Scientific Grand Challenges

DISCOVERY IN BASIC ENERGY SCIENCES: THE ROLE OF COMPUTING AT THE EXTREME SCALE

August 13-15, 2009 • Washington, D.C.

U.S. DEPARTMENT OF
ENERGY

Sponsored by the Office of Basic Energy Sciences and the Office of Advanced Scientific Computing Research

DISCLAIMER

On the cover: Lawrence Berkeley National Laboratory's Cray XT4™ supercomputer. The computer is named Franklin in honor of Benjamin Franklin, one of the first American scientists. The Franklin is at the National Energy Research Scientific Computing Center, which is managed by Lawrence Berkeley National Laboratory for the U.S. Department of Energy's Office of Science. The Franklin's computing power makes it one of the largest and most powerful supercomputers in the world. Future reports in the Scientific Grand Challenges workshop series will feature different Office of Science computers on their covers.

DISCOVERY IN BASIC ENERGY SCIENCES: THE ROLE OF COMPUTING AT THE EXTREME SCALE

Report from the Workshop Held August 13-15, 2009

Sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences and the Office of Advanced Scientific Computing Research

Chair, **Giulia Galli**
University of California, Davis

Chair, **Thom Dunning**
University of Illinois at Urbana-Champaign

Co-Lead, Correlation and Time Dependence, **Martin Head-Gordon**
University of California, Berkeley, and Lawrence Berkeley National Laboratory

Co-Lead, Correlation and Time Dependence, **Gabriel Kotliar**
Rutgers University

Co-Lead, Photovoltaic Fundamentals, **Jeffrey C. Grossman**
Massachusetts Institute of Technology

Co-Lead, Photovoltaic Fundamentals, **Kai-Ming Ho**
Ames Laboratory and Iowa State University

Co-Lead, Energy Storage, **Mei-Yin Chou**
Georgia Institute of Technology

Co-Lead, Energy Storage, **Michel Dupuis**
Pacific Northwest National Laboratory

Co-Lead, Dynamics, **Mark Asta**
University of California, Davis; University of California, Berkeley; and Lawrence Berkeley National Laboratory

Co-Lead, Dynamics, **Carlos Simmerling**
Stony Brook University

Representative, Office of Basic Energy Sciences, **Mark Pederson**
Representative, Office of Basic Energy Sciences, **James Davenport**
Representative, Office of Advanced Scientific Computing Research, **Lali Chatterjee**

EXECUTIVE SUMMARY

The U.S. Department of Energy's (DOE) Office of Basic Energy Sciences (BES) and Office of Advanced Scientific Computing Research (ASCR) workshop in August 2009 on extreme-scale computing[1] provided a forum for more than 130 researchers to explore the needs and opportunities that will arise due to expected dramatic advances in computing power over the next decade. This scientific community firmly believes that the development of advanced theoretical tools within chemistry, physics, and materials science—combined with the development of efficient computational techniques and algorithms—has the potential to revolutionize the discovery process for materials and molecules with desirable properties. Doing so is necessary to meet the energy and environmental challenges of the 21st century as described in various DOE BES Basic Research Needs reports.[2]

Furthermore, computational modeling and simulation are a crucial complement to experimental studies, particularly when quantum mechanical processes controlling energy production, transformations, and storage are not directly observable and/or controllable. Many processes related to the Earth's climate and subsurface need better modeling capabilities at the molecular level, which will be enabled by extreme-scale computing.

To provide a far-reaching plan for this new era of computing, the "Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale" workshop was jointly sponsored by BES and ASCR in August 2009.[1]

The purpose of the workshop was to accomplish the following:

1. Identify forefront scientific challenges in basic energy sciences and identify those problems that could be solved by high-performance computing at the extreme scale
2. Describe how high-performance computing capabilities could address issues at the frontiers of basic energy sciences
3. Provide basic energy science researchers an opportunity to influence the development of high-performance computing
4. Provide input from the BES community for planning the development of a future high-performance computing capability by ASCR.

The workshop consisted of plenary talks that provided perspective and identified challenges and opportunities in the areas of photovoltaics, superconductivity, catalysis, combustion, materials in extreme environments, and a computer-science session that outlined how computer architectures would likely evolve over the next decade. Next, four panel breakout groups examined the relation of these presentations to more fundamental scientific issues. Each breakout group provided priority research directions intended to guide future investments in extreme-scale computing and scientific endeavors.

---

[1] "Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale," August 13-15, 2009, Washington, D.C.

[2] http://www.sc.doe.gov/bes/reports/list.html

This report underscores the scientific community's recognition that advances in our ability to simulate molecular and materials systems and identify yet undiscovered avenues toward new energy technologies depends on many factors. One of those factors is the increasingly capable computers that, in accordance with ASCR's goals, are expected to reach exaflop/s within a decade. However, the community noted that hardware alone is not the only factor and further posited that several other issues are at least equally pressing. In particular, the need to advance theoretical models of physical and chemical objects and processes, and to develop algorithms that effectively enable those models to be simulated on modern computing systems was highlighted as well. Success in this endeavor necessarily mandates support of scientists that can bridge the gap between chemistry and materials science and computer science and engineering. Any new research initiatives must continue to support an appropriate balance between small-scale, medium-scale, and large-scale computational research efforts. A focus on only large-scale efforts would be detrimental. Sustained funding is required for successful software development, evolution, maintenance and distribution.

Workshop participants identified the following topical areas as the most pressing and critical—where development in computational modeling and simulation is needed, and extreme-scale computations could have great impact:

- Excited states and charge transport
- Strongly correlated systems
- Free energy landscapes, rare events, and phase space sampling
- Bridging time and length scales
- Materials, molecules, and nanostructures by scientific design
- Systems and processes out of equilibrium
- Materials properties, including phase diagrams, solvent effects and dielectric properties.

Priority research directions in each of these areas are presented in this report.

These areas have potential for significant advances through extreme-scale computing; foreseeable advances are well beyond the scope of smaller computer systems. However, effective success does require advances in the models, algorithms, and computer programs necessary for laying the groundwork for mission-oriented applications that are not possible today. Without such work on models, algorithms, and software development, the impact of extreme-scale computing on the solution of scientific problems, particularly in the energy arena, may be minor. In addition, the overall impact of extreme-scale computing is intimately connected to advances in computing at all scales, ranging from medium-size computer clusters used for daily exploratory and analysis work to those anticipated at the extreme scale.

The findings of these panel breakout sessions point to two major themes underlying advances in basic energy sciences:

- computational quantum mechanics of energy transformations in materials
- computational dynamics of processes encompassing long time scales, reactive, and rare events.

Both themes have major computational needs summarized in this report.

Computing technology is continuing to evolve and the best path to extreme-scale computing for BES research requires continuous reconsideration and reflection throughout the transition to extreme-scale computing. A BES extreme-scale working group is needed to collaborate on the following: 1) track the evolution of computing technology and determine its impact on BES scientific efforts; and 2) work closely with ASCR to enable its plans for exascale computing to have maximum impact on BES's scientific programs.

TABLE OF CONTENTS

INTRODUCTION

Over the next decade, the scientific community anticipates that significant advances will be made in computing technology that will enable increases in computing performance by orders of magnitude. These advances will have a major impact on the ability of scientists and engineers to solve critical scientific and technological problems.

This workshop report is one of a series resulting from the Scientific Grand Challenges Workshops hosted by the U.S. Department of Energy (DOE) Office of Advanced Scientific Computing Research (ASCR) in partnership with other DOE Office of Science programs. The workshop series focuses on the grand challenges of specific scientific domains and the role of extreme-scale computing in addressing those challenges. Dr. Paul Messina, interim director of science at the Argonne Leadership Computing Facility, is overseeing the workshop series.

Starting in late 2008, the ASCR workshop series provided a forum for scientists to relate opportunities in extreme-scale computing to the research challenges in various fields, including climate science, nuclear energy, high-energy physics, biology, and basic energy sciences.[1] In particular, the use of efficient computational techniques within chemistry, physics, and materials science has the potential to accelerate the discovery of materials and molecules with desirable properties and thus meet the challenges outlined in the various DOE Office of Basic Energy Sciences Basic Research Needs reports. Furthermore, computational modeling and simulation are a crucial complement to experimental studies, particularly when quantum mechanical processes controlling energy production, transformations, and storage are not directly observable and/or controllable (see Figure 1). Finally, many processes related to the Earth's climate and subsurface need better modeling capabilities at the molecular level that will be enabled by extreme-scale computing.

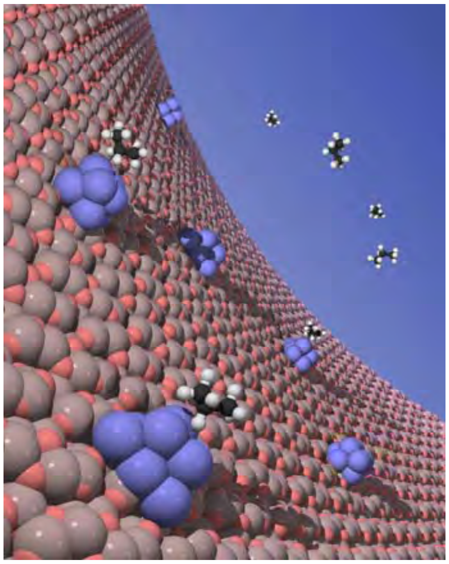


Figure 1. Improvement of catalysts involving clusters supported on substrates requires new computer algorithms that couple chemically accurate quantum-mechanical calculations for the reactive area with first-principles methods for the crystalline states. Image courtesy of Larry Curtiss (Argonne National Laboratory).

---

[1] http://extremecomputing.labworks.org.

WORKSHOP

The “Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale” workshop was jointly sponsored by the U.S. Department of Energy’s Office of Basic Energy Sciences (BES) and the Office of Advanced Scientific Computing Research (ASCR). The workshop was held August 13-15, 2009, in Bethesda, Maryland, to accomplish the following:

1. Identify forefront scientific challenges in basic energy sciences and identify those problems that could be solved by high-performance computing at the extreme scale
2. Describe how high-performance computing capabilities could address issues at the frontiers of basic energy sciences
3. Provide basic energy sciences researchers an opportunity to influence the development of high-performance computing
4. Provide input from the BES community for planning the development of a future high-performance computing capability by ASCR.

Workshop participants were encouraged to review the results of previous BES workshops, particularly those targeted at Basic Research Needs (BRN) for Energy (see Appendix 1 for a list). These reports are not focused on computation; instead, most outline computational and data management needs in their focus areas.

The workshop opened with six plenary talks that were followed by four panel breakout sessions. Conclusions about important directions in computational research were apparent from these talks.

Speakers described research needs in several important areas:

- **Photovoltaics for solar energy conversion**. Improved efficiency and lower cost for organic and inorganic materials, charge transfer and exciton dynamics, and the role of defects and interfaces.
- **Superconductivity: transmission and storage**. Superconductors with higher transition temperatures and critical magnetic fields, mechanism of high temperature superconductivity, oxide phase diagrams, and the role of stoichiometry.
- **Catalysis**. Energies to chemical accuracy (1 kcal/mol), reaction pathways and dynamics, development of heavy fossil and biological feedstock, conversion of ligno-cellulose, and computational design of new catalysts.
- **Combustion**. Heavy fossil fuels and biofuels, turbulent combustion, reacting Navier Stokes simulations, direct injection, homogeneous charge compression ignition, and cyber-infrastructure for sharing large data sets.

Extreme scale in this context means computing beyond today’s fastest machines—that is beyond one petaflops = 10^{15} floating point operations/sec. We include the planned development of exaflops machines (10^{18} flops) but also the expectation that petaflop machines will become available to many individual research groups and departmental computing centers, and enable a new generation of simulation and computation.

- **Advanced nuclear materials and systems; materials in extreme environments**. Microstructure of nuclear fuel, grain boundaries, voids in uranium dioxide, radiation damage, f-electron physics and chemistry, and high temperature and pressure.

The following talk summarized the likely shape of future computing hardware and software.

- **Evolution of high-performance computing architectures over the next decade and challenges to their effective utilization**. Petaflop (10^{15} flops) machines are available now, and exaflop (10^{18} flops) machines are expected to be available in 8-10 years. Such machines will have architectures substantially different from current ones and will require a significant rethinking of application code design and implementation. In particular, exascale computers are expected to be massively parallel; consist of billions of processing units; have no significant increase in processor clock speed; be populated with multicore chips; and use software techniques such as openMP and Pthreads. From the programmer's perspective, exascale machines will provide abundant and inexpensive flops – but impose high penalties for data movement. For further details, see the following reports:
    - ExaScale Computing Study: Technology Challenges in Achieving Exascale Systems (DARPA 2008)[1]
    - The International Exascale Software Project Roadmap 1.0 (Dongarra et al. 2010).[2]

With these plenary talks as background material, the four panel breakout groups convened and discussed the following topics:

- Correlation and Time Dependence
- Photovoltaics, Solar Energy Conversion and Solid-State Lighting
- Chemical and Electrical Storage for Energy and Environment
- Molecular Dynamics and Reaction Dynamics.

---

[1] http://www.er.doe.gov/ascr/Research/CS/DARPA%20exascale%20-%20hardware%20(2008).pdf.

[2] http://www.exascale.org/mediawiki/images/4/42/IESP-roadmap-1.0.pdf.

FINDINGS

CHALLENGES AND OPPORTUNITIES IN BASIC ENERGY SCIENCES

Workshop participants identified the following topical areas as the most pressing and critical where development in computational modeling and simulation are needed, and where extreme-scale computations could have great impact:

- excited states and charge transport
- strongly correlated systems
- free energy landscapes, rare events, and phase space sampling
- bridging time and length scales
- materials, molecules, and nanostructures by scientific design
- systems and processes out of equilibrium
- materials properties, including phase diagrams, solvent and dielectric media.

All of these areas have potential for significant advances via extreme-scale computing; the foreseen advances are well beyond the scope of smaller computer systems. However, effective success does require advances in the models, algorithms, and computer programs necessary for laying the groundwork for mission-oriented applications that are not possible today. Without such work on models, algorithms, and software development, the impact of extreme-scale computing on the solution of scientific problems, particularly in the energy arena, may be minor. In addition, the overall impact of extreme-scale computing is intimately connected to advances in computing at all scales, ranging from medium-size computer clusters used for daily exploratory and analysis work to those anticipated at the extreme scale.

The findings of these panel breakout sessions point to two major themes underlying advances in the basic energy sciences: computational quantum mechanics of energy transformations in materials, and computational dynamics of processes encompassing long time scales, reactive, and rare events. Both of these themes have major computational needs that are summarized in “Crosscutting Issues.”

CROSSCUTTING ISSUES

“Challenges and Opportunities in Basic Energy Sciences” summarizes the output of the four panel breakout sessions. Panel members also discussed several issues that underlie the priority research directions and must be considered when developing research programs to address these research directions. Three major issues were identified:

- Any new research initiatives must continue to support an appropriate balance between small-scale, medium-scale, and large-scale computational research efforts. A focus on only large-scale efforts would be detrimental for the following reasons:
  - Many innovative and unexpected new ideas emerge from single investigator or small research group initiatives. For example, in the field of strongly correlated electron systems, scientists

  have learned that simultaneous consideration of multiple interactions and coupling can lead to unexpected simplified collective behavior that often forms the basis of new technological ideas and capabilities.

  - Much scientific computing is performed at the midscale—for software development, preliminary investigative research, analysis of large-scale simulations, etc. Large-scale computing systems are not appropriate for—nor should they be used for—this type of work.

- Sustained funding is required for successful software development, evolution, maintenance and distribution. It is essential to recognize and support the long life cycle of any large-scale scientific software. The life span of such software far exceeds the life span of any particular generation of computer hardware, and the software must be constantly updated and revised as the scientific questions and computing systems change.
- Computing technology is continuing to evolve and the best path to extreme-scale computing for the U.S. Department of Energy's Office of Basic Energy Sciences (BES) research is unclear (see "Algorithmic and Software-Hardware Issues"). An extreme-scale computing working group is needed to 1) track the evolution of computing technology and determine its impact on BES scientific efforts; and 2) work closely with DOE's Office of Advanced Scientific Computing Research (ASCR) to enable its plans for exascale computing to have maximum impact on BES' scientific programs. For more information on this extreme-scale computing working group, see "Algorithmic and Software-Hardware Issues."

ALGORITHMIC AND SOFTWARE-HARDWARE ISSUES

Exciting new scientific opportunities provided by extreme-scale computing clearly pose great, largely unknown challenges for software development. Although multicore processors with large, fully functional cores and large per-core memories enabled the development and deployment of petascale computers, this technology will not scale to exascale computers—the compute performance is not sufficiently dense and the power requirements are prohibitive. Additionally, some of the critical performance characteristics (e.g., the cost of a floating-point operation versus the cost of moving data) will dramatically change. Exascale computers will require the development of new computing technologies. Although the details of these future technologies are unknown, they are likely to resemble the many-core technologies used in today's graphics processing units or some combination of multicore and many-core technologies. To achieve exascale performance levels, a computer will likely have tens to hundreds of millions of cores and a billion or more execution threads. Exploiting this level of parallelism in science and engineering applications will be a daunting challenge.

Use of these new technologies in exascale computers will require substantial revision of the application codes widely used today in chemical and materials sciences. This statement is accurate despite that some of the highest performing codes on Jaguar, the petascale computing system at Oak Ridge National Laboratory, are chemical and materials science codes. Achieving another factor of 1000 in parallelism will require new algorithms and likely even new mathematical and/or computational approaches to modeling chemical and materials systems. Development of these new approaches and algorithms, as well as a clear understanding of the impact of computing technologies that underlie extreme-scale computing, will require close collaborations between software developers in the computational chemical and materials sciences with computer scientists and applied mathematicians.

To ensure that BES' research programs derive maximum benefit from the development and deployment of exascale computers by ASCR, it is recommended ASCR and BES jointly fund two to four exascale software development projects in computational chemistry and materials sciences. These projects will begin the development of chemistry and materials science applications for the anticipated trans-petascale computing systems to be fielded by ASCR—a 20-50 petaflops system in 2012-2013 and a 200-500 petaflops system in 2015-2016. Project team leaders would be key members of the BES extreme-scale computing working group. In addition to providing feedback to ASCR on the extreme-scale computing hardware and software—a key ingredient of the co-design approach being adopted by ASCR—another key responsibility of these project teams is to provide outreach to the larger BES chemistry and materials science community, informing the community of new algorithms and approaches that can fully exploit the power of exascale computers.

CONCLUSIONS

Computations at the extreme scale—the exascale and beyond—will greatly contribute to understanding and predicting properties and processes in materials and molecules related to the optimal use of current energy technologies and the development of new energy sources. Concurrently, the success of extreme-scale computing for basic energy science research programs will require investments in software and algorithms to exploit the extreme level of concurrency available by extreme-scale computing systems, as well as in continued and increased investments in theory and small- to medium-scale computing facilities. Workshop participants determined there was a need for a concerted effort in investments both at the extreme and small to medium scales. Connections and cross-fertilization between small-, medium-, and extreme-scale computing, in terms of interconnected theory and algorithmic and code development, need to be carefully planned and effectively established. Formation of an extreme-scale working group, composed of members of the basic energy science community, would facilitate coordination and communication required for effective design and the balanced use of future extreme-scale architectures.

Figure 2 illustrates how advanced computer simulations are helping researchers in the basic energy sciences field. Extreme-scale computing can advance this research.

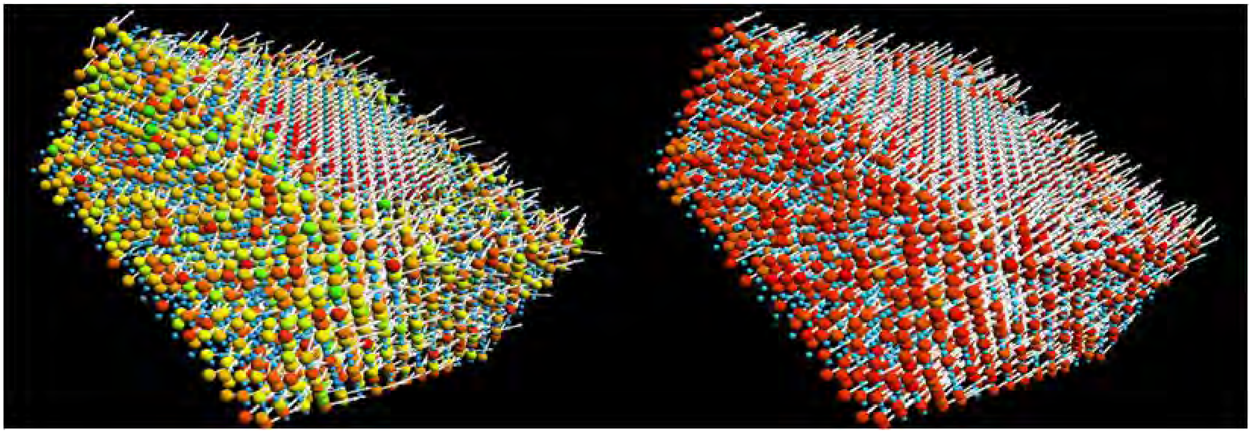


Figure 2. Calculated magnetic spin dynamics in an iron-platinum nanoparticle embedded in a random alloy. Left image is initial state (nonmagnetic); right image is final state (ferromagnetic). Image courtesy of Malcolm Stocks, Aurelian Rusanu, Markus Eisenbach, and Don Nicholson (Oak Ridge National Laboratory); and Yang Wang and Greg Foss (Pittsburgh Supercomputer Center).

Three major issues were identified:

- Computing technology is continuing to evolve and the best path to extreme-scale computing for basic energy science research could be multifold. The science community should stay aware, informed, and involved as much as possible in the evolution of computing technology and in its realization in extreme-scale computing systems to maximize science output.
- New research initiatives must continue to support an appropriate balance between small-scale, medium-scale, and large-scale research efforts for the following reasons:
  - Many of the most innovative new ideas emerge from single investigators or small research group initiatives. For example, in the field of strongly correlated electron systems, scientists learned

  that unexpected results from new computational implementations of theory often require access to less-structured programming environments that are more often available on small- to medium-scale platforms.

  - Much scientific computing is performed at the midscale, such as software development, preliminary investigative research, and analysis of large-scale simulations. Major computing systems are not appropriate—nor should they be used for—this type of work.

- Sustained funding is required for successful software development and maintenance. It is essential to recognize and support the long life cycle of any large-scale scientific software. In particular, the life span of such software far exceeds the duration of any particular generation of computer hardware and must therefore be constantly updated and revised, with new functionality being added as needed.

The exciting new capabilities associated with extreme-scale computing clearly pose great, largely unknown challenges for software development. Close collaborations between software developers in different basic energy sciences areas, computer scientists, and applied mathematicians (perhaps in a variation of the Scientific Discovery through Advanced Computing model) will be needed to meet these challenges; a clear understanding of the computing technologies that underlie extreme-scale computing will be required as well. The challenge of creating more productive and reusable software for scientific and engineering applications must be faced in light of the current, rapid evolution of computing technology.

Workshop participants also recognized three additional pressing challenges:

1. Establish specific, problem-driven connections between extreme-scale computing and Energy Frontier Research Centers missions to enable computational solutions of important energy problems not only among theoreticians and computer scientists, but also with experimentalists and eventually with engineers.
2. Establish specific problem-driven connections with the U.S. Department of Energy Office of Science experimental facilities such as the light-source, neutron-sources, and nanoscience activities.
3. Create a renewed focus and investment in code verification and data validation. Reproducibility and repeatability of calculations and transparency of results will be increasingly more difficult at the extreme scale, and devising specific plans and algorithms to validate the computational results is an essential need. A concrete validation and verification strategy and its execution are critical to the success of computation at the extreme scale in general, particularly for energy problems.

PRIORITY RESEARCH DIRECTIONS

CORRELATION AND TIME DEPENDENCE

PHOTOVOLAIC FUNDAMENTALS

STORAGE FOR CLEAN ENERGY TECHNOLOGIES

DYNAMICS

CORRELATION AND TIME DEPENDENCE

The panel identified the **treatment of strongly correlated and far from equilibrium systems** as major challenges. In particular, the following priority research directions (PRDs) were identified:

- **Develop methodologies to predict the total energies, excitation spectra, and correlation energy of solids and molecules with properties that are dominated by electron correlation effects**. The use of density functional theory (DFT) for a broad range of problems where strong electron correlations are less critical is one of the great successes of computational quantum physics and chemistry over the last 30 years. However, DFT-based calculations lack sufficient accuracy to describe and predict the properties of strongly correlated materials (e.g., many metal oxides) and strongly correlated multireference molecules (e.g., low-spin biradicaloids and polyradicals). A future challenge is to advance methods for computationally modeling materials and molecules where electron correlation effects are dominant, such as the dynamical mean field theory, the quantum Monte Carlo method, and the coupled-cluster theory. These much more computationally intensive methods can then be applied to strongly correlated systems much as DFT is applied today to weakly correlated materials.
- **Develop accurate methods for modeling electronic excitations, surface crossings, and nonradiative couplings in large molecules and materials**. While harnessing light energy is central to future energy needs, accurate modeling of electronic excitations is currently restricted to the smallest systems. Advances in theory and leveraging developments in computational capabilities can lead to breakthroughs in modeling the creation, evolution and destruction of excitations, all of which may be strongly influenced by electron correlation effects. Concurrently, development of theoretical spectroscopy tools for direct computation of experimental observables should be advanced. A greater synergy between computational developments and present and next-generation U.S. Department of Energy (DOE) national experimental facilities will emerge if computational tools are developed to predict the spectra of materials and molecules. These tools will greatly assist in interpreting the spectroscopy of a broad range of materials, particularly of strongly correlated materials and their time-dependent behavior.
- **Advance theory and computational models of driven and open systems for the control of matter on very short time scales**. A key challenge is to extend the existing and emerging methods for isolated systems to include interactions with external driving fields, and the coupling of materials and molecules to external reservoirs. Advances in these areas will result in applications to modeling next-generation information processing devices, solid-state thermoelectrics, organic and biomimetic materials, and strong field coherent control of materials and molecular processes.
- **Develop multiscale and multiphysics capabilities to treat physical and chemical phenomena requiring modeling over multiple length and time scales**. Many macroscopic phenomena are driven by processes that occur on molecular length and time scales. Examples of materials and processes requiring models capable of describing systems over multiple length and time scales include chemically inhomogenous systems; e.g., reactor materials, materials subject to damage, or correlated materials present in modern batteries.

Figure 3 illustrates how the catalytic conversion of acetylene to benzene is accomplished via a series of complex reactions. Combining advanced computational techniques and experiment using extreme-scale computing will enable researchers to identify complex chemical reactions (Figure 3).

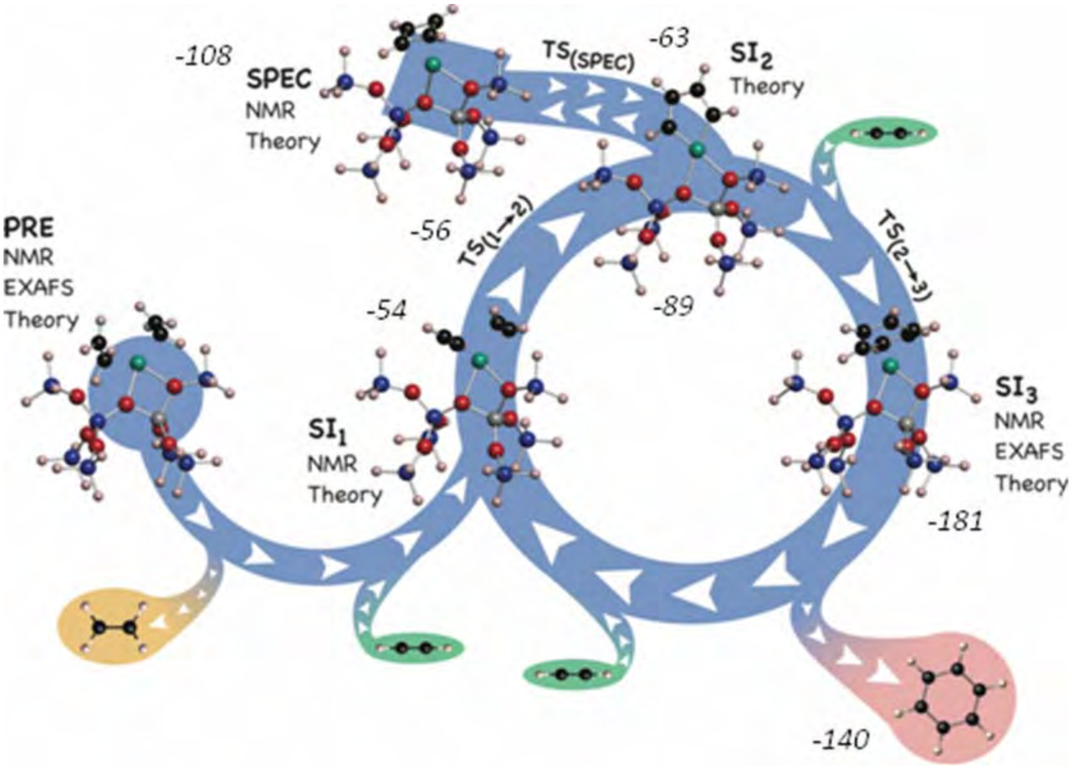


Figure 3. Catalytic conversion of acetylene to benzene is accomplished via a series of complex reactions. Combining advanced computational techniques and experiment allows for the identification of the complicated path followed and reactions that occur during the process. Image courtesy of David A. Dixon (The University of Alabama), Bruce C. Gates (University of California-Davis) and James F. Haw (University of Southern California). Source: Kletnieks et al. (2007).

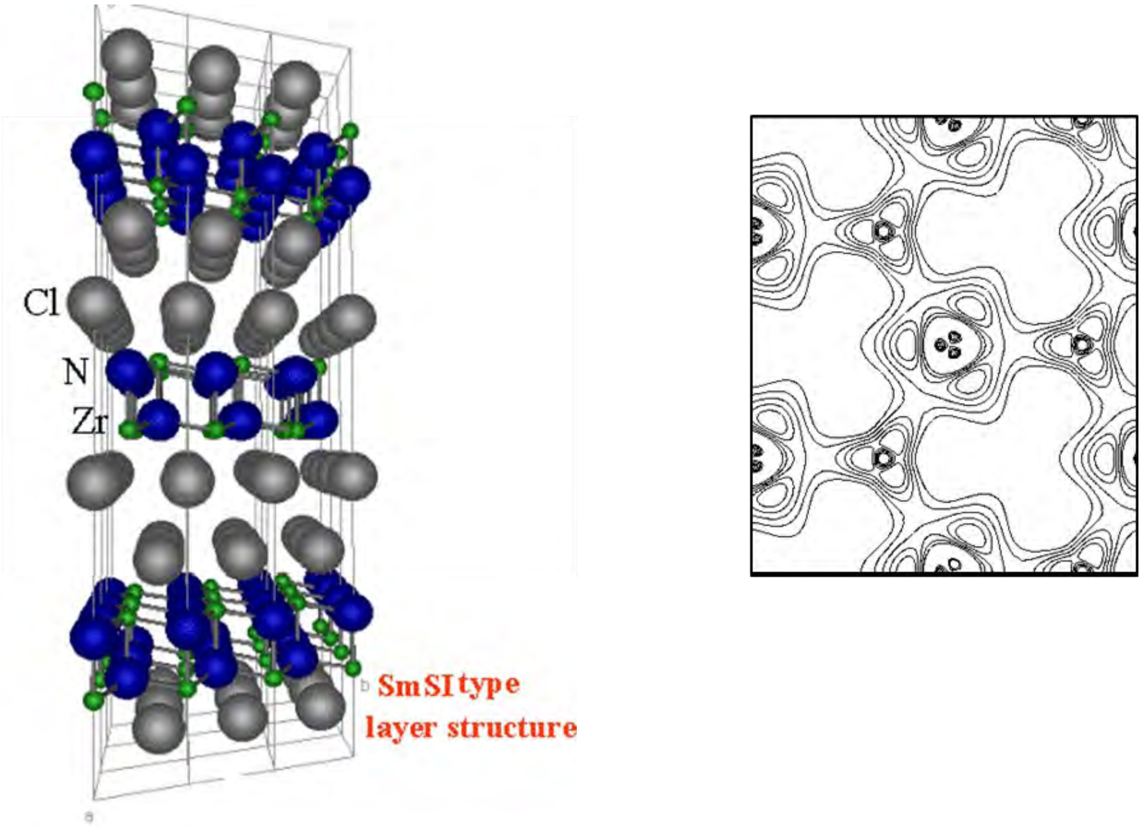


Figure 4. Crystal structure and charge density of a compound of zirconium, nitrogen and chlorine displays superconductivity at a remarkably high temperature that requires fundamental understanding. Image courtesy of Warren Pickett (University of California, Davis).

