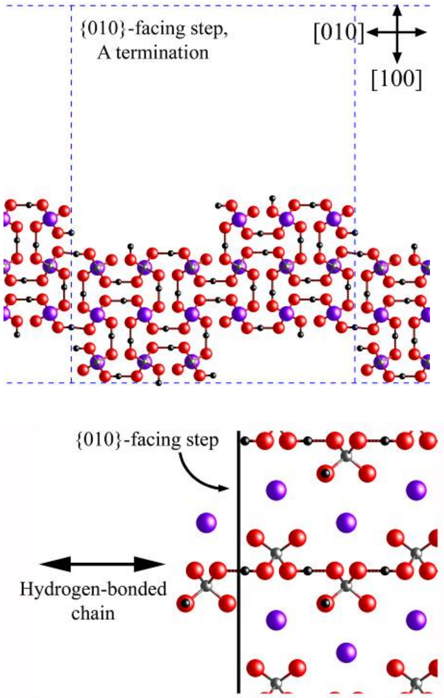

Figure 1. Atomic structures of the KDP surface. Potassium atoms are shown as purple spheres, oxygen atoms are red spheres, phosphorous atoms are grey spheres, and hydrogen atoms are black spheres. Hydrogen bonds are shown with alternating grey and white stripes linking the $H_2PO_4^-$ molecules. Blue dashed lines indicate the supercell boundaries. Top: A step facing the {010} on the {100} surface, viewed down the [001] axis. Bottom: Same step viewed from looking down the [100] axis, with an adsorbed growth unit. Only the top-most layer is shown. The double-ended arrow shows the direction of hydrogen-bonded phosphate chains.

Calculated detachment energies of the {010}-facing step were +4.2 and +4.5 eV (for two different terminations of the step) and +3.8 eV for the {001}-facing step. A more unfavorable detachment energy indicates a less-labile growth unit and a larger net rate of step advancement. Because the calculated detachment energies of the {010}-facing steps are larger than the {001}-facing step, this indicates that the {010}-facing step should have a higher net rate of growth. This finding is in qualitative agreement with experimental results. The detachment energies of subsequent growth units show that the energy stays approximately the same for the {010} face, but goes up (+5.1 eV) for the {001} face. Therefore, it is likely that in the slow {001} direction, the initial adsorption of new material to the step is limiting the rate, and once it has been adsorbed, the second unit adsorbs very quickly and reproduces the step.

By examining the hydrogen bond chains and their directionality on the different steps, this work proposes that the first growth unit on the {001}-facing step has a lack of hydrogen bonds to the step edge, which increases its lability. This study provides a qualitative picture of how crystal structure may control growth morphology of KDP and emphasizes the importance of anisotropic hydrogen bonding in the system.

This research was supported by the National Science Foundation and performed in part using the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory.

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Parallel Reactive Transport Modeling of Radioactive Waste Form Weathering Using the STORM Code

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Understanding the weathering of vitrified waste at U.S. Department of Energy sites, such as the Hanford Site Integrated Disposal Facility, is critical for cleanup activities. The STORM code is an effective tool for assessing performance of proposed waste forms, and simulations reveal release rates from radioactive mixed-waste storage tanks.

The Subsurface Transport Over Reactive Multiple Phases (STORM) code (Bacon et al. 2004), a parallel, coupled non-isothermal multiphase flow and reactive transport simulator, is used to calculate waste form release rates for immobilized low-activity waste (ILAW) created during processing of stored radioactive waste at the U.S. Department of Energy's Hanford Site in southeastern Washington.

A large inventory of radioactive and mixed waste is stored in the 177 underground single- and double-shell tanks at Hanford. During cleanup activities, liquid waste recovered from these tanks will be pretreated to separate the low-activity fraction from high-level and transuranic wastes. The low-activity waste will be immobilized in glass and placed in a near-surface disposal facility at Hanford. Before the ILAW can be disposed of, however, a waste form that effectively protects both human health and the environment over the extremely long storage period must be selected. Thus, the STORM code is an effective tool for assessing performance of proposed waste forms.

The underlying mathematics in STORM are contained in a set of coupled nonlinear partial differential equations that describe 1) the rate of change of the solute concentrations of pore water in a variably saturated, non-isothermal porous medium, and 2) the alteration of waste forms, packaging materials, backfill, and host rocks. STORM provides full coupling between unsatuarated flow and reactive chemical transport, global-implicit reactive transport for large time steps, node-by-node iteration for a small Jacobian matrix and fast convergence, and a capability for parallel execution on multiple processors. Results from execution of STORM include:

- waste form release rates that directly apply to the ILAW performance assessment
- simulated weathering of waste glass, packaging materials, backfill materials, and host rocks
- solutions for extremely complex systems; for example, a typical simulation involves 4 million unknown factors and 100,000 time steps.

STORM has been used to simulate the weathering of vitrified waste in the Integrated Disposal Facility (IDF) at Hanford, and is currently being validated against a 14-year field experiment of vitrified waste corrosion at a site in Russia. In addition, STORM will be used to conduct waste form release calculations for the 2005 IDF Performance Assessment.

Figure 1 shows a few of the unknown factors (including distribution of a radioactive waste product [technetium-99]) solved for a typical simulation that involved 37 aqueous species, 19 equilibrium aqueous reactions, and 20 kinetic mineral reactions at 120,000 locations.

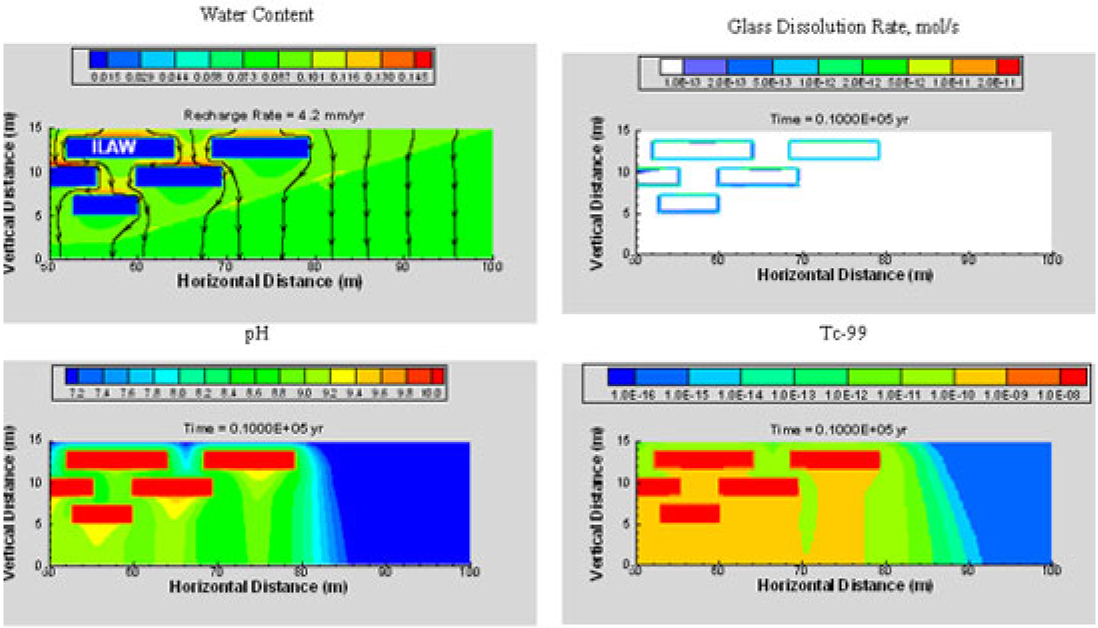

Figure 1. A few of the unknown factors (including distribution of a radioactive waste product [technetium-99]) solved during a typical STORM simulation.

Performance assessment simulations are run for 10,000-year time spans. Because time steps are usually limited to less than one month by either advection rates or mineral reaction rates, more than 100,000 time steps are required. Therefore, simulations may take weeks or even months when run in serial mode, and may be too large to run on a desktop workstation. These extreme compute requirements make running simulations on parallel processor systems highly desirable, and in fact test simulations have shown computing times decrease to 90 minutes as the work is divided among 256 processors. These simulation times drastically increase the number of computations that can be run in a reasonable amount of real time.

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It's All in the Water

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The energetics and properties of water are critical to many chemical and nearly all biological processes. Development of accurate potentials will greatly increase our fundamental understanding of the chemistry of these processes.

