

Materials Chemistry

Portfolio Description

This program supports research on materials with a focus on the role of chemical reactivity, chemical transformation, and chemical dynamics in material composition, structure, function, and lifetime across the range of length scales from atomic to mesoscopic. The overarching goals of materials chemistry research are to elucidate fundamental chemical aspects of materials' composition-structure-property relationships and to provide the knowledge needed to design and produce materials with tailored properties from first principles.

Program emphases are on hypothesis-driven basic research on the chemistry-based synthesis of materials and/or morphologies that have the potential to enable next-generation, energy-relevant technologies, and on the chemical transformations that occur in functional materials in operating environments. Included are the study of chemical processes that direct and control the covalent and non-covalent assembly of materials, the discovery of the mechanistic detail of chemical transformations and dynamics in materials, the utilization of chemistry to control interfacial properties and interactions of materials, and the development of science-driven tools and techniques to achieve fundamental real-time understanding of materials assembly pathways and materials properties. New approaches to materials discovery involving the integration of theory and experiment are supported within the portfolio.

Scientific Challenges

The Materials Chemistry research activity seeks to explore and advance the frontier of accessible functional materials, through the application of the methods and principles of chemistry. Doing so requires addressing specific scientific challenges and opportunities, such as those identified in the BES Advisory Committee's reports (<https://science.energy.gov/bes/community-resources/reports/>), including *Directing Matter and Energy: Five Challenges for Science and Imagination* and *From Quanta to the Continuum: Opportunities for Mesoscale Science*.

Challenges and opportunities identified in these reports include:

- Discovering new methods to design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties, taking advantage of the recent and ongoing development of theoretical methods and tools;
- Characterizing and controlling matter far away from equilibrium;
- Mastering defect mesostructure and its evolution by characterizing and controlling the patterns and evolution of mesoscale heterogeneity;
- Directing assembly of hierarchical functional materials through the integration of disparate materials classes across a range of length scales from molecular to macroscopic.

Each of these challenges and opportunities may potentially be addressed by the application of chemical principles to the design, synthesis, and transformation of materials.

Projected Evolution

The overarching goal of materials chemistry research is to provide the knowledge needed to design and produce materials with tailored properties from first principles. This program will make progress towards that goal by continuing to emphasize hypothesis-driven research on the chemistry-based synthesis of materials and/or morphologies that have the potential to enable next-generation energy-relevant technologies, and research on the chemical transformations

occurring in functional materials in the operating environment. Major scientific areas of interest include: fundamental aspects of the chemical assembly of material structures and control of multi-scale material morphology; synthesis and characterization of new classes of organic, inorganic, polymeric, and composite materials (crystalline and non-crystalline) with novel functionality; control of surface and interfacial chemistry and morphology; fundamental electrochemistry of solid-state materials; chemical dynamics and transformations of functional materials in operational environments; and development of new, science-driven laboratory-based analytical tools and techniques for the elucidation of chemical processes in materials, particularly *in situ* or *in operando*, in energy-relevant applications.

Research primarily aimed at the optimization of synthetic methods or of properties of materials for applications, and research with a primary goal of device fabrication and testing, will be discouraged.

Significant Accomplishments

The Materials Chemistry research activity has resulted in a variety of scientific accomplishments, including the discovery of new superconducting materials, the discovery of the first organic magnet above room temperature, and the demonstration of new analytical techniques for surfaces and interfaces that have had significant impact in their respective fields.

Recent accomplishments include:

- Discovery of a new class of materials, a porous polymer/metal organic framework(MOF) hybrid material, termed ‘polyMOFs,’ that were shown to exhibit effective gas separation properties;
- Developing a synthetic route to ultra-fine jagged Pt nanowires with highly stressed, under-coordinated surface configurations, that exhibit record high mass activity for the oxygen reduction reaction, doubling the previous record;
- Design of nanostructured MoS₂ electrodes having pathways for both fast ion and electron transport that show dominantly capacitive behavior, allowing for fast charging times;
- Creation of a new crystalline porous material with designed pore partitions that exhibits near-record carbon dioxide uptake;
- Demonstration that controlling the nanostructures of the layered dichalcogenides, MoS₂ and WS₂, dramatically enhances their catalytic activity toward the hydrogen evolution reaction;
- 3-D imaging of nanoparticles rotating freely in a liquid with near-atomic resolution that enables understanding of their growth mechanisms in order to advance the development of nanomaterials for energy applications;
- First demonstration of a MOF material that shows both stable micropores and good charge mobility, relevant to energy storage technologies; and
- Discovery of single-crystal nanowires composed of hybrid organic-inorganic lead halide perovskites as the most efficient nanowire lasers known.