PHOTOVOLTAIC FUNDAMENTALS

Characterization of **materials properties related to the fundamental mechanisms in photovoltaic cells**, which are particularly challenging to experimentally characterize, is a major challenge in photovoltaic science. Hence, the ability to study these properties computationally is crucial, as illustrated in Figure 5.

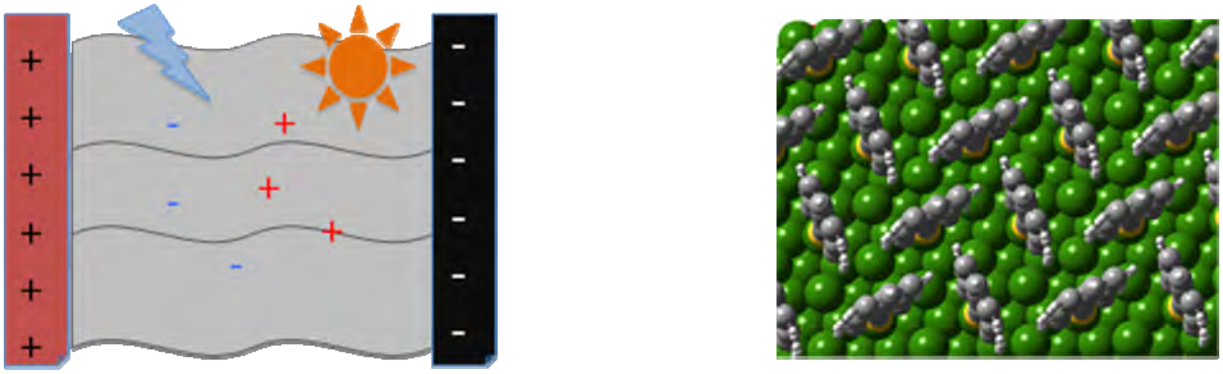


Figure 5. New photovoltaic materials require understanding organic-inorganic interfaces brought about by more sophisticated methods for modeling light-matter interactions and for calculating transfer of energy from a collective many-electron excitation to an activated adsorbate. Image courtesy of Hai-Ping Cheng (University of Florida/Quantum Theory Project).

The critical properties and phenomena that have been identified are as follows:

- **Excited-state phenomena**. Every step in the conversion process of light to electrical energy involves excited states of complex heterogeneous materials. Extreme-scale computation can create a breakthrough in the accurate prediction of the combined effects of multiple, interacting structures and their effects upon electronic excitation and ultimate performance of a photovoltaic cell. Some specific challenges include the *development of scalable semiempirical methods and accurate first-principles methods for computing energies and forces in excited states;* and *the development and implementation of DFT for improved band gaps, and electronic level alignment prediction.*

- **Carrier relaxation, recombination, and transport**. To increase the efficiency of photovoltaic materials, the recombination of carriers must be reduced and the probability of carrier transport and collection increased. Extreme-scale computing can contribute to the development and use of *efficient computational quantum mechanical methods for studying carrier dynamics*. This will enable scientists to address issues such as exciton lifetime and carrier transport in complex nanostructures and organic solar cells, as well as electron-phonon coupling, radiative and nonradiative recombination in inorganic solar cells.

- **Defects and doping**. Control of defects and doping is critical for photovoltaic materials research and the photovoltaic industry; this control would enable lower-cost design with more efficient photovoltaic materials. Advances in photovoltaic research require an accurate description of point defects that couple strongly to the electronic and structural degrees of freedom of the material, as well as extended defects at different length scales. Simulating defect-defect interactions and mesoscopic scale migration of defects are challenges that cannot be addressed without extreme-scale computing.

Extreme-scale computing will also allow for *rapid screening of many candidate structures of complex defects* in systems with many degrees of freedom.

- **Interface morphology and dynamics of formation and growth**. Cost-effective photovoltaic systems involve complex, multicomponent, heterogeneous, nonstoichiometric materials and multiple phases; e.g., polycrystalline, amorphous, organic, and hybrids. The morphology in these systems often eludes experiment. As a consequence, the formation and evolution processes of these systems are poorly understood. Extreme-scale computing can enable innovation in *computational methodology and programming paradigms to evolve the large number of degrees of freedom for long-time scales and thus to achieve efficient sampling of configuration space*. By employing accurate multiscale methods, scientists will be able to generate the understanding necessary to optimize growth conditions to control uniformity, design percolation networks and multijunction cells, induce fluctuations in stoichiometry, and control doping and grain boundary/sizes for limiting electron-hole recombination.

Figure 6 illustrates how new theoretical methods can be used to predict band-gaps in photovoltaic crystals. Researchers could analyze such complex chemical compounds further using extreme-scale computing.

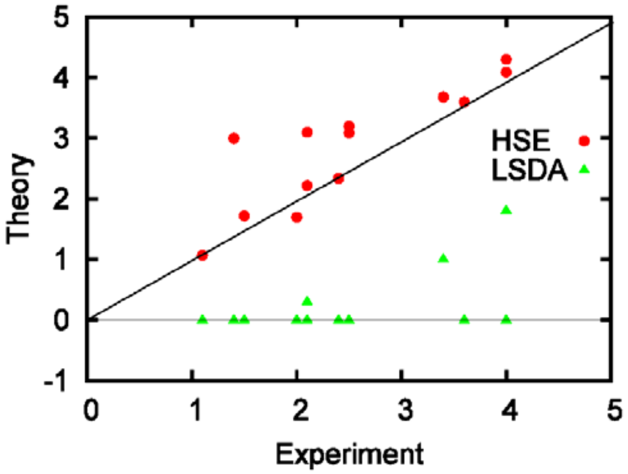


Figure 6. New theoretical methods for predicting band-gaps in photovoltaic crystals can be improved by carefully combining density-functional and correlated methods. Image courtesy of Gustavo E. Scuseria (Rice University) and Richard L. Martin (Los Alamos National Laboratory).

STORAGE FOR CLEAN ENERGY TECHNOLOGIES

The Storage for Clean Energy Technologies panel examined research opportunities for the use of extreme-scale computing in the field of energy storage and focused on four domain sciences: fuel cell science, batteries and capacitors, energy storage in chemical bonds, and geological CO_2 sequestration. For each of these domain sciences, key issues to be addressed computationally—at the extreme scale—were identified.

- **Fuel cell science**. Fuel cells play an important role in an energy economy, where chemical energy carried by a fuel (e.g., H_2 or CH_3OH) is transformed into electrical energy. Fuel cells are especially well suited for this task because they operate with high efficiency, do not produce pollutants, and provide electrical power that can be tailored to a wide variety of applications—from large stationary plants to portable and consumer power sources. Two major research areas have been identified for this domain science: 1) electrode catalysis with the goal of finding alternate catalysts based on nonprecious metals (for H_2 or CH_3OH oxidation, and O_2 reduction) in lieu of Pt-based catalysts; and 2) the transport of protons through membranes in complex molecular environments.
- **Batteries and capacitors science**. These energy storage devices are in need of revolutionary new materials to attain higher energy and power densities, better stability and safety, and longer lifetimes. Achieving breakthroughs in the development of electrode materials and electrolytes require a fundamental understanding and control of the coupled charge and ion transport through the electrode material, of phase transformations and reactions.
- **Chemical bond energy storage science**. Energy storage in chemical bonds and its release inevitably requires efficient chemical transformations, often within complex crystalline mixtures, amorphous structures, or molecular liquids. In this context, quantitative predictions of materials performance are needed (including thermodynamic, kinetic, and structural evolution) during complete energy storage cycles.
- **Geological CO_2 sequestration science**. The essence of this domain science is the capture and storage of CO_2 and other greenhouse gases in deep geologic formations to prevent release to the atmosphere from fossil fuel combustion for geologically relevant time scales. Implementing carbon capture and storage technologies requires reliable predictive modeling of the temporal and spatial evolution of reacting fluids and corresponding transport pathways, including accompanying structural and phase changes of heterogeneous geological systems under nonequilibrium conditions, at all relevant scales.

Figure 7 illustrates how realistically simulating chemical and material processes through extreme-scale computing is needed in basic energy sciences.

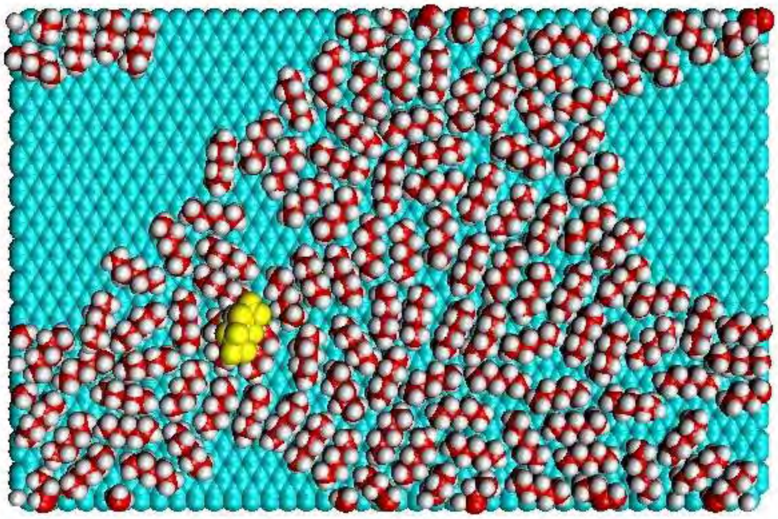


Figure 7. The problem of realistically simulating chemical and materials processes—often relevant to catalysis and combustion—that depend on rare events is an example of an incompletely solved problem where unpredictable inspirational breakthroughs are needed. Image courtesy of Kristen Fichthorn (Pennsylvania State University, Department of Chemical Engineering).

A single, overarching grand challenge emerged in all three domain sciences listed above: **inverse methods for materials design**, whereby a material with specific function and property is sought. Four priority research directions were identified to advance the realization of this grand challenge:

- **Develop simulation techniques to control chemical interactions at the molecular levels**. This requires advances in phase-space sampling techniques, quantum mechanical chemical rate calculations, and rare-events characterization.
- **Develop simulation techniques for transport of matter in heterogeneous environments**. This requires simulation techniques dealing with the coupled dynamics of electrons, protons, ions, and molecules at the nanoscale and at the macro- and field-scale.
- **Develop general and robust multiscale modeling techniques**. Techniques will be used for the description of integrated, complex materials.
- **Develop knowledge discovery techniques**. Techniques will be used that rely on machine learning to connect materials properties with the details of materials structure (unit cells, grain boundaries, etc.).

DYNAMICS

Extreme-scale computing, combined with the requisite advances in theoretical methods and algorithms, are anticipated to lead to fundamental breakthroughs in scientists' ability to predict rare-event kinetics, excited-state and charge-transport dynamics, and multiscale phenomena. These advances are central to expanding the role of dynamics modeling that will impact the understanding and design of new materials and chemical systems for future energy technologies.

Motivated by specific application areas in basic energy sciences, the following needs were identified:

- **Rational design and synthesis of multifunctional catalysts**. For fuel production from new and increasingly complex feedstocks, new catalysts with multiple functionalities are required. To guide discovery and design of these catalysts, a predictive computational framework is necessary. In particular, two major needs are identified: 1) develop systematic approaches for constructing and characterizing the molecules and materials designed to act as catalysts, and 2) develop the necessary understanding for controlling or directing chemical reactions in complex media.
- **Computational combustion**. To describe the chemical processes involved in combustion of existing and alternative fuels, high-quality *ab-initio* descriptions of stationary points and reaction paths on complex potential ground and excited-state energy surfaces are required from which reactions rates, product branching ratios, and final-state distributions can be obtained through dynamics calculations. Also required is a framework for integrating these basic quantities into sophisticated models that couple thousands of reactions together with fluid dynamics models to simulate fuel combustion (Figure 8). While supramolecular-scale combustion modeling has already demonstrated the utility of petascale modeling and is likely to be among the first investigations on any new-generation computational platform, the aforementioned integration will significantly enhance the ability to design clean and efficient internal combustion engines for this new generation of alternative fuels.

Figure 8. Direct numerical simulation of turbulent reactive flows reveals fundamental new insight into combustion. Image courtesy of Jacqueline Chen, Chun Sang Yoo, and Hongfeng Yu (Sandia National Laboratories).

- **Computational geosciences**. New modeling strategies for predicting geochemical and geophysical processes and properties at the microscopic scale (e.g., complex fluids and their reactions at mineral interfaces) are needed to analyze the long-term storage of greenhouse gases and nuclear waste. As most geochemical processes occur on atomistic time and length scales, while being observed on much larger scales, developments in effective multiscale methods are required. Figure 9 illustrates how new modeling capabilities can advance research in geosciences.

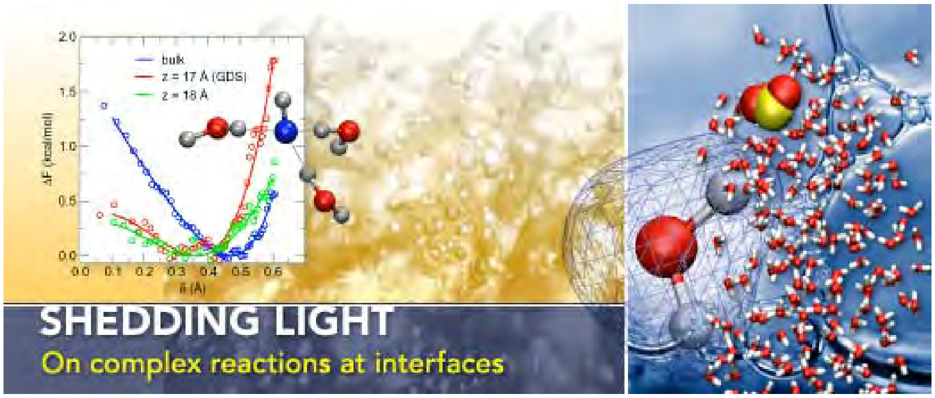


Figure 9. The chemistry of the air-water interface critically important for geoscience, involves many complex reactions that require new modeling capabilities. Image courtesy of Christopher Mundy (Pacific Northwest National Laboratory).

- **Materials under extreme environments**. Fundamental understanding of the behavior of materials under extreme conditions of temperature, stress, and corrosive environments underlies advances in a wide range of technologies relevant to energy generation and efficiency—from combustion of hydrocarbon fuels to the generation of electricity from nuclear energy. Progress requires methods to simulate the mechanical and mechano-chemistry properties of materials with heterogeneous grain, phase, and defect microstructures under conditions that are far from equilibrium.
- **Materials for nuclear energy**. Developing new materials for nuclear energy applications includes the development of multiscale methodologies for computing thermo-mechanical properties of nuclear fuel materials, accounting for the concurrent effects of irradiation and microstructure evolution.

PANEL REPORTS

CORRELATION AND TIME DEPENDENCE

PHOTOVOLTAIC FUNDAMENTALS

ENERGY STORAGE

DYNAMICS

CORRELATION AND TIME DEPENDENCE

Co-Leads: Martin Head-Gordon, University of California, Berkeley, and Lawrence Berkeley National Laboratory
Gabriel Kotliar, Rutgers University

Panel Members: Gerald Baumgartner, Louisiana State University; Jacqueline Chen, Sandia National Laboratories; Erik Deumans, University of Florida, Quantum Theory Project; Thomas Devereaux, SLAC National Accelerator Laboratory; Massimiliano Di Ventra, University of California, San Diego; Brett Esry, Kansas State University; Bruce Harmon, Ames Laboratory; Robert Harrison, Oak Ridge National Laboratory; Mark Jarrell, Louisiana State University; Karol Kowalski, Pacific Northwest National Laboratory; Wei Ku, Brookhaven National Laboratory; John Ludlow, Auburn University; Richard L. Martin, Los Alamos National Laboratory; Spiridoula Matsika, Temple University; Stephen Miller, Oak Ridge National Laboratory; Lubos Mitas, North Carolina State University; Mike Norman, Argonne National Laboratory; Joseph Oefelein, Sandia National Laboratories; Kyungwha Park, Virginia Tech; Thomas Schulthess, ETH Zurich; David Schultz, Oak Ridge National Laboratory; Sadasivan Shankar, Intel Corporation; Rick Stevens, Argonne National Laboratory; Malcolm Stocks, Oak Ridge National Laboratory; and David Yarkony, Johns Hopkins University

CURRENT STATUS

Understanding the behavior of electrons in systems ranging from molecules to solid-state materials is central to U.S. Department of Energy (DOE) mission challenges ranging from solar energy, to catalysis science, to nuclear energy and beyond. Theoretical and computational chemistry, physics, and materials science have the potential to accelerate the discovery of materials and molecules with properties to meet the challenges outlined in various DOE Office of Basic Energy Sciences (BES) Basic Research Needs (BRN) reports.[1] Furthermore, computational modeling based on the fundamental principles of quantum mechanics is an invaluable complement to experimental tools, particularly when key factors controlling electron behavior are not directly observable.

Value of Existing First-Principles Simulations and Their Limitations

The tremendous value of predictive quantum mechanical simulations is evident from the extraordinary success achieved by the description of solids and molecules in terms of a mean field model (electrons moving in an effective potential) with corrections to account for electron-electron correlation. Density functional theory (DFT) (Jones and Gunnarsson 1989) in particular, has become a ubiquitous simulation method in both quantum chemistry and condensed matter physics over the past 20 years due to three factors. The first factor is development of functionals that are sufficiently accurate to treat a wide range of problems in electronic structure theory (from the determination of catalytic reaction paths to the prediction of band structure and spectroscopy). The second factor is the broad availability of both public domain and commercial software that efficiently implements these models, including the ability to not only predict the energies of the systems, but also responses of the energy to perturbations such as moving

---

[1] See http://www.er.doe.gov/bes/reports/abstracts.html.

atoms or applied electromagnetic fields. The third factor is the wide availability of computers that enable DFT calculations to be routinely performed in both computational and experimental laboratories. Development of DFT as a ubiquitous tool is illustrated in Figure 10, which shows citation statistics for common functionals and programs.

Of course, development of DFT and methods built on a DFT foundation are not at a standstill. There is intense activity to develop new functionals that include aspects of physics that are not present in the functionals widely used today. For example, the notorious self-interaction error, which leads to artificial delocalization of odd electrons or holes (a crucial defect for the treatment of electron transfer relevant to light harvesting) is being addressed in functionals currently under development. The missing long-range correlations that give rise to dispersion interactions, which are responsible for self-assembly in nanoscale systems, are being added to new functionals in a variety of ways.

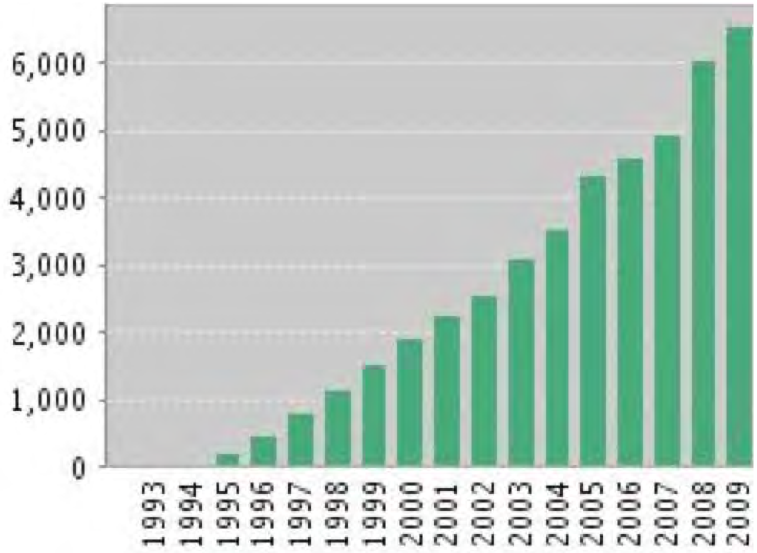


Figure 10. Impact of density functional theory calculations on computational simulations, as measured by the number of citations for a popular functional from the chemistry community (the Becke hybrid functional, B3LYP) and a popular functional from the physics community (the Perdew-Burke-Ernzerhof generalized gradient approximation) (Cramer and Truhlar 2009). As impressive as these citation counts are, this simple measure greatly underestimates the overall use of density functional theory for applications in computational chemistry, physics, and materials science. However, it conveys the growing impact of these efficient, first-principles methods.

Algorithms have been developed to treat time-dependent and transport phenomena, and they are being steadily improved to permit larger and larger-scale calculations. Extreme-scale computing will further enable this development, and the energy problems discussed in other panel reports on photovoltaics, catalysis, energy storage, and dynamics all envisage at least partial reliance on DFT in the future. The central theme of this panel report, however, is that advances in alternative simulation methods are essential to facilitate applications to a broad and important class of systems where DFT is inadequate. In these systems, correlation between electrons are of primary rather than secondary importance and it is for these challenging systems—called strongly correlated materials—that extreme-scale computing will have the most impact.

The Challenge of Strong Correlation in Chemistry and Physics

Of particular interest to basic energy science scientists are solids and molecules in which the delicate balance of competing interactions between electrons have resulted in remarkable and unexpected phenomena, such as high temperature superconductivity in materials based on copper oxide or iron arsenide layers. Addressing the problems related to energy conversion and storage also requires the treatment of systems in the presence of external fields and or in contact with external reservoirs, and therefore are not in equilibrium. The treatment of strongly correlated and far from equilibrium systems are challenging areas, which requires advanced modeling methods and—in some cases—new concepts and algorithms that have to be implemented, tested, and made available on state-of-the-art computers.

In the past decade, enormous conceptual algorithmic and computational advances have produced a new set of tools to address strongly correlated electron materials. Understanding, describing, and predicting the behavior of these materials has opened new avenues in materials research and has had great impact in the way basic energy science scientists develop novel materials to address the pressing energy needs described in various BES BRN reports.[1] In the forthcoming decade, the related and overlapping fields of computational chemistry, physics, and materials science are poised to make many more significant advances in the treatment of strongly correlated materials.

This panel report summarizes the challenges identified by the Correlation and Time-Dependence panel members.[2] Progress on these challenges requires advances in the models, algorithms, and computer programs necessary to lay the groundwork for mission-oriented applications that are not possible today. All of these areas are intimately connected to advances in computing at all scales, ranging from medium-size computer clusters to those anticipated at the extreme scale.

In the field of strongly correlated electron systems, both in physics as well as in chemistry, discoveries have often occurred by serendipity, and the search for new materials is usually conducted by trial and error. For example, the recent discovery of high-temperature superconductivity in FeAs layers in Japan was the outcome of a well-funded research project to search for more transparent conductors, and the rapid increase in critical temperature obtained in China was the result of very labor-intensive explorations in the newly identified area.

Concerted investment in the area of computational materials, physics and chemistry will facilitate the development of tools that will accelerate the design of new, correlated electron solids and molecules with desirable properties and impact the areas of research described in the BES reports.[1] For example, a promising direction for improving the harvesting of solar energy is provided by quantum dots in regimes where the Coulomb interactions have to be treated more accurately than by mean field methods. Many of the proposed ingredients of fourth-generation nuclear fuels, which hold promise for developing proliferation-resistant, high-efficiency nuclear reactors, involve actinides and their oxides that are archetypical strongly correlated electron materials. Many promising new catalysts are mixed valence elements and compounds. Expanding the scope of electronic structure and quantum chemistry methods to cope with this class of problems provides a high payoff investment opportunity that impacts a broad range

---

[1] See http://www.er.doe.gov/bes/reports/abstracts.html.

[2] "Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale," August 13-15, 2009, Washington D.C. Additional information at http://extremecomputing.labworks.org/basicenergy/index.stm.

of areas in energy research. The following section provides additional background and some broad research avenues underpinning this research opportunity and the outstanding challenges in this area.

BASIC SCIENCE CHALLENGES AND RESEARCH NEEDS

Developing Methodologies to Predict the Energies, Spectra, and Properties of Strongly Correlated Solids and Molecules

The "Introduction" section of this report notes the widespread success of DFT calculations for an enormous range of problems where strong electron correlations are not critical is one of the great successes of computational quantum physics and chemistry. However, current DFT methods cannot properly describe strongly correlated materials (many metal oxides, for instance), as well as strongly correlated molecules (organic polyradicals and many metal-containing catalysts, for instance). The challenge is to advance the most promising methods for treating strongly correlated systems (discussed in "Perspective from Condensed Matter Physics" and "Perspective from Quantum Chemistry") so they can be applied to these challenging systems with the same ease with which DFT is applied today to weakly correlated materials.

Perspective from Condensed Matter Physics

Dynamical Mean Field Theory (DMFT) (Kotliar et al. 2006) simplifies the full many-body problem by assuming the irreducible quantities have a restricted range. It has been very successful in combination with model Hamiltonians and its combination with high-quality band structure methods involving advanced basis sets is a subject of intensive research with promising results. For example, theoretical predictions of the phonon spectra of delta plutonium (Dai et al. 2003) supported by DOE BES, was shown to be surprisingly accurate by later inelastic x-ray scattering measurements (Wong et al. 2003) (see Figure 11). This was in spite of the approximations involved in the calculations and the fact that delta plutonium is stabilized by small amounts of impurities. The computed photoemission spectra of delta plutonium is also in good agreement with the experimental results, as shown by recent calculations using advanced impurity solvers (Marianetti et al. 2008). These calculations, using continuous time quantum Monte Carlo as the impurity solver, were only possible because of the one-time availability of massive computational resources in the Atlas Grand Challenge program at Lawrence Livermore National Laboratory (100,000 central processing unit-hours a week for 6 months). Further advances in computational facilities and algorithms would allow the extension of these calculations to predict the finite temperature phase diagrams of actinides and their alloys and oxides that are involved in advanced nuclear fuel cycles.

Another grand challenge is to achieve a seamless integration of DMFT into accurate electronic structure methods. This would result in a fully controlled diagrammatic approximation to the quantum many-body problem that is free from any adjustable double-counting parameters that is the central limitation of the current approach.

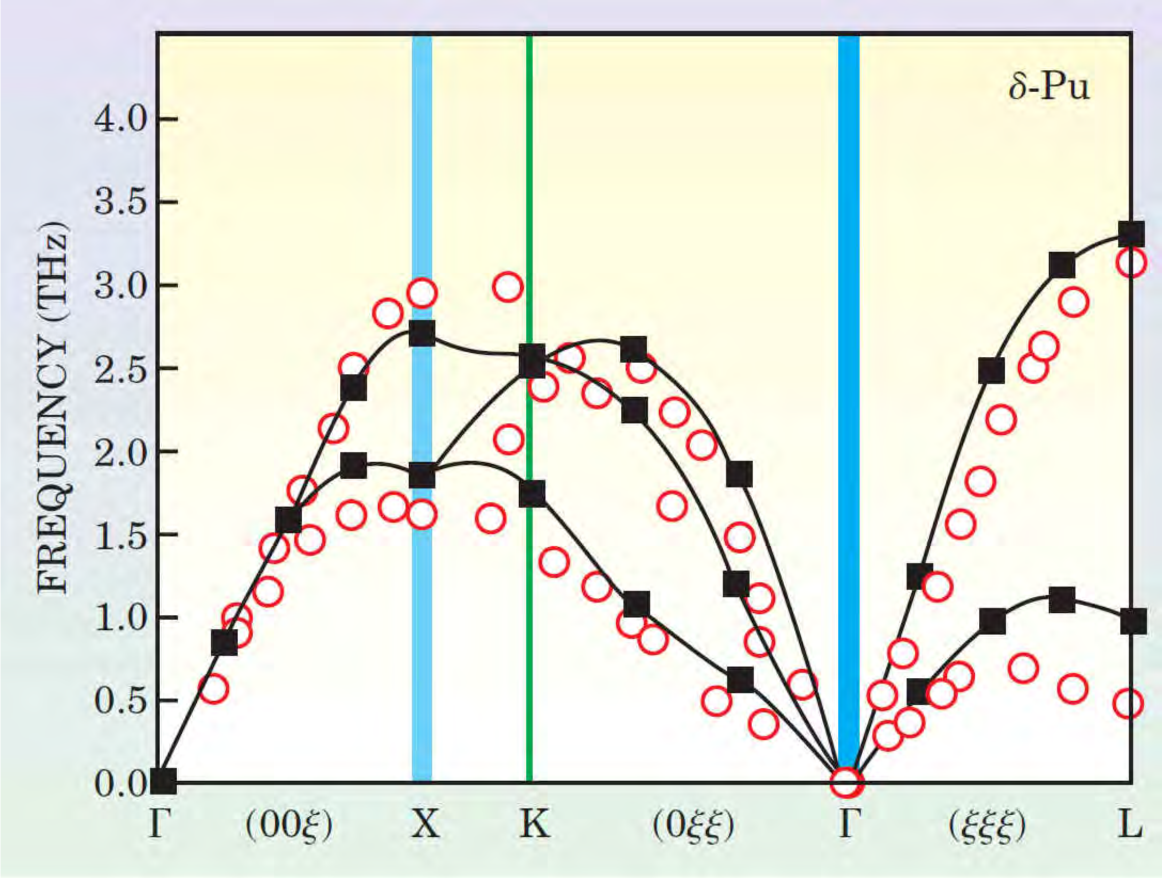


Figure 11. Predicted zero temperature phonon spectrum of the delta phase of plutonium (red open circles) calculated using DMFT compared to subsequent experimental values (solid squares) of this material at room temperature with 0.05% Ga doping. The experiments were conducted using state-of-the-art inelastic X-ray facilities at the European Synchrotron Radiation Facility. The dispersion curves plotted here map the vibrational frequencies of the atoms in momentum space. The frequencies vary with the wave vectors and are evident in the branches as one moves in a particular Brillouin zone direction. The delta phase of plutonium is not magnetic and is not stable in DFT. This important material therefore requires methods that more accurately treat electron correlation. Predicting the chemical trends of plutonium-based nuclear fuels is important for the design of high-efficiency, proliferation-proof nuclear power plants. Reprinted with permission from Gabriel Kotliar and Dieter Vollhardt, *Physics Today* Vol. 57, page 53 (2004). Copyright 2004, American Institute of Physics.