Because of its ubiquitous nature and importance in many biological and chemical processes, water is one of the most studied media. For many years scientists have attempted to construct simplified descriptions of the intermolecular interactions between water molecules in an effort to gain insight into water's unique properties from molecular simulations. One bottleneck in this effort is the lack of experimental energetic information regarding the interaction between water molecules that can be used to assess the accuracy of the proposed models.

Researchers at Pacific Northwest National Laboratory are constructing models that accurately describe the interaction between water molecules and are using the models to obtain macroscopic structural and thermodynamic properties for its liquid phase. For the first time, an empirical potential describing the interaction between water molecules has been constructed from the results of high-level, first-principles electronic structure calculations. The developed potential reproduces the converged—as regards electron correlation and basis set—binding energies of water clusters up to 21 water molecules to within an impressive less than 0.5% accuracy, which is far better than than the accuracy achieved by any other model. The liquid simulations of water are performed by combining this intermolecular potential with quantum statistical mechanics techniques. The simulations use centroid dynamics, a variation of the path integral method, combining molecular dynamics on 256 water molecules with periodic boundary conditions and a representation of the statistical sampling of each atom with a set of 32 replicas or 'beads.' Liquid water properties obtained included the radial distribution function (RDF), dielectric constant, diffusion coefficient, and enthalpy of vaporization (Figure 1).

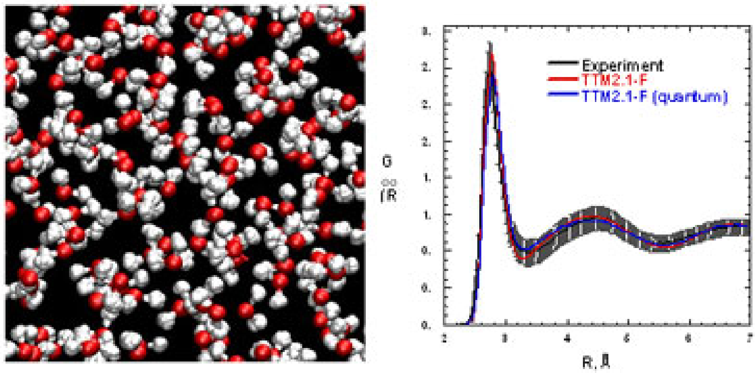

Figure 1. Left: Graphical representation of the liquid (32 beads per atom) at a single time step. Right: Calculated radial distribution function compared to experiment.

The calculation of accurate binding energies for water clusters from electronic structure calculations and subsequent centroid path integral quantum dynamical simulations using the developed potential is truly a computational Grand Challenge. The achievement is made possible by the Molecular Science Computing Facility's supercomputer and the in-house-developed software NWChem, which have enabled researchers to efficiently perform electronic structure calculations to be performed in parallel on 256 processors. Initial tests have shown that the calculation scales to thousands of processors, but at a lower efficiency. Even using 256 processors, it took 24 days to obtain a molecular dynamics simulation of 350 picoseconds. On a single processor, this would have taken more than 20 years to calculate. The data of the first 350-picosecond simulation allowed the researchers to calculate an RDF that is in close agreement with experimental data.

Ab Initio Study of Catalytic Guanosine Triphosphate Hydrolysis

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Enzymes that can bind guanosine triphosphate are critical in cellular signaling processes, transmitting messages that lead to cell proliferation. This work examines the mechanism by which the cell signal is turned off when guanosine triphosphate is hydrolyzed to become guanosine diphosphate. Future mutation studies will lead to increased understanding of tumor formation.

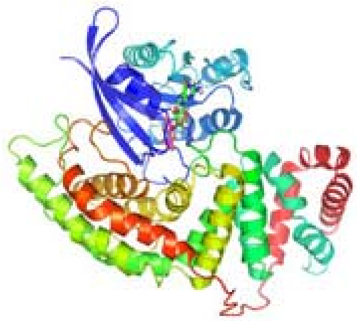

Figure 1. Snapshot of the Ras-GTP and GAP-334 complex at 100 picosecond step of classical molecular dynamics simulation.

The GTPases, a large family of enzymes of which Ras is a member, can bind guanosine triphosphate (GTP) and then hydrolyze it to guanosine diphosphate (GDP) (Figure 1). The overall formal hydrolysis reaction is $GTP^{4-} + H_2O \rightarrow GDP^{3-} + H_2PO_4^-$. GTPases play an important role in a number of biologically important processes such as signal transduction at the intracellular domain of transmembrane receptors, control and differentiation during cell division, and translocation of proteins through membranes. In the active GTP conformation, these proteins transmit a signal to an effector molecule that leads to cell proliferation. The slow intrinsic hydrolysis rate is accelerated by GTPase-activating proteins (GAPs) by a factor of 10^{3-6}. The native p21 Ras is an essential growth regulating component of eucaryotic cells, but single residue mutations are sufficient to convert the Ras genes to oncogenic genes.

Although there are three possible mechanisms, the exact mechanism of the hydrolysis reaction is still not well established, and the roles of RasGAP and glutamine in position 61 (Gln61) in the reaction at the molecular level have not been fully elucidated. It has been postulated that the mechanism is an S_N2 in-line attack of a water molecule in the active site on the γ-phosphate of GTP. We studied a mechanism where Gln61 uses a proton from a catalytic water, and Gln61 serves as a proton shuttle from the catalytic water site to the γ-phosphate. Sondek and co-workers (1994) suggested this 'Gln61-proton shuttle' mechanism based on analysis of the crystal structure of transducin α-GTP activated with aluminum fluoride, which resembled a pentavalent intermediate for GTP hydrolysis. This mechanism is a variant of the general base mechanism.

Because the currently available experimental results and theoretical calculations are not conclusive in terms of the mechanism of GTP hydrolysis, we have used *ab initio* electronic structure theory at the density functional theory (DFT) level to study the mechanism. The latest generation of supercomputers and software (NWChem) (Kendall et al. 2000) allowed us to study a large model of the active site at a high level of theory.

All *ab initio* electronic structure calculations were performed using the NWChem program package. The calculations were done at the DFT level with the B3LYP exchange-correlation functional and the double zeta balance with polarization basis set. To provide a better model of the active site, dielectric continuum calculations using a self-consistent reaction field approach were performed with the continuum solvation conductor-like screening model. In total, the calculations required about 75,000 CPU hours on the HP Linux cluster with Itanium-2 processors and a Quadrics Elan3 switch, housed in the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory. Most of the calculations were done in parallel with 64 processors.

Our calculations predict that the GTP hydrolysis in RasGAP is a multiple-step, dissociative reaction. In the first step, the γ-phosphate dissociates and the catalytic water forms hydrogen bonds with Gln61 and Thr35. The proton is successively transferred to Gln61 and then to γ-phosphate. Thus, Gln61 serves as a proton shuttle. There is no evidence that the proton transfers directly from the catalytic water to the γ-phosphate. Our findings support the "Gln61-proton shuttle" theory originally suggested by Sondek and co-workers (1994). The results are consistent with experimental data and mutant studies. To definitively answer the question of the actual mechanism for GTP hydrolysis in Ras and RasGAP, further experimental and computational work are needed.

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Structure and Energetics of Aluminum Nanoparticles

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(a) University of Minnesota, Minneapolis, Minnesota

Understanding the reactions of carbon, hydrogen, and oxygen on an aluminum nanocluster is important to the development of powdered aluminum as a rocket fuel. In this study, models with excellent energetics were developed for aluminum cluster up to Al_{177}.

The usefulness of nanoscale materials is well established, and the development of nanotechnology applications are under way in a variety of fields ranging from molecular biology to materials science. In this project, we focus on aluminum nanoparticles, developing in partnership with experimentalists and engineers computational tools that are designed to improve our understanding of the reaction dynamics of molecules and radicals composed of carbon, hydrogen, and oxygen at the aluminum surface. These processes are of great importance for energy development because of the use of powdered aluminum as a rocket fuel. Furthermore, the general methodologies (e.g., computer algorithms, parameterization, and validation schemes) are of broad applicability and general interest to nanoparticle and energetic research.

The dynamics of nanoparticles are very challenging to model computationally because they have unique properties that prohibit the use of methods developed for bulk materials, and they are far too large to be modeled by methods that have been developed for molecular systems. To overcome these issues, we have adopted a bootstrap methodology in which we first validate approximate methods such as density functional theory (DFT), against high-level *ab initio* calculations for small systems. A validated DFT method can then be used to model larger systems and validate even more approximate methods such as semiempirical tight-binding models and analytic potential energy functions, which can in turn be applied to systems that contain many thousands of atoms.