Unique Aspects

Research supported in this program advances fundamental knowledge in the materials sciences that underpins many energy-related technologies such as energy harvesting, conversion, transmission, and storage devices; high-efficiency catalysts and electrocatalysts; friction and

lubrication materials; high-efficiency electronic devices; advanced photonic materials; light-weight, high-strength materials; and materials for advanced separations. The focus on chemistry-based formation and control of new materials and morphologies is complementary to the BES Biomolecular Materials research activity (with an emphasis on discovery of materials and systems using concepts and principles of biology) and the Synthesis and Processing Science research activity (with a focus on physical, rather than chemical, control of structure and properties, and on bulk synthesis, crystal growth, and thin films). The researchers supported by the program benefit from significant use of BES-supported scientific user facilities with their advanced x-ray, neutron scattering, electron microscopy and nanoscience tools.

Mission Relevance

The Materials Chemistry program supports research to generate fundamental knowledge based on the principles of chemistry about the creation, manipulation, and functional behavior of materials that will underpin the future development of energy-relevant technologies including systems for energy harvesting, storage, transformation, and utilization, with levels of performance superior to the current state of the art.

Relationship to Other Programs

The fundamental research supported by the Materials Chemistry program serves as an interface between chemistry, materials science, physics, and engineering. It is necessarily interdisciplinary and cultivates a number of relationships, within BES and DOE, and within the larger federal research enterprise:

- Within BES, this research activity sponsors—jointly with other core research activities, the Energy Frontier Research Centers program, and the Joint Center for Energy Storage Research (JCESR), as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops.
- There are active interactions with the DOE Offices of Energy Efficiency and Renewable Energy (EERE) and Fossil Energy (FE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Within the larger federal research enterprise, program coordination is through the Federal Interagency Materials Representatives (FIMaR), the Federal Interagency Chemistry Representatives (FICR), and the Interagency Polymer Working Group.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).
- There are particularly active interactions with the National Science Foundation (NSF) through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Biomolecular Materials

Portfolio Description

This activity supports fundamental research in the discovery, design, and synthesis of functional and hierarchical materials, including the materials aspects of energy conversion processes based on principles and concepts of biology. Since biology provides a blueprint for translating atomic and nanoscale phenomena into mesoscale materials that display complex yet well-coordinated collective behavior, the major programmatic focus is on the hypothesis-driven creation of energy-relevant versions of these materials optimized for harsher, non-biological environments. New fundamental science approaches are sought that will lead to predictable and scalable synthesis of novel, hierarchically structured polymeric, inorganic, and hybrid functional materials *in vitro* with controllable morphology, content, behavior, and performance.

Major thrust areas include: harnessing or mimicking the energy-efficient synthesis approaches of biology to generate new optimized materials for a broad range of non-biological conditions; bioinspired self-, directed-, and dissipative-assembly approaches with control of mechanisms and kinetics to form materials that display novel, unexpected properties that are far from equilibrium; adaptive, resilient materials with self-repairing capabilities; and development of science-driven tools and techniques to achieve fundamental real-time understanding of synthetic and assembly pathways, and to enable active, precise manipulation of structure and function. Integrated theoretical and experimental approaches to understand how materials complexity leads to new functionalities, development of new design ideas, and opportunities for accelerated discovery are emphasized.