Another important technique capable of treating strong correlations from first-principles is quantum Monte Carlo (QMC) methods (Foulkes et al. 2001). The methods compute the exact wave function by systematically improving variational wave functions. The approach is based on an exact mapping of the Schrödinger equation onto an equivalent stochastic process, which is then simulated. The QMC method enables scientists to treat light nuclei—such as hydrogen—quantum mechanically. An application of QMC to the computation of the equation of state of iron oxide (FeO) is shown in Figure 12.

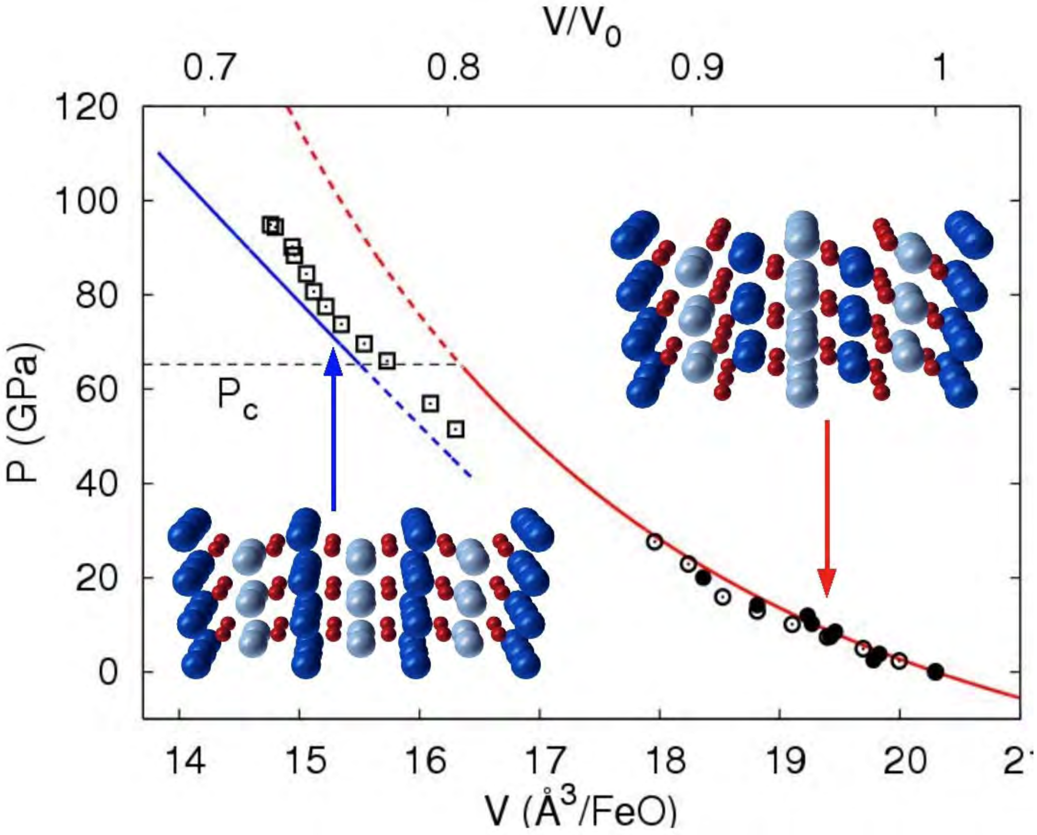


Figure 12. Equation of state (pressure versus volume) of FeO at low temperatures. The QMC results for the transition pressure, P_c = 65-70 GPa, is in close agreement with experimental measurements that vary between 70 and 100 GPa. The upper-right corner shows antiferromagntic rocksalt equilibrium structure while the lower-left corner illustrates the high-pressure tetragonal structure. Image courtesy of Jindrich Kolorenč and Lubos Mitas (North Carolina State University). (Source: Kolorenč and Mitas 2008).

Deriving high quality, trial wave functions for variational Monte Carlo calculations with accurate nodal surfaces will continue to be an important challenge in this field. Other challenges involve gaining insights into the factors that govern the topology of the exact nodal surface in strongly correlated materials, and on methods for releasing those nodal surfaces without encountering the so-called "sign" problem.

The use of molecular dynamics in conjunction with methods to compute total energies that provide more accuracy than DFT is feasible in relatively simple systems. In more complex systems, progress can be made by using hybrid schemes where forces are obtained from DFT and energies are obtained from QMC, as demonstrated recently in the evaluation of the heat of vaporization for 32 water molecules (Grossman and Mitas 2005). Integration of molecular dynamics with methods for computing energies and forces in strongly correlated materials is a frontier of materials research with great potential to advance the discovery of new materials. These studies will become more widespread as algorithms advance and extreme-scale computational resources become increasingly available.

Perspective from Quantum Chemistry

There are several well-established methods used for treating strongly correlated electrons in molecules. One very powerful approach is the "complete active space" (CAS) method that solves the Schrödinger equation in a small space of chemically relevant orbitals, called the active space (Roos et al. 1980; Cramer 2002). While the active space should in principle include all valence electrons, in practice the exponential cost of CAS methods with increasing numbers of electrons and orbitals means there is an upper limit of about 16 orbitals. This restriction means that not all important configurations of the strongly correlated electrons can be included in the calculations. This leads to challenges that are well known to practitioners of CAS methods. Tractable CAS calculations are difficult to attain because many different active spaces must be investigated until sensible results are obtained—a rather ad hoc process.

An example of a difficult, but ultimately tractable, CAS calculation is the complex bonding that describes the uranium dimer (Gagliardi and Roos 2005). In some instances, however, CAS calculations are not feasible because the required active spaces are simply too large. An example is the oxygen-evolving complex of Photosystem II, a Mn_4O_5 cluster with 20 metal *d* orbitals, plus additional participating ligand orbitals. Unfortunately, in many of these cases, extreme-scale computing will only be of modest help—in the Mn_4O_5 problem, applying 1000 times more computing resources would only permit the addition of one more active orbital to the conventional CAS calculation.

Alternative approaches for treating strongly correlated molecules must be found. From the quantum chemistry community, a diverse set of approaches are emerging that are directed towards treating these problems. It is too early to predict specific methods as either winners or losers, but based on the surge in novel ideas over the past few years, it is not too early to forecast this is an extremely important research frontier that has the potential to address important applications areas. A few examples of promising directions are in the following paragraph.

First, the coupled-cluster method (Cizek 1966; Bartlett 1981; Oliphant and Adamowicz 1993) has long been recognized as capable of treating strongly correlated problems, and active research is proceeding on novel truncations of the full coupled-cluster hierarchy to permit the treatment of ever larger molecular systems with strongly correlated electrons. Second, QMC methods, given a trial function that can describe strong correlations, is another area where there has been recent activity (Hammond et al. 1994). Third, the density matrix renormalization group (DMRG) approach (Schollwöck 2005) has been shown to be capable of describing strong correlations in very large systems that have one-dimensional connectivity. Scientists are investigating extensions of this approach to higher dimensions, such as projected entangled pair state (PEPS) and multiscale entanglement renormalization ansatz (MERA). Fourth, reduced density matrix methods (Mazziotti 2006) are another direction that promises to enable treatment of large molecules.

Advancing Theory and Models of Driven and Open Systems for the Control of Matter on Very Short Time Scales

Attosecond Science

Experimental advances have pushed laser-matter interactions into new domains of space and time, creating enormously strong electromagnetic fields that act on tremendously short time scales. This defines the emerging regime of attosecond science, where the structure of matter can be measured on the subnanometer-length scale characteristic of electrons in molecules, and time resolution can be pushed into the attosecond (10^{-18}) range (Corkum and Krausz 2007). At the same time, the fields generated by attosecond pulses can be as strong or stronger than the internal electric fields experienced by electrons in stable molecules; thus, nonperturbative treatment of the matter-field interactions are essential.

Attosecond pulses create new avenues for time-domain studies of multielectron dynamics in atoms, molecules, clusters, and solids on their natural, quantum mechanical time scales and at dimensions even shorter than molecular scales. New phenomena result, including high-harmonic generation, which involve very strongly perturbed resonance states where correlation effects are important. These new avenues have important implications for measurement—possibly being able to follow chemical reactions or transformations in real time, as well as the possibility of controlling the behavior of matter through new pump-probe techniques. These experimental opportunities lead to strong challenges to theory. Electron correlation effects are of obvious importance, but we are no longer considering the ground state as in the previous section. Indeed, we are no longer considering a stationary state at all. The system is driven by fields that demand nonperturbative solution of the time-dependent Schrödinger equation. To date, this has been accomplished for only the smallest molecules—two electron systems. Extreme-scale computing is likely to enable new predictions that will be invaluable to experimental advances. This will be a new form of the computational spectroscopy discussed more generally in the following section. The opportunities briefly reiterated here have been addressed in previous BES reports – the key point emphasized here is the need for development of methods that properly treat electron correlation to accurately model attosecond phenomena.

Materials Design – Driven and Open Systems

Materials (solids, nanostructures, and molecules) are the fabrics used to tailor devices to a given specification. To understand how to optimally make these devices, scientists require advances in the theory and models of externally driven and open systems out of thermodynamical equilibrium. Panel members identified several areas where computational and algorithmic advances that extend the scope of existing methodologies away from equilibrium could result in applications that are relevant to current industrial efforts. For example, the design of the next generation information processing devices or solid-state thermoelectric devices requires a thorough understanding of material properties both from *synthesis* and *performance* perspectives.

The *International Road Map for Semiconductors 2007 Edition* stressed the importance of new materials and listed the various materials challenges in the section on “Emerging Research on Materials” (ITRS 2007). For example, high k dielectrics have already replaced SiO_2 as the dielectric in the MOSFET device. Now, complex oxides of transition metals and inner transition metals are being evaluated for the next generation dielectrics to further reduce the leakage current and reduce power consumption. This class of materials (unlike Si and SiO_2 that have served the industry well over in the last four decades) are not well described by DFT. Theoretical developments such as those described in “Perspective from Condensed Matter Physics” and “Perspective from Quantum Chemistry” are needed for progress. The need to address these problems in external fields and in contact with reservoirs makes the strong correlation problem even more challenging.

Efficient energy generation, storage and conversion represent a global challenge that encompasses all aspects of technology and society. Similar to the information processing devices above, these systems are materials and molecular systems that not in equilibrium (i.e., they are time dependent and/or open systems). Strongly correlated materials are a promising avenue to search for breakthroughs in this area. These points are illustrated with an example from thermoelectric devices. The efficiency of such devices is quantified by a figure of merit proportional to the thermoelectric power squared and the electrical conductivity (or inversely proportional to the resistivity). For many years, the optimal figure of merit in these materials was not substantially improved over the results obtained by A. Ioffe in the 1950s. In the past few years, several advances—such as density of states engineering and nanostructuring—have been used to reduce thermal conductivity without significantly increasing resistivity. The use of strongly correlated elements to increase the thermoelectric power of these devices has resulted in significant increases in the figures of merit. Of particular interest is the use of thorium (Th), a mixed valence element, as a dopant in PbTe (Heremans et al. 2008) where the increase in thermoelectric power can be due to the charge Kondo effect, an interesting strong correlation effect. Many industries are currently interested in the use of thermoelectrics to produce electricity from the heat that is being currently dissipated.

Maintaining leadership in the area of new materials for information processing and energy storage is essential to retain the economic competitiveness of the U.S. computational exploration of multidimensional material landscapes that could result in a huge economic advantage and catalyze a revolution in materials research. It is essential for DOE to support this area of research given the critical role it could play in achieving energy independence. Progress on modeling correlated and time-dependent systems, coupled with advances in extreme-scale computing, could result in the following: 1) *computer-aided design of realistic devices from first-principle material simulations*, including their driving forces and dissipative effects; and 2) *systematic exploration of the composition and performance of complex materials* under the conditions in which they operate. This will accelerate the production of novel materials and devices.

These points can be extended to other areas important to the development of information devices and devices for the energy industry. These main points are very general:

1. All devices operate out of equilibrium.
2. Strong correlation leads to properties that need to be well understood for optimization.
3. Nanodevices are being considered for the above applications and the smaller dimensions of these devices increases the role of correlation.

Even weakly correlated materials can become strongly correlated on the nanoscale. The methodologies to be developed are general and can be applied to all of the challenges described in previous DOE energy challenges reports.[1] Investments in this area have a potentially huge payoff because it can completely alter the methodology used in the design of materials and devices.

Developing Theoretical Spectroscopy for Direct Computation of Experimental Observables

DOE BES operates nine synchrotron radiation and high-flux neutron sources. In addition, BES supports five nanoscale science research centers and another three electron beam centers. In 2008, these user facilities enabled over 10,000 researchers to perform experiments, which in turn, engaged thousands of collaborators in the analysis of the data from the experiments. Common to these facilities is the

---

[1] See http://www.er.doe.gov/bes/reports/abstracts.html.

production of experiment data, and the need for users to access, process, analyze these data, and interpret the results to extract the relevant insights and information.

This need becomes more pressing as experimental methods become able to control the statics and dynamics of complex correlated electronic systems probed in and out of equilibrium. Here, the conceptual framework and the computational tools to interpret the results of the experiments are still being developed. Compelling evidence of the need for theory associated with fourth-generation light sources and the advanced neutron facilities supported by DOE has been carefully documented in previous BES reports. Theory and computation play an important role in driving and interpreting experimental results. In addition, theoretical studies can help optimize the designs and specifications of the experiments themselves, particularly in identifying and proposing new physical processes that will become accessible using ultrafast and ultra-intense light sources.

The scope of this report did not include providing recommendations to achieve these goals, which could include increasing university-national facilities interactions, development of a U.S. theoretical spectroscopy facility similar to the European spectroscopy facility, or increasing the size of the theory groups in the national laboratories. Instead, from a broad perspective, scientists stress the importance of developing “theoretical spectroscopies” that will enable *in silico* “experiments” similar to those conducted in the laboratory.

First, theoretical spectroscopy will provide the context and the means for understanding the spectroscopy of strongly correlated materials. A profound fact about correlated electron materials is that—under many circumstances—they are not described by Fermi liquid theory and new paradigms must be sought to replace this important model from twentieth-century physics. In this case, it is not possible to think in terms of poles of the Green function and instead requires the use of spectral functions. Different spectroscopies weigh this crucial information with different matrix elements, and probe different regions of the sample (surface versus bulk) with different weights. Detailed modeling of the various spectroscopies is the vital link to theoretical frameworks. Naïve interpretations of the experiments in terms of models based on a one-particle picture can be very misleading.

Second, theory and computation will also provide the context for understanding spectroscopy in the time-domain. This requires significant extensions of all of the electronic structure codes to treat systems far from equilibrium. It will require modeling transients and steady states rather than stationary states. This is described in the previous research direction, “Advancing Theory and Models of Driven and Open Systems for the Control of Matter on Very Short Time Scales.”

Third, instrumental advances are resulting in increased spatial and temporal resolution, and of the variables that the experiment can control. For example, out of equilibrium angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscope (STM) can now probe, via suitable matrix elements, selected aspects of the spectral function of the electron as a function of two- or three-dimensional spatial variables and two-time variables. Introducing nonequilibrium effects (i.e., additional temporal variables) and strong correlation effects (making the frequency and the wave vector independent variables as a result of the breakdown of the quasi-particle model that relates these quantities in weakly correlated materials) greatly increases the amount of information that needs to be processed computationally. This is not just a quantitative problem—it is also a qualitative problem. Without a theoretical framework to replace the quasiparticle model, it is not possible to extract meaningful information from the experimental spectroscopic results.

This poses a dual problem. First, there is the problem of managing and analyzing large data sets, followed by organization and visualization of this knowledge. These data challenges require interdisciplinary developments to design new algorithms, optimization techniques, advanced statistical analysis methods, methods of automated data mining, multidimensional histogramming techniques, data inversion, and image reconstruction. This interaction can lead to the introduction of advanced visualization techniques to facilitate real-time analysis of experimental data. This interaction can also lead to development of novel methods; for example, identifying significant scattering events in sparse data to highlight dispersion surfaces and Brillouin zone boundaries embedded within multidimensional data volumes.

The second problem is the need for development of new theoretical paradigms for extracting meaningful simplified models to systematize the data that are being acquired. These ideas have to be implemented in algorithms and codes. Ideally, the codes would be open source and support a vibrant interaction between theoretical and experimental spectroscopies.

Developing Accurate Methods for Calculating Electronic Excitations, Surface Crossings and Nonradiative Couplings for Large Molecules and Materials

Harnessing light energy for solar energy production is central to addressing the nation’s future energy needs, as discussed in the panel report titled “Photovoltaic Fundamentals.” In addition to solar cell research where the goal is conversion of photons to electrons, another issue to address is the central role of excitations in the direct conversion of photons to fuels. Modeling solar energy conversion involves describing the creation, evolution, and destruction of excitations. Competing processes must also be considered, including photodissociation, photoionization, and internal conversion. Models of molecules in strong fields may also be required. For a comprehensive understanding of these processes, methods must be developed to describe excited states and the associated interstate interactions. All of these processes involve treatment of strong electron correlation. As an example, carotenoids in natural light-harvesting are deactivated by a state in which two electrons are excited (Polivka and Sundström 2004).

Advances in theory and leveraging developments in computational capabilities can lead to breakthroughs in modeling the creation, evolution, and destruction of excitations, all of which are often associated with strong electron correlations. While strong correlations are the undercurrent of this entire panel report, it is important to distinguish the treatment of excited states, which correspond to higher eigenstates of the Schrödinger equation, from the description of the ground state. Substantially different theoretical methods are generally required for the treatment of excited states. Methods that can generate accurate multichannel coupled potential energy surfaces will be required, as the fate of excited states usually involves a number of different channels, from electron-hole recombination to the ground state to photodamage such as bond-dissociation, charge-transfer, or spin-crossing to a long-lived intermediate excited state. Simulations should be capable of predicting the branching ratios amongst these diverse paths to enable simulation-based chemical modification to enhance the desired outcome of the initial excitation and reduce undesirable outcomes such as energy loss and damage.

At present, accurate methods exist only for the smallest molecules. For example, excited state versions of the CAS procedures already exist and have been used successfully for applications to excited states, conical intersections of potential energy surfaces, and radiationless couplings of small molecules. They have the same exponential increase of cost with molecule-size discussed for CAS methods previously, with the additional challenge of obtaining a consistent set of orbitals for all states considered. The latter is achieved—somewhat unsatisfactorily—by optimizing the orbitals to minimize an energy that is the average over a chosen number of states. The CAS methods can be combined with trajectory-based methods that propagate the time-dependent Schrödinger equation for the multichannel problem, such as surface-hopping or wave-packet based approaches. In isolated molecules, this approach can lead to predictions of product ratios resulting from light absorption. In materials, further consideration must be given to transport, as discussed in the panel report, "Photovoltaic Fundamentals."

Methods for simulating these processes in large molecules and extended systems are currently much more approximate. Applicable techniques include time-dependent density functional theory (TDDFT) and simplified configuration interaction methods. These methods are often reasonable for excited states that involve promotions of a single electron from a ground state that is not strongly correlated, but are deficient for several problems of critical importance. For instance, these methods cannot correctly describe the conical intersections of an excited state with the ground state, and they cannot correctly describe excited states that have significant contributions from the promotion of two or more electrons. These deficiencies prevent TDDFT from being an appropriate method for studying the dynamics of light harvesting, although it is a useful tool for understanding the initial states that are accessed as a result of photon absorption.

Extreme-scale computing will enable the use of more accurate methods on moderate size systems. It would enable the scale-up of existing CAS-type methods that obtain "the right answer for the right reason" to model the dynamical processes necessary to understand the fate of electronic excitations. This type of work is important because it will provide insights on model systems, even if the molecules are much smaller than those used in organic photovoltaics. Furthermore, the results of these calculations will provide benchmarks against which new and necessarily more approximate methodologies can be assessed.

There is no doubt improved excited state methods that scale better with system size and allow the treatment of challenging problems where multiexcitonic effects are involved must be developed. In the molecular context, scientists can begin to see the first emergence of methods that at least accomplish this goal for bi-excitonic states, such as double spin-flip approaches that can potentially describe singlet fission or triplet-triplet fusion. While the outlook is promising, it must be emphasized that because the treatment of systems with strongly correlated ground states is still challenging and a priority research direction in itself, it follows that the development of methods for describing excited states that are strongly correlated are at an earlier stage of development. Thus, application of existing methods to energy-related problems—despite their known deficiencies—must proceed in sync with the search for new excited-state simulation methods that lift those limitations.

Developing New Multiscale and Multiphysics Capabilities to Treat Physical and Chemical Phenomena that Requires Modeling over Multiple Length and Time Scales

Examples of multiscale, multiphysics/chemistry problems connected to DOE challenges abound in chemically inhomogeneous systems such as reactor materials, or materials subject to damage, or correlated materials such as modern battery materials. Advances in computational methods to treat these problems, as well as their implementation on state-of-the-art computers, are needed to contribute to the solution of these challenges.

Multiscale modeling is an important research area in materials science, physics and chemistry. A well known example in materials science is modeling of material strength and fracture. This problem requires the modeling of bonds and cohesion on an atomic scale, dislocations and grain boundaries on a mesoscopic microstructural scale, and distribution of dislocations at a macroscopic length scale. First-principles modeling of materials require the simultaneous modeling of various scales with various techniques; for example, the core of a dislocation is defined on a microscopic scale, while the long-range strain field it generates far away from the core can be described by elasticity theory and phase field models. Parallel problems arise in chemistry where hybrid quantum mechanics/molecular mechanics techniques have been—and continue to be—developed and implemented in community codes such as Code Amber[1], the CHARMM Code[2], and commercial products such as Gaussian to treat large molecular assemblies and their chemical reactions in solvents.

The importance and challenge of modeling materials and phenomena at different length and time scales has been recognized in several BES workshops and reports (*Final Report Second DOE Workshop on Multiscale Problems* [DOE 2004a]). Here, scientists highlight several reasons why strong correlations are very important for multiscale modeling and—in turn—why multiscale modeling is crucial for understanding many aspects of correlated electron materials. This is a largely unexplored area of research where much work is required before actual devices can be built from strongly correlated electron materials.

1. Most of the multiscale methods bridge between implementations of DFT to model quantum mechanical short distance, short time behavior, and molecular dynamics to model the longer time, longer scale behavior. More accurate treatment of strong correlations will result in more accurate forces, whose accuracy limits the accuracy of multiscale modeling of complex molecules and materials.
2. Defects and impurities have served as important probes of the physics of strongly correlated materials. Adding a nonmagnetic atom (such as zinc) to a nonmagnetic copper-oxide layer nucleates spins in the vicinity of the impurity. Multiscale modeling is essential to tackle these problems.
3. Many strongly correlated electron materials develop inhomogeneities at different length scales. This is the result of competing ground states, which gives rise to a complex phase diagram and unusual sensitivity to external perturbations. A prime example of this behavior is the colossal magnetoresistance materials.
4. Strong correlations can emerge near defects in otherwise weakly correlated systems. A time-honored example is dilute-doped semiconductors, such as phosphorus-doped silicon, that displays a metal insulator transition at low temperature that is not well understood by scientists.
5. Multiscale many-body techniques are being rapidly developed to treat, with different accuracy, different many body effects on different lengths scales. Examples include the following:
    a. Combination of GW approximation (to treat long wavelength Plasmon modes) and DMFT (to treat local Hubbard correlations) in an *ab initio* treatment of solids

---

[1] Code Amber alerts computer users nationwide when an Amber Alert is issued. An Amber Alert is issued when a child is reported missing to law officials.

[2] CHARMM (Chemistry at Harvard Macromolecular Mechanics) is the name of a widely used set of force fields for molecular dynamics.

6. Combination of the dynamical cluster approximation and other cluster DMFT methods to treat short-range correlations and Flex to treat spin and charge collective modes in Hubbard-like models (Maier et al. 2005).

Describing each of these extremes, and more importantly, bridging the disparate length and time scales associated with them (multiscale modeling) poses a grand challenge in computational chemistry, physics and materials science. Multiscale modeling issues emerge in many other areas of chemistry, physics and material science, including the modeling of chemical reactions, combustion, and nuclear reactor design.

CONCLUSIONS

To fulfill the promise of solving energy-related problems by accurate predictive methods in cases where electronic structure methods (primarily DFT) currently fail, three steps are required. The first step is robust support for the development of new methodologies. As stated throughout this panel report, much groundwork has been completed, but promising methods such as DMFT and coupled-cluster theory for strongly correlated problems are not yet fully mature. Furthermore, this is the source of new game-changing innovations for the future, without which the following two steps will not succeed.

The second step is the incorporation of new methodological advances into software packages (accessible to both experts and nonexperts) so that the strengths and weaknesses of these methods can be understood in detail through application to a greater range of problems than their developers alone can accomplish. This mechanism was used to clarify both the virtues and deficiencies of DFT. At least as important at this stage, new energy-related science can also begin to be accomplished using the new methods.

The third step is the extension of software from conventional computers towards extreme-scale computers. This may require entirely new algorithms, and the experts in this area are often not the same as the experts in methodology development. Therefore, building teams that have the appropriate expertise is important to enable state-of-the-art methodology on state-of-the-art computers.

In this panel report, the focus has primarily been on the first of the three issues discussed above, although the other two areas cannot be ignored if the long-term goal of enabling a new generation of scientific advances in energy-related science through simulation is to be realized. Despite the innumerable existing successes of DFT-based simulations, these techniques fail in systems where electron correlations are strong. This applies to many molecular catalysts, metal oxide and heavy element solids, as well as to the excited states that are involved in light-harvesting and energy conversion. This also applies to nonstationary states that are involved in energy transfer, and the interaction of molecules and materials with strong and ultrafast electromagnetic fields, as are being probed in next generation light sources. It is these considerations that are encapsulated in the five priority research directions presented in this panel report.

The following are some recommendations on how to achieve the goals in the priority research directions. Three general principles should be incorporated into the development plans:

1. Any new research initiatives should support small-scale, medium-scale, and large-scale research efforts. A focus on only large-scale efforts would be a mistake, as scientists anticipate a continuation of the historical pattern of many of the most innovative new ideas emerging from single investigator initiatives. In the field of strong correlations, scientists have learned to expect the unexpected.

2. Sustained funding is required for successful software development and maintenance. It is essential to recognize and prepare for the long life cycle of any large-scale scientific software. The life cycle of scientific software far exceeds the life span of any particular generation of computer hardware.
3. Balance extreme-scale computing with synergistic improvements at the medium-scale. Most scientific computing is performed at the midscale, and it is important to leverage advances at the leading edge of extreme-scale computing to benefit the larger trailing vortex.

Immediate investments in the field of computational materials science, chemistry, and physics are essential because the United States is rapidly losing, or may have already lost, its competitive edge in this area. For example, all of the large-scale electronic structure codes for solids in use today were developed in Europe, while the most exciting discoveries in the field of high-temperature superconductivity are now occurring in China and Japan. The relevance of the field of computational chemistry, physics, and materials science to modern society, as well as many of the other basic points in this panel report, have already been stated in previous BES reports, but are worth re-emphasizing.

PHOTOVOLTAIC FUNDAMENTALS

Co-Leads: Jeffrey Grossman, Massachusetts Institute of Technology
Kai-Ming Ho, Ames Laboratory and Iowa State University

Panel Members: Wanda Andreoni, CECAM/Centre Européen de Calcul Atomique et Moléculaire; Tunna Baruah, University of Texas at El Paso; James Chelikowsky, University of Texas; Hai-Ping Cheng, University of Florida, Quantum Theory Project; Lori Diachin, Lawrence Livermore National Laboratory; Xin-Gao Gong, Fudan University; So Hirata, University of Florida, Quantum Theory Project; Richard M. Martin, University of Illinois at Urbana Champaign; Glen Martyna, IBM Research; Gustavo Scuseria, Rice University; Annabella Selloni, Princeton University; Lin-Wang Wang, Lawrence Berkeley National Laboratory; John Wu, Lawrence Berkeley National Laboratory; Weitao Yang, Duke University; Shengbai Zhang, Rensselaer Polytechnic Institute; and Alex Zunger, National Renewable Energy Laboratory

CURRENT STATUS

For solar energy to become a truly viable alternative to carbon-based fuels for producing electricity, it must become cost competitive. Despite substantial advances in efficiency and cost over the past three decades, solar energy from existing photovoltaic cells is still considerably more expensive per kilowatt-hour than power from coal, gas, or oil (Wadia et al. 2009). Many of the properties related to the fundamental mechanisms in photovoltaic (Figure 13) are particularly challenging to characterize experimentally, which makes the ability to predict them computationally crucial. Calculations therefore have an opportunity to play a substantial role in this global-scale challenge, working together with experiment, to provide basic understanding while concomitantly allowing for greatly accelerated materials design and discovery.

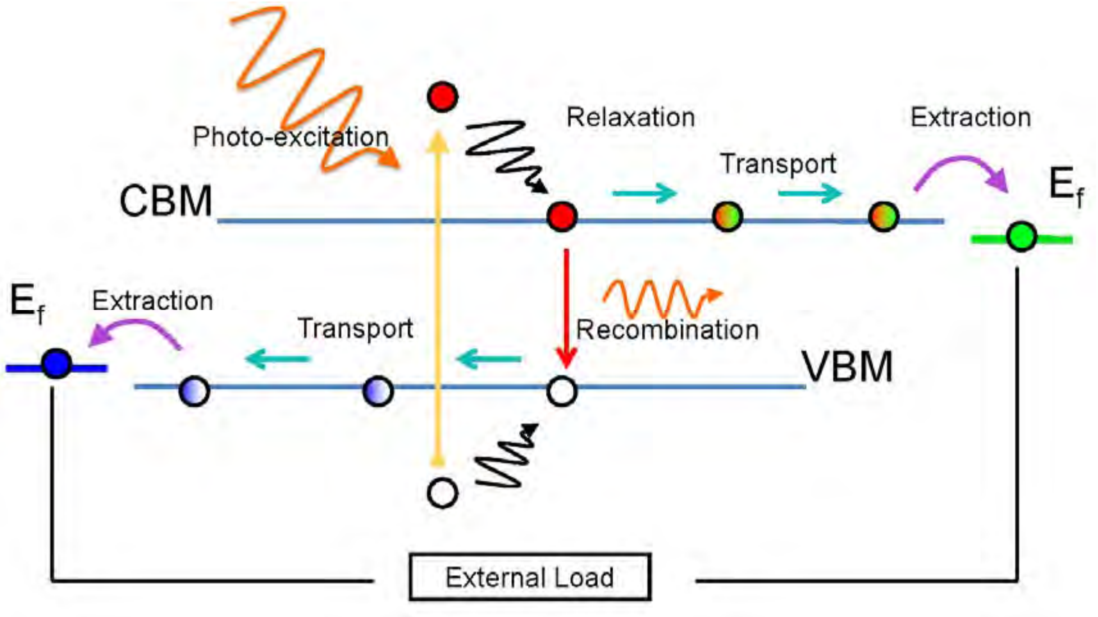


Figure 13. Schematics of physical processes involved in photovoltaics. Image courtesy of Jeffrey C. Grossman (Massachusetts Institute of Technology).