Because of the relatively small amount of experimental and high-level theoretical data in the literature for small aluminum clusters (Figure 1), we elected to test all of our methods against accurate *ab initio* data. We tested a wide variety of multilevel methods (e.g., CBS-Q//B3, CBS-4, MCG3/3, G3, and G3X) against a database of previously published energies that were extrapolated from CCSD(T)/X , where X = aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ, for Al_2 – Al_4. We found that MCG3/3 was the most accurate method (with an average error of 0.01 eV/atom) and also the second-most cost-efficient multilevel method. Using MCG3/3, we constructed a much larger database of energies for Al_n ($n = 2 – 7$) clusters. We then tested a large number of DFT methods and found that the PBE0 functional with the MG3 basis set (6-311+G(3d2f) for Al) to be the most accurate, with an average error of only 0.01 eV/atom.

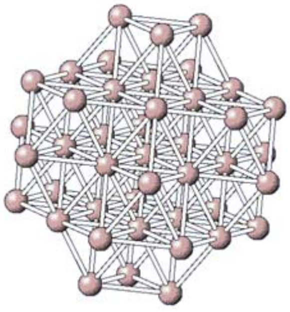
Figure 1. Sample aluminum cluster.

A PBE0/MG3 calculation, although much more efficient than the multilevel methods discussed above, is cost-prohibitive for systems larger than approximately 13 aluminum atoms. To overcome this constraint, we tested several popular effective core potential methods against a database of energies calculated with the PBE0/MG3 method for Al_n ($n = 2 – 13$) and found that they were too inaccurate for quantitative work. We have therefore parameterized a newly developed effective core potential and valence electron basis set for aluminum against the database of Al_n ($n = 2 – 13$) energies along with some additional Al_nX ($n = 1 – 2$ and X = H, C, and O) data calculated with PBE0/MG3. Our effective core potential method is called Minnesota effective core (MEC) and has an accuracy of 0.01 eV/atom.

Crucial to the success of this project was the development of the MEC method and the computational facilities at the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL), which are particularly well-suited for these studies. Specifically, the ability to efficiently run NWChem (Kendall et al. 2000) on anywhere from 10 to more than 200 processors has allowed us to develop a large database of structural and energetic data for aluminum clusters and nanoparticles that range in size from 2 to almost 200 aluminum atoms. Our largest calculation to date has been a partially optimized structure of Al_{177}. Converging electronic structure calculations for metal nanoparticles is especially challenging because of the presence of low-lying excited states, and success requires sophisticated strategies for obtaining estimates for the initial wave function, accurate integration grids, and efficient convergence algorithms. We have had previous difficulties with the large clusters using a Gaussian approach because of inefficient self-consistent field routines and unstable integration grids. Because these critical elements are implemented in NWChem at EMSL, we have been able to develop a database containing quantitatively accurate energies for aluminum nanoparticles. The database has been used to parameterize and validate approximate methods, as discussed below. In addition, by analyzing trends in the database, researchers can study fundamental differences between aluminum nanoparticles and molecular and bulk aluminum.

The nanoparticle database has allowed us to make significant progress in the area of analytic potential energy functions. Specifically, we have tested more than 30 different functional forms for the analytic potentials and identified several promising functionals. Our most accurate potential has an error of only 0.03 eV/atom when tested against our large database of aluminum data and against the experimental energy of bulk aluminum. This potential is ideal for simulating nanoparticles because it can accurately predict the energies and structures of small clusters that will constitute the building blocks of larger nanoparticles, and it can also correctly predict the energies of nanoparticles and the bulk limit. We believe that this potential is the first well-validated potential for metal nanoparticles.

Reference

Kendall RA, E Aprà, DE Bernholdt, EJ Bylaska, M Dupuis, GI Fann, RJ Harrison, J Ju, JA Nichols, J Nieplocha, TP Straatsma, TL Windus, and AT Wong. 2000. "High Performance Computational Chemistry: An Overview of NWChem, a Distributed Parallel Application." *Computer Physics Communications* 128(1-2):260-283.

Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons in Groundwater

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(a) Pacific Northwest National Laboratory, Richland, Washington

Understanding the reactions of hydrocarbons in groundwater is critical to the cleanup of sites across the nation that are contaminated with chlorinated hydrocarbons.

The reactions $OH^{-}(H_2O)_m + CHCl_3$ and $OH^{-}(H_2O)_m + CCl_4$ (m = 0-2) present significant challenges for high-level electronic structure theory because of the many electrons in the systems. We have used the high-performance computers in the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory to perform calculations at the MP2, MP3, and CCSD(T) levels of theory with basis sets up to aug-cc-pVQZ. Full geometry optimizations at the MP2/aug-cc-pVDZ level of theory were performed for reactant complexes, transition states, and products for the nucleophilic substitution (S_N2) and proton transfer reactions. By employing a series of single-point calculations at the MP2, MP3, and CCSD(T) levels of theory with the aug-cc-pVXZ series of basis sets, we obtained a complete basis set limit estimate of the energetics for each critical point along the reaction path. The results of these calculations are summarized in Figure 1, where we show the energetics (relative to the energy of the reactants with $OH^{-}(H_2O)_m$ infinitely separated from the chlorinated hydrocarbon) for the S_N2 and proton transfer reactions. In each case, the results clearly show that the effect of microsolvation is a decrease in the energy for forming the reactant and product complex and an increase in the energy of the transition state.

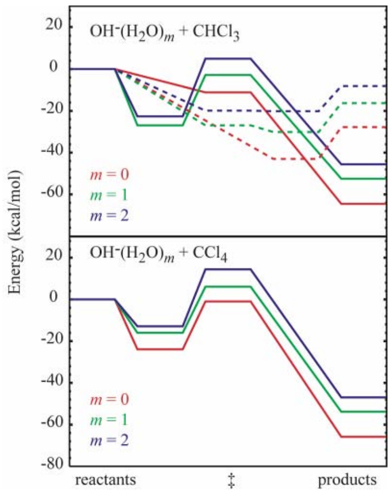

Figure 1. Relative energies of the S_N2 (solid line) and proton transfer (dotted line) reactions.

We have subsequently used these high-level electronic structure theory results to parameterize a newly developed hybrid semiempirical 'self-consistent, field-neglect of diatomic differential overlap' (SCF-NDDO) method to accurately model the microsolvation energetics of several ions and chlorinated hydrocarbons (CHCs). The new method combines aspects of both NDDO-based self-consistent field techniques and classical descriptions of polarization to describe the diffuse nature of the electronic wavefunction in a self-consistent manner. The additional description of molecular dispersion developed as a second-order perturbation theory expression has also been included within the theory. Our current work extends the parameterization of the water-water interaction to the current *ab initio* results. We observe notable improvements in incremental hydration energy for the chloride anion and several CHCs over the standard NDDO-based methods. The work here represents a significant step toward the accurate modeling of the reaction dynamics of CHCs in the aqueous environment using carefully benchmarked approximate methods.

Improving Combustion Systems through Modeling

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Understanding the complex chemical reactions involved in combustion can lead to the design of more efficient combustion systems that balance efficiency and emissions. In this study, the basic reaction information is fed into chemical mechanisms that are used for numerical simulations of engine designs. Reaction thermodynamics and kinetics change the reaction flows and efficiency of combustion.

As the cost of foreign oil increases, so does the need for more efficient use of other fuel resources. Understanding the complex chemical reactions involved in combustion can lead to the design of more efficient combustion systems. Researchers at the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) and the University of Alabama, Tuscaloosa (UA), are carrying out quantum chemical calculations using a state-of-the-art parallel computing system to accurately predict thermodynamic information vital to understanding complex combustion reactions.

In one of the largest simulations ever focused on this problem, EMSL and UA researchers performed pioneering first-principles calculations needed to predict the heat of formation of octane, a fairly simple molecule and a key component of gasoline (Figure 1).

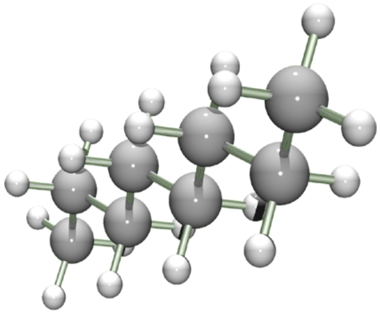

Figure 1. Octane molecule (C_8H_{18}).