Scientific Challenges

Since biology has already figured out ways in which matter, energy, entropy, and information are organized and/or manipulated across multiple length scales, the challenge for us is to understand, adapt, and improve upon them so that they will become valuable and practical under a broader range of harsher, non-biological conditions. The major scientific challenges that drive the Biomolecular Materials activity directly correspond to the scientific challenges laid out in the report *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* (<https://science.energy.gov/bes/community-resources/reports>):

- Realizing targeted functionality in materials by mastering spatial and temporal control of the synthesis and assembly of hierarchical architectures and beyond-equilibrium matter, and so build into synthetic materials a new level of information content approaching that of biological materials.
- Development of predictive models, including the incorporation of metastability, to guide the creation of beyond-equilibrium matter, and pursue the opportunity to go even beyond what nature has achieved to advance the frontiers of energy science.
- The development of methods for in situ characterization of spatial and temporal evolution during synthesis and assembly.

Programmatic challenges also directly correspond to four of the five scientific grand challenges in basic energy sciences, as described in the report, *Directing Matter and Energy: Five Challenges for Science and Imagination* (<https://science.energy.gov/bes/community-resources/reports>):

- How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?
- How do remarkable properties of matter emerge from complex correlations of the atomic and electronic constituents and how can we control these properties?
- How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living systems?
- How do we characterize and control matter away--especially very far away--from equilibrium?

Additional challenges directly correspond to the objectives laid out in the reports *From Quanta to the Continuum: Opportunities for Mesoscale Science* and *Computational Materials Science and Chemistry* (<https://science.energy.gov/bes/community-resources/reports>):

- Discovering, controlling, and manipulating complex mesoscale architectures and phenomena to realize new functionality.
- The development and use of powerful new theory/modeling and physical/chemical characterization tools that can accelerate materials discovery.

Projected Evolution

The activity will expand research on methods to create mesoscale materials with high fidelity and in appreciable quantities. For dissipative- and directed-assembly approaches, programmatic focus will be on: spontaneous assembly-disassembly and reconfiguration, the ability to respond *en masse* to directed and environmental cues, coordination of collective response to multiple signals, defect management, ability to self-repair and rebuild structure, and capability for self-replication and autonomous function. This activity will also expand research to design and create next-generation materials for energy conversion and storage with programmable selectivity and transport based on biological gating and pumping functions, and to understand and precisely control bioinspired mechanisms for directing synthesis and function at organic-inorganic interfaces.

Research that does not have a clear focus on materials science or is aimed at optimization of materials properties for any applications, device fabrication, sensor development, tissue engineering, and biomedical research will be discouraged.

Significant Accomplishments

Although relatively new within BES, the Biomolecular Materials activity has produced accomplishments that show promise of significant impact:

- A process for inserting short, narrow, subnanometer carbon nanotubes (CNTs) that mimic biological ion channels into synthetic lipid membranes. The confined water in the CNTs formed one-dimensional water wires that drastically boosted the proton transport rate to an order of magnitude faster than bulk water and faster than the state-of-the-art membrane in fuel cells.
- A new strategy for modulating entropic and enthalpic attractive interactions between particles that enables crossover between two distinct assembly pathways.
- Synthesis of defect-free, 2-dimensional protein crystals using a simple chemical-bonding and design strategy that display highly desired counterintuitive mechanical behavior—they expand or contract equally in both directions when stretched or compressed. Such

materials absorb vibration; resist shear, indentation, and fracture; may enable active tuning; and are attractive for use in highly resilient, tunable, lightweight packaging and electronics.

- A new self-regulating process for polymer self-healing using a fluid secretion process inspired by wound-healing processes of living systems.
- A new class of 3D porous, crystalline framework materials formed by spherical protein nodes that assemble as designed through directed interactions between these nodes, metal ions, and organic linkers.

Unique Aspects

Basic research supported in this activity underpins DOE's mission to develop future, transformative energy technologies in areas such as energy conversion, transduction, and storage; light-weight/high-strength materials; efficient membranes for highly selective separations; and energy-efficient, low-temperature synthesis of materials. Current scientific thrusts balance grand challenge and use-inspired basic research, and require strong interactions among biology, chemistry, physics, and computational science disciplines. This activity's focus on new energy-related materials by exploiting biological principles and concepts is complementary to the focus on chemistry-based formation and control of new materials and morphologies of the Materials Chemistry research activity, and to the emphasis on physical, rather than chemical, control of structure and properties and on bulk synthesis, crystal growth, and thin films of the Synthesis and Processing Science research activity. The Biomolecular Materials activity's focus on the intersection of biology and materials sciences complements the Physical Biosciences activity in the Chemical Sciences, Geosciences, and Biosciences Division, which focuses on biochemical, chemical and molecular biological approaches to further our understanding of the ways plants and/or non-medical microbes capture, transduce, and store energy.