Despite the high degree of basic and applied research in this area, the power conversion efficiencies and costs of solar cell materials falls far short of what is required for large-scale applications and a significant impact on the global energy crisis. An important reason for this is that many of the fundamental mechanisms shown in Figure 13 are only partially understood; examples include the efficiency of interfacial charge separation, the impact of impurities on energy-level alignment and transport, optimal contact configuration, the effects of quantum confinement, and excitonic effects.

Because of the many significant advances in high-performance computing, as well as methodological improvements in a wide range of computational approaches over the past several decades, it is now possible to investigate materials properties derived from atomistic details, and, in some cases, to predict and design new materials with the desired properties. Atomistic and quantum calculations can therefore play a substantial role in accelerating advances in photovoltaic research by providing a much needed basic understanding of their key properties.

However, further development of general frameworks for predicting structural, electronic, and optical properties at the necessary levels of accuracy are greatly needed. For example, because electrons are quantum mechanical particles, scientists must calculate their properties by solving the multidimensional differential Schrödinger equation. However, few cases can be solved exactly, even with today’s supercomputers, and typically a number of theoretical and numerical approximations are used to obtain approximate solutions. Thus, the utility of computed materials properties depends on the accuracy of such calculations. Even though in recent decades, atomic-scale calculations have greatly expanded their role in advancing current understanding of materials, the “bottlenecks” challenging scientists today in photovoltaic research underline the importance of developing methods with greater accuracy, broader applicability, and new capabilities in computing. Combined with the potential for extreme-computing environments, these advances—the specific needs for which are discussed below—could lead to brand new progress in photovoltaic research.

BASIC SCIENCE CHALLENGES AND RESEARCH NEEDS

The Photovoltaic Fundamentals panel examined research opportunities for the use of extreme-scale computing to address issues at the frontier of photovoltaic science. The panel consisted of approximately 20 theoretical and computational scientists with expertise covering a broad background in the photovoltaic area. The following four priority research directions (PRDs) were identified.

Excited-State Phenomena. Every step in the conversion process of light to electrical energy involves excited states of the electrons in complex heterogeneous materials. Extreme-scale computation can create a breakthrough in accurately predicting the combined effects of multiple, interacting structures and their behavior upon electronic excitation and ultimate performance. Some specific challenges are to develop 1) scalable semiempirical methods and accurate first-principle methods for computing energies and forces in excited states, and 2) density functional theory (DFT) with efficient implementation for improved band gaps and level-alignment prediction.

Carrier Relaxation, Recombination, and Transport. For efficient photovoltaic materials, it is desirable to reduce the recombination of carriers and increase the probability of carrier transport and collection. Extreme-scale computing can contribute to the development of efficient computational quantum mechanical methods for studying carrier dynamics in time domain to address issues such as exciton lifetime and carrier transport in complex nanostructures and organic solar cells, as well as electron-phonon coupling and radiative and nonradiative recombination in inorganic solar cells.

Defects and Doping. Greater control of defects and doping is one of the most important challenges in photovoltaic materials research and for the photovoltaic industry because it could enable both lower cost design and higher efficiencies. Advances in photovoltaic research require an accurate description of point defects that couple strongly to the electronic and structural degrees of freedom, as well as extended defects at different length scales, which are present in realistic photovoltaic materials. Defect-defect interactions and mesoscopic scale migrations that combine the effects of different defects are challenges that cannot be addressed without extreme-scale computing. Extreme-scale computing will also allow rapid screening of many candidate structures of complex defects in systems with many degrees of freedom.

Interface Morphology and Dynamics of Formation and Growth. Cost-effective photovoltaic systems involve complex, multicomponent, heterogeneous, off-stoichiometric materials and phases; e.g., polycrystalline, amorphous, organic, and hybrids. The morphology in these systems often eludes experiment; their formation and evolution processes are not well understood. Extreme-scale computing can enable innovation in computational methodology and programming paradigms to evolve the large number of degrees of freedom for long time scales to achieve efficient sampling of configurational space. By employing accurate multiscale methods, scientists will be able to generate tools necessary to optimize growth conditions to control uniformity, design percolation networks and multijunction cells, induce fluctuations in stoichiometry, and control doping and grain-boundary/sizes for limiting electron-hole recombination.

Excited-State Phenomena

The underlying scientific challenge in photovoltaic research is to predict the properties of realistic materials and heterosystems that are essential for efficient conversion of light to electrical energy. As previously discussed, several key steps in the energy conversion process involve excited states of electrons and holes in complex heterogeneous materials with defects that can play important roles. Thus, critical needs for predictive capabilities include the following:

1. Band gaps and spectrum of electronic excitations of the component materials that determine the absorption of light
2. Atomic-scale structures of interfaces, grain boundaries, and extended defect complexes
3. Alignment of the bands of different components that are essential for separating positive and negative carriers
4. Essential modes of transport of the neutral excitations created by the light and the charge carriers to the electrodes
5. Creation of multiple excitations that can be beneficial by multiplying the production of carriers or detrimental when the electronic excitations decay releasing energy into heat
6. Understanding and reducing the effects of degradation due to ultraviolet (UV) excitation in organic photovoltaics.

The computational challenge in this area is to make accurate predictions for electronic states of large-scale, heterogeneous systems. This includes the extension of existing first-principle methods to vastly larger systems, which will require a combination of new algorithms and exascale computing. Such advances are also needed to transfer information from simpler systems to treat the multiple time and length scales of the dynamics of defects and transport in complex systems. A true breakthrough that could be accomplished by computation at the exascale is to predict the combined effects of multiple, interacting structures upon electronic excitation and ultimately, upon photovoltaic performance.

To address the simulation challenges for exploring exited-state phenomena in realistic photovoltaic materials, it will be necessary to develop theory and computational methodology in the following areas:

- **Improved Functionals in DFT**. DFT, currently the main tool in realistic simulations of materials, has had great success in wide-range applications; recently, much progress has been made in predicting band gaps and optical absorption with hybrid and screened hybrid functionals. DFT still suffers from critical failures in many issues related to photovoltaic—for example, it significantly underestimates charge transfer excitation energies, and gives unreliable band alignment and defect predictions. These failures originate from deficiencies of currently used exchange-correlation functionals. Recently, a clear understanding of these errors from the most basic principles has been developed for simple systems (Cohen et al. 2008), and the investigations of sources of errors for various classes of systems is an active field of research. Theoretical research in correcting DFT errors and therefore improving the functional approximations will be most significant, with broad applicability in material simulations, including excited-state phenomena.
- **Predictive Electronic Structure Methods and "Beyond DFT**.**"** New theories and algorithms are required for predictive theoretical methods executable on next-generation, peta, and exascale supercomputers. The desired characteristics of these methods include unprecedented accuracy based on rigorous many-body methods, as well as novel density functionals mentioned above. The many-body methods include the coupled-cluster, Green's function (including many-body perturbation theory at the GW approximation level), density matrix renormalization group (DMRG), and quantum Monte Carlo (QMC) methods. Novel density functionals must address the well-known weakness of existing functionals in quantitatively computing energy bands, charge transport, and optical properties without impairing their strengths. These properties include functions such as inherent computational efficiency and transparent physical pictures. These methods must be capable of computing with predictive accuracy energy bands, structures, and optical and transport properties of general organic and inorganic solids that are currently in use as photovoltaic-based materials and other candidate materials.
- **Predictive Dynamics Simulations**. A general, multiscale dynamic theory and corresponding algorithms with which to computationally elucidate the time-resolved, electronic mechanisms of photovoltaic processes (such as exciton dynamics and charge transport) are needed. These properties should be addressed through accurate, predictive electronic structure methods for reactive electrons in all involved electronic states while using appropriate quantitative methods to account for environmental effects originating from 10,000 or more atoms. Dynamics must be conducted over a sufficiently long period to address coupled electronic and nuclear motion, as well as multiple electronic states. Nonadiabatic couplings between these states, especially those involving conical intersections, must be included. The simulations also need to be repeated a number of times to verify adequate statistical sampling.

- **Algorithmic Breakthroughs**. The desired methods discussed above are currently not applicable or even in existence for realistic simulations of photovoltaic materials, but could be devised and made applicable by algorithmic breakthroughs and massive parallel implementations on next-generation supercomputers. Scientists anticipate the improved algorithms may take advantage of the distance-based decay of chemical interactions of different types of bonding environments (covalent, metallic, ionic, van der Waals, etc.). The algorithms will break down computational tasks through molecular fragmentations and thereby attempt to drastically reduce the scaling (size dependence of computational cost). Such algorithms must be applicable to periodic solids that are either insulating or metallic as well as to nonperiodic (nano)-structured materials.
- **New Paradigms for Program Implementation and Execution**. Computational algorithms for extreme-scale hardware with millions of cores and complex, hierarchical device architectures require novel strategies for their implementation, execution, and validation. Conventional development of massively parallel electronic structure methods is extremely challenging even on existing terascale and petascale architectures. To have scalable codes on petascale or exascale hardware, scientists need to take full advantage of the hierarchical structures in interprocessor communication network, cache, and memories. This necessitates versatile middleware to be developed that analyzes the patterns of computations, data access, and interprocessor communication so as to facilitate the optimal use of hardware and minimize human intervention. With millions of processors, codes must also have measures against inevitable hardware and operating software failures. This may be achieved partly by middleware that implements general fault-tolerant measures and possibly by automated code synthesis that recognizes relatively independent, compartmentalized (and thus non-fault-propagating) compute tasks (e.g., in local-basis, linear-scaling algorithms) and distributes them to processor groups.

The potential impact of the above advancements will affect the design of new photovoltaic materials with high efficiency. The optimized materials will possess large cross sections for photo-absorption with solar flux and significantly improved carrier generation. At the same time, the capabilities for simulating the excited-state phenomena will help in reducing photo-induced structural degradation.

Carrier Relaxation, Recombination, and Transport

The focus here is on carrier dynamics, including relaxation (after the initial photon absorption), recombination, and transport/collection. In solar cells, the efficiency is often controlled by quantum yield (how many electron hole pairs can be collected for each phonon absorbed?), and by how fast the voltage drops from the open circuit voltage when the current increases. Both are related to carrier dynamics. For efficient photovoltaics, it is essential to reduce the recombination of carriers and increase the carrier transport and collection. It might also be desirable to generate multiple excitons from high-energy photon absorption to exceed the Shockley-Queisser limit. For nanostructure-based solar cells, it could be useful if no bound excitons are formed after the initial carrier relaxation and thermal cooling process, and the free carriers can be collected directly by the electrodes. The carrier dynamics discussed in this section are directly related to the quantum efficiency in a solar cell.

While scientists are now able to calculate the electronic structures and optical absorption spectra for many systems, little is known about carrier dynamics, especially in complex systems such as nanostructures, highly defected systems, and organic/inorganic mixed structures. Carrier dynamics involve many-body problems with strong electron-hole interactions and electron-phonon couplings, often with multiple phonons. For bulk-like systems with itinerant carriers, the Boltzmann equation can be used to describe the coherent carrier transport. Alternatively, for a highly disordered system where the carrier wave functions are localized, the hopping transport picture—or Marcus theory—can be used to describe the incoherent electron movement. However, in organic systems, recent evidence indicates there might be cases where the carrier transport does not fall into either of these two simple cases. Thus, direct simulations might be crucial to understand the correct dynamics. The availability of extreme computing capability will change the way scientists simulate carrier dynamics. Rather than relying on simple models and analytical approximations, direct simulations—including all the phonon modes and electron-phonon couplings—might become the norm. Time-domain simulations with electrons following the time-dependent Schrödinger equation while nuclei following molecular dynamics might also become feasible. Such simulations can incorporate both coherent and incoherent transport within the same framework.

Understanding Carrier Relaxation from the Initial Instant of Photon Absorption

To date, theoretical descriptions of carrier relaxation remain phenomenological with many unknown parameters. The priority in this area is to change phenomenological approaches into *ab initio*-based realistic simulations where many-body Coulomb effects and electron-phonon coupling are fully incorporated. In addition, to study multiexciton generation (MEG) processes, scientists need to go beyond single exciton calculations and incorporate many-body wave functions with multiple electrons and holes. The relaxation process is basically a phonon emission process. Thus, the calculation of electron-phonon coupling is essential. The challenge is to combine many-body effects with electron-phonon coupling effects to study the behavior of exciton or multiexciton systems. Theoretical frameworks need to be developed first before large-scale computation can be deployed. Then, given that the number of degrees of freedom in the related calculations will be enormous, extreme-scale computation will become essential.

Carrier Recombination from the Exciton Wave Function and its Radiative and Nonradiative Decay

Nonradiative decay is one of the main sources for carrier loss. Understanding this process is extremely important for accurately predicting photovoltaic efficiency. While it is straightforward to model radiative decay, describing multiphonon nonradiative decays is much more challenging. There are analytical formulas for multiple phonon processes for one given phonon mode, but if many phonon modes are involved, direct numerical simulations are necessary. So far, there are not many such direct simulations in the literature. It might be necessary to reformulate the problem to make direct numerical calculations more tractable. In addition, calculations are complicated by the need to predict defect atomic structures or surface atomic structures where the carrier-wave function is localized, and the nonradiative decay occurs.

Carrier Transport, Including Free-Carrier Transport in General and Exciton Transport in Organic Systems or Nanostructures

In both inorganic (nano)-systems and organic systems, a critical exciton dissociation process is involved where the exciton is separated into free electron and hole carriers. The exciton binding energy can be extremely large—several tenths of electron volts (eV)—in organic systems and inorganic nanostructures. Such exciton binding energy is much larger than room temperature, and a gentle electric field as in a bulk p-n junction is not enough to dissociate the exciton. As a result, the exciton dissociation often happens at a type-II interface with donors on one side and acceptors on the other side. However, the real process might be more complicated because the electric field might also be involved at the interface. Thus, the simulation of excitons' dissociation at finite temperature can be a computational challenge because it involves thermo activation processes, tunneling, and electron-hole Coulomb interaction effects. Another complication for all carrier transport is the so-called polaron effect. This might affect both exciton and free-carrier transport. While in simple cases, the polaron transport can be described by the Marcus theory, it is not clear how to describe it in a realistic case where many degrees of freedom might be involved. For weak electron-phonon coupling, free-carrier transport can be described by either the Boltzmann equation or localized state hopping, but there are cases in organic systems where neither picture appropriately describes the system. An additional problem is how to incorporate electron-phonon coupling in the exciton dynamics (besides the Förster resonance energy transfer [FRET] process). Finally, the carrier collection by the electrode is the most important part in solar cell design, encompassing several issues: static electronic structure problems like band alignment, identification of interfacial states, Fermi-level pinning and Schottky barriers, and dynamic problems of charge transfer crossing the semiconductor/metal interface. It might also be possible that the exciton itself—not just a free carrier—is present at the electrode contact interface where it may lose one carrier, and therefore, the exciton dissociation and charge collection process may be simultaneous. The description of the charge-transfer process crossing the contact interface is a very active field of research. To study the exciton dynamics at organic bilayer heterojunctions, approximate dynamics can be implemented within mean-field (Ehrenfest) or surface-hopping methods. The Ehrenfest method is accurate for very short time scales, and it has been used to describe polaron and soliton dynamics in conjugated polymers. Surface-hopping methods were developed to study nonadiabatic chemical processes, and they have been applied to the study of electron dynamics in polymer-C60 composites. Implementing the Ehrenfest method by directly propagating the density matrix, combined with the time-dependent density functional theory (TDDFT) approach, may be an efficient way to address interfacial electron-hole separation processes. The evolution process can be studied by following the polarization cloud of the exciton in real-time and computing the density currents via the variation in time of the molecular wave function. This will enable the study of charge transfer, as well as exciton and electron-hole delocalization and transport processes at organic interfaces.

In all calculations appearing to date, models and approximated methods have been used to calculate each of the processes described above. However, such simulations are usually fragmented and narrow in scope. One possible general approach to overcome these drawbacks is to use time-domain simulations. In this method, the electron will be propagated following the time-dependent Schrödinger's equation while the nuclei will follow *ab initio* molecular dynamics (MD). The state collapse from nonadiabatic states to the adiabatic state will incorporate the incoherent (hopping) process, while the coherent process is represented by the time-dependent carrier wave function evolution following Schrödinger's equation. Such an approach is similar to the real-time implementation of TDDFT simulations, except that in addition to describing the evolution of wave functions, state collapsing is also included within stochastic processes.

TDDFT is generally considered less accurate—but more computationally affordable—to describe excited states, compared to other first-principle methods, such as the many-body perturbation theory at the GW level or the Bethe Salpeter equation (BSE). Advances in functionals to be used at the TDDFT level, which are targeted at organic and inorganic nanosystems, will be required as well as expanding codes to photovoltaic systems that can accommodate heterogeneity. Formulations of many-body perturbation theory (MBPT) are also needed to accurately describe spatial and energetic properties of excitons as well as of charge-transfer excitations. These may be obtained by solving the BSE. A first goal will be to accurately predict the light absorption of organic semiconducting polymers and the excitations supported by heterojunctions with TDDFT, possibly by adopting hybrid-like functionals. Several research groups have successfully implemented TDDFT and have applied it to a wide variety of systems—from molecules to clusters to quantum dots. However, TDDFT remains a computationally intensive technique that often scales poorly and cannot describe properly; for example, excitons in solids and charge-transfer excitations. Currently, the application of TDDFT is limited to roughly several hundred atoms when using techniques based on density functional perturbation theory. A smaller number of atoms can usually be processed when using other direct implementations. Thus, extending TDDFT to systems with thousands of electrons requires both algorithm developments and increases in computer power. The realization of exascale computing is essential in this pursuit. Currently, real-time TDDFT calculations may be run for only a few femtoseconds. To extend this to the picoseconds or nanoseconds regime is another challenge that requires the deployment of exascale computation.

Besides requiring large computational effort, additional challenges exist in how to implement the collapse of the nonadiabatic state (hopping), especially when an approximate nonlinear Schrödinger's equation like the DFT Kohn-Sham equation is used (instead of the original many-body wave functions in the linear Schrödinger's equation). In terms of computation, approximations might become necessary given the large computational cost and the large system size needed. In addition to increasing the size of the system, the simulation time needs to be speeded up. New algorithms are needed for this temporal speed-up using massively parallel computations. Finally, a multiscale approach might be necessary to describe the carrier dynamics in a realistic system with more than a few thousand atoms. To develop such a multiscale approach, besides the direct time-domain simulation, it might be possible to integrate the piece-meal simulations for different processes. For example, by calculating many electron states, one can study Coulomb interaction many-body effects, including the inverse Auger multiexciton generation. By calculating electron-phonon couplings, scientists can simulate the initial thermal cooling in carrier relaxation, and can describe the carrier hopping transport and the nonradiative decay through multiple phonon processes. By calculating the exciton wave functions and their binding energies, scientists can estimate its dissociation energy related to charge separation. By calculating the polaron energy and wave function, scientists can study its transport. All these simulation steps could be incorporated into a multiscale integrated system to therefore simulate the device-level carrier flow of a solar cell, thus obtaining a comprehensive picture of how the solar cell works, based completely on parameter-free *ab initio* methods.

Defects and Doping

Understanding and controlling the fundamental photovoltaic mechanisms call for an accurate description of point defects that couple strongly to the electronic and structural degrees of freedom of the system. For example, we must be able to describe accurately the shallow-to-deep transition (involving polaron formation [Du and Zhang 2009 and references therein]) of a dopant that hinders the capability to dope a promising photovoltaic material. It is also critical to obtain an accurate description of extended defects that couple the physics at different length scales. Defect-defect interactions and mesoscopic scale migrations that combine the effects of different defects are additional challenges. Without exascale computing, scientists cannot even imagine first-principle simulations and the modeling of such phenomena. Exascale computing also enables *ab initio* MD for large systems relevant to realistic photovoltaic materials and the application of beyond the local density approximation (LDA) and generalized gradient approximation (GGA) approaches for large systems. The computational challenge is to port the current algorithms and codes (which have not yet been designed for petascale computing) to the exascale platform and develop new algorithms. Another difficult task with the complexity of defect and doping studies is the need for rapid screening of many candidate structures that is intrinsic to systems with large degrees of freedom.

One research direction is to develop reliable electronic structure methods for defects. It could be an integration of the currently available methods such as LDA/GGA, GW quasiparticle, and QMC methods. It could also be a completely new method particularly designed for defects and doping with the exascale perspective built in its construction. Another direction is continuing to develop new approaches for multiscale simulations of very large systems. This would allow, for example, for treating dislocation core quantum mechanically, with the surrounding environment treated either atomistically or as continuum media, and for defect dynamics over many orders of time scale.

The development of new methodology for localized states in complex materials is far beyond just the present problem of defects in photovoltaic materials. This methodology can be applied to other mathematical and computational problems where inhomogeneity is a critical issue. Even within the photovoltaic community, by revealing the underlying physics and chemistry of defects and doping as well as their spatial and time correlation, new designs and functionalities can result. The rendering of defect theory beyond LDA and GGA can lead to routine computer screening of defects and impurities in photovoltaic materials with desired accuracy, and lend their abilities to other areas of defect researches such as electronics, optoelectronics, and spintronics.

Controlling defects and doping is a crucial challenge for photovoltaic materials research and for the photovoltaic industry as it develops a lower-cost design more efficient than current photovoltaic materials. The reason the two seemingly contradicting factors (i.e., low cost and high efficiency) can work together is that defects can be both bad (e.g., being recombination centers [Fischer and Pschunder 1973, p. 405] and causing lower optical absorption) and good (e.g., assisting or enabling charge separation and removing gap states [Zhang et al. 1997]). Controlling defects may also enhance the dopability of the material (e.g., reducing the spontaneous formation of charge-compensating defects) (Zhang 2002). Doping is necessary for p-n junction formation for the transparent conduction oxides. An intentionally introduced intermediate (defect) band inside photovoltaic material can also increase photocarrier generation, thus significantly increasing solar cell efficiency.

Interface Morphology and Dynamics of Formation and Growth

Currently, an extraordinary amount of time and resources is spent connecting the desired photovoltaic device properties to the manufacturing process—almost exclusively through experimental trial and error. Numerical simulation can significantly reduce the time to design and engineer the production processes as well as to optimize the manufacturing procedures by predicting optimal design and control strategies. In addition, computer simulations can contribute to basic research by elucidating the fundamental relationships of these multiscale systems.

The grand challenge is to develop accurate, robust, and scalable computational tools to support the basic research, engineering, and manufacturing processes of photovoltaic materials. The simulation tools must link *manufacturing process variables* at the reactor scale to the *material properties* and *performance* described by electronic structure, microstructure nucleation, and evolution models at the mesoscales, nanoscales, and atomic scales. These are large-scale, computationally intensive simulations that can benefit from the availability of exascale computing.

Examples Related to Inorganic Photovoltaic

Multi-junction solar cells hold the record (>40%) for energy conversion efficiency (King et al. 2007; Geisz et al. 2008). However, there is room for improvement up to the theoretical thermodynamic efficiency of ~60%. Developing effective strategies that stabilize strained multi-junction structures against the formation and growth of dislocations is critical to the success of the inverted lattice-mismatched (iLMM) III-V multi-junction solar cell approach (King et al. 2007; Geisz et al. 2008). Particular areas that require fundamental understanding are 1) the structure, movement, and interaction of misfit dislocations at the interfaces between two lattice-mismatched layers; 2) the mobility and electronic properties of threading dislocations traveling through the 1-eV GaInAs absorber layer; and 3) kinetic pathways and barriers for the nucleation and growth of dislocation loops at heterojunction interfaces.

An alternative approach to lower the costs of photovoltaic systems is to grow polycrystalline thin films. However, the efficiency of thin-film solar cells is limited by defect-related detrimental processes, such as recombination at grain boundaries, low mobility, and materials degradation under illumination (Möller 1993). It is very clear that controlling thin-film structure is the key to low-cost manufacture of high-performance photovoltaic cells. Computational modeling and numerical simulations can significantly reduce the time to design and engineer the production processes. In recent research, semiconductor films are grown on inexpensive substrates such as alumina or glass with a buffer layer. Again, theoretical modeling of the evolution of the interface between the substrate or buffer layer with the growing semiconductor thin film will be of great assistance in developing cost-effective inorganic thin-film growth.

The development of film growth models that can incorporate effects at the atomic scale (such as energies and diffusion barriers of atomic steps) and kinks together with larger length-scale effects (such as elastic strain and grain boundaries) is needed to address this problem. Because of the multiple length and time scales present in the problem, this will be a challenging problem where exascale computing can make an impact.

Examples Related to Organic Photovoltaic

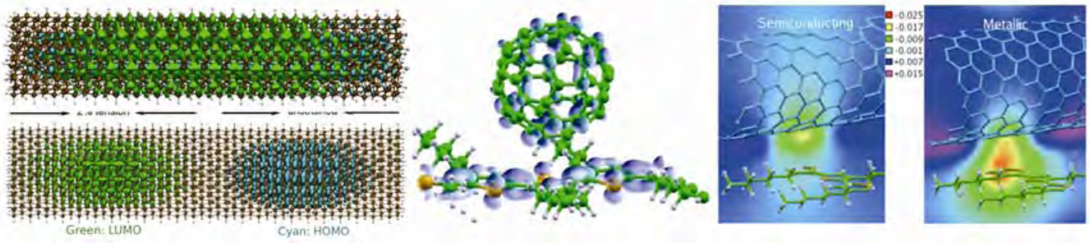
In organic photovoltaic, the difficulty resides precisely in the feature that makes these materials technologically interesting—the bonding between constituent organic molecules is very weak. The ultimate result of this property is that the processing of organic molecules into ordered materials does not require much energy and does not have to overcome any significant energy barriers. However, the formation of crystalline materials from these constituents requires long times, low temperatures, and high purity. Relaxing these conditions results in disorder and impurities. There is a competition between minimizing the cost and complexity of materials synthesis and forming sufficiently controlled and ordered materials that function efficiently as photovoltaic devices. Both theory and experiment are greatly challenged with the question of precisely how much and what order is necessary to explain and then improve the functionality of these materials, and what is superfluous.

These materials are not highly crystalline and are not in the limit of dilute defects in a well-defined lattice. They are also generally not in the opposite extreme of a random packing of randomly conformed molecules. The success of specific material combinations (such as regioregular poly(3–hexylthiophene)/ phenyl-C61-butyric acid methyl ester [P3HT/PCBM]) under specific synthesis conditions (such as post-synthesis thermal annealing) has led to the hypothesis that local order on the scale of nanometers may play an essential role in the physics of these devices and ultimately in their efficiency. The authors of this panel report believe that major advances in the molecular-level mechanistic understanding of interfacial processes in organic photovoltaics nanomaterials will not be possible without guidance and interpretation using theory and simulation. Applying computational approaches is generally a formidable task for complex materials, which may contain large numbers of atoms arranged on multiple length scales, but remarkable progress has been made by implementing novel algorithms designed for advanced computational platforms.

Separating the Charge in Solar Cells

When sunlight strikes a solar cell, the energy from the photon forces a negative charge (or electron) to become "excited" and leave behind a positive charge (hole). In bulk systems, such as silicon, the attraction between this electron and hole is small, and the charges become essentially "free" carriers very rapidly. However, in many nanomaterials and organic materials, the excited electron and hole are tightly bound, on the order of approximately 1 electron volt.

Quantum mechanical calculations help predict how the attraction between these positive and negative charges can be overcome such that they can be separated from one another and pulled out of the solar cell at the metal electrodes. New opportunities arise for efficient charge separation at the nanoscale that can lead to novel, efficient photovoltaic materials.



Understanding and controlling charge separation at the nanoscale. Examples shown from calculations: strain in a nanowire (left), type-II heterojunction between a polymer and a fullerene (middle), and the difference between semiconducting vs. metallic carbon nanotubes at a heterojunction (right). Image courtesy of Jeffrey C. Grossman (Massachusetts Institute of Technology).

CONCLUSIONS

The behavior of photovoltaic materials poses difficult challenges in the simulation and prediction of excited state phenomena, carrier relaxation, recombination and transport. The problems are exacerbated by the important role of defects and complex interface morphology that can be affected by the dynamics of formation and growth of the material. Significant progress in this area requires the availability of extreme-scale computing for the modeling of complex systems with many degrees of freedom, as well as development of new approaches for accurate prediction of excited state phenomena and quantum evolution in systems where strong electron-hole interactions and electron-phonon coupling play important roles in determining the dynamics of the system.

ENERGY STORAGE

Co-Leads: Mei-Yin Chou, Georgia Institute of Technology
Michel Dupuis, Pacific Northwest National Laboratory

Panel Members: Larry Curtiss, Argonne National Laboratory; Bert de Jong, Pacific Northwest National Laboratory; David Dixon, University of Alabama; Stefano Fabris, CNR DEMOCRITOS, SISSA; Maria Fernandez-Serra, SUNY Stony Brook; Stephen Garofalini, Rutgers University; Al Geist, Oak Ridge National Laboratory; Jeffrey Grossman, Massachusetts Institute of Technology; William Hager, University of Florida; Gus Hart, Brigham Young University; Maciej Haranczyk, Lawrence Berkeley National Laboratory; Yu Jiao, Oak Ridge National Laboratory; Kwiseon Kim, National Renewable Energy Laboratory; Jens Kortus, TU Bergakademie Freiberg; Paul Maupin, U.S. Department of Energy, Office of Science; Andrew McIlroy, Sandia National Laboratories; Jeffrey Nichols, Oak Ridge National Laboratory; Jim Roberto, Oak Ridge National Laboratory; David Sholl, Georgia Institute of Technology; John Wu, Lawrence Berkeley National Laboratory; and Zhenyu Zhang, Oak Ridge National Laboratory

CURRENT STATUS

Effective solutions to the world's overwhelming demand for sustainable energy will not be possible without the development of new energy storage cycles to connect intermittent or distributed energy input (e.g., solar, wind) with end-use applications (e.g., vehicular transportation). This is particularly important because energy resources such as solar, wind, and water are unevenly distributed around the country, typically incongruent with the geographic locations of high-energy demand. The potential societal impact of new energy storage cycles is almost impossible to overstate. Challenges facing the global society in terms of discovering and implementing energy supplies that are economically and ecologically sustainable are immense, and can only be met if the research community can bring its full, creative resources to emerge in this area. Computational efforts are essential and indispensable in this endeavor.

The research domains discussed by the Energy Storage panel members at the "Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale" workshop[1] include proton-exchange membrane fuel cell science, batteries and capacitors, energy storage in chemical bonds, and geological carbon dioxide (CO_2) sequestration. The topic of CO_2 sequestration was included in this panel due to the similar computational challenges involved.

---

[1] "Scientific Grand Challenges - Discovery in Basic Energy Sciences: The Role of Computing at the Extreme Scale," August 13-15, 2009, Washington, D.C.

BASIC SCIENCE CHALLENGES AND RESEARCH NEEDS

Research opportunities in the area of energy storage (with a focus on fuel cell science, batteries and capacitors, energy storage in chemical bonds, and geological CO_2 sequestration) encompass four underlying computational challenges that have great potential impact from extreme-scale computing. They are as follows:

- accurate and reliable theories at varied scales
- multiscale modeling (length and time)
- knowledge discovery (data analytics)
- scalable computing technologies.