This study would not have been possible without the combination of the NWChem software developed by EMSL researchers and the multiple-processor computing resource available in EMSL's Molecular Science Computing Facility.

For comparison, running the calculation using the best single-processor desktop computer would have required a three and a half years and 2.5 terabytes of memory. Instead, the calculation performed using 1400 parallel processors in the Molecular Science Computing Facility took 23 hours to complete and achieved a sustained efficiency of 75%, an astonishing feat when compared to the 5 to 10% efficiency of most codes. NWChem achieves high efficiency in this computation by taking advantage of efficient algorithms and communication schemas and is ideally suited for massively parallel computers.

This initial benchmark study served two primary purposes: it validated the approach and helped define its limitations. These initial calculations also helped identify the level of theory needed for subsequent efforts to reliably predict the heats of formation of larger alkanes (e.g., the components of diesel fuel), for which there is very little experimental data, and for the heats of formation of key reactive intermediates, such as alkyl and alkoxy radicals, for which no experimental data is available.

Reliable Electronic Structure Calculations for Heavy Element Chemistry: Molecules Containing Actinides, Lanthanides, and Transition Metals

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Understanding the molecular structures, properties, and reactivity of compounds containing actinides, lanthanides, and other heavy elements is critical to the development of remediation technologies in areas containing large repositories of nuclear waste materials. Simulations can shed light on the motility of and possible separations strategies for heavy element waste.

The computation of heavy elements is made difficult by the need to compute relativistic effects for many electron systems. The work presented here, the ground- and excited-state structures, energetics, vibrational frequencies, and nuclear magnetic resonance (NMR), excitation, and ionization spectra of compounds containing actinides, lanthanides, and other heavy elements were studied.

Carbon-uranium-oxide (CUO) has become a system of interest because the ground and excited states are very difficult to determine computationally, and CUO is the first molecular system that was found to bind to argon, krypton, and xenon (Li et al. 2002), thus changing the way scientists view bonding in noble gasses. To better understand the ground state of isolated CUO, highly accurate computations were performed using all-electron, fully relativistic coupled-cluster methods (e.g., coupled clusters with singles, doubles, and approximate triples) (Infante and Visscher 2004). These computations, in contrast to previous work, show agreement with the experimental finding that the ground state is a singlet that lies 58.2 kJ/mol below the first excited state.

Interestingly, the ground state of CUO is strongly dependent on the strength of its interaction with various noble gasses. Recent computational and theoretical results show that Ne-CUO complexes remain in the singlet state. However, if any argon gas is present in the complex, a stronger interaction is formed and the ground state is a triplet. Experimentally, atomic uranium is excited by laser ablation and reacts with CO in excess neon to produce the novel CUO molecule, which forms weak complexes CUO(Ne)$_m$ with neon and stronger complexes CUO(Ne)$_x$(Ng)$_n$ (Ng = argon, krypton, xenon) when the heavier noble gas atoms are present. The heavier CUO(Ne)$_{m-1}$(Ng) complexes are identified through the effects of CO isotopic and Ng substitution on the neon matrix infrared spectra and by comparison to density functional theory (DFT) frequency calculations on the model complexes CUO(Ng) (Ng = neon, argon, krypton, xenon). These experimental results and calculations indicate that the ground-state reversal of CUO is a consequence of multiple coordination of CUO by heavy noble gas atoms.

To further explore the multiple coordination of heavy noble gas atoms to the CUO molecule, we performed systematic DFT calculations on CUO(Ng)$_4$ and CUO((Ne)$_n$(Ng)$_{4-n}$ (n = 0, 1, 2, 3, 4; Ng = neon, argon, krypton, xenon) species using an extremely fine integration grid and very tight energy and gradient criteria for convergence. We have shown that the unique ground state reversal of the CUO molecule is caused by two major stabilizing effects to the triplet state: the U-Ng bonding and the spin-orbit coupling. The spin-orbit coupling splits the CUO triplet state so the low-energy component of the triplet becomes closer in energy to the singlet ground state. The coordination of neon, argon, krypton, and xenon atoms stabilizes both the singlet and the triplet states of CUO, but the triplet states are stabilized more than the singlet. The binding energies for Ng atoms bonded to the CUO triplet and singlet states is larger for argon, krypton, and xenon than for neon, which explains why neon atom coordination is not enough to reverse the ground state of CUO from singlet to triplet.

To further understand the interaction of uranium compounds with noble gasses, UO$_2$ in argon (Li et al. 2004) and UO$_2^+$ in both neon and argon (Wang et al. 2004) were examined experimentally and computationally. Scalar-relativistic DFT and CCSD(T) calculations reveal that the ^3H_g excited state of UO$_2$ exhibits significant bonding to noble gas atoms in UO$_2$(Ar) and UO$_2$(Ar)$_5$, thus achieving the ground state upon coordination of argon, krypton, and xenon atoms. The results strongly suggest that the ground electron configuration of UO$_2$ changes from 5f^{1}7s^1 to 5f^2 when the matrix host is changed from neon to argon. Experimental and theoretical evidence shown Figure 1 also lead to the conclusion that U-Ng bonding in UO$_2$(Ng)$_n^+$ complexes is stronger than the U-Ng bonds involving neutral CUO and UO$_2$, because of the combined electron-donation and ion-induced dipole interactions.

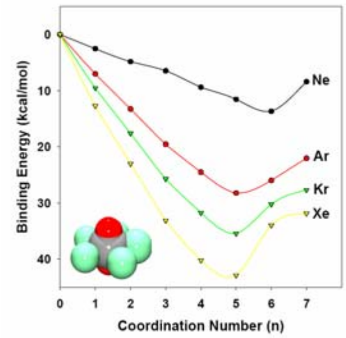

Figure 1. Binding energy curves for UO$_2$(Ng)$_n^+$.

The study of these relatively small systems described above has provided unique insights into the fundamental bonding properties of actinide-containing systems. The majority of the molecular systems in this project of which the structures, binding energetics, and properties were studied were considerably larger. For example, DFT calculations have been performed to investigate the solvent effects on the hydration of trivalent and tetravalent actinide ions and uranyl systems by including and fully optimizing a complete second hydration shell. The optimized structures show that the inclusion of the second hydration shell improves the actinide-O bond distances between the actinide center and the water molecules in the first shell by 0.02 to 0.05 Å compared to the experimental extended x-ray absorption fine structure results. For the UO_2^{2+} system, a full second hydration shell $[UO_2^{2+}(H_2O)_5(H_2O)_{10}]$ decreases the U-O first-shell bond distance by 0.06 Å; the calculated first-shell U-O distance is now 2.43 Å, which is in excellent agreement with the experimental data.

Another example involves understanding the separation of heavy elements, an activity of direct importance to the cleanup effort. Americium and curium are chemically similar to the lanthanide elements and thus present a challenge for their separation from the lanthanides in nuclear wastes. Organodithiophosphinates have great selectivity for americium over the lanthanide elements. Experiments show there is an extra water in the first ligand shell of lanthanides compared with americium. The structural difference is suggested as the basis for the selectivity. The calculated structural differences are consistent with experimental results. The results also show significant differences in the role of f orbitals in bonding, providing electronic structure evidence for the observed structural and extraction differences.

In separation chemistry, finding efficient ligands for binding actinide and lanthanide ions is of fundamental importance. We performed relativistic density functional calculations to explore the geometries, electronic structures, and physico-chemical properties of some actinide and lanthanide cations with various Kläui ligands. We investigated the geometry preferences, stabilities, and electronic structures of a series of complexes with one or two Kläui ligands (Figure 2) for group IV transition metals and the tetravalent actinides, thorium, protactinium, and uranium. We found that the group IV transition metals prefer linear sandwich geometries, whereas the tetravalent actinides prefer slightly bent sandwich complexes, which paves the way for additional ligand coordination to saturate the coordination sphere. The calculated formation energies indicate that the Kläui ligands have robust binding ability toward actinide ions.

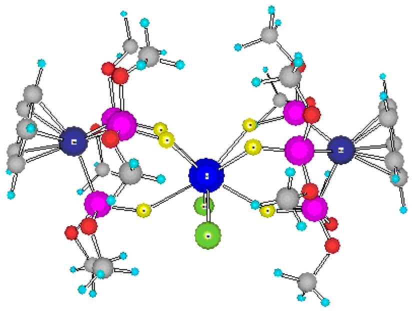

Figure 2. Optimized geometry structure of a $U(Kläui)_2Cl_2$ complex.