Mission Relevance

Biology offers an extraordinary source of inspiration for the development of new materials with precise control of collective self-healing, self-regulating, catalytic, and energy-harvesting, -conversion, -transduction, and -storage behavior. Basic research supported by the Biomolecular Materials activity underpins development of a broad range of energy-relevant materials and technologies such as lighter and stronger materials to improve fuel economy, materials to control transport across membranes and make separations and purification processes more efficient, energy-efficient synthesis and assembly of functional materials, and processes that can convert light, carbon dioxide, and water to fuels.

Relationship to Other Programs

The Biomolecular Materials program is a vital interdisciplinary component of the materials sciences that interfaces materials sciences with biology. This interfacing results in active relationships within BES, within DOE, and within the larger federal research enterprise:

- Within BES, this research activity sponsors—jointly with other core research activities, the Energy Frontier Research Centers program, and the Joint Center for Energy Storage Research (JCESR), as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops.

- There are active interactions with the DOE Offices of Energy Efficiency and Renewable Energy (EERE) and Fossil Energy (FE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Within the larger federal research enterprise, program coordination is through the Federal Interagency Materials Representatives (FIMaR), the Federal Interagency Chemistry Representatives (FICR), and the Interagency Polymer Working Group.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).
- There are particularly active interactions with the National Science Foundation (NSF) through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Synthesis and Processing Science

Portfolio Description

This program supports research to understand the physical phenomena and unifying principles in different classes of materials that underpin their synthesis, including diffusion, nucleation, and phase transitions, often using *in situ* diagnostics, and development of new techniques to synthesize materials with tailored structure and desired properties. An important element of this activity is the development of real-time monitoring tools, diagnostic techniques, and instrumentation that can provide information on the progression of structure and properties as a material is formed, in order to understand the underlying physical dynamic mechanisms and to gain atomic-level control of material synthesis and processing. The emphasis is on fundamental research to enable discovery of new functional materials, and development of new crystal growth methods and thin-film deposition techniques to create complex materials with targeted structure and properties.

Scientific Challenges

With recent developments toward high-precision, *in situ*, dynamic, real-time, ultra-fast and ultra-small characterization tools and with increased accessibility of computational resources, synthesis and processing materials can be transformed to a science with a higher level of understanding. The time is ripe to address many open challenges in this field, including:

- Developing robust predictive thermodynamic and kinetic tools. How do we accurately incorporate dynamic processes and near-equilibrium phenomena into new or existing tools? Can experiment and theory be bridged to construct accurate models of the evolution of materials away from equilibrium, and thus pave the way for new states of matter?
- How can we enable the fabrication and understanding of artificially structured materials with hierarchical arrangement and attain novel functionality?
- Can we more deeply characterize and understand the non-idealities that inevitably occur during synthetic processes for model materials? How can we effectively utilize these defects to synthesize useful structures, and thereby strengthen our ability to deal with the complexity of systems operating under more realistic conditions?
- *In situ* characterization of materials synthesis from the atomic to the micron scale. How do we measure *in situ* processes at their relevant length and time scales?

Finally, BES Basic Research Needs workshop reports (<https://science.energy.gov/bes/community-resources/reports>), especially the *Basic Research Needs for Synthesis Science for Energy Relevant Technology* due this year and the BES Advisory Committee's report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science*, provide additional discussion on these and other challenges.

Projected Evolution

The Synthesis and Processing Science activity continues to focus on the area of predictive design and synthesis of materials across multiple length scales, with particular emphasis on the mesoscale, where functionalities begin to emerge. Proposals to accelerate progress in understanding synthesis pathways and in the discovery of new materials through coupling creative physical experimental synthesis and processing techniques, computational approaches, and/or *in situ* diagnostic tools and characterization techniques developed in the laboratory or at DOE-BES user facilities, are encouraged. The program has an increasing focus on understanding the kinetics and mechanisms of materials growth, including bulk material processes, organic and inorganic film deposition, plasma synthesis, and the organization of mesoscopic assemblies across a range of length scales, especially underpinning many energy-related technological areas.