Accurate and reliable theories are at the center of the computational characterization of the phenomena underlying all of these domains of energy storage technologies. Accuracy and reliability are essential for the predictive control of chemical interactions at the molecular level. Linking the models directly to experimental observables requires that models capture the essential features of the real systems, thus creating the need to design more complex and realistic systems on which to perform modeling. The ensuing efforts will require increased computer time, which would clearly benefit from extreme-scale computing.

To achieve understanding, predictions and control will require advances in methods to describe electronic structure, reactivity, and dynamics in complex molecular materials, and interfacial environments. The electronic structure cannot be limited to the ground state, but must also include electronic excitations, surface crossings, and nonradiative couplings to accurately describe the physics and chemistry that mediate these phenomena. Usually the systems are driven by external fields or are open, thus requiring new theories to account for the correct physics. Such advances usually bring more complex theories and computer codes that require increased computer power.

Multiscale modeling over length and times scales is present among the four domains of science. Limiting simulations to one spatial scale and/or over a short-time scale is often not enough to link the modeling findings directly to the experimental observation. The most accurate theories and methods lead to computational requirements that scale prohibitively with system size and are therefore not amenable to simulations on large systems in cases where the underlying interactions depend upon the quantum behavior. Further, this approach is not desirable in many situations and coarse-grain theories often prove more beneficial as they focus on more insightful parameters. The systematic development of multiscale and multiphysics capabilities that treat physical and chemical phenomena over multiple length and time scales is thus required. This is an essential ingredient needed to make the connection to experimental observables. The methods and approaches must be robust and capable of addressing integrated and complex materials.

Knowledge discovery encompasses techniques that rely on data analytics to connect materials properties with the details of materials structure (e.g., unit cells, grain boundaries, etc.) and composition. Data analytics focuses on inference, the process of drawing a conclusion based on knowledge obtained through computational investigations. The challenges are primarily in the high throughput requirement in establishing the database.

Scalable computing is critical to extracting the benefit of extreme-scale computing. Codes that compute the fundamental theories and methods—such as advanced electron-correlated methods and density functional theory—must be highly scalable. Extreme-scale computing will comprise hundreds of thousands of cores, the power of which will need to be harnessed through parallel constructs and parallel algorithm. Robustness, fault tolerance, and restart capabilities are integral requirements of the algorithms and their implementations. It is unlikely current computer codes that scale up to thousands of processors can be directly extended to extreme scalability. New algorithms will have to be invented and totally new computer codes may have to be designed and implemented from conceptual development.

In summary, the computation needs for the science domains in energy storage are shown in Table 1. The left column lists the science domains of interest to the U.S. Department of Energy (DOE) Office of Basic Energy Sciences (BES) while the top row lists the computing domains that offer challenges to the DOE Advanced Scientific Computing Advisory Committee. This two-dimensional matrix captures the benefits that advances in computing technologies, software or hardware offer to the science domains, albeit in different ways and to different degrees.

Table 1. Computation Needs for Science Domains in Energy Storage

ASCR/BES	**Accuracy/ Theories**	**Multiscale Modeling**	**Knowledge Discovery (Data Analytics)**	**Scalable Codes**
Fuel cells	X	X	X	X
Batteries and capacitors	X	X	X	X
Chemical bond energy storage	X	X	X	X
CO_2 sequestration	X	X	--	X

SUMMARY OF RESEARCH DIRECTIONS

The following summarizes the specific issues and computational challenges in the research domains discussed by the Energy Storage panel members.

Proton Exchange Membrane Fuel Cell Science

Fuel cells are a key step in a new energy-based economy—the chemical energy of a fuel (e.g., hydrogen or methanol) is transformed into electrical energy. The building block of a fuel cell is an electrochemical cell (Figure 14) consisting of two electrodes separated by an ion-conducting medium (or membrane). The conducting medium can be an acid, base, or salt (in molten forms) or a solid ceramic that conducts ions, depending on the fuel, the temperature of operation, and the specific application of the technology. Fuel enters the cell on the anode side and oxygen enters on the cathode side. Reaction products (water and perhaps CO_2, depending on the fuel and type of cell) must also exit the cell. As fuel is oxidized to form protons, electrons travel through the circuit to the cathode, where molecular oxygen consumes the electrons. A major use for fuel cells in a hydrogen economy is in portable and mobile applications in which compact and efficient power sources are needed. DOE has established target performance specifications for demonstration and implementation of transportation fuel cell technologies. These goals underscore the difficult technical challenges to the development of automotive fuel cells that are sufficiently inexpensive, effective, and durable to displace current internal combustion engines.

This domain science encompasses two research areas that address the following: 1) the science of catalysis at the electrodes with the goal of finding alternate catalysts based on nonprecious metals (for H_2 or CH_3OH oxidation; O_2 reduction) in lieu of platinum-based catalysts, with low over-potential and increased tolerance to "poisoning" chemistry; and 2) the science of transport of protons through membranes that are complex molecular environments operating under varied temperature and hydration levels while retaining material stability and transport selectivity.

Theory and modeling of electrochemical reactions, catalysis, surface interactions of fuel, and ionic conduction in membranes have the potential to provide substantial insight in understanding, controlling, and enhancing the fundamental processes involved in fuel-to-electricity conversion sciences. The application of theory and simulation to electrocatalysis is complicated by the presence of an aqueous/metal interface in an electric field that forms as a result of the potential at the interface. There is a need to simulate systems under constant potential in contrast to the usual constant number of electrons. The theoretical description of proton transport in general is challenging because of the inherent complexity of proton transfer, a combination of vehicular and Grotthuss mechanisms (concerted hydrogen bond breaking and formation, at least in aqueous environments), the morphology of the environment, the level of hydration, and the multiple length and time scales involved. Extreme-scale computing offers the opportunity for computational tractable models that capture the right physics and afford more complex and realistic models at longer-size scales and time scales than are currently available.

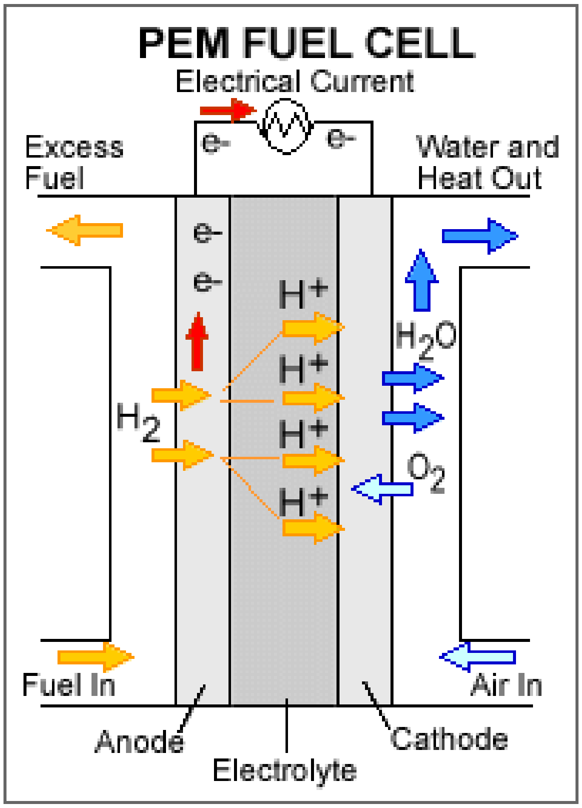


Figure 14. The membrane conducts protons from anode to cathode in proton exchange membrane fuel cells (PEMFC). Image from the U.S. Department of Energy.

Electrode Catalysis

The electrodes contain the electrocatalytic materials that facilitate the reaction of the fuel at the anode and of oxygen at the cathode. Current low-temperature fuel cell electrodes consist of porous composites of ionic/electronic conductors with embedded nanosize particles of the electrocatalyst, thus providing high electrical power from small amounts of precious metal. The electrode also contains open pores for the fuel (and any waste products) to enter or exit the electrode. Producing electrodes that offer optimal performance is challenging. Despite extensive research, fuel cells that operate near room temperature still contain platinum. One goal is to replace the expensive platinum with cheaper materials.

Regardless of the material used as the cathode electrocatalyst, the over potential for the reduction of oxygen at operating currents is too high. This over potential is caused by the slow electrochemical kinetics of oxygen reduction, and it represents an additional driving force to overcome. The result is a decrease in cell voltage, with a loss in efficiency. The problem is especially severe in low temperature fuel cells in which the only cathode catalysts that are currently acceptable and used are platinum or platinum-based alloys. Dramatic improvements in overall performance, efficiency, and cost can be achieved by reducing the over potential. New insights from theory and modeling and new ideas for new materials are required to realize these improvements.

Another important issue in electrocatalysis is “electrode poisoning” by impurities in the hydrogen feed stream such as sulfur, hydrocarbons, and carbon monoxide (CO). The over potential for the oxidation of high-purity H_2 is quite small—much smaller than for the cathode. Impurities that react with the anode, however, can substantially increase the over potential. A higher tolerance of impurities would allow the use of less-pure H_2, reducing the cost of hydrogen production. Carbon monoxide tolerance of current catalysts needs to be improved.

More details can be found in “Advances in Computational Approaches for Electrocatalysis” in the DOE BES report titled, *Basic Research Needs: Catalysis for Energy* (DOE 2008).

Proton Transport

A critical component of low temperature fuel cells is the polymer electrolyte membrane or proton exchange membrane (PEM) that conducts protons from anode to cathode. Practical technical challenges exist in the following:

1. Currently, PEM fuel cells operate below 100°C because the membranes require water for proton conduction. In this temperature range, the electrode catalysts are inefficient, and the cathode is flooded while the anode is dehydrated because of electro-osmotic drag of water.
2. Operating above 120°C could help overcome CO poisoning of platinum-based electrode catalysts, but it would also dehydrate and degrade the membrane.
3. Current membrane materials are expensive and let fuel cross over. Thus, there is a need to develop membranes that conduct protons in the absence of water; do not degrade upon prolonged operation at elevated temperatures; offer selective ionic transport to avoid fuel and oxygen crossover; and are more economical. Presently, membranes are primarily based on perfluoro sulfonic acid (PFSA), such as Nafion®.[1] These membranes are expensive; suffer from deficiencies such as methanol crossover

---

[1] Nafion is a registered trademark of E. I. du Pont de Nemours and Company.

and electro-osmotic drag of water; and exhibit degradation under high power, high temperature, and cyclic (on/off) operation. As previously indicated, the desired membrane properties for this application include high-proton conductivity at low-hydration levels; thermal, mechanical, and chemical stability; durability under prolonged operation; and low cost. None of the existing membranes meet all the requirements. Decades of PEM research have centered on incremental alterations to sulfonic acid-type membranes with unsatisfactory results, and have led mostly to a phenomenological understanding of membrane performance. There is a pressing need to develop novel membranes based on a *fundamental understanding of membrane chemistry, morphology, and dynamical properties* to enable widespread adoption of this promising technology. Such an understanding would form the basis for a rational design and provide input to the desired atomic level characteristics of polymeric materials with controlled and reliable properties.

Advances in Computational Approaches for Fuel to Electricity Conversion

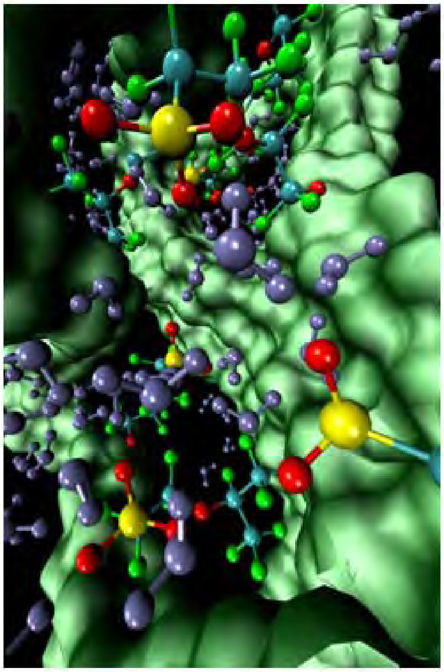


Image courtesy of Ram Devanathan (Pacific Northwest National Laboratory).

Chemical energy conversion to electricity and electrical energy storage are two critical elements in a global energy management for sustained energy sources in the future. In an electrochemical fuel cell, the chemical energy of the fuel is transformed into electrical energy. The fuel (H_2 or CH_3OH for example) is oxidized at the anode into electrons that travel through the open circuit and protons that transport across an electrolyte membrane to the cathode where they recombine with the electrons and O_2 to form water. Grand scientific challenges for greater import of this technology reside in 1) the quest for nonprecious metal catalysts at the electrodes to replace the currently used platinum-based catalysts; and 2) the development of proton-exchange membranes that operate under varied temperature and hydration levels while retaining material stability and transport selectivity. The extension of theory and simulation to electrocatalysis is complicated by the presence of an electrified aqueous/metal interface, which forms as a result of the potential at the interface. To this end, theories that capture increasing aspects of the correct physics in more complex models are needed. Such was the case for a recently developed constant-potential *ab-initio* density functional based-approach (Filhol and Neurock 2006; Taylor et al. 2006). The approach mimics a half-cell electrochemical system used to simulate the electrooxidation and reduction of water at various transition metal surfaces to make a theory-based prediction that a novel PtRuAu alloy would lead to significantly improved methanol oxidation activity at the anode of the direct methanol polymer electrolyte membrane fuel cell. The scientific grand challenge in designing proton exchange membranes (PEMs) is in the characterization of the relationship between membrane nanostructure, local chemistry around acidic sites, proton transfer, and proton and small molecule transport in PEMs. Because of the different chemical interactions, as well as length and time scales that characterize these factors in PEMs, modeling from the molecular level to the mesoscale is essential to provide insights toward the development of membrane materials with selective transport, good conductivity, and stability for operation in low hydration conditions (Kreuer 2001). The theoretical description of these processes is challenging because of the need to capture the quantum mechanical nature of proton transfer and proton hopping, the diversity of transport mechanisms (vehicular and Grotthuss), the influence of the complex environment, and the computational cost of modeling realistic environments over relevant time lengths. The work is computationally intensive and benefits from access to massively parallel computers.

Computer simulations have an important role to play in the rational design of membrane materials. The theoretical description of proton transport in general is challenging because of the inherent complexity of proton transfer (a combination of vehicular and Grotthuss mechanisms, at least in aqueous environments), the morphology of the environment, the level of hydration, and the multiple length and time scales involved.

Batteries and Capacitors Sciences

Advanced batteries will play a significant role in the energy and economic security of the United States. This critical crosscutting technology for domestic applications will enhance environmental friendliness and reduce national dependence on foreign oil. The development of advanced battery technologies for use in the transportation sector of the economy has been a focused research area for DOE. This includes advanced lithium-ion battery technologies for hybrid electric, plug-in hybrid electric, and pure electric vehicles. Many technical topics are discussed in *Basic Research Needs for Electrical Energy Storage* (DOE 2007a). Overall, batteries and capacitors are an important player in advanced energy storage technologies for use with solar, wind, and other renewable sources of energy.

Although batteries and capacitors have been available for many decades, there are still many fundamental issues in understanding reaction processes at the atomic and molecular level that govern their operation, performance limitations, and failure. In the area of lithium-ion batteries, there are several opportunities for the development of advanced materials that will improve the performance, life, and inherent safety of this technology and render the technology more broadly acceptable for use in transportation applications. The process of developing these new materials by conventional experimental methods has been quite successful but requires a considerable amount of time, effort, and funding. The extremely complex behavior occurring in batteries has also prevented complete understanding of all the correlated mechanisms. Advancement in new battery technology requires fundamental understanding of charge transport (electronic and ionic), reduction-oxidation behavior, phase transformations, microstructure evolution, and surface and interface reactions occurring in these compositionally and structurally heterogeneous materials.

The virtual design of new materials enabled by high-performance computing at the extreme scale and the development of advanced computational methodologies offers unprecedented opportunity for theory and modeling to play a major role in combination with experiment in the development of new materials for advanced batteries and capacitors. Computational simulations will be enabled through use of the next generation of high-performance computing resources; new, highly parallelized electronic structure codes; development of adaptive simulations; incorporation of data across time and size scales; and software for storage, retrieval, and analysis of calculated data.

When combined with new techniques for synthesis and characterization having atomic level precision, computation provides a powerful approach for designing new materials for future-generation batteries. For example, tailoring the interface between the electrode and electrolyte in the lithium-ion battery is extremely important to improving the safety and reliability of the lithium-ion batteries that will be used in the next generation of electric vehicles. Similarly, conversion reactions in lithium-ion batteries involve *in-situ* transformations of a metal halide plus lithium composite into a lithium halide and metal nanocomposite. These conversions include all the valence changes in the metal ion from high-charge valence to zero state. These involve large particles that evolve into nanoparticles, creating interfaces and reaction zones different from the starting microstructure. Description of these conversion materials require new interatomic potentials that can capture the changes that occur, new techniques describing electron transport in solid phases in conjunction with ion transport, *in-situ* phase changes and recovery, ion transport in different phases, and correlations over multiple particles and complex heterogeneous compositions. Computational simulations at the extreme scale will be able to help provide insight into the nature of the interfaces and into the design of new solid-electrolyte interfaces that can achieve safety goals.

Another example is the lithium-air battery for which discovery of new catalytic materials for the Li-O_2 reaction is one of the grand challenges for the development of this new battery technology with potentially much larger energy densities than lithium-ion batteries. Computational efforts can provide useful guidance to experiment in design and discovery of new catalytic materials, as well as other key components of the lithium-air battery. Theory-based design of new materials with desired functional properties has the potential to revolutionize the materials discovery process and play a key role in developing materials for electrochemical energy storage as well as other materials.

High-surface area materials—such as nanoparticles or nanoporous materials—are used in high-power capacitors. However, behavior of ions and liquids in nanoconfinement is different from bulk solutions, requiring significant enhancement in scientists' understanding of this behavior using advanced computational techniques. Complicating behavior are features associated with different crystallographic orientations on reactions, crystalline versus amorphous phases, transport, solid electrolyte interphase (SEI) formation, and the correlations between these different features on each other. This local heterogeneity in composition and structure requires computing at the extreme scale to combine all parts of the system and to evaluate the correlations among them, which are fed into larger-scale calculations for system evaluation and design.

In summary, batteries and capacitors as energy storage devices are in need of revolutionary new materials for higher energy and power densities, better stability and safety, and longer lifetimes. Achieving breakthroughs in the development of electrode materials and electrolytes requires a fundamental understanding and control of the coupled charge and ion transport through the electrode material, phase transformations, and reactions. Computational approaches can effectively complement experimental efforts and provide insight into mechanisms, predict trends, identify new materials, and guide experiments. Computation at the extreme scale has the potential to integrate methods at different time and length scales to provide a fundamental understanding of underlying processes in batteries and capacitors, such as phase transitions in electrode materials, ion transport in electrolytes, charge transfer at interfaces, and electronic transport in electrodes.

Energy Storage Cycles Using Chemical Bonds

Chemical bonds are nature's most efficient tool for storing energy at high densities on a per weight basis. An additional advantage of storing energy by chemical means is in its ease in energy distribution that can be disseminated over large length scales, potentially using the current petroleum infrastructure with minimal energy loss. Therefore, energy storage using chemical bonds has been recognized as an essential component in energy research.

In this research domain, development of energy storage cycles can be viewed as the manipulation of material transformations through cyclic processes that vary in the number and identity of chemical bonds. Examples of these storage cycles include the use of metal hybrids or chemical hybrids to store and release hydrogen, and the creation of liquid fuels from renewable resources for use in combustion or fuel cells. In metal hybrids, the ability to cycle many times between loaded and unloaded end states is required, while in the second example, a “one pass” chemical transformation is sufficient. In both metal and chemical hybrids, the goal is to develop a system that releases H_2 spontaneously and controllably at suitable pressures and temperatures in amounts consistent with the needs of a fuel cell of a size sufficient to run an automobile or light truck. For such a system, it is equally important the spent material be reprocessed or recycled efficiently. Many issues are presented in *Basic Research Needs for the Hydrogen Economy* (DOE 2004b).

A common feature of all energy storage cycles is the storage material must pass through multiple chemically distinct states on a time scale relevant for the desired application at acceptable economic cost. Materials being considered are usually complex combinations of states of matter including crystalline solids, amorphous materials, molecular liquids, etc. Therefore, the scientific challenge that pervades the development of new energy storage cycles is the need for efficient materials discovery. Arguably, the most important role for computational science in this area is to enable and facilitate this effort of materials discovery, a task that requires models of sufficient fidelity to describe the entire energy storage cycle so that experimental development of promising new materials can be accelerated. Although the implementation of improved methods within individual modeling domains (e.g., electronic structure theory) is a necessary requirement for this overarching goal, these methods alone will not be sufficient. The greatest challenge for using extreme-scale computing to unlock the potential for computationally driven materials discovery in this area is in the efficient integration of individual domain-specific applications. This integration is essential to describe energy storage cycles in materials with complex atomic-scale structures that vary strongly in their physical characteristics over the course of energy storage and release. In addition, regeneration management of spent fuel is critical for any energy capture, utilization, and storage system. Many aspects of this challenge are also critical in closely related scientific areas, such as catalysis.

One important example of the challenges that will require careful integration of modeling schemes is the efficient sampling of physical configurations in a complex material. The core capacities of describing the properties of a material after the atomic configuration is specified are relatively well developed, although the scaling of existing domain-specific computational materials modeling tools (e.g., electronic structure theory, molecular dynamics) to extreme-computing environments will certainly require significant efforts. This activity includes the capability to capture, with reasonable accuracy, atomic interactions that mix strong interactions (chemical bonding) and weak interactions (dispersion interactions) that are challenging with current computational resources. In complex materials, however, the task of identifying the *relevant* atomic configurations among a huge search space is extremely difficult but absolutely essential. The task of crystal structure prediction for molecular species is one specific example of this kind of task, requiring effective computational tools for exploring the high-dimensional configuration spaces defined by the potential atomic configurations. These problems are ubiquitous in energy storage materials both in understanding the detailed structure of individual materials, but also in describing the net transformation of materials during cycles of energy and release. The computational power of extreme computing has potential to open entirely new conceptual approaches to this important problem. In addition, there is a critical need to develop new algorithmic approaches that will unlock this capability.

The ability to reliably predict the performance of genuinely new materials in energy storage applications throughout entire energy storage and release cycles has the potential to revolutionize materials development in this important area. Storing energy in chemical bonds remains an attractive, viable option in energy storage. Many physical issues the research community must address in this application area are also shared in related topics such as catalysis and the development of materials for the mitigation of greenhouse gas emissions. The future acceleration of materials development in energy storage applications will be tightly coupled to the ability to use computational tools to drive materials discovery. Although experiments will remain the ultimate benchmark for the viability of a new material or process, computational modeling will continue to grow in importance as an indispensable enabling technology in driving materials discovery in problems with large search spaces.

Geological CO_2 Sequestration

The capture and storage of carbon dioxide and other greenhouse gases in deep geologic formations represents one of the most promising options for mitigating the impacts of greenhouse gases on global warming owing to the potentially large capacity of these formations and their broad regional availability (Bachu 2008). A critical issue is to demonstrate that CO_2 will remain stored over the long term in the geological formation where it is injected. The complexity and dynamics of mineral-water interfaces are a priority research direction (PRD) identified by the DOE workshop on the *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems* (DOE 2007b). The DOE BES sponsored symposium, *Computational and Numerical Geosciences*,[1] provided a forum for scientists to discuss developing research objectives and approaches in these areas in more detail and the important role of advanced computational methods at the atomic- and molecular-scale in addressing them.

Meeting CO_2 sequestration measurement, monitoring and verification (MMV) requires the ability to model the temporal and spatial evolution of fluids and corresponding transport pathways within heterogeneous geological systems. All subsurface science models involve multiple poorly separated length and time scales, and complex coupled physical phenomena. To model processes at one scale requires that scientists understand the important variables at smaller scales to ensure these variables are accurately represented at the larger scale. The coupling of mathematical models between different scales (atomistic, pore, laboratory, and field) plays a defining role in understanding subsurface phenomena related to CO_2 sequestration. Currently, direct numerical simulation from fundamental scales to field scale is impossible.

The computational challenge is therefore to model the temporal and spatial evolution of reacting fluids and corresponding transport pathways, including structural changes (e.g., pore blocking) as well as phase changes within heterogeneous geological systems under nonequilibrium conditions at all relevant scales. A key aspect will be the integration of molecular level theory and experiment to provide unique insight into the microscopic phenomena that occur, and to establish a basis for how such molecular level processes can be represented at the macroscopic level. The geological storage of CO_2 is inherently multiscale in time and space, and addressing the scientific and technological problems they pose requires experts from multidisciplinary fields. In the future, accurate and realistic models of reaction mechanisms can help bridge scales and disciplines. However, constraints imposed by current computing power do not currently allow the scale of calculations required to make these connections.

Research on mineral-fluid interaction for subsurface CO_2 storage includes both the aqueous phase; i.e., reactivity with aqueous solutions or brines containing dissolved CO_2, and wet nonaqueous fluids of supercritical CO_2 that is highly diffusive owing to its low viscosity. A key issue for the latter is to unravel

---

[1] May 2007, Gaithersburg, Maryland.

the molecular mechanisms governing the reactivity of mineral phases with variably wet supercritical CO_2 as a function of T, P, mineral structure/composition, and solution phase composition. The computational science efforts will include the development of knowledge discovery tools, which will be necessary to provide reliable estimates of uncertainty from different sources including models, data, and the simulation.

Important questions center on how water and dissolved species behave at mineral surfaces and in nano-confinement by different mineral surfaces. Current understanding of hydrated mineral-water interfaces is incomplete. Molecular-scale information is difficult to obtain experimentally due to the nature of the materials (e.g., interfacial and bulk structural disorder, the presence of molecular scale dynamical disorder with characteristic time scales that span many orders of magnitude, the physical limitations on the samples that can be effectively examined, and the difficulty of experiments under extreme conditions). Mineral surfaces themselves vary by the arrangements and reactivity of individual surface functional groups and the specific adsorption of inorganic and organic ions. Connecting computational and experimental results is crucial in addressing these questions and in bridging the gap between the atomic- and nanometer-scales and the micron- and larger scales that is essential for environmental, geochemical, and energy applications of practical importance. In addition, the interaction with experimentalists is imperative for verifying theoretical models and guiding larger-scale simulation efforts.

Computational research in the United States concerning mineral-fluid systems has advanced significantly in the past decade but even greater strides can be made if there are substantial improvements in computational resources and software that can run on these resources. Computer simulations at the atomic- and molecular-scales, often coupled to experimental results, have provided otherwise unobtainable perspective into the structure, dynamics, and energetics of fluid-mineral systems. Computational approaches range from traditional quantum chemical methods to classical molecular dynamics (MD) and Monte Carlo simulations using semiempirical interaction potentials to emerging methods including quantum molecular dynamics, metadynamics, and reactive force fields for molecular-scale modeling. Critical questions currently revolve around the following:

- effect of solid surfaces on the properties of near-surface and nano-confined fluids
- structural and chemical modification of the surface by the fluid
- pathways of chemical reactions at surfaces and in fluids
- connections between these reactions and fluid structure and dynamics
- consequent effects on the pathways of dissolution and precipitation.

There is a growing consensus that the idealized mineral-fluid interfaces used in MD and Monte Carlo simulations and the relatively small assemblages used in these models and in quantum calculations are at least an order of magnitude too small in characteristic length (three orders of magnitude in volume) to effectively address many critical questions. A typical size of the systems currently simulated is on the order of a few nanometers (nm), but may reach up to 20 nm for classical force-field-based MD simulations that can probe the systems evolution over tens of nanoseconds. However, the application of quantum MD is limited to the sizes < 1.5-2 nm and time periods ~10 picoseconds. The inability to effectively model realistic compositional and structural complexity is significantly impeding further progress. Particle edges, surface defects, the surface roughness on length scales of 10 to 100 nm play central roles in determining the energetics and kinetics of dissolution, precipitation, sorption, and catalytic reactions at mineral interfaces, but these phenomena are currently modeled only very rarely and with limited success. Petascale supercomputing capability will allow such molecular simulations to achieve truly realistic system sizes and time scales, thus significantly increasing their value. Other parameters that can be effectively addressed only with very large-scale simulations include variable composition, crystal defects, low crystal symmetry, stacking disorder, and nonplanar interfaces.

PRIORITY RESEARCH DIRECTIONS

Based on the panel discussions on the computational challenges for the four research domain sciences, a single overarching grand challenge emerges: "Inverse Materials Design," whereby a material with specific function and property is sought. The search for optimal materials is of central importance in all four research domain sciences. In practice, four PRDs were identified to advance the realization of this grand challenge.

Develop Simulations Techniques to Control Chemical Interactions at the Molecular Levels

This PRD requires advances in fundamental theories, phase space sampling techniques, quantum mechanical chemical rate calculations, and rare events characterization. In addition, the simulation of dynamical processes is central to the modeling of a wide variety of phenomena in the materials and chemistry science associated with energy storage. In most cases, the calculation of reaction rates must go beyond the simplest theory of activated processes and requires accurate and efficient treatment of phase space sampling to extract accurate free energies, discovery, and characterization of rate events through automated searches, and finally calculation of quantum mechanical effects. These steps traditionally consume huge computer power, and extreme-scale computing will have a huge impact on characterization of dynamics.

Develop Simulation Techniques for Transport of Matter in Heterogeneous Environments

This PRD addresses the dynamics of electrons, protons, ions, and molecules at the nanoscale and the overall dynamics at the macro- and field-scale. The focus on transport of matter (electron, protons, ions, and molecules) requires long-time simulations of the dynamics of these species in heterogeneous environments at the nanoscale and beyond. These challenges are compounded by the fact that in many cases, the dynamics of these species, electrons, protons, and ions are coupled. For example, advancement in new battery technology requires fundamental understanding of both electronic and ionic charge transport. No established methodologies exist to describe the coupled dynamics, and innovative methods need to be developed. The scale of the computing power required can only be realized by advances in high-performance computing capacities.

Develop General and Robust Multiscale Modeling Techniques for the Description of Integrated, Complex Materials

Multiscale modeling over a range of scales of length and time is critical in dealing with multiphase description of the domain science, and in some cases toward real system characterization. Various schemes have been proposed in connecting properties over different length and time scales, but these techniques need to be further improved to increase the accuracy and robustness.

Develop Knowledge Discovery Techniques

Techniques are needed that rely on machine learning to connect materials properties with the details of materials structure (unit cells, grain boundaries, etc.) and composition. Given the high cost of synthesis, computational materials design can greatly improve the efficiency of the search process for new energy storage materials and have a major impact in this important field. Computational techniques will enable high fidelity, descriptor-based screening of many candidates for new and improved materials for energy storage applications with improved stability, safety, and energy densities.

CONCLUSIONS

This panel covered four research domains in energy storage: proton-exchange membrane fuel cell science, batteries and capacitors, energy storage in chemical bonds, and geological CO_2 sequestration. The workshop discussions identified four underlying computational challenges in these research domains that have great potential for impact from extreme-scale computing: 1) accurate and reliable theories at varied scales; 2) multiscale modeling (length and time); 3) knowledge discovery (data analytics); and 4) scalable computing technologies. Specific issues and computational challenges for these research domains were presented. One single overarching grand challenge of “Inverse Materials Design” emerged from the panel discussions. Panel members recognized that the search for optimal materials is of central importance in all four research domain sciences. To address this challenge, panel members identified four priority research directions: 1) the development of simulations techniques that permit the control of chemical interactions at the molecular level; 2) the development of simulation techniques to permit the prediction of the transport of matter in heterogeneous environments; 3) the development of general and robust multiscale modeling techniques for the description of integrated, complex materials; and 4) the development of knowledge discovery techniques. Extreme-scale computing is expected to bring critical advances in all four priority research directions.