In addition to understanding the structures and energetics of these heavy element systems, the computation of properties aids in collaboration with experimental work. In work by Cho and co-workers (2004), the temperature and isotope dependencies of the technetium-99 chemical shift were examined. Temperature dependencies are a result of the changes in vibrational motion of the molecular structure. The property and potential energy surfaces need to be calculated to determine the effect of the vibrational (and rotational) motion on the molecular properties and structure in solution at a finite temperature and for various isotopes. The results for the temperature dependence in pertechnetate are shown in Figure 3.

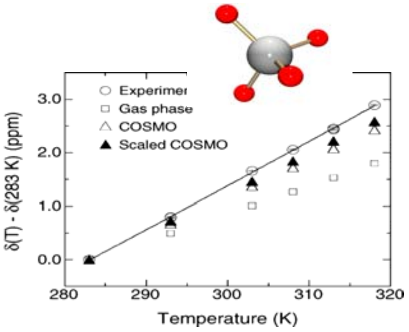

Figure 3. Theoretical vs. experimental NMR shielding temperature dependence in pertechnetate of the technetium-99 chemical shift.

The calculated results show the correct trends but slightly underestimate the dependencies. This is caused by the dynamics of the molecular environment, and rough calculations confirm this. The isotope dependencies were found to be in very close agreement with experimental data. Similar calculations were performed for the technetium-oxygen indirect spin-spin coupling values. The temperature dependence is much smaller, but calculations match very well with experimental data. The isotope dependence is too small to be measured, but it can be calculated. This isotope dependence and the combined isotope-temperature dependence have been calculated as predictions for future, more accurate NMR measurements.

In addition to the pertechnetate, the electric field gradient and the chemical shift tensor of the uranium-bonded ^{17}O (oxygen directly bonded to uranium) have been calculated for the experimental crystal structures of rutherfordine, a uranyl carbonate structure (Figure 4). The calculated NMR property tensors for ^{17}O in uranyl carbonate systems predicted a large chemical shift anisotropy of around 1500 ppm. This anisotropy will dominate the shape of the NMR spectrum of the ^{17}O NMR signal in uranyl carbonate crystals and produce a very broad NMR signal of around 1600 ppm. The predicted broad signal suggests that experimental measurement of ^{17}O in uranyl compounds requires a long sampling time.

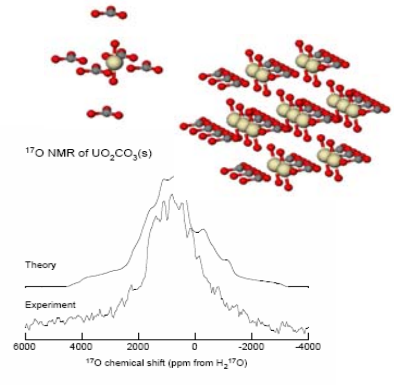

Figure 4. (Top, right) Rutherfordine, a uranyl carbonate structure. (Bottom) NMR spectrum of rutherfordine: theory vs. experiment.

Herman Cho used the W.R. Wiley Environmental Molecular Sciences Laboratory's High-Field Magnetic Resonance Facility to perform experiments on rutherfordine. The experimentally obtained spectrum is shown in Figure 4. This figure also contains the spectrum generated from calculated results. For these calculations the molecular structure in the left top portion of Figure 4 was used. There is already a reasonable agreement between theory and experiment, although some features are missing. To account for those features, the local environment around the central uranyl molecule needs to be accounted for in a more extensive manner. During the course of the project, calculations were started using the crystal structure model in the right top portion of Figure 4. This substantial calculation with 187 atoms (including 17 uranium atoms) is a true grand challenge calculation that will be continued next year.

Finally, the chemical shift of the central carbon in $[C(Au\text{-}PPh_3)_6]^{2+}$ illustrated in Figure 5 was computed. This system has fascinated experimentalists and theoreticians since its discovery in 1988.

The chemical shift of the central carbon was estimated experimentally to be in the arene region at about 135 ppm. These computations have

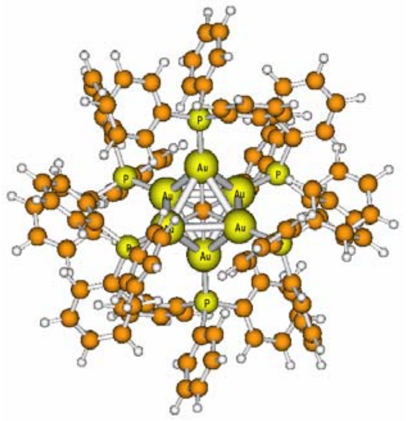

Figure 5. $[C(Au\text{-}PPh_3)_6]^{2+}$ complex.

uncovered that the central carbon shift is very sensitive to approximations in the computational model. Calculations on the complex as well as numerous model systems have shown that it is necessary to consider the full system, not model complexes, to reproduce the shift with acceptable accuracy. The best calculated value is 129 ppm, and neglected effects from the use of polarization on the phenyl ligands are thought to be responsible for the difference. Spin-orbit NMR DFT calculations have shown that without the PR_3 (where R = H, CH_3, and C_6H_5) ligands, the gold cage would induce a large shielding, leading to a chemical shift of -300 ppm. This shielding is almost exclusively caused by spin-orbit coupling in the gold 5*d* shells. Because of the interaction with the PR_3 ligands, the spin-orbit shielding is completely quenched. The mechanism is similar to the trans effect for spin-spin coupling that we have investigated previously.

In conclusion, significant new insights have been gained in the structure, energetics, and properties of heavy element systems based on computational and experimental results.

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Multifluid Flow and Multicomponent Reactive Transport in Heterogeneous Subsurface Systems

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Long-term, scientifically defensible predictions of subsurface contaminant fate are critical to the development of remediation alternatives that can accelerate the cleanup of the U.S. Department of Energy's waste storage sites and reduce costs and risks to people and the environment. The new knowledge and capabilities developed by this research enhance the Department of Energy's ability to understand, assess, and manage the risks of contaminated soil and groundwater.

This project has developed new capabilities that advance the understanding of processes and properties controlling contaminant behavior in complex environments in the subsurface. New science that expands the robustness and range of subsurface process modeling has been included in our simulations. Advanced parallel programming tools, utilities, and interfaces have been designed and implemented to increase usability, computational performance, and efficiency of the simulation software used in this research. These accomplishments were achieved with 416,689 CPU hours of computation on the Linux cluster MPP2 computing system in the Molecular Science Computing Facility in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL).

Radionuclide Migration at the Nevada Test Site

The parallel code PFLOTRAN for modeling reactive flows in porous media was developed by Peter Lichtner at Los Alamos National Laboratory and tested on the EMSL MPP2 system. PFLOTRAN is based on the Portable Extensible Toolkit for Scientific computation (PETSc) parallel libraries developed at Argonne National Laboratory by Balay and co-workers (2004).

Preliminary results for a field-scale problem describing radionuclide migration from the BENHAM underground test at the Nevada Test Site were obtained using the EMSL MPP2 system. A relatively small three-dimensional problem with 926,250 degrees of freedom was run on MPP2 twice, once using 64 processors and then using 128 processors. Excellent scaling was obtained with run times of 50 and 25 minutes, respectively. Results based on an effective porous medium model suggested that plutonium moved more rapidly compared to other radionuclides based on fit-to-breakthrough data collected from a limited set of observations from nearby groundwater monitoring wells.

Multifluid Subsurface Flow and Transport

CO_2 Injection at the Mountaineer Power Plant Site. The parallel Fortran 90 version of Subsurface Transport over Multiple Phases (STOMP), a scalable, parallel-processing implementation of the multifluid subsurface flow and transport simulator, was developed by Mark White at Pacific Northwest National Laboratory (PNNL) for investigating carbon dioxide injection, redistribution, and sequestration in deep geologic reservoirs. It was used for a pilot study at American Electric Power's Mountaineer Power Plant in New Haven, West Virginia (White et al. 2004a). The comprehensive and detailed numerical simulations will be used to support integrated risk assessments and design guidance for injection strategies, protocols, and permits for a demonstration project for carbon dioxide injection in these deep saline aquifers.

Residual Nonaqueous Phase Liquid Migration Processes. High-resolution STOMP90 simulations were used to investigate the historical migration of carbon tetrachloride at the Hanford Site 200 West Area during the disposal period (beginning in 1954) to date, including the soil vapor extraction activities (Figure 1), and to predict the current distribution and fate. This work successfully demonstrated a scientifically defensible scalable simulator for three-phase, three-component, aqueous-nonaqueous phase liquid (NAPL)-gas systems undergoing phase transitions (White et al. 2004b).

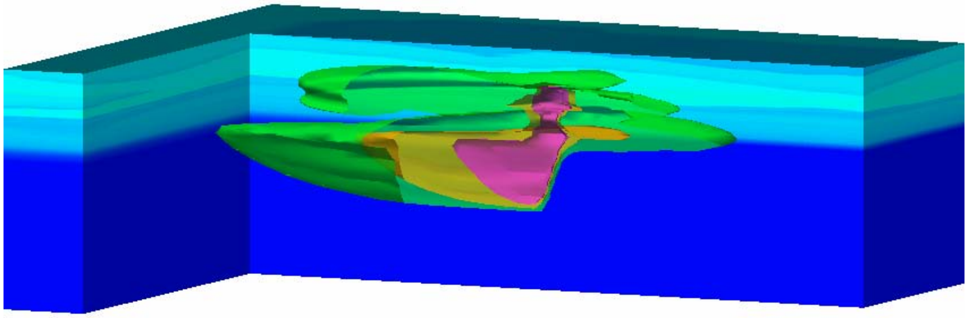

Figure 1. Simulation of carbon tetrachloride migration and remediation beneath the 216-Z-9 trench on the Hanford Site using soil vapor extraction.

Coupled Multifluid Flow and Reactive Transport

The parallel processing CRUNCH multicomponent reactive transport simulator is a joint development between Lawrence Berkeley National Laboratory and PNNL and has a variety of attributes that make it ideal for investigating movement of different contaminants simultaneously in complex geochemical environments (Fang et al. 2004).

This simulator was combined with the STOMP simulator to model the migration of high-ionic strength waste from a historical leak beneath the SX-Tank Farm at the Hanford Site. A simulation using 1 million grid cells with 29 chemical species predicted the formation of an uncommon mineral, cancrinite, which has been observed to form at elevated temperature (Figure 2).

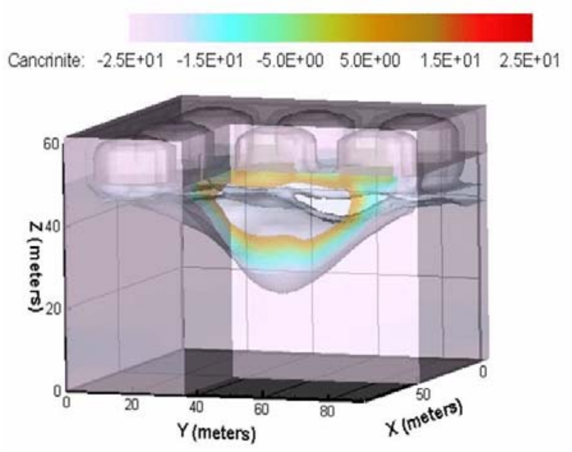

Figure 2. Predicted cancrinite concentrations.

Unsaturated Flow and Multicomponent Strontium Ion Exchange. At the Army Loop Road Vadose Zone Test Site in the Hanford Site 200 East Area, a combined CRUNCH/STOMP simulation (Figure 3) was used to study strontium ion exchange in the soil zone above the water table (i.e., the vadose zone).

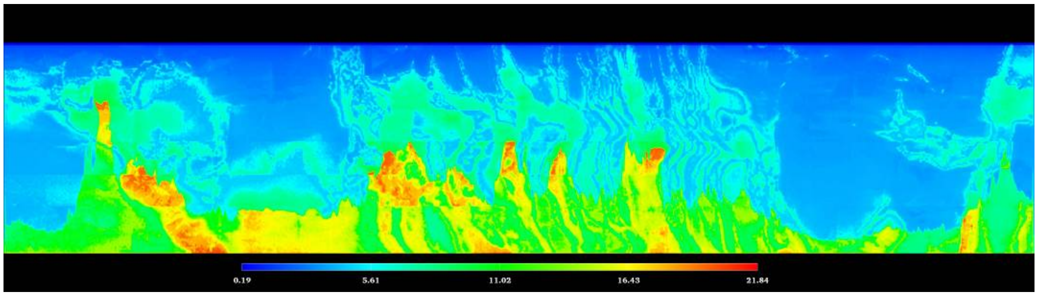

Figure 3. Calcium ion exchange sites after six days of infiltration of high strontium and magnesium solution (equivalents per cubic meter). Red and yellow represent higher calcium concentrations, and blue and green represent lower concentrations.

New PETSc Algorithm

PNNL's implementation of the block Krylov solver, developed by Joel Malard for subsurface multifluid modeling under this Grand Challenge project, was recently adopted by the PETSc.

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Superparameterization: A New Paradigm for Climate Modeling

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This research has produced data that enable the evaluation of the treatment of cloud processes and properties in global climate models. These processes are the key uncertainty in simulations of future climate change resulting from the increasing concentration of greenhouse gases in the atmosphere. Results from this research contribute directly to improving our understanding of climate change.

All current global climate model simulations simulate atmospheric properties, such as temperature and moisture, on horizontal grids with a spatial resolution of hundreds of kilometers. This coarse resolution is dictated by the speed of current computers. Because cloud processes occur at much smaller scales, the properties of clouds are not computed directly; instead, they are diagnosed at each time step in each grid cell using a combination of simple theory and empirical, fitted constants that we call a cloud parameterization. Differences in model cloud parameterizations are largely responsible for differences in the results obtained from simulations of climate change.

A recent advance in climate modeling has replaced the cloud parameterizations in each grid scale with a two-dimensional (height and longitude) cloud model. The cloud model we use has 64 columns with each column having a horizontal resolution of 4 km. The result is a computationally intensive 'nested' model, with cloud properties computed at high resolution while other atmospheric properties are computed at low resolution (Figure 1).

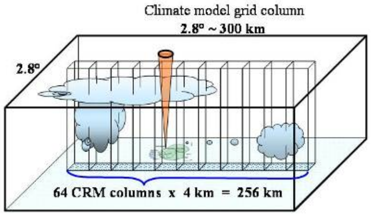

Figure 1. A schematic of the nested model structure in the MMF, with an outer coarse grid and nested cloud model. The cone schematically represents the scale of the ground-based observations on the island of Nauru.

This project has simulated 31 months of weather using the computationally intensive nested model called the Multiscale Modeling Framework (MMF), also called super-parameterization, and 92 months of weather with a traditional climate model for comparison using the observed sea-surface temperatures as the bottom boundary condition.

These runs have generated over 16 terabytes (1 terabyte = 1 trillion characters) of climate data for further analysis. Generating these data, which are stored in the archive file system (NWfs) in the Molecular Science Computing Facility at the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL), consumed more than 235,000 CPU-hours on the EMSL MPP2 parallel computing system.

The results of our analysis are encouraging but are not conclusive. We find that MMF provides a superior representation of some aspects of climate compared to the parent climate model. (We define the parent model as the conventional climate model that provided the outer coarse-resolution grid along with its cloud parameterizations.) MMF provides an improved simulation of cloud occurrence in the tropics (Figure 2), as well as precipitation in the tropics. Simulations of mid-latitude land precipitation, however, were not improved.

MMF is a model very much in its early development stage. Our evaluation is intended to provide insight into its successes and failures, and guidance for improvement.

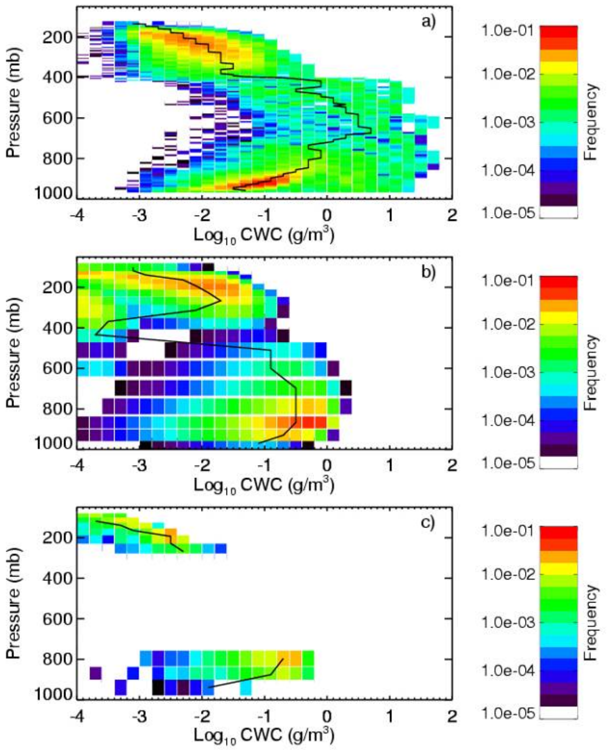

Figure 2. Frequency distribution of condensed water content (CWC) from a) Atmospheric Radiation Measurement Program ground-based observations in Nauru, b) clouds simulated by MMF, and c) clouds simulated by the parent climate model. The solid black line indicates the median CWC at each pressure level. The CWC distributions are plotted at the midpoint of each vertical level. White areas indicate no clouds.