DYNAMICS

Co-Leads: Mark Asta, University of California, Davis; University of California, Berkeley; and Lawrence Berkeley National Laboratory
Carlos Simmerling, Stony Brook University

Panel Members: Sebastian Boutet, Linac Coherent Light Source, SLAC National Accelerator Laboratory; Marc Meserschmidt, Linac Coherent Light Source, SLAC National Accelerator Laboratory; Bruce Garrett, Pacific Northwest National Laboratory; Todd J. Martinez, Stanford University and SLAC National Accelerator Laboratory; Julius Su, California Institute of Technology; Rigoberto Hernandez, Georgia Institute of Technology; Kristen A. Fichthorn, Department of Chemical Engineering, Penn State University; Renata Wentzcovitch, University of Minnesota; Talat S. Rahman, University of Central Florida; Christopher J. Mundy, Pacific Northwest National Laboratory; Priya Vashista, University of Southern California; Rajiv Kalia, University of Southern California; Aiichiro Nakano, University of Southern California; Andrew Canning, Lawrence Berkeley National Laboratory; Dieter Wolf, Idaho National Laboratory; Anter El-Azab, Florida State University; John Pask, Lawrence Livermore National Laboratory; Eric J. Bylaska, Pacific Northwest National Laboratory; Vincenzo Lordi, Lawrence Livermore National Laboratory; Joel Bowman, Emory University; A. D. (Tony) Rollett, Carnegie Mellon University; Gregory A. Voth, University of Utah; Bruce Harmon, Ames Laboratory and Iowa State University; Paul Whitney, Pacific Northwest National Laboratory; Francois Gygi, University of California, Davis; George Fann, Oak Ridge National Laboratory; Joe Oefelein, Sandia National Laboratories; and John Bell, Lawrence Berkeley National Laboratory

CURRENT STATUS

Simulating dynamical processes is central to modeling a wide variety of phenomena in materials science and chemistry. In the context of basic energy sciences, dynamical simulations find widespread use in applications including catalysis, combustion, environmental and geochemistry, and advanced structural materials. Over the past decade, significant advances have been realized in simulating reaction kinetics, diffusion in condensed phases, the dynamics of interfaces and crystalline defects, and molecular self-assembly. However, substantial computational and algorithmic challenges have limited applications of existing methods to relatively idealized systems and often very short time scales. Extreme-scale computing, combined with the requisite advances in theoretical methods and algorithms, are anticipated to lead to fundamental breakthroughs in scientists' ability to predict rare-event kinetics, excited-state and charge-transport dynamics, and multiscale phenomena. These advances are central to expanding the role of dynamics modeling to impact the understanding and design of new materials and chemical systems for future energy technologies.

The Dynamics panel examined research opportunities for the use of extreme-scale computing to understand modeling and prediction of dynamical processes in materials and molecules for renewable energy applications. The panel identified five priority research directions (PRDs):

- Rational design and synthesis of multifunctional catalysts
- Opportunities and challenges for combustion science at the exascale

- Computational challenges in Geosciences
- Thermo-mechanical behavior of materials under extreme conditions
- Materials for nuclear energy.

These PRDs are described in more detail in the following sections.

BASIC SCIENCE CHALLENGES AND RESEARCH NEEDS

Rational Design and Synthesis of Multifunctional Catalysts

Scientific Challenge and Computational Challenge

As feedstocks for fuel production become more complex, the need arises for catalysts with multiple functionalities that can catalyze a sequence of reaction steps in a concerted manner. Developing such catalysts is a response to the two grand challenges identified in the 2007 Basic Research Needs workshop report on catalysis science (DOE 2008):

1. Understanding mechanisms and dynamics of catalyzed transformations: Connect catalytic and photocatalytic reaction rates and selectivities to the kinetics, energetics, and dynamics of individual elementary steps, and relate these to the structure and dynamics of the catalytic sites involved.
2. Design and control synthesis of catalytic structures: Use theory as a predictive design tool, develop systematic approaches to construct and to characterize at the atomic level the molecules and materials designed, and develop the necessary understanding to control or direct chemical reactions in complex media.

The underlying computational challenges include scalable algorithms for electronic structure and dynamics calculations that will allow larger, more reliable models of catalytic systems to be treated than is presently possible. The next generation of exascale computing presents significant challenges to the software development associated with advancing this science. Such a resource will likely not be a simple capacity-computing machine, but will rather consist of heterogeneous cores connected hierarchically. As such, the requisite algorithms to handle systems with many electrons, many particles, and many coarse-grained components simultaneously will have to be mapped onto such hierarchies. Indeed, the software and hardware developers will need to work together to optimize the relative distribution of cores and memory, as well as their topology to the computational science algorithms. (With a thousand-fold more capacity, so-called *ab initio* molecular dynamics, could—for example—be performed for systems with up to 100,000 atoms.)

Another challenge would be to extract useful information from the multitude of data acquired from petascale and exascale computing. Handling large-scale datasets for this purpose would be done in collaboration with computer scientists and applied mathematician experts in those areas.

Summary of Research Direction

The major scientific research direction is to integrate dynamics, statistical mechanics, and electronic structures, including the treatment of long-time dynamics and nonequilibrium systems. Understanding the fundamentals of reaction mechanisms and designing and synthesizing new catalysts requires the following computational tools:

- Accurate and scalable electronic structures
- Reliable molecular mechanics potentials
- Efficient methods for free-energy calculations, including effects of vibrational dynamics
- Efficient, robust methods for characterizing potential energy surfaces (e.g., rare kinetics events)
- Scalable methods for electronically nonadiabatic processes, including concerted multielectron/multi-ion motion, and photocatalysis
- Methods to couple temporal and spatial scales (e.g., coarse-graining methods), ranging from those relevant at the molecular scale to those in macroscopic systems, leading to an understanding of catalytic behavior as a function of reaction conditions.

The scaling of computation expense with system size for electronic structure methods currently limits the model size to only tens to hundreds of atoms with current computational tools and resources. The parallel scaling of current electronic structure codes is limited to thousands of cores so that new approaches to parallel implementation of electronic structure need to be developed. The primary computational research directions needed to address these issues include the following:

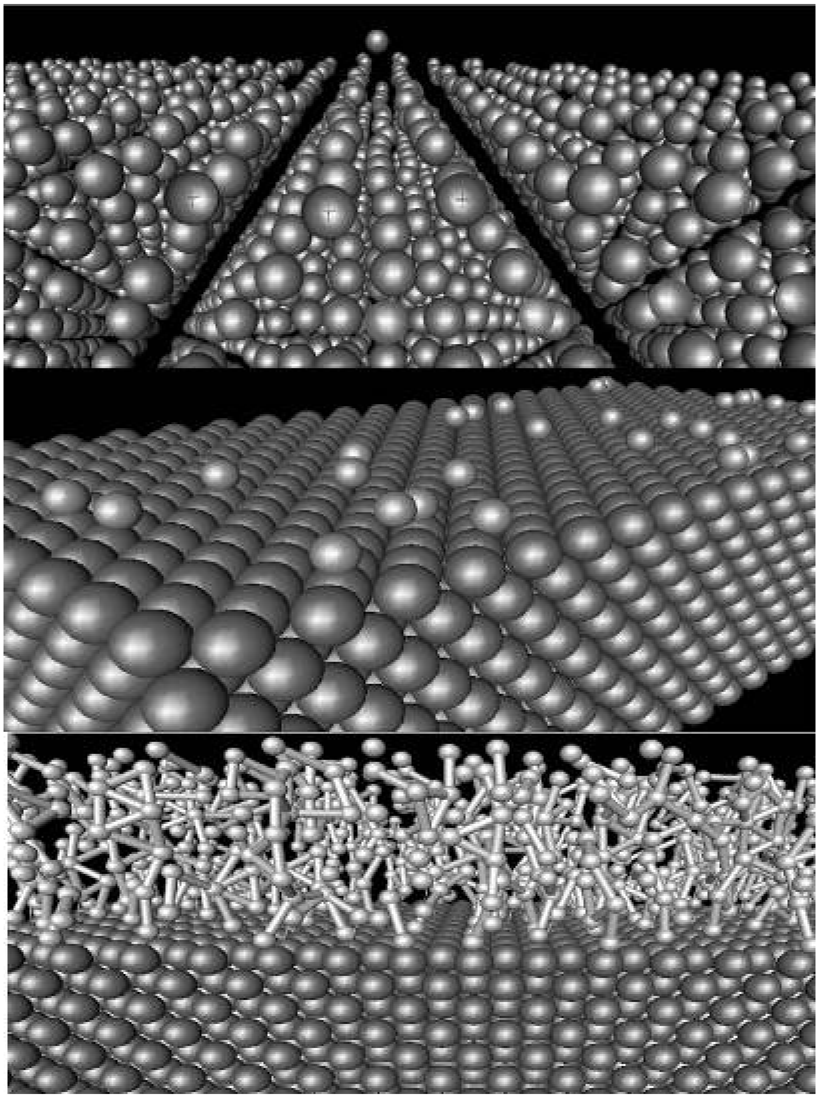
- concurrency between different techniques and at different length and time scales
- parallel scalability of electronic structure and dynamics algorithms
- advanced mathematical and computer science tools (e.g., scalable solvers, accelerated dynamics, methods for handling large data sets, and integrators for long time scales).

Expected Computational and Scientific Outcomes

Scientists do not currently understand how multifunctional catalysts that promote a cascade of reaction steps will behave in real catalyst systems. The proposed research directions are expected to unveil emergent behavior from complex, cooperative networks of reactions in these systems. Developing the integrated capabilities described above will provide predictive capabilities that will greatly accelerate the design of realistic catalysts. Further, these capabilities are required to understand self-assembly for synthesizing multifunctional, nanostructured catalysts. The computational outcome of this effort will be an integrated computational framework for describing reactive molecular processes in complex, multiphase systems.

Current exascale computers can handle idealized, model systems with approximate (and sometimes inappropriate) levels of theory; the extension to computers with extreme-scale capabilities will enable system sizes to be addressed that realistically represent the systems of interest, including defects and inhomogeneities. In addition, new methodologies for accurate and scalable treatment of excited state and electronically nonadiabatic dynamics, which currently represent a deficiency in theory and computation, are expected. Furthermore, computing with a large-scale capacity will likely play a role as well because statistical mechanical sampling and free energies are fundamental aspects of the required computations.

Catalysis

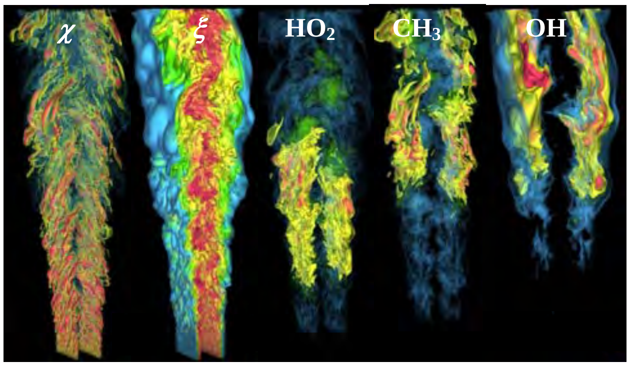


The description of catalytic processes using computational models and molecular dynamics simulations requires treating the heterogeneous surface (which may be the catalyst itself or contain catalytic sites) and the reaction partners at given surface coverage, and perhaps also increasing the numbers of tertiary molecules physisorbed on the surface to modify the kinetic properties of the catalyst. The three pictures (left) illustrate a progression of increasing complexity in the size and number of adsorbates on a surface. The appropriate treatment of these systems requires an accurate description of the underlying surface, complicated because the number of atoms (or molecules) must be large enough to remove finite-size effects through the transition from the surface to the bulk. The surface is usually terraced and/or structured, which necessitates even more layers for the description. The interactions between the surface atoms also require an appropriate treatment of electrons, particularly if properties such as conductance are of interest. This is further complicated by the increasing complexity and heterogeneity that arises from the adsorbates at a given surface coverage with varying structure (such as when the adsorbates are oligomers or polymers). The relative time and distance scales for the relevant motions of all these processes can vary by factors as high as 10^{10}, and therefore, it will be necessary to increase the computational power and advancing algorithms. Image courtesy of Rigoberto Hernandez (Georgia Tech).

Potential Impact on Energy Science Field

Over the next 5 to 10 years, computational tools will enable us to predict thermodynamics and kinetics for progressively more complex (realistic) catalytic systems. In addition, there is the need to capture the vast amount of information about catalytic systems and use this knowledge to develop design rules for catalysts. Finally, the long-term goal is to develop the fundamental understanding needed to design new multifunctional catalysts with unprecedented control over the transformation of complex feedstocks into useful, clean energy sources.

Stabilizing a Lifted Turbulent Jet Flame in a Heated Coflow as Revealed by the Domain Name System



DNS of a lifted ethylene-air jet flame in a heated coflow at a Reynolds number of 10,000. Instantaneous volume rendering from left to right: scalar dissipation rate, mixture fraction, mass fractions of HO_2, CH_3, and OH.

Many familiar flames are stabilized by heat loss to a burner. At higher flow velocities, a jet flame can be stable even when it is lifted off the burner, but it is not always clear what is causing the stabilization. At still higher velocities, the flame blows out. Lifted flames are used in many high-power applications, including direct-injection automotive engines, in part to reduce the thermal load on the fuel injector. The details of mixing upstream of the flame influences the combustion and soot-formation processes downstream. The position of the flame is highly sensitive to the ignition chemistry of the fuel. For example, in a diesel jet flame, the preignition “cool flame” chemistry may help to stabilize the flame. However, “cool flame” chemical kinetics is relatively slow and may be modulated by turbulent strain and mixing. Petascale simulation provides a way to study fundamental issues related to small-scale combustion processes in well-defined laboratory configurations and gives information that is difficult or impossible to measure. The domain name system (DNS) was used (see figure) to understand how a lifted autoignitive flame is stabilized (Yoo et al. 2010a, 2010b) at atmospheric pressure. Concentrations of 22 chemical species were computed at 1.28 billion grid points for this three-dimensional flame where Re=10,000, requiring 7.5 million central processing unit hours on a Cray XT4 supercomputer at Oak Ridge National Laboratory. The results reveal that autoignition in a fuel-lean mixture immediately upstream of the flame is the main source of stabilization. A fundamental understanding of this issue, provided by detailed scalar and velocity statistics from the DNS and many others, is needed to develop robust and reliable combustion models for the combustion regimes observed under low-temperature combustion engine environments. Exascale computing will enable DNS to be performed at engine pressures, and with more complex chemistry representative of low-temperature ignition kinetics. With petascale computing, it is currently feasible to transport 20 to 60 species. With exascale computing, greater numbers of species and reactions will be possible, $O(\sim 100)$. It will also enable parametric studies to be performed, varying the co-flow temperature, jet velocity, pressure, and ignition quality of the fuel (by varying the fuel, dilution, and additives in the vitiated gases). Fuels under consideration include oxygenated fuels like dimethyl ether and biodiesel; e.g., bio-butanol. Previous-strained counterflow *n*-heptane ignition studies at diesel pressures show strong sensitivity of the thermal dissociation reaction $H_2O_2 \rightarrow OH + OH$ to fluctuations in local mixing conditions, and hence differences in the ignition quality of fuels may play a significant role in the duration of the induction period before thermal runaway, thereby modulating lift-off heights in diesel jets and downstream sooting processes. After validation against experiment, the DNS will be used to validate engineering Large Eddy Simulation and Reynolds-Averaged Navier-Stokes (RANS) approaches applied to higher Reynolds number flames at high pressure.

Opportunities and Challenges for Combustion Science at the Exascale

The U.S. Department of Energy (DOE) Basic Energy Sciences workshop report on *Basic Energy Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels* (DOE 2007c) identified a single overarching grand challenge: to develop a “validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications." To meet this challenge, combustion scientists must focus on the science underlying the development of nonpetroleum-based fuels, including carbon-neutral biofuels, and their optimal use in transportation. This science intrinsically involves chemistry with transport at conditions far from equilibrium and at extreme pressures, as well as a coordinated multiscale approach for understanding and predicting combustion in turbulent environments.

The urgent need for a concerted effort to develop nonpetroleum-based fuels is mandated by recent concerns over energy sustainability, energy security, and global warming. Drastic changes in the fuel constituents and operational characteristics of energy conversion systems are needed over the next few decades as the world transitions away from petroleum-derived transportation fuels. Conventional empirical approaches to developing new engines and certifying new fuels have only led to incremental improvements, and as such, they cannot meet these enormous challenges in a timely, cost-effective manner. Achieving the required high rate of innovation will require computer-aided design, as is currently used to design the aerodynamically efficient wings of airplanes and the molecules in ozone-friendly refrigerants. The diversity of alternative fuels and the corresponding variation in their physical and chemical properties, coupled with simultaneous changes in energy-conversion device design/control strategies needed to improve efficiency and reduce emissions, pose immense technical challenges. These challenges are particularly daunting because energy-conversion efficiencies and emissions are governed by coupled chemical and transport processes at multiple-length scales ranging from nanoscale particulate formation to turbulent fuel/air mixing.

Combustion in practical devices covers a myriad of time and length scales, from the scale of the electron to those of the largest scales of turbulence dependent upon the geometry of the device. To tackle this daunting challenge and complexity, a multiscale approach is adopted wherein experiments, theory, and direct computation are brought to bear on a limited range of scales (four to five decades), and fundamental physical insights gained are encapsulated in reduced-order parameterizations that are used to upscale knowledge to bridge the scales. Several of the relevant computational approaches are shown in Figure 15, including atomistic and continuum methods. Each of these computational approaches currently use petascale and exascale computing that would greatly facilitate higher fidelity or access to more practically relevant parameter regimes.

Nanoparticle Scale/Molecular Dynamics and Kinetic Monte Carlo Approaches to Soot/Nanoparticle Formation

When molecules become very large, with length scales of nanometers rather than Angstroms—as happens in particulate formation processes—it becomes impractical to compute every possibility in detail using quantum mechanics. Therefore, different approximations and approaches must be taken to estimate the nanoparticle properties and reaction rates. At the nanoparticle scale, there are still some effects of molecular "graininess"; statistical mechanics methods such as kinetic Monte Carlo and molecular dynamics can capture some of those effects. The size of nanoparticles is often comparable to or smaller than the molecular mean free path (~10 to 100 nm) so that their transport properties are significantly different from the continuum properties important at larger length scales.

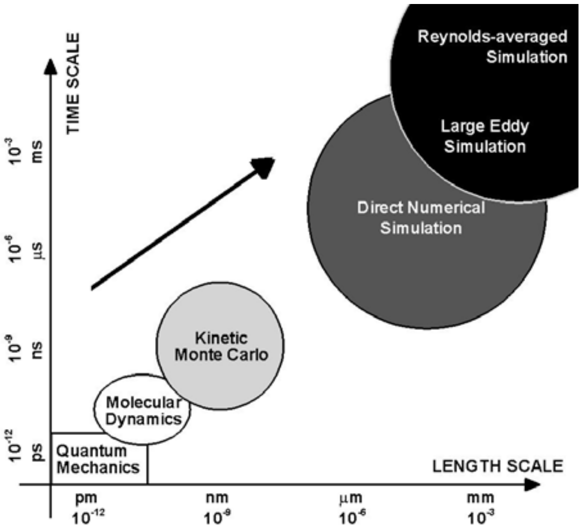


Figure 15. Multi-scale combustion simulation methods for bridging decades in length and time scales in practical combustors. Source: DOE (2007c).

Soot Simulation: A Multiscale Problem

In combustion environments, soot formation is a fascinating multiscale problem of nanoparticle growth, both in length scale and in time scale. Soot formation is initiated by reactions of carbon-based fuel molecules produced by partial fuel combustion. These initial reactions produce large organic molecules containing carbon rings that are referred to as polycyclic aromatic hydrocarbons (PAHs). Large PAHs associate and condense to form small nascent particles in the size range of 5 nm. These incipient particles grow in size to form carbon spheres in the size range of 15 to 50 nm and aggregate to form larger branched-chain particles of widely varying size. A typical size for a soot particle produced by a modern conventional diesel engine is ~200 nm. At higher temperatures, soot particles react rapidly with oxygen, and under some conditions can be completely oxidized before being incorporated into the exhaust stream (Homann and Wagner 1968). The fundamental challenge in predicting soot formation is in the fact that soot formation is a heterogeneous process at even atomic length scales [$\sim O(10^{-10}\,\text{m})$], which has an enormous impact on the soot morphology and overall yield.

Recent work reported in Violi (2004) and Izvekov and Violi (2005) has revealed how chemical changes and transformation can propagate upward in scale to help define the function of the particle structures. In particular, the morphology of the nanoparticles is critical in determining the overall growth and agglomeration behavior of higher molecular structure compounds. Figure 16 shows photos obtained using molecular dynamics simulations of nanoparticle agglomeration in high-temperature regimes (Izvekov and Violi 2006; Fiedler et al. 2007). The sheet-like particles 1) do cluster in small agglomerates while the round particles 2) tend to cluster, showing a preferred orientation that is back-to-back. Current models report a simplified notion of the coagulation process in which two particles coagulate after collision if the kinetic energy of the particles is lower than their interaction potential, which depends on van der Waals attraction and Born repulsion forces (Narsimhan and Ruckenstein 1985). Particle morphology plays an important role on the clustering process, and this information is necessary to build a realistic model for particle formation.

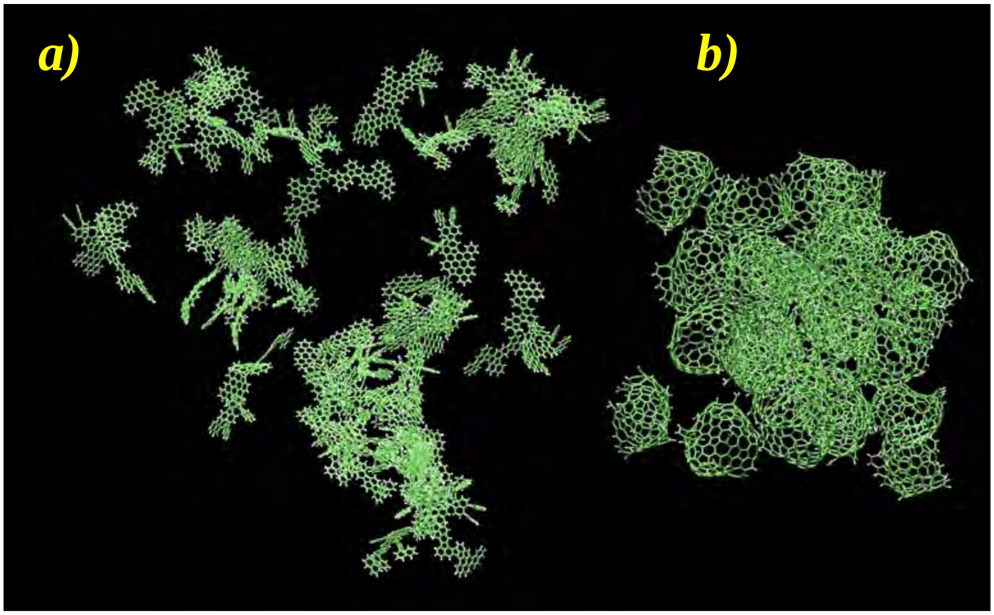


Figure 16. Soot particle morphology: a) sheet like and b) cluster. Image courtesy of Angela Violi (University of Michigan).

Soot modeling approaches present in the literature (Kazakov and Frenklach 1998; Singh et al. 2006; Hall et al. 1997; Patterson and Kraft 2007) are not suitable frameworks for including morphology-dependent nucleation, surface growth, and agglomeration processes. Novel Monte Carlo or molecular dynamics (Violi 2004; Izvekov and Violi 2005; Violi and Venkatnathan 2006) calculations have been developed to bridge the time scales in soot formation (Chung and Violi 2007). This approach traces out trajectories of soot particle growth that, with appropriate sampling, can lead to representations of soot particle shapes and distributions.

To extract realistic information on the formation of particles, multiple independent simulations of the Atomistic Model for Particle Inception (AMPI) code need to be conducted to obtain statistically significant averages. Preliminary studies have shown the need of 10^8 calculations per point to obtain convergence on particle formation with an average diameter of 4 to 5 nm. In addition, for realistic predictions of soot formation, soot clusters of size approaching 1 μm are needed, resulting in a huge increase of the number of realizations. Simulating such a large system of nanoparticles is already well beyond the range of current petaflop computing systems. However, with exascale computing, scientists can begin to approach these requirements.

Current computation on petascale machines addresses the formation, growth, and destruction of PAHs, nanoparticles, and soot during combustion. The interaction between PAHs and particles is generated by AMPI. The system size is reduced by using a high density and neglecting the majority of gaseous species, except for a few critical ones for computational feasibility. The current methodology includes molecular dynamics simulation with an empirical force field, and a combination of molecular dynamics simulation and the kinetic Monte Carlo method (AMPI). The current size of the problem that can be simulated is approximately 1000 to 10,000 molecules per system.

It will be possible on a 20 petaflop machine to investigate the formation, growth, and destruction of PAHs, nanoparticles, and soot during combustion with realistic density and gaseous concentrations. A reactive potential will be used instead of the empirical force field to catch some aspects of the chemical process. The methodology will include molecular dynamics simulation with a reactive force field and a combination of molecular dynamics simulation and the kinetic Monte Carlo method (AMPI). The size of the problem that could be simulated is approximately 5000 to 50,000 molecules per system.

Finally, on an exascale machine, full-scale molecular dynamics simulation with an *ab-initio* force field would be feasible. It would be possible to investigate the combination of physical and chemical processes affecting nanoparticle and soot-formation processes. The methods used would include *ab-initio* molecular dynamics simulation where the size of the affordable problem would be greater than 1000 molecules (depending upon the performance of the quantum potential).

Computational Challenges in Geosciences

As reviewed in the Basic Energy Sciences report on *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems* (DOE 2007b), the challenge of meeting global energy needs while reducing emissions of greenhouse gases to the atmosphere requires fundamental scientific advances in the geosciences. Strategies for carbon sequestration and containment of the waste materials generated by expanded use of nuclear energy inevitably involve different forms of subsurface storage. Outstanding fundamental questions must be addressed to understand and predict how mineral formations will perform as such storage systems over the envisioned long-application time scales.

Dynamical modeling on exascale platforms has the potential to revolutionize research addressing scientific grand challenges in the geosciences. New modeling strategies for predicting geochemical and geophysical processes and properties at the fundamental scale are needed to analyze long-term storage of greenhouse gases and nuclear waste. In addition, these strategies will likely be able to provide important new understandings of the properties of complex materials found in the earth’s core. Most geochemical processes are dependent on chemistry processes that occur on time and length scales related to the atomic structure (time scales of 10 to 100 picoseconds and length scales of tens of nanometers) of the system, but are observed on much larger time and length scales (e.g., minutes to tens of years, and inches to miles). These events contribute to processes important to the transport of toxic species, the formation of soils, the isolation of nuclear waste products, and carbon dioxide sequestration in mineral formations. While there is significant averaging involved in reducing the dimensionality and coarsening time resolution in these problems, the specificity of the atomic-level chemistry is evident and essential to predicting the behavior of the system at larger scales.

Current Status

At the finest scale, interactions between atoms in geochemical systems typically reflect complex many-body chemistry. To capture this behavior in a predictive manner, it is generally necessary to calculate forces using *ab initio* theory. These forces may be used to provide a predictive dynamical model on the time scale of molecular motion, either by using quantum mechanical potential evaluations to develop analytical interaction potentials or by using *ab initio* force calculations on the fly in a dynamical algorithm (*ab-initio* molecular dynamics [AIMD]). The systems of interest are often defected on an atomic scale or are amorphous. Large numbers of atoms are therefore required to accurately represent the structural features. The requirements of large system sizes and dynamical information lead to an extremely computationally intensive problem.

For many applications, it is becoming clear the lower levels of exchange correlation potentials presently used in most AIMD simulation software are unable to reliably predict the properties of many materials relevant to geochemistry. Higher levels of exchange-correlation potential that are augmented with some fraction of exact exchange (hybrid-density functional theory [DFT]) are therefore needed. Examples of interest to the DOE Geosciences Research Program include charge localization in transition elements with tightly bound *d* electrons in oxide materials (see Figure 17 [Bylaska et al. 2009]), the underestimation of reaction barriers and band gaps in solids, and accurate predictions of spin structure of solids and nanoparticles. Considerable progress has been made in recent years in developing AIMD methods (Marx and Hutter 2000) tailored to treat actinide and geochemical problems for system sizes up to ~1000 atoms for tens of picoseconds, including very efficient implementations of exact exchange, spin-orbit, AIMD/molecular mechanics (MM), and new parallel algorithms that scale to +10,000 CPUs. Simulations using these approaches have been able to produce results that are in remarkable agreement with measured data without the need to develop complex phenomenological descriptions of atomic interactions that have limited predictive capabilities.

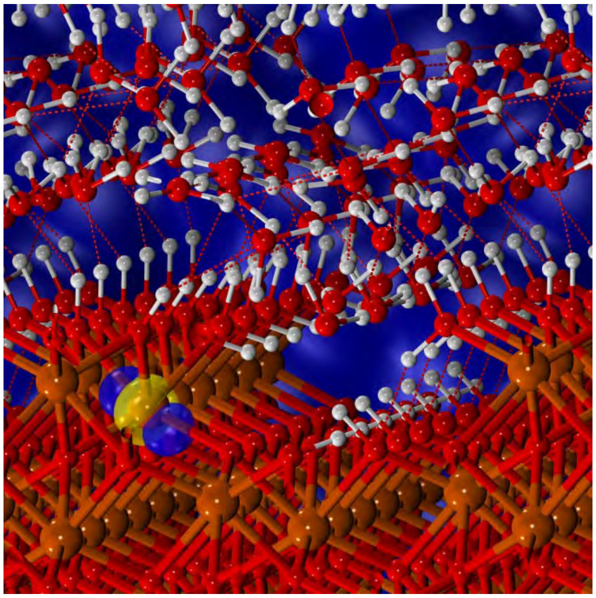


Figure 17. Illustration of a localized electron (i.e., polaron) on the surface of hematite calculated with a higher and more expensive level (e.g., hybrid DFT) of AIMD. Lower levels of AIMD will predict a delocalized electron. Image courtesy of Eric Bylaska (Pacific Northwest National Laboratory).

A more difficult problem with the DFT method is that long-range, nonbonded (van der Waals) interactions are not included formally in the theory. These interactions dominate many problems of interest to subsurface modeling. They can be treated by using high-accuracy molecular orbital-based methods; e.g., MP2, or Coupled-Cluster with Single and Double and Perturbative Triple excitations CCSD(T) (Bartlett 2005), or quantum Monte Carlo methods (Grossman and Mitas 2005). While quantum mechanics (QM)/MM techniques may broaden their applications to much more complex systems,[6] these methods are currently too expensive.