Biomolecular Simulation of Base Excision Repair and Protein Signaling

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The broad goal of this project is to study the effects of environmental factors, including ionizing radiation, that contribute to continuous damage of cellular DNA. Failure of correct and timely repairs to these damaged DNA sites can result in cell death, carcinogenesis, or genetic diseases. Resulting mutations in cell signal transduction enzymes can lead to uncontrolled cell proliferation or differentiation.

One objective of this work is to investigate the effect of damage induced by oxidative stress on the structure and dynamics of DNA. Damage-induced structural and dynamical changes are very difficult to study experimentally; hence, modeling can play a crucial role in advancing our understanding of the biochemistry of DNA base excision repair processes. Recent progress in the simulation of nucleic acids because of force-field improvements and a more accurate treatment of long-range electrostatic interactions enables a stable molecular dynamics simulation of DNA for up to several tens of nanoseconds. Such simulations can complement experimental studies on nucleic acids because they allow the extraction of DNA structural and dynamical properties that can not easily be obtained from experiment.

Another objective of this work is to understand signaling processes in cells. Mutations in cell signal transduction enzymes can lead to uncontrolled cell proliferation or differentiation. For example, mutations in Ras, the molecular switch in several growth-factor signaling pathways, have been found in about 30% of human tumors. These signaling pathways often involve a chain of protein kinases that activate or deactivate each other through phosphorylation reactions, eventually controlling the activation of transcription factors in the cell nucleus.

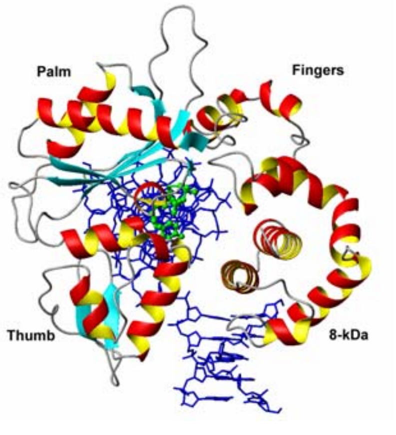

Figure 1. The human DNA polymerase β structure (ribbons) in complex with DNA (dark blue) and ddCTP substrate analog (green).

Multifluid Subsurface Flow and Transport

Molecular dynamics simulations were performed on ternary complexes of polymerase β, a key enzyme in base excision repair, bound to gapped DNA (Figure 1) and each of the four possible deoxynucleoside-triphosphate substrates. The starting structure that differed most radically from the crystal structure was the binary complex, modeled by removing the 2',3'-dideoxycytidine triphosphate substrate. An extended duration simulation was carried out to search for clear evidence of thumb opening, which decreases the catalytic effect of the active site. Because there are no crystal structures available for polymerase β ternary complexes bound by a mismatched substrate, we believe these simulations shed light on the probable response of the enzyme-DNA complex to the presence of an incorrect nucleotide in the active site and, thus, provide a means of testing one proposed mechanism of fidelity assurance. In the proposed 'induced-fit' mechanism of fidelity assurance, the thumb subdomain is expected to reopen if the correct substrate (matching the template base) is not in place. Both structural and essential dynamics analyses of the 5.2-nanosecond trajectory did not provide direct evidence of thumb/subdomain movement. However, certain specific interactions across the thumb/8k Da domain interface showed signs of weakening as the simulation progressed. It is estimated that motion of the 8-kDa lyase domain in solution probably occurs on a time scale between 3 and 8 nanoseconds. Because opening of the thumb requires the breaking of multiple attractive interactions, a 5.2-nanosecond simulation may well be too short to observe a definite opening movement.

Molecular Dynamics Simulation of the Complete Nucleosome

A molecular dynamics simulation of a complete nucleosome has been performed. The simulation system consists of 147 base pairs of DNA, several histone proteins, ions, and several thousand water molecules, and is based on the high-resolution structure by Richmond and Davey (2003). A simulation time of 15 nanoseconds was achieved and allowed the characterization of the local and global mobility of the nucleosome particle (Figure 2) on the nanosecond time scale at atomic resolution. The study of the dynamics of packed DNA also is of fundamental importance for understanding the effect of DNA damage because DNA in the cell is not free but, to a large degree, is associated with proteins that form a compact structure only partially accessible. Simulation studies on such a large structure are only possible by using supercomputing resources as are available at the Molecular Science Computing Facility in the W.R. Wiley Environmental Molecular Sciences Laboratory. The simulation will be extended in the current Grand Challenge phase and could also form the basis to study DNA damage in the context of a packed DNA structure.

Figure 2. Simulation start structure of the nucleosome core particle in cartoon representation.

Molecular Docking of Balanol to Dynamic Snapshots of Protein Kinase A

Even if the structure of a receptor has been determined experimentally, it may not be in the conformation to which a ligand would bind when induced-fit effects are significant. In this work, we evaluated the use of an ensemble of receptor conformations generated from a molecular dynamics simulation for molecular docking of the inhibitor balanol to dynamics snapshots of protein kinase A (PKA). Two molecular dynamics simulations were carried out to generate snapshots for PKA: one with the ligand bound, and the other without the bond. The ligand, balanol, was then docked to conformations of the receptors presented by these trajectories.

The Larmarkian genetic algorithm (Morris et al. 1998) in Autodock (Goodsell et al. 1996) was used in the docking. Three ligand models were used: 1) rigid, 2) flexible, and 3) flexible with torsional potentials (Figure 3). When the snapshots were taken from the molecular dynamics simulation of the protein-ligand complex, the correct docking structure was found in all cases. On the other hand, when the snapshots were taken from the simulation of the protein alone, several clusters of structures were found. Out of the 10 docking runs for each snapshot, at least one structure was close to the experimental complex structure when the flexible ligand models were used. However, the lowest energy structures, according to Autodock, did not always correspond to the correctly docked structure. Rescoring using a more sophisticated Generalized Born electrostatics model did not improve the identification of the correctly docked structure. On the other hand, we found that the correctly docked structure appeared more frequently as the lowest energy structures with the Autodock scoring function. This can provide a useful criterion for selecting the correctly docked structure from clusters of structures obtained from molecular docking experiments.

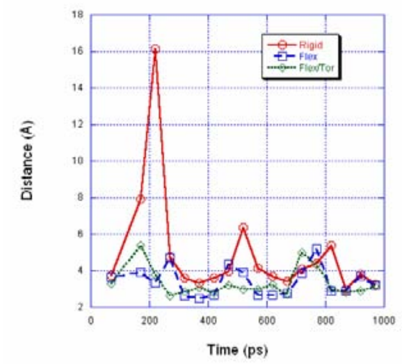

Figure 3. Best docking structures for each snapshot.

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Amorphization Mechanism of Icosahedral Metal Nanoclusters

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Clusters of transition and noble metals are interesting for their physical and chemical properties, and for technical applications. In this context, platinum clusters are of great importance because of their role in many catalytic processes.

The starting point for understanding cluster properties is the determination of their structure, which is usually a non-trivial task because clusters can assume a wide variety of structures (Figure 1).

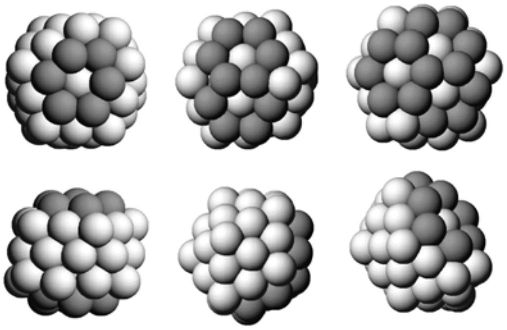

Figure 1. From left to right, front (top row) and side (bottom row) views of the double opposite rosette, of the double paired rosette, and of the triple rosette, as obtained within the RGL description. Atoms belonging to the hexagonal rosette rings are depicted in darker gray.