Even with optimistic projections of improvements in performance of first-principle simulation tools, the time scales required to analyze many geochemical processes may be several orders of magnitude longer than can be achieved directly by molecular-dynamics (MD) simulation. Strategies must be developed to extend the time frames of simulations while retaining the chemical specificity of the materials involved.

An effective way to extend time scales, while retaining an atomistic level of description, is to introduce rare-event methods. In these approaches, it is presumed the important changes in the system are dominated by the rare occurrence of single concerted events (e.g., chemical reactions). There are a number of ways to search for these rare events. However, most of these have been designed for problems with few degrees of freedom. One class of methods accelerates or makes more efficient the exploration of phase space, either by using higher temperature dynamics or by modifying the energy landscape so that rare events become more probable (Voter et al. 2002). This class of methods has the advantage that local minima in the system do not have to be determined before the search starts. In another class of methods, it is presumed that the local minima are known (very often this is the case in chemical reactions with known mechanisms), and the focus of the method is on determining the barrier to transition. There are several algorithms for doing this, such as the Nudged Elastic Band (NEB) method (Henkelman and Jonsson 2000). These methods work well for systems with few degrees of freedom. However, in a noisy system with many degrees of freedom, a method of averaging out unimportant environmental variations in the structure is necessary.

While atomic detail is an essential starting point, averaged (thermodynamic) behavior is required for practical long-term prediction. In geosciences, equations of state (EOS) are used to summarize the averaged behavior at the atomic level by providing thermodynamic potentials and related kinetic properties as a function of pressure, temperature, and composition that are required in higher level predictive tools (e.g., reactive flow simulators). While the development of EOS has been a topic of research for many years (Christov and Moller 2004; Felmy and Rai 1999; Pitzer 1987; Pople 1954; Weare 1987), adequate EOS for many of the key mixtures encountered in storage applications are not available. Obviously, these equations must incorporate the yet-to-be-discovered behavior of the complex systems that will be encountered in these storage problems. Unfortunately, because present EOS methods are poorly based in theory, they do not provide a very large range of extrapolation or interpolation and are highly dependent on the availability of data.

Basic Science Challenges and Research Needs

While the state of the art in dynamical simulations in the geosciences has advanced enormously over the past decade, significant outstanding challenges must be addressed to exploit these methods in predicting the properties of complex minerals and fluids as well as mineral-fluid interfaces. Advances in this area are critical to predicting the performance of subsurface storage systems in the context of carbon sequestration and nuclear energy. The associated scientific and computational challenges form the context for the panel members' recommendation of a PRD in "Computation for the Geosciences." Scientific grand challenges in this area include predicting structural, elastic, thermodynamic, and transport in complex multicomponent and multiphase minerals and fluids, as well as processes at mineral-fluid interfaces. The associated computational challenge of the simulation of such systems is to predict their behavior for very large length and time scales while retaining chemical information from the atomic level.

A key computational need is the continued improvement of the efficiency of present methods based on DFT. In the realm of computational mineral physics, such advances will facilitate applications of relatively modest AIMD simulations to investigate the properties of minerals in a wide range of pressures, temperatures, chemical compositions, atomic configurations (in the case of solid solutions), and strains (in the case of elasticity). Such studies involve computational studies with high-throughput parameter sampling requiring ~10^4 small- to medium-scale first-principles parallel calculations, each one using ~10^2

to 10^3 processors. These studies are well suited for exascale platforms, but equally well suited for distributed environments because these runs are decoupled in different stages of the calculations. Melt and transport (mass, energy, and charge) properties, such as viscosity, radiative and conductive heat transport, and ionic diffusivity, are larger scale calculations that will need to be addressed in variable ranges of pressure, temperature, and composition as well.

In addition, new higher level approximations to the solution of the Schrödinger equation will be required to provide quantitative estimates of the geochemical processes involved in waste mobilization and migration. A critical research area is the development of higher levels of approximation for the electronic Schrödinger equation that can be used with dynamic methods in a computationally efficient manner. Until recently, it was infeasible to contemplate such computations. However, as the exaflop milestone is approached, scientists can think about coping with the high computational costs through vastly increased parallelism.

New methods need to be developed that search for reaction pathways, including minima in noisy, many-dimensional environments. These are required to extend dynamical simulations to much larger time scales. An example of such a method combines a minimum free-energy path with finding and sampling to average out the environmental noise (Weinan et al. 2003). Given rare event paths, methods may be introduced to calculate the free energy and estimate the reaction rate using absolute rate theory. With these rate estimates, much longer time scales can be simulated using kinetic Monte Carlo dynamics (Voter et al. 2002).

A key synergistic role of theory will be to inform the development of EOS (see Gubbins 1985 for a review). Appropriate equations need to be developed that can more efficiently describe the chemical and physical properties of gaseous, liquid, and solid mixtures. Nevertheless, reliable EOS will, for the foreseeable future, have to be heavily based on experimental data and will require inverse modeling techniques and associated uncertainty assessments. The scientific outcome of these computational and associated technical developments includes higher fidelity modeling and inference of planetary structure and dynamics with associated uncertainty assessments. These, in turn, will be useful for providing spatial and time assessments to make predictions and manage energy production (e.g., geothermal) and in environmental quality (e.g., sequestration of carbon dioxide and radioactive wastes in geological formations).

Thermo-Mechanical Behavior of Materials Under Extreme Conditions

As reviewed in the BES report on *Basic Energy Needs for Materials under Extreme Environments* (Wadsworth et al. 2008), future energy technologies will require revolutionary new materials to be designed and optimized for service under extreme conditions. Many advanced energy technologies require materials that can withstand substantially higher temperatures and stresses in the presence of highly reactive environments, high electromagnetic fields, and/or sustained radiation fluxes.

Discovering and designing new materials for such applications will require expanded basic research to develop fundamental understanding of the mechanisms underlying the mechanical response and stability of materials under extreme thermomechanical and chemically reactive (corrosive) environments. This, in turn, requires breakthroughs in fundamental understanding of the dynamics of individual defects under conditions of high stresses, temperatures, and chemical driving forces. This also includes the collective behavior resulting from the interactions between large ensembles of such defects with each other and with the internal grain boundaries and heterophase interfaces that are ubiquitous in the microstructures of advanced structural materials. Such scientific understanding is needed, not only to help guide the selection of optimal compositions and microstructural elements in materials design, but also to discover ways in which new highly nonequilibrium processing routes can be exploited in materials synthesis.

Dynamical simulation methodologies that can exploit extreme-scale computing platforms offer a framework for greatly expanding current fundamental understanding of the properties of materials under thermomechanical and mechanochemical extremes, as well as for aiding in the design of new materials for such applications. Simulations in this area will require advances in the development of atomistic, mesoscale, and continuum techniques for modeling plasticity, crack propagation and fracture, and multiscale approaches for integrating these methods in the modeling of complex polycrystalline and multiphase materials. The current state of the art and future challenges underlying the applications of such methods in the context of materials under extreme environments are summarized below.

Current Status

Dynamical simulations have been applied extensively in the study of thermomechanical properties of materials. At the atomic scale, first-principle calculations based on electronic DFT and classical MD simulations have been applied in studies of a range of properties, including the intrinsic cohesive strength of bulk crystals and interfaces, dislocation core structures and mobilities, point-defect formation energies and diffusion, and fracture and defect interactions (see Mishin et al. 2010 for a recent review). With increases in computer power, such simulations have been extended most recently to tackle larger systems, such as nanocrystalline materials, longer time scale phenomena (e.g., involving lower strain rates), and extrinsic effects arising from impurities. As a specific example representing the current state of the art in such simulations, a hierarchy of atomistic simulation methods based on MD have been developed that are scalable on petaflops parallel supercomputers and are expected to scale on future exaflops architectures (i.e., metascalable)—recent benchmark tests have achieved parallel efficiency well over 0.95 on 212,992 IBM BlueGene/L processors at Lawrence Livermore National Laboratory for 218 billion-atom MD, 1.7 billion-atom reactive force field (ReaxFF) MD, and 19.2 million-atom (1.68 trillion electronic-degrees-of-freedom) DFT-based quantum-mechanical MD simulations (Normura et al. 2009). An example of production runs employing such simulations is shown in Figure 18, taken from a 48-million-atom ReaxFF MD simulation on 65,536 IBM BlueGene/P processors at Argonne National Laboratory, to study embrittlement induced by sulfur segregation of nickel grain boundaries, which is relevant in the context of the design of corrosion-resistant materials for next-generation nuclear reactors.

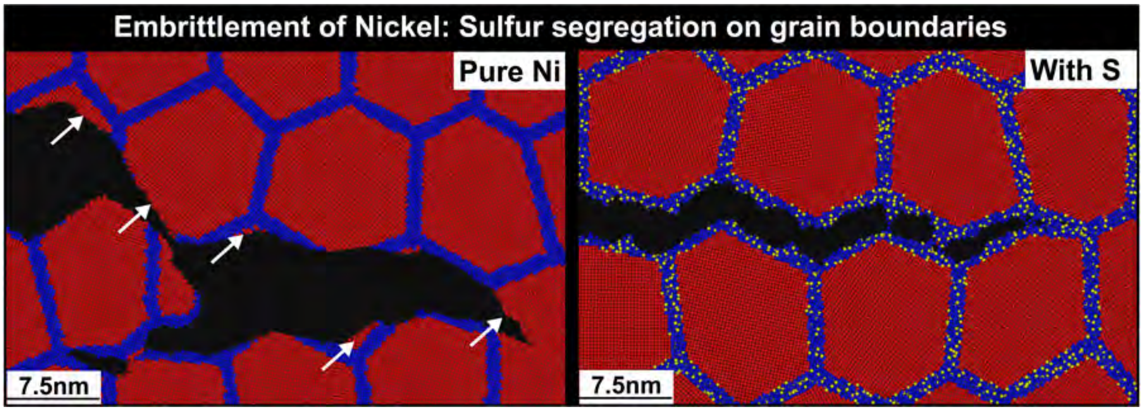


Figure 18. Close-ups of fracture simulations for nanocrystalline nickel without and with amorphous sulfide grain-boundary phases, obtained from a 48-million-atom ReaxFF-MD simulation. Red, blue, and yellow colors represent nickel atoms inside grains (>0.5 nanometers from grain boundaries), nickel atoms within 0.5 nm from grain boundaries, and sulfur atoms, respectively. The figure shows a transition from ductile, transgranular tearing to brittle, intergranular cleavage. White arrows point to transgranular fracture surfaces. Image courtesy of Priya Vashishta (University of Southern California).

Despite this important progress, significant challenges remain in extending atomistic simulations to the much larger length and time scales required to predict macroscopic thermo-mechanical properties in many engineering materials. For the simulation of such properties, complementary coarse-grained techniques are indispensable. At the mesoscopic and continuum scales, dynamical simulation methods include discrete dislocation dynamics simulations (Bulatov and Cai 2006), phase-field models for plasticity and fracture (Wang and Li 2010; Spatschek et al. 2007) and more conventional continuum finite-element approaches (e.g., Wang et al. 2009; Qidwai et al. 2009). Recently, considerable effort has been invested to use such simulation techniques to quantify the impact of materials microstructure on thermo-mechanical response. The focus of much of this work has been to go beyond simple average properties such as plastic strength and to examine higher moments (e.g., “hot-spots” in a complex microstructure), which are particularly relevant to response under extreme conditions. Major challenges in such simulations are associated with 1) the need for very fine mesh densities to numerically resolve highly nonuniform stress, strain, and thermal fields; and 2) the need to compute the properties of measured microstructures and to build in realistic response functions for relevant interfaces. Although current three-dimensional experimental materials characterization produces images of the order of 5123 voxels, scientists can expect to be working with 20,483 size images in the near future (Suter et al. 2008).

For problems where there is a clear separation of length and time scales, information from atomic-scale simulations can be incorporated for developing coarse-grained mesoscale models to form a “hierarchical” multiscale modeling framework. For some classes of problems related to the thermomechanical properties of materials, phenomena at different length scales are intimately coupled such that “concurrent” multiscale approaches are required. Examples can be found in the modeling of fracture (e.g., Kermode et al. 2008; Ogata et al. 2001). As a specific example, the above-mentioned metascalable simulation framework has been used to develop multiscale QM/MD/finite element (FE) simulations in which divide-and-conquer DFT calculation are embedded within MD simulations only when and where high accuracy is required. MD simulation in turn is embedded in FE calculation (Ogata et al. 2001). A multiscale QM/MD simulation has been performed for the high-energy beam oxidation of silicon on a grid of six supercomputer centers in which the number of processors changed dynamically on demand, and computations were automatically migrated between remote supercomputers in response to unexpected faults.

Basic Science Challenges and Research Needs

The basic science challenges for materials under extreme environments are associated with the need to greatly extend current understanding of stability and mechanical response under extreme conditions of temperature, stress, and reactive environments. This requires an atomistic to mesoscale understanding of material damage from void and crack nucleation, defect generation, stress-strain response, and defect dynamics under far-from-equilibrium conditions. The computational challenges in this area are associated with a need to develop, implement, and apply multi-core algorithms that can fully exploit computational platforms consisting of hundreds of thousands of nodes with hundreds of cores per node with dynamic load balancing, data management, and visualization.

These scientific and computational challenges form the context for the panel members' recommendation for a PRD on computation of materials under extreme environments. Research in this area should address the theoretical, methodological, and computing challenges required to extend and integrate molecular dynamics simulations, electronic structure and electron dynamics calculations, force field development, and mesoscale modeling for applications involving large chemical and mechanical driving forces. This will require substantial rethinking and development to extend current state-of-the-art methods to exascale computing platforms. However, such rethinking and development will be crucial to the near-term progress of all associated research. Equally important for longer-term breakthroughs will be to develop new computational methods and algorithms with more favorable asymptotic scaling—e.g., robust and general $O(\mathrm{N})$ methods will become increasingly important. Successfully accomplishing all of the above will depend critically upon the development and availability of improved theory, robust and scalable numerical libraries, and hardware for larger memory bandwidth applications. To guide advances in this area, there is also a critical need for community codes and development projects targeting multiscale-materials simulations specifically.

Developing materials for applications under extreme environments have potential impacts on a broad range of energy science fields, including energy efficiency, energy generation, and ultrafast experimental characterization. The time scale for impact of the PRD outlined in this section is anticipated to be as short as 5 to 10 years. This time scale for impact is expected to be accelerated by parallel developments of engineering scale codes being pursued within the framework of Integrated Computational Materials Engineering (ICME), as documented in a recent National Materials Advisory Board report (Committee on Integrated Computational Materials Engineering, National Research Council 2008). The research in this PRD would address a number of shortcomings in existing materials design software required to extend the ICME approach to developing materials for applications under extreme environments.

Materials for Nuclear Energy

The vital role of computational materials modeling in basic research for nuclear energy was detailed in the recent Basic Energy Sciences report, *Basic Research Needs for Advanced Nuclear Energy Systems* (Roberto et al. 2006). A grand challenge is to model the complex microstructure evolution processes taking place in fuel and cladding materials under the aggressive radiation environments characteristic of nuclear reactors. The function of the fuel is to produce heat through fission. This heat must be transferred through and out of the fuel, crossing through a number of interfaces, for eventual power conversion. Fission processes produce high levels of atomic-displacement damage, leading to the generation of solid and gaseous fission products. These microstructural changes are responsible for the continuous deterioration of the fuel's thermomechanical performance; these changes also give rise to fuel swelling, leading to severe mechanical interactions with the cladding that impact its integrity and, ultimately, its ability to retain harmful fission products.

Apart from large empirical databases, a predictive materials-science basis that connects "structure" across all the relevant length- and time scales with the thermomechanical behavior of the fuel and its cladding does not currently exist. What is particularly lacking is a comprehensive multiscale, multiphysics model that captures how defect generation and evolution, as well as microstructure development during irradiation, affects thermomechanical performance. The grand challenge is to tie the fundamental microstructural damage mechanisms to the macroscopic degradation of the fuel components through a detailed multiscale understanding of the complex processes of dynamical microstructure evolution occurring in aggressive irradiation environments.

Current Status

The past two decades have witnessed significant developments in the modeling of microstructure evolution dynamics and the associated impact of microstructural changes on thermomechanical properties. The previous section, "Materials for Nuclear Energy," includes a review of the current status for incorporating microstructural information in the modeling of thermomechanical properties (see also Roters et al. 2010)—this section focuses on dynamical modeling of microstructure evolution.

The most widely used approach in simulating microstructure evolution dynamics involves formulating "phase-field" models in which microstructural elements (e.g., grains, precipitates, voids) are described by field variables that evolve under either conserved or nonconserved dynamics in response to generalized driving forces described by gradient-thermodynamic formalisms. Predictive models require knowledge of bulk and interfacial free energies for relevant stable and metastable phases, as well as bulk diffusivities and interface mobilities. These parameters are often difficult to measure directly from experiment, and in such cases, they must be derived from atomistic calculations (Mishin et al. 2010). Phase-field modeling has been applied in studies of the dynamics of grain and phase microstructures accompanying a variety of phase transformation or deformation processes (Wang and Li 2010; Steinbach 2009). To date, however, radiation effects on microstructural evolution have been modeled in only a relatively limited number of cases (see Ye et al. 2006; Rokkam et al. 2009; Stan 2009). Such studies require, in addition to the bulk and interfacial thermodynamic parameters listed above, knowledge of the highly nonequilibrium atomistic processes associated with defect generation induced by a radiation flux.

Basic Science Challenges and Research Needs

The final PRD relates to modeling of materials for nuclear energy. The main scientific challenge associated with this PRD is *the development of a comprehensive understanding of microstructure dynamics under irradiation*. This theme captures and builds on the significant computational advances (described above) in understanding microstructural processes and elucidating the underlying mechanisms across relevant length and time scales involved.

A vision for how a predictive nuclear fuel modeling capability can be developed by an atomistically informed mesoscale approach that, in turn, is linked to the continuum level is summarized in Figure 19.

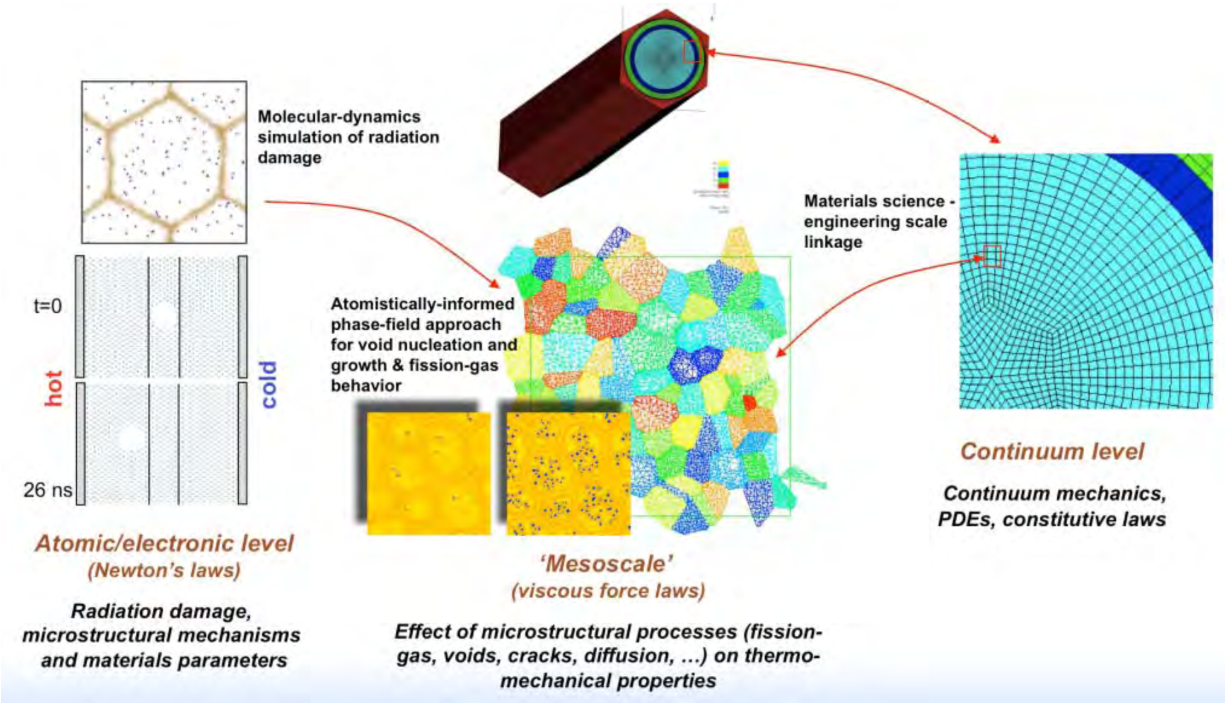


Figure 19. Hierarchical multi-scale simulation approach for materials-physics–based prediction of the performance, degradation, and lifetime of nuclear materials. Image courtesy of Dieter Wolf (Argonne National Laboratory).

The approach requires bridging between three distinct time- and length-scale regimes, each involving distinct technical approaches and associated computational challenges. Methodological challenges include the need to develop the following:

1. Atomic-scale interatomic-potential models capable of describing the complex chemistry of actinide-based materials

2. Refined algorithms for atomistic simulations of radiation-induced damage evolution occurring on collision to diffusion time scales

3. Predictive mesoscale models incorporating irradiation effects through Langevin "noise" source terms

4. Efficient homogenization schemes for incorporating microstructure-related variations in materials properties into continuum models of bulk thermomechanical properties.

Computational challenges include the need to develop massively parallel algorithms to numerically solve phase-field equations together with the corresponding free-energy functional that captures all the coupled, simultaneously occurring microstructural processes. This includes all of the relevant kinetic phenomena associated with atomic transport, alloy-species redistribution, Soret effect, etc.

Historically, fuel performance modeling has employed engineering-scale calculations that use a combination of empirically derived models and constitutive equations closed by material property data. It is anticipated that the development and experimental validation of the type of computational modeling approach described in this PRD would have immediate impact on the development of a materials-physics based capability to predict the performance and lifetime of nuclear materials in general and nuclear fuel in particular.

CONCLUSIONS

In conclusion, the role of “dynamics” in materials simulations goes beyond time dependence—in many cases, it provides the connection between the atomistic scale and macroscopic properties. Thus, thermodynamic properties, such as free energy or entropy, and mechanical properties, such as Young’s modulus or stiffness, are often calculated by methods termed “dynamical.” This is in addition to the explicitly dynamical properties, such as chemical reaction rates. This section has shown that there are many opportunities to expand on the calculation properties critical to chemistry, materials, and geosciences by using extreme-scale computing.

REFERENCES

Bachu S. 2008. “CO_2 Storage in Geological Media: Role, Means, Status and Barriers to Deployment.” *Progress in Energy and Combustion Science* 34(2): 254-273.

Bartlett RJ. 2005. “How and Why Coupled-Cluster Theory Became the Pre-Eminent Method in *Ab-Initio* Quantum Chemistry: Theory and Application of Computational Chemistry.” Chapter in *Theory and Applications of Computational Chemistry: The First Forty Years*, eds C Dykstra, G Frenking, K Kim, and G Scuseria. Elsevier, Amsterdam, p 1191.

Bartlett, RJ. 1981. “Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules.” *Annual Reviews of Physical Chemistry* 32:359-401.

Bulatov VV and W Cai. 2006. *Computer Simulations of Dislocations*. Oxford University Press, New York.

Bylaska EJ, K Glass, D Baxter, S.B. Baden, and JH Weare. 2009. “Hard Scaling Challenges for *Ab Initio* Molecular Dynamics Capabilities in NWChem: Using 100,000 CPUs per Second.” *Journal of Physics: Conference Series* 180:Art. No. 012028.

Christov C and N Moller. 2004. “A Chemical Equilibrium Model of Solution Behavior and Solubility in the H-Na-K-Ca-OHCl-HSO_4-SO_4-H_2O System to High Concentration and Temperature.” *Geochimica Et Cosmochimica Acta* 68(18):3717-3739.

Chung SH and A Violi. 2007. “Insights on the Nanoparticle Formation Process in Counterflow Diffusion Flames.” *Carbon* 45(12):2400-2410.

Cizek J. 1966. “On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods.” *Journal of Chemical Physics* 45(11):4256-4266.

Cohen AJ, P Mori-Sanchez, and WT Yang. 2008. “Insights into Current Limitations of Density Functional Theory.” *Science* 321:792-794.

Committee on Integrated Computational Materials Engineering, National Research Council. 2008. *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*. The National Academies Press, Washington, D.C.

Corkum PB and F Krausz. 2007. “Attosecond Science.” *Nature Physics* 3:381-387.

Cramer CJ and DG Truhlar. 2009. “Density Functional Theory for Transition Metals and Transition Metal Chemistry.” *Physical Chemistry Chemical Physics* 11:10757-10816. Art. No. 10757. DOI: 10.1039/b907148b.

Cramer CJ. 2002. *Essentials of Computational Chemistry*. John Wiley & Sons, New York.

Dai X, SY Savrasov, G Kotliar, A Migliori, H Ledbetter, and E Abrahams. 2003. “Calculated Phonon Spectra of Plutonium at High Temperatures.” *Science* 300(5621):953-955. DOI:10.1126/science.1083428.

DARPA (Defense Advanced Research Projects Agency). 2008. *ExaScale Computing Study: Technology Challenges in Achieving Exascale Systems*. Prepared by the Exascale Study Group for the Defense Advanced Research Projects Agency Information Processing Techniques Office, and the Air Force Research Laboratory, Washington, D.C. Accessed June 1, 2010, at http://users.ece.gatech.edu/~mrichard/ExascaleComputingStudyReports/exascale_final_report_100208.pdf.

DOE. 2004a. *Final Report Second DOE Workshop on Multiscale Problems - Broomsfield, Colorado July 20-22, 2004*. U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.math.colostate.edu/~estep/doe_multiscale/IIDOEWMP_final_report_v8.pdf.

DOE. 2004b. *Basic Research Needs for the Hydrogen Economy*. U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.er.doe.gov/bes/reports/files/NHE_rpt.pdf.

DOE. 2007a. *Basic Research Needs for Electrical Energy Storage*. U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.er.doe.gov/bes/reports/files/EES_rpt.pdf.

DOE. 2007b. *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems.* U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.er.doe.gov/bes/reports/files/GEO_rpt.pdf.

DOE. 2007c. *Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels: Report of the Basic Energy Sciences Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels*. U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.er.doe.gov/bes/reports/files/CTF_rpt.pdf.

DOE. 2008. *Basic Research Needs: Catalysis for Energy*. PNNL-17214, U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C. Accessed April 1, 2010, at http://www.er.doe.gov/bes/reports/files/CAT_rpt.pdf.

Dongarra J, P Beckman, and T Moore, et al. 2010. *International Exascale Roadmap 1.0 Software Project.* UT-CS-10-654, Electrical Engineering and Computer Science, University of Tennessee, Knoxville, Tennessee. Accessed July 1, 2010, at http://www.exascale.org/mediawiki/images/4/42/IESP-roadmap-1.0.pdf.

Du M-H and SB Zhang. 2009. “Impurity-Bound Small Polarons in ZnO: Hybrid Density Functional Calculations.” *Physical Review B* 80:115217.

Fiedler SL, S Izvekov, and A Violi. 2007. “The Effect of Temperature on Nanoparticle Clustering.” *Carbon* 45(9):1786-1794.

Felmy AR and D Rai. 1999. "Application of Pitzer's Equations for Modeling the Aqueous Thermodynamics of Actinide Species in Natural Waters: A Review." *Journal of Solution Chemistry* 28(5):533-553.

Filhol JS and M Neurock. 2006. "Elucidation of the Electrochemical Activation of Water over Pd by First Principles." *Angewandte Chemie International Edition* 45:402-406.

Fischer H and W Pschunder. 1973. *Proceedings of the 10th IEEE Photovoltaic Specialists Conference*, Palo Alto, California, p. 13. Institute of Electrical and Electronics Engineers, New York.

Foulkes WMC, L Mitas, RJ Needs, and G Rajagopal. 2001. "Quantum Monte Carlo Simulations of Solids." *Reviews of Modern Physics* 73(1):33-83.

Gagliardi L and BO Roos. 2005. "New Look for Chemical Bonds." *Nature* 433:848.

Geisz JF, DJ Friedman, JS Ward, A Duda, WJ Olavarria, TE Moriarty, JT Kiehl, MJ Romero, AG Norman, and KM Jones. 2008. "40.8% Efficient Inverted Triple-Junction Solar Cell With Two Independently Metamorphic Junctions." *Applied Physics Letters* 93:123505.

Grossman JC and L Mitas. 2005. "Efficient Quantum Monte Carlo Energies for Molecular Dynamics Simulations." *Physical Review Letters* 94(5): Art. No. 056403. DOI:10.1103/PhysRevLett.94.056403.

Gubbins KE. 1985. "Theory and Computer-Simulation Studies of Liquid-Mixtures." *Fluid Phase Equilibria* 20:1-25.

Hall RJ, MD Smooke, and MB Colket. 1997. "Predictions of Soot Dynamics in Opposed Jet Diffusion Flames." In Chapter 8 of *Physical and Chemical Aspects of Combustion*, eds FL Dryer and RF Sawyer, Gordon and Breach Science Publishers, India.

Hammond BJ, WA Lester, and PJ Reynolds. 1994. *Monte Carlo Methods in Ab Initio Quantum Chemistry*. World Scientific Publishing Company, Singapore.

Henkelman G and H Jonsson. 2000. "Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points." *Journal of Chemical Physics* 113(22):9978-9985.

Heremans JP, V Jovovic, ES Toberer, A Saramat, K Kurosaid, A Charoenphakdee, S Yamanaka, and GJ Snyder. 2008. "Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States." *Science* 321:554-557. DOI:10.1126/science.1159725.

Homan KH and HG Wagner. 1968. "Chemistry of Carbon Formation in Flames." *Proceedings of the Royal Society London Series A, Mathematical and Physical Sciences* 307:141-152.

ITRS. 2007. *International Road Map for Semiconductors 2007 Edition*. Accessed April 1, 2010, at http://www.itrs.net/Links/2007ITRS/Home2007.htm.

Izvekov S and A Violi. 2005. "Systematic Coarse-Graining of Nanoparticle Interactions in Molecular Dynamics Simulation." *Journal of Physical Chemistry B* 109(36):17019-17024.

Izvekov S and A Violi. 2006. “A Coarse-Grained Molecular Dynamics Study of Carbon Nanoparticle Aggregation.” *Journal of Chemical Theory and Computation* 2(3):504-512.

Jones RO and O Gunnarsson. 1989. “The Density Functional Theory Formalism, its Applications and Prospects.” *Reviews of Modern Physics* 61(3):689-746. DOI:10.1103/RevModPhys.61.689.

Kazakov A and M Frenklach. 1998. “Dynamic Modeling of Soot Particle Coagulation and Aggregation: Implementation With the Method of Moments and Application to High-Pressure Laminar Premixed Flames.” *Combustion and Flame* 114:484-501.

Kermode JR, T Albaret, D Sherman, N Bernstein, P Gumbsch, MC Payne, G Csanyi, and A De Vita. 2008. “Low-Speed Fracture Instabilities in a Brittle Crystal.” *Nature* 455(7217):1224-1227.

King RR, DC Law, KM Edmondson, CM Fetzer, GS Kinsey, H Yoon, RA Sherif, and NH Karam. 2007. “40% Efficient Metamorphic GaInP/GaInAs/Ge Multijunction Solar Cells.” *Applied Physics Letters* 90(18):183516.