In this research (Apra et al. 2004), the amorphization mechanism of icosahedral platinum nanoclusters is investigated by a combination of molecular dynamics simulations using a Rosato-Guillopé-Legrand (RGL), many-body, atom-atom potential (Rosato et al. 1989) and density functional theory (DFT) calculations. A general mechanism for amorphization that involves rosette-like structural transformations at fivefold vertices is proposed.

In the rosette, a fivefold vertex is transformed into a hexagonal ring. This work shows that, in the case of icosahedral platinum nanoclusters, this transformation is associated with an energy gain, so their most favorable structures have a low symmetry even at icosahedral magic numbers and the same mechanism underlies the formation of amorphous structures in gold.

Accurate DFT calculations, using the Becke functional for exchange (Becke 1988), the Perdew-Wang (Perdew et al. 1992) functional for correlation, and a Gaussian-type orbital basis set, showed that icosahedral platinum clusters indeed have a tendency toward amorphization. The amorphization mechanism takes place through the generation of (eventually multiple) rosette motifs at the fivefold vertices. The rosette motif allows an efficient relaxation of the internal atoms, which overcomes a surface energy penalty. In the case of platinum, the driving force favoring the rosette is enhanced by bond directionality effects caused by *d-d* orbital interactions. All DFT calculations were carried out using the NWChem code (Kendall et al. 2000).

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User Projects

Collaborative Development of Software for Electronic Structure Calculations

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Calculated Rates of Water-Exchange on Large Aqueous Aluminum Nanoclusters

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Coupled Quantum Simulation Techniques for Studying Nanostructured Materials

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Correlation of Structure and Function of Zinc Metalloproteins Via Solid-State Nuclear Magnetic Resonance Methods

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Computational Biology Applied to the Murine Right Ventricle

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Fast-OS PetaScale Linux

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Single Enzyme Nanoparticle Crosslinking Polymerization

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Sub-Grid Modeling of Diesel Particulate Filtration Using the Lattice-Boltzmann Method

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Computer Simulation of Optical Spectroscopy

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Integrated Multiscale Modeling of Molecular Computing Devices

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Animation for Morphing Catalysis

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Reliable Electronic Structure Calculations for Heavy Element Chemistry: Molecules Containing Actinides, Lanthanides, and Transition Metals

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Immobilization of Radionuclides in Oxides

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A Computational Approach to Understanding Aerosol Formation and Oxidant Chemistry in the Troposphere

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Biomolecular Simulation of Base Excision Repair and Protein Signaling

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Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons in the Groundwater

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Thermochemistry of Arsenic Compounds

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Large-Scale Code Development Applied to Building a Geometry-Based Computational Framework for Biology and Ecology Applications

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Computational Thermochemistry and Benchmarking of Reliable Methods

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DOE Science Grid Operational Development and Testing

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Ab Initio Characterization of Unreduced and Reducted (012) Surfaces of Hematite

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Development of GASNet Communication System on the Quadrics Interconnect

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Benchmarking Climate and Weather Modeling Codes on the Pacifc Northwest National Laboratory Cluster

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Effects of the Presence of Helium on Silicon Carbide

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Geometry Optimizations of Aqueous Aluminum Clusters

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Determining the Phase Behavior of Polarizable Water Models

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Bioinformatics and Genome Analysis on U.S. Department of Energy Science Grid Computational Resources

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Relativistic Many-Electron Theories

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New Approach to Extract and Visualize Discontinuities from Two- and Three-Dimensional Seismic and Imagery Data Sets

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Intrusion Detection Video

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Computational Fluid Dynamics Applied to Airflow Problems in Animal and Human Lungs

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Ab Initio Calculations of GTP Hydrolysis by Using NWChem and TAO Components

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Local Motions in Protein Structures

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Electronic Structure Calculations of Hydrogen Bonding in Biological Macromolecules

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A Grid-Based Exact or High-Accuracy Solution of the Electronic Schrodinger Equation

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Regional Scale Atmospheric Modeling

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Rapidly Deployable Sensor Network

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Computational Study of Polycyclic Aromatic Hydrocarbons and Their Derivatives

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Computer Simulation of Radiation Effects in Zircon

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Optimization of Peptide Identification from Tandem Mass Spectral Data

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Complex Enzymatic Reactions Studied by Molecular Modeling and Electronic Structure Calculations

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Benchmarking Localized Coupled Cluster Methods in the NWChem Package

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Superparameterization: A New Paradigm for Climate Modeling

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Molecular Computational Studies in Environmental Chemistry, Geochemistry, and Biogeochemistry

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Nanostructure Formation, Aggregation, and Reactivity

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Reliable Electronic Structure Prediction of Molecular Properties

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Direct Dynamics Simulations: From Molecules to Macromolecules and Condensed Phases

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Computational Design of Catalysts: The Control of Chemical Transformation

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Multiscale Modeling of Biochip Systems

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Modeling Complex Bacterial Cell Systems Through Development of Segregated Models with Spatial Localization

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Multifluid Flow and Multicomponent Reactive Transport in Heterogeneous Subsurface Systems

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Image Processing, Modeling, and Simulation of Complex Biological Systems Using Volume-Filling and Boundary-Fitted Mesh Based Methods

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Computer Simulations of Chemical Reactions in Confined Environments and Mesoscopic Clusters

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Developing High-Performance Parallel Languages on the SGI Altix

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Molecular Energetics of Clustered Damage Sites in DNA

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Parallel Reactive Transport Modeling of Radioactive Waste Form Weathering Using the STORM Code

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NMR Chemical Shift Calculations for Novel Bioactive Metabolites from an Acid Mine Waste Organism

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Computational Fluid Dynamics Code Performance Testing

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Computed Frequencies to Support Experimental Quests for Novel Molecules

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Ab Initio Calculations on a Proposed Gating Mechanism for the KcsA Channel

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Common Architecture Chemistry Components for Terascale Simulations

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Rosetta *Ab Initio* Protein Folding

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Computational Characterization of Two Lesions in DNA: 8-Oxo-Adenine and Abasic Site

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A New Approach to Protein Folding by Reducing Dimensionality of Protein Conformational Space

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Advanced Sorbent Deployment

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Computational Study of Protein-Protein Interaction Dynamics

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Animation and Three-Dimensional Illustrations for the Atmospheric Radiation Measurement Program

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Multi-Region Reactive Transport Due to Strong Anisotropy in Unsaturated Soils with Evolving Scales of Heterogeneity

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Deploy Lustre as a Global File System on the HPCS2 Supercomputer

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Epidermal Growth Factor Receptor Dimerization

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Ab Initio Simulations of the Catalytic Mechanism in Protein Kinases

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Fundamental Assessment of the Accuracy of Time-Dependent Density Functional Theory

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Defects, Defect Processes, and Ion-Solid Interactions in Ceramics

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Computational Chemical and Materials Science to Study Nanoscale Surface Reactivity and Radiation Resistance of Metal Oxides

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Direct Numerical Simulations of Turbulent Combustion-Temperature Inhomogeneity Effects on the Autoignition of Hydrogen/Air Mixtures in the Spontaneous Ignition Regime

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Quantum and Classical Simulations of Clusters, Self-Assembly, Nano-Scale Manipulations, Nanotribology, and Biological Processes

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A Combined Approach for Protein Structure Prediction

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Radiation Detection Portals for Border Security

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Multimedia for Investigator Training

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Aerosol Model Data Storage

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Investigating Three-Dimensional Coupled Geophysical Processes of the Subsurface

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Oxidation and Radiation Damage in Nucleic Acid Bases

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Electronic Structure Study of Platinum Clusters

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NAMD Benchmarking on EMSL Molecular Science Computing Facility for Molecular Dynamics Simulations

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Chemical Discovery Through Advanced Computing

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Energetics, Bonding Mechanism, and Electronic Structure of Metal/Ceramic Interfaces

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Impact of Spray Cooling Microprocessors on Nodes in a High-Performance Computing Cluster

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Pacific Northwest National Laboratory Next-Generation Chemistry/Meteorology/Aerosol Model

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Accurate *Ab Initio* Determinations of Thermochemical Properties of Environmental and Biological Molecular Systems for Benchmarking with Experiments

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Bioinformatics Tools to Define the Proteomic State of the Cell

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Immune Response to Environmental Factors: Molecular Dynamics Simulations of Antibody Structure

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Simulation of the Conformation of Single Conjugated Polymer Molecules with Varying Conjugation Length in a Nematic Liquid Crystal

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