Kletnieks P, A Liang, R Craciun, J Ehresmann, D Marcus, V Bhirud, M Klaric, M Hayman, D Guenther, O Bagatchenko, D Dixon, B Gates, and J Haw. 2007. “Molecular Heterogeneous Catalysis: A Single-Site Zeolite-Supported Rhodium Complex for Acetylene Cyclotrimerization.” *Chemistry – A European Journal* 13(26):7294–7304. DOI: 10.1002/chem.200700721.

Kolorenč J and L Mitas. 2008. “Quantum Monte Carlo Calculations of Structural Properties of FeO Under Pressure.” *Physics Review Letters* 101(18): Art. No. 185502.

Kotliar G and D Vollhardt. 2004. “Strongly Correlated Materials: Insights from Dynamical Mean-Field Theory.” *Physics Today* 57 (3):53.

Kotliar G, SY Savrasov, K Haule, VS Oudovenko, O Parcollet, and CA Marianetti. 2006. “Electronic Structure Calculations with Dynamical Mean-Field Theory.” *Reviews of Modern Physics* 78(3):865-951. DOI:10.1103/RevModPhys.78.865.

Kreuer KD. 2001. “On the Development of Proton Conducting Polymer Membranes for Hydrogen and Methanol Fuel Cells.” *Journal of Membrane Science* 185:29-39.

Maier T, M Jarrell, T Pruschke, and MH Hettler. 2005. “Quantum Cluster Theories.” *Reviews of Modern Physics* 77(3):1027-1080. DOI:10.1103/RevModPhys.77.1027.

Marianetti CA, K Haule, G Kotliar, and MJ Fluss. 2008. “Electronic Coherence in δ-Pu: A Dynamical Mean-Field theory Study.” *Physical Review Letters* 101(5): Art. No. 056403. DOI:10.1103/PhysRevLett.101.056403.

Marx D and J Hutter. 2000. “Ab-Initio Molecular Dynamics: Theory and Implementation.” *Modern Methods and Algorithms of Quantum Chemistry*, NIC Series, 1:301-449.

Mazziotti DA. 2006. “Elucidation of Residue-Level Structure and Dynamics of Polypeptides via Isotope-Edited Infrared Spectroscopy.” *Accounts of Chemical Research* 200 39(3):169-229.
DOI: 10.1021/ar050135f.

Mishin Y, M Asta, and J Li. 2010. "Atomistic Modeling of Interfaces and Their Impact on Microstructure and Properties." *Acta Materialia* 58:1117-1151.

Möller HJ. 1993. *Semiconductors for Solar Cells.* Artech House, Norwood, Massachusetts.

Narsimhan G and E Ruckenstein. 1985. "The Brownian Coagulation of Aerosols over the Entire Range of Knudsen Numbers Connection between the Sticking Probability and the Interaction Forces." *Journal of Colloid and Interface Science* 104(2): 344.

Nomura K, H Dursun, R Seymour, W Wang, RK Kalia, A Nakano, P Vashishta, F Shimojo, and LH Yang. 2009. "A Metascalable Computing Framework for Large Spatiotemporal-Scale Atomistic Simulations." In *Proceedings of IEEE International Parallel & Distributed Processing Symposium* (IPDPS 2009), Institute of Electrical and Electronics Engineers, Rome, Italy.

Ogata S, E Lidorikis, F Shimojo, A Nakano, P Vashishta, and RK Kalia. 2001. "Hybrid Finite-Element/Molecular-Dynamics/Electronic-Density-Functional Approach to Materials Simulations on Parallel Computers." *Computer Physics Communications* 138(2):143-154.

Oliphant N and L Adamowicz. 1993. "Multireference Couples-Cluster Method for Electronic-Structure of Molecules." *International Reviews in Physical Chemistry* 12(2):339-362.

Patterson RIA and M Kraft. 2007. "Models for the Aggregate Structure of Soot Particles." *Combustion and Flame* 151(1-2):160-172.

Pitzer KS. 1987. "A Thermodynamic Model for Aqueous-Solutions of Liquid-Like Density." *Reviews in Mineralogy* 17:97-142.

Polivka T and V Sundström. 2004. "Ultrafast Dynamics of Carotenoid Excited States−From Solution to Natural and Artificial Systems." *Chemical Reviews* 104(4):2021-2072. DOI:10.1021/cr020674n.

Pople JA. 1954. "The Statistical Mechanics of Assemblies of Axially Symmetric Molecules. 2nd Virial Coefficients." In *Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences* 221(1147):508-516.

Qidwai MAS, AC Lewis, and AB Geltmacher. 2009. "Using Image-Based Computational Modeling to Study Microstructure-Yield Correlations in Metals." *Acta Materialia* 57(14):4233-4247.

Roberto J, T Diaz de la Rubia, R Gibala, S Zinkle, JR Miller, S Pimblott, C Burns, K Raymond, R Grimes, K Pasamehmetoglu, S Clark, R Ewing, A Wagner, S Yip, M Buchanan, G Crabtree, J Hemminger, J Poate, JC Miller, N Edelstein, T Fitzsimmons, G Gruzalski, G Michaels, L Morss, M Peters, and K Talamini. 2006. *Basic Research Needs for Advanced Nuclear Energy Systems*. Report of the Workshop on Basic Research Needs for Advanced Nuclear Energy Systems, July 31-August 3, 2006. U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C.

Rokkam S, A El-Azab, P Millett, and D Wolf. 2009. "Phase Field Modeling of Void Nucleation and Growth in Irradiated Metals." *Modelling and Simulation in Materials Science and Engineering* 17(6):18.

Roos BO, Taylor, PR and Siegbahn, PEM. 1980. "A Complete Active Space SCF Method (CASSCF) Using a Density Matrix Formulated Super-CI Approach." *Chemical Physics* 48(2):157-173.

Roters F, P Eisenlohr, L Hantcherli, DD Tjahjanto, TR Bieler, and D Raabe. 2010. "Overview of Constitutive Laws, Kinematics, Homogenization and Multiscale Methods Crystal Plasticity Finite-Element Modeling: Theory, Experiments, Applications." *Acta Materialia* 58:1152-1211.

Schollwöck U. 2005. "The Density-Matrix Renormalization Group." *Reviews of Modern Physics* 77(1):259-315. DOI:10.1103/RevModPhys.77.259.

Singh J, RIA Patterson, M Kraft, and H Wang. 2006. "Numerical Simulation and Sensitivity Analysis of Detailed Soot Particle Size Distribution in Laminar Premised Ethylene Flames." *Combustion and Flame* 145(102):117-127.

Spatschek R, C Mueller-Gugenberger, E Brener, and B Nestler. 2007. "Phase Field Modeling Of Fracture and Stress-Induced Phase Transitions." *Physical Review E* 75(6): Art. No. 066111.

Stan M. 2009. "Discovery and Design of Nuclear Fuels." *Materials Today* 12:36-44.

Steinbach I. 2009. "Phase-Field Models in Materials Science." *Modeling and Simulation in Materials Science and Engineering* 17(7): Art. No. 073001.

Suter RM, CM Hefferan, SF Li, D Hennessy, C Xiao, U Lienert, and B Tieman. 2008. "Probing Microstructure Dynamics with X-Ray Diffraction Microscopy." *Journal of Engineering Materials and Technology, Transactions of the ASME* 130(2):0210071-0210075.

Taylor CD, SA Wasileski, JS Filhol, and M Neurock. 2006. "First Principles Reaction Modeling of the Electrochemical Interface: Consideration and Calculation of a Tunable Surface Potential from Atomic and Electronic Structure." *Physical Review B* 73, Art. No. 165402.

Violi A. 2004. "Modeling of Soot Inception in Aromatic and Aliphatic Premixed Flames." *Combustion and Flame* 139:279-287.

Violi A and A Venkatnathan. 2006. "Combustion-Generated Nanoparticles Produced in a Benzene Flame: A Multiscale Approach." *Journal of Chemical Physics* 125:0544302.

Voter AF, F Montalenti, TC Germann. 2002. "Extending the Time Scale in Atomistic Simulation of Materials." *Annual Review of Materials Research* 32:321-346.

Wadia C, AP Alivisatos, and DM Kammen. 2009. "Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment." *Environmental Science & Technology* 43(6):2072–2077.

Wadsworth J, GW Crabtree, and RJ Hemley, M Buchanan, R Falcone, I Robertson, J Stringer, P Tortorelli, GT Gray, M Nicol, J Lehr, SW Tozer, T Diaz de la Rubia, T Fitzsimmons, JS Vetrano, CL Ashton, S Kitts, C Landson, B Campbell, G Gruzalski, D Stevens. 2008. *Basic Research Needs for Materials under Extreme Environments*. Report of the Basic Energy Sciences Workshop for Materials Under Extreme Environments, June 11-13, 2007, U.S. Department of Energy, Office of Basic Energy Sciences, Washington, D.C.

Wang L, SR Daniewicz, MF Horstemeyer, S Sintay, AD Rollett. 2009. "Three-Dimensional Finite Element Analysis Using Crystal Plasticity for a Parameter Study of Microstructurally Small Fatigue Crack Growth in a AA7075 Aluminum Alloy." *International Journal of Fatigue* 31(4):651-658.

Wang Y and J Li. 2010. "Phase Field Modeling of Defects and Deformation." *Acta Materialia*, 58:1212-1235.

Weare JH. 1987. "Models of Mineral Solubility in Concentrated Brines with Application to Field Observations." *Reviews in Mineralogy* 17:143-176.

Weinan E, B Engquist, and ZY Huang. 2003. "Heterogeneous Multiscale Method: A General Methodology for Multiscale Modeling." *Physical Review B* 67(9): Art. No. 092101.

Wong J, M Krisch, DL Farber, F Occelli, AJ Schwartz, TC Chiang, M Wall, C Boro, and RQ Xu. 2003. "Phonon Dispersions of FCC δ-Plutonium-Gallium by Inelastic X-Ray Scattering." *Science* 301(5636):1078-1080. DOI: 10.1126/science.1087179.

Ye J, P Bellon, and RA Enrique. 2006. "Nanoscale Patterning of Composition and Chemical Order Induced by Displacement Cascades in Irradiated Alloys." *Nuclear Instruments and Methods in Physics Research B* 242(1-2):265-269.

Yoo CS, R Sankaran, and JH Chen. 2010a. "3D Direct Numerical Simulation of a Turbulent Lifted Hydrogen/Air Jet Flame in Heated Coflow: Stabilization and Structure." *Journal of Fluid Mechanics* 460:453-481.

Yoo CS, ES Richardson, R Sankaran, and JH Chen. 2010b. "A DNS Study of the Stabilization Mechanism of a Turbulent Lifted Ethylene Jet Flame in Highly-Heated Coflow." *Proceedings of the Combustion Institute* (In Press).

Zhang SB. 2002. "Microscopic Origin of the Doping Limits in Semiconductors and Wide-Gap Materials and Recent Developments in Overcoming These Limits: A Review." *Journal of Physics: Condensed Matter* 14:R881.

Zhang SB, S-H Wei, and A Zunger. 1997. "Stabilization of Ternary Compounds Via Ordered Arrays of Defect Pairs." *Physics Review Letters* 78(21):4059-4062.

APPENDICES

APPENDICES

APPENDIX 1: WHERE TO FIND BASIC RESEARCH NEEDS DOCUMENTS

Abstracts of Basic Energy Sciences Workshop and Technical Reports

A full list of Basic Research Needs (BRN) workshop reports (and abstracts) sponsored by the U.S. Department of Energy's Office of Basic Energy Sciences is provided at http://www.sc.doe.gov/BES/reports/abstracts.html. Not all of the reports listed at this website are part of the BRN workshop series.

BES Basic Research Needs Reports

The 10 BRN reports, plus Energy Challenges (New Science for a Secure and Sustainable Energy Future), Grand Science Challenges (Directing Matter and Energy: Five Challenges for Science and the Imagination), and Foundational Report (Basic Research Needs to Assure a Secure Energy Future), (13 total) are at http://www.sc.doe.gov/BES/reports/list.html.

The BRN list—with shortened descriptive titles—are as follows:

- Advanced Nuclear
- Catalysis
- Combustion
- Electrical Energy Storage
- Energy Challenges
- Extreme Environments
- Foundational
- Geosciences
- Grand Science Challenges
- Hydrogen Economy
- Solar
- Solid State Lighting
- Superconductivity

Archives of BES Workshop and Technical Reports

The archives of BES workshop and technical reports are at http://www.sc.doe.gov/BES/reports/archives.html.

APPENDIX 2: WORKSHOP PROGRAM/AGENDA

Wednesday, August 12, 2009

Time	Session	Lead	Room
6:00 - 7:30 p.m.	Pre-Workshop Dinner (Organizers, Panel Leads, & Speakers)		Middlebrook

Thursday, August 13, 2009

Time	Session	Lead	Room
7:30 - 8:30 a.m.	Registration/Morning refreshments		Foyer D
8:30 - 9:30 a.m.	Opening remarks from Office of Science, BES, ASCR		Salon D
Plenary Talks			
9:30 - 10:10 a.m.	Technology and Architectures for Future Large-Scale Computing	Rick Stevens	Salon D
10:10 a.m.	General Discussion		Foyer D
10:30 - 11:10 a.m.	Parallel Algorithms for Bridging the Meso and Engineering Scales in Nuclear Fuel Performance Modeling	Dieter Wolf	Salon D
11:10 - 11:50 a.m.	Direct Numerical Simulation of Turbulent Combustion at the Extreme Scale - Opportunities and Challenges	Jacqueline Chen	
11:50 - 12:30 p.m.	Outstanding Fundamental Issues in Inorganic Photoconversion Addressable via Computations: Nanostructures, Thin-Films, and Transparent Conductors	Alex Zunger	
12:30 - 1:30 p.m.	Working Lunch: Plenary discussions and preparation for breakouts		Foyer D & Salon D
1:30 - 3:30 p.m.	Breakout Sessions		
	Correlation & Time Dependence (A)	Martin Head-Gordon	Salon B
	Correlation & Time Dependence (B)	Gabriel Kotliar	Salon C
	Photovoltaic Fundamentals	Kai-Ming Ho & Jeffrey Grossman	Salon F
	Energy Storage	Mei-Yin Chou & Michel Dupuis	Salon G
	Dynamics	Mark Asta & Carlos Simmerling	Salon H
3:30 p.m.	General Discussion		Foyer D
4:00 - 5:00 p.m.	Continue Breakout Sessions (return to breakout rooms)		
5:00 - 6:00 p.m.	Preliminary reports		Salon D
6:30 - 8:00 p.m.	Working Dinner: Organizational meetings		Salon E
8:00 p.m.	End of Day 1		

Friday, August 14, 2009

Time	Session	Lead	Room
7:30 - 8:30 a.m.	Morning Refreshments & Summary of Day 1 and Expectations for Day 2		Foyer D
Plenary Talks			
8:30 - 9:10 a.m.	Superconductivity & Electrical Energy Storage (Batteries, Hydrogen and Capacitors)	Warren Pickett	Salon D
9:10 - 9:50 a.m.	Theory and Computation for Catalysis Science	Bruce Garrett	
9:50 a.m.	General Discussion		Foyer D
10:15 - 12:15 p.m.	Breakout Sessions		
	Correlation & Time Dependence	Martin Head-Gordon & Gabriel Kotliar	Salons B & C
	Photovoltaic Fundamentals	Kai-Ming Ho & Jeffrey Grossman	Salon F
	Energy Storage	Mei-Yin Chou & Michel Dupuis	Salon G
	Dynamics	Mark Asta & Carlos Simmerling	Salon H
12:15 - 1:30 p.m.	Working lunch: Panel breakout sessions		Foyer D & Salon D
1:30 - 3:00 p.m.	Continue Breakout Sessions (return to breakout rooms)		
3:00 p.m.	General Discussion		Foyer D
Plenary Session			
3:30 - 5:30 p.m.	Presentations from Breakout Session Leaders		Salon D
6:00 - 7:30 p.m.	Working Dinner: Discussion and breakout closeouts		Salon E
7:30 p.m.	End of day 2		

Saturday, August 15, 2009

Time	Session	Lead	Room
7:30 - 8:30 a.m.	Morning Refreshments & Preparation for writing session		Foyer & Salon B
8:30 - 10:00 a.m.	Report Writing Session for Chairs, Panel Leads, and Writers		Salon B
10:00 - 10:20 a.m.	General Discussion		Foyer & Salon B
10:20 - 12:30 p.m.	Report Writing Session (Continued)		Salon B
12:30 - 1:30 p.m.	Working Lunch: Report Writing discussion		Foyer & Salon B
1:30 - 3:30 p.m.	Report Writing Session (Continued)		Salon B
3:30 - 3:50 p.m.	General Discussion		Foyer & Salon B
3:50 - 6:00 p.m.	Report Writing Session (Continued)		Salon B
6:00 p.m.	Meeting ends		

APPENDIX 3: WORKSHOP PARTICIPANTS

First Name	Last Name	Email	Affiliation
Wanda	Andreoni	wanda.andreoni@epfl.ch	CECAM/Centre Européen de Calcul Atomique et Moléculaire
Mark	Asta	mdasta@ucdavis.edu	University of California, Davis
Arun	Bansil	arun.bansil@science.doe.gov	U.S. Department of Energy, Office of Science
Tunna	Baruah	tbaruah@utep.edu	University of Texas at El Paso
Gerald	Baumgartner	gb@lsu.edu	Louisiana State University
John	Bell	jbbell@lbl.gov	Lawrence Berkeley National Laboratory
Joel	Bowman	jbowma@emory.edu	Emory University
Ben	Brown	ben.brown@science.doe.gov	U.S. Department of Energy, Office of Science
David	Bruce	dbruce@clemson.edu	Clemson University
Eric	Bylaska	eric.bylaska@pnl.gov	Pacific Northwest National Laboratory
Andrew	Canning	canning@nersc.gov	Lawrence Berkeley National Laboratory
Jonathan	Carter	jtcarter@lbl.gov	Lawrence Berkeley National Laboratory
Lali	Chatterjee	lali.chatterjee@science.doe.gov	U.S. Department of Energy, Office of Science
James	Chelikowsky	jrc@ices.utexas.edu	University of Texas
Jacqueline	Chen	jhchen@sandia.gov	Sandia National Laboratories
Hai-Ping	Cheng	cheng@qtp@ufl.edu	University of Florida/Quantum Theory Project
Mei-Yin	Chou	meiyin.chou@physics.gatech.edu	Georgia Institute of Technology
Ronald	Cohen	cohen@gl.ciw.edu	Carnegie Institute, Geophysical Laboratory
Larry	Curtiss	curtiss@anl.gov	Argonne National Laboratory
James	Davenport	james.davenport@science.doe.gov	U.S. Department of Energy, Office of Science
Bert	DeJong	bert.dejong@pnl.gov	Pacific Northwest National Laboratory
Erik	Deumans	deumans@qtp.ufl.edu	University of Florida/Quantum Theory Project
Thomas	Devereaux	tpd@slac.stanford.edu	SLAC National Accelerator Laboratory
Massimiliano	Di Ventra	diventra@physics.ucsd.edu	University of California, San Diego
Lori	Diachin	diachin2@llnl.gov	Lawrence Livermore National Laboratory
David	Dixon	dadixon@bama.ua.edu	University of Alabama
Thom	Dunning	tdunning@ncsa.uiuc.edu	NCSA, University of Illinois at Urbana-Champaign
Michel	Dupuis	michel.dupuis@pnl.gov	Pacific Northwest National Laboratory
Brett	Esry	esry@physics.ucsd.edu	Kansas State University
Stefano	Fabris	fabris@democritos.it	CNR DEMOCRITOS, SISSA
George	Fann	fanngi@ornl.gov	Oak Ridge National Laboratory

First Name	Last Name	Email	Affiliation
Maria	Fernandez-Serra	maria.fernandez-serra@stonybrook.edu	Stony Brook University, Physics & Astronomy
Kristen	Fichthorn	fichthorn@psu.edu	Pennsylvania State University, Dept. of Chemical Engineering
Gregory	Fiechtner	gregory.fiechtner@science.doe.gov	U.S. Department of Energy, Office of Science
Giulia	Galli	gagalli@ucdavis.edu	University of California, Davis
Stephen	Garofalini	shg@glass.rutgers.edu	Rutgers University
Bruce	Garrett	bruce.garrett@pnl.gov	Pacific Northwest National Laboratory
Al	Geist	gst@ornl.gov	Oak Ridge National Laboratory
Bonnie	Gersten	bonnie.gersten@science.doe.gov	U.S. Department of Energy, Office of Science
Evelyn	Goldfield	egoldfie@nsf.gov	National Science Foundation
Xin-Gao	Gong	xggong@fudan.edu.cn	Fudan University
Jeffrey	Grossman	jcg@mit.edu	Massachusetts Institute of Technology
Francois	Gygi	fgygi@ucdavis.edu	University of California, Davis
William	Hager	hager@math.ufl.edu	University of Florida
Glen	Hansen	glen.hansen@inl.gov	Idaho National Laboratory
Maciej	Haranczyk	mharanczyk@lbl.gov	Lawrence Berkeley National Laboratory
Bruce	Harmon	harmon@ameslab.gov	Ames Laboratory
Robert	Harrison	harrisonrj@ornl.gov	Oak Ridge National Laboratory
Gus	Hart	gus.hart@gmail.com	Brigham Young University
Angela	Hatton	angela.hatton@pnl.gov	Pacific Northwest National Laboratory
Martin	Head-Gordon	mhg@bastille.cchem.berkeley.edu	UC Berkeley / Lawrence Berkeley National Laboratory
Rigoberto	Hernandez	hernandez@gatech.edu	Georgia Institute of Technology
So	Hirata	hirata@qtp.ufl.edu	University of Florida/Quantum Theory Project
Kai-Ming	Ho	kmh@ameslab.gov	Ames Laboratory/Iowa State University
Linda	Horton	linda.horton@science.doe.gov	U.S. Department of Energy, Office of Science
James	Horwitz	james.horwitz@science.doe.gov	U.S. Department of Energy, Office of Science
Leland	Jameson	ljameson@nsf.gov	National Science Foundation
Mark	Jarrell	jarrellphysics@gmail.com	Louisiana State University
Yu (Cathy)	Jiao	jiaoy@ornl.gov	Oak Ridge National Laboratory
Gary	Johnson	garymichaeljohnson@gmail.com	Computational Science Solutions
Moe	Khaleel	moe.khaleel@pnl.gov	Pacific Northwest National Laboratory
Kwiseon	Kim	kwiseon.kim@nrel.gov	National Renewable Energy Laboratory
Jens	Kortus	jens.kortus@physik.tu-freiberg.de	Institut für Theoretische Physik
Douglas	Kothe	kothe@ornl.gov	Oak Ridge National Laboratory
Gabriel	Kotliar	kotliar@physics.rutgers.edu	Rutgers University
Karol	Kowalski	karol.kowalski@pnl.gov	Pacific Northwest National Laboratory

First Name	Last Name	Email	Affiliation
Jeffrey	Krause	jeff.krause@science.doe.gov	U.S. Department of Energy, Office of Science
Wei	Ku	weiku@bnl.gov	Brookhaven National Laboratory
Harriet	Kung	harriet.kung@science.doe.gov	U.S. Department of Energy, Office of Science
Michael	Lee	michael.lee@science.doe.gov	U.S. Department of Energy, Office of Science
Vincenzo	Lordi	lordi2@llnl.gov	Lawrence Livermore National Laboratory
John	Ludlow	ludlow@physics.auburn.edu	Auburn University
Richard M.	Martin	rmartin@illinois.edu	University of Illinois at Urbana Champaign
Todd	Martinez	toddmtz@slac.stanford.edu	SLAC National Accelerator Laboratory
Glen	Martyna	martyna@us.ibm.com	IBM Research
Osni	Marquez	oamarques@ascr.doe.gov	U.S. Department of Energy, Office of Science
Spiridoula	Matsika	smatsika@temple.edu	Temple University
Hope	Matthews	hope.matthews@pnl.gov	Pacific Northwest National Laboratory
Andrew	McIlroy	amcilr@sandia.gov	Sandia National Laboratories
Marc	Messerschmidt	mcmesser@slac.stanford.edu	Stanford University
Paul	Messina	messina@mcs.anl.gov	Argonne National Laboratory
Stephen	Miller	millersd@ornl.gov	Oak Ridge National Laboratory
Raul	Miranda	raul.miranda@science.doe.gov	U.S. Department of Energy, Office of Science
Lubos	Mitas	lubos_midas@ncsu.edu	North Carolina State University
Lester	Morss	lester.morss@science.doe.gov	U.S. Department of Energy, Office of Science
Sue	Morss	helaine.morss@science.doe.gov	U.S. Department of Energy, Office of Science
Jeffrey	Nichols	nicholsja@ornl.gov	Oak Ridge National Laboratory
Mike	Norman	norman@anl.gov	Argonne National Laboratory
Lucy	Nowell	lucy.nowell@ascr.doe.gov	U.S. Department of Energy, Office of Science
Joseph	Oefelein	oefelei@sandia.gov	Sandia National Laboratories
Karen	Pao	karen.pao@science.doe.gov	U.S. Department of Energy, Office of Science
Kyungwha	Park	kwungwha@vt.edu	Virginia Tech
John	Pask	pask1@llnl.gov	Lawrence Livermore National Laboratory
Mark	Pederson	mark.pederson@science.doe.gov	U.S. Department of Energy, Office of Science
Warren	Pickett	pickett@physics.ucdavis.edu	University of California, Davis
Walt	Polansky	walt.polansky@science.doe.gov	U.S. Department of Energy, Office of Science
Talat	Rahman	talat@physics.ucf.edu	University of Central Florida

First Name	Last Name	Email	Affiliation
Douglas	Ray	doug.ray@pnl.gov	Pacific Northwest National Laboratory
Dan	Reed	daniel.reed@microsoft.com	Microsoft Corporation
Jim	Roberto	robertojb@ornl.gov	Oak Ridge National Laboratory
Eric	Rohlfing	eric.rohlfing@science.doe.gov	U.S. Department of Energy, Office of Science
Anthony	Rollett	rollett@andrew.cmu.edu	Carnegie Mellon University
Benoit	Roux	roux@uchicago.edu	University of Chicago
Ahmed	Sameh	sameh@cs.purdue.edu	Purdue University
John	Sarrao	sarrao@lanl.gov	Los Alamos National Laboratory
Thomas	Schulthess	schulthess@cscs.ch	ETH Zurich
David	Schultz	schultzd@ornl.gov	Oak Ridge National Laboratory
Gustavo	Scuseria	guscus@rice.edu	Rice University
Yukiko	Sekine	yukiko.sekine@science.doe.gov	U.S. Department of Energy, Office of Science
Tamar	Seideman	seideman@chem.northwestern.edu	Northwestern University
Annabella	Selloni	aselloni@princeton.edu	Princeton University
Sadasivan	Shankar	sadasivan.shankar@intel.com	Intel Corporation
Sheryl	Shea	sheryl.shea@pnl.gov	Pacific Northwest National Laboratory
David	Sholl	david.sholl@chbe.gatech.edu	Georgia Institute of Technology
Carlos	Simmerling	carlos.simmerling@gmail.com	Stony Brook University
Marvin	Singer	marvin.singer@science.doe.gov	U.S. Department of Energy, Office of Science
Wade	Sisk	wade.sisk@science.doe.gov	U.S. Department of Energy, Office of Science
Ellen	Stechel	ebstech@sandia.gov	Sandia National Laboratories
Thomas	Sterling	tron@cct.lsu.edu	Louisiana State University
Rick	Stevens	stevens@anl.gov	Argonne National Laboratory
Malcolm	Stocks	stocksgm@ornl.gov	Oak Ridge National Laboratory
Julius	Su	jsu@calteche.edu	California Institute of Technology
Dimitri	Sverjensky	sver@jhu.edu	Johns Hopkins University
Thiyaga P.	Thiyagarajan	p.thiyagaragan@science.doe.gov	U.S. Department of Energy, Office of Science
Priya	Vashishta	priyav@email.usc.edu	University of Southern California
Greg	Voth	voth@chem.utah.edu	University of Utah
Lin-Wang	Wang	lwwang@lbl.gov	Lawrence Berkeley National Laboratory
Renata	Wentzcovitch	wentzcov@cems.umn.edu	University of Minnesota
Paul	Whitney	paul.whitney@pnl.gov	Pacific Northwest National Laboratory
Dieter	Wolf	d.wolf@anl.gov	Idaho National Laboratory
Nicholas	Woodward	nick.woodward@science.doe.gov	U.S. Department of Energy, Office of Science
John	Wu	kwu@lbl.gov	Lawrence Berkeley National Laboratory
Weitao	Yang	weitao.yang@duke.edu	Duke University
David	Yarkony	yarkony@jhu.edu	Johns Hopkins University

First Name	Last Name	Email	Affiliation
Shengbai	Zhang	zhangs9@rpi.edu	Rensselaer Polytechnic Institute
Zhenyu	Zhang	zhangz@ornl.gov	Oak Ridge National Laboratory
Jane	Zhu	jane.zhu@science.doe.gov	U.S. Department of Energy, Office of Science
Alex	Zunger	alex.zunger@nrel.gov	National Renewable Energy Laboratory

APPENDIX 4: ACRONYMS AND ABBREVIATIONS

AIMD	*ab-initio* molecular dynamics
AMPI	Atomistic Model for Particle Inception
ARPES	angle-resolved photoemission spectroscopy
ASCR	DOE Office of Advanced Scientific Computing Research
BES	DOE Office of Basic Energy Sciences
BRN	Basic Research Needs
CAS	complete active space
CCSD(T)	Coupled-Cluster with Single and Double and Perturbative Triple excitations
CO	carbon monoxide
CO_2	carbon dioxide
DCA	dynamical cluster approximation
DFT	density functional theory
DMFT	Dynamical Mean Field Theory
DMRG	density matrix renormalization group
DNS	domain name system
DOE	U.S. Department of Energy
EOS	equations of state
eV	electron volts
FE	finite element
FeO	iron oxide
FRET	Förster resonance energy transfer
GGA	generalized gradient approximation
ICME	Integrated Computational Materials Engineering
iLMM	inverted lattice-mismatched
LDA	local density approximation
MBPT	many-body perturbation theory
MD	molecular dynamics

MEG	multiexciton generation
MERA	multiscale entanglement renormalization ansatz
MM	molecular mechanics
MMV	monitoring and verification
NEB	Nudged Elastic Band
nm	nanometer(s)
P3HT/PCBM	poly(3–hexylthiophene)/ phenyl-C61-butyric acid methyl ester
PAH	polycyclic aromatic hydrocarbon
PEM	proton exchange membrane
PEMFC	proton exchange membrane fuel cells
PEPS	projected entangled pair state
PFSA	perfluoro sulfonic acid
PRD	priority research direction
QMC	quantum Monte Carlo
SEI	solid electrolyte interphase
STM	scanning tunneling microscope
TDDFT	time-dependent density functional theory
Th	thorium
UV	ultraviolet

U.S. DEPARTMENT OF
ENERGY

Office of Science

Office of Advanced Scientific Computing Research
Office of Basic Energy Sciences

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Production support provided by Pacific Northwest National Laboratory,
Fundamental & Computational Sciences Directorate

PNNL-19902