Projects aimed at engineering scale-up, properties optimization, device fabrication, and device development are not encouraged.

Significant Accomplishments

The Synthesis and Processing Science research activity has many notable accomplishments. Some have already made an impact of scientific and technological significance:

- A new rapid processing method was developed for consolidating ceramic materials that stabilizes the processing temperature by applying an external pressure on the material through a press, equalizing the distribution of temperature. The uniform temperature resulted in almost instantaneous densification of the ceramic with only limited grain growth, confirming theoretical calculations.
- A new material that displays electrically controlled magnetism at room temperature was created by assembling alternating atomic layers of two oxide materials by exploiting geometric factors and atomic lattice distortions between the alternate materials.
- A new reversible chemical conversion reaction mechanism, similar to what powers lead-acid car batteries, was discovered and used to successfully manipulate the chemical balance in manganese oxide and zinc system. The battery could be charged-discharged over 5,000 cycles, while retaining 92 percent of its initial storage capacity, demonstrating its potential for ultra-low cost rechargeable batteries.
- A new fabrication method takes disordered (amorphous) solid glass and turns it into crystals with a single orientation (single crystals). A focused laser is used to heat the glass that allows controlled nucleation as the temperature increases from room temperature to the temperature at which a crystal is formed (below the melting temperature). The method suppresses excessive nucleation and allows for a single crystal seed to grow until the entire line or surface has a single orientation.
- Organic glasses were shown to have substantially increased photostability (resistance to changes in their molecular structure when exposed to light) when prepared by vapor deposition. The vapor deposited glasses are more densely packed in comparison with the more loosely-packed liquid-cooled glasses.
- Thousands of lanthanum strontium copper oxide compound samples were prepared by molecular beam epitaxy and characterized to reveal that the mechanism for high temperature superconductivity depends on the density of electron pairs that challenges the standard theory that superconductivity depends on the strength of electron pairing interactions.

Unique Aspects

Basic research supported in this activity underpins DOE's mission to develop future, transformative energy technologies in areas such as energy conversion, transduction, and storage; high-efficiency electronic devices; advanced photonic materials; and light-weight, high-strength materials.

Research in materials synthesis furthers our capabilities in single crystal growth and preparation of high-quality specimens used by other investigators funded by BES, often at the DOE x-ray synchrotron and neutron facilities. Current scientific thrusts balance grand challenge and use-inspired basic research, and require strong interactions among engineering, chemistry, physics, and computational science disciplines. This activity emphasizes physical control of material structure and properties, and bulk synthesis, crystal growth, and thin-film deposition to obtain new materials. The research is complementary to the Materials Chemistry research activity that focuses on chemistry-based formation and control of new materials and morphologies and the Biomolecular Materials research activity that emphasizes discovery of materials and systems using concepts and principles of biology.

Mission Relevance

Synthesis and processing science is a key component in the discovery and design of a wide variety of energy-relevant materials. In this regard, the activity supports DOE's mission by uncovering the mechanisms and kinetic factors for synthesis and by configuring materials through prediction, thus enabling the study of unique properties. Some examples of basic materials synthesis that support DOE's mission in energy include a wide range of semiconductors for solid-state lighting and photovoltaics; light-weight metallic alloys and nanocomposites for transportation applications; novel, designer materials for electrical energy storage; and ceramics processing including high-temperature superconductors for near-zero-loss electricity transmission. The research activity aims at providing new synthesis and processing capabilities to enable the manipulation of individual spin, charge, and atomic configurations to probe the atomistic basis for materials properties.

Relationship to Other Programs

The Synthesis and Processing Science program is a critical element of materials sciences that have emphasis in the physical sciences. This connection results in especially active interactions:

- Within BES, this research activity sponsors—jointly with other core research activities, the Energy Frontier Research Centers program, and the Joint Center for Energy Storage Research (JCESR), as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops. Research efforts in this program are closely coordinated with other core research activities in BES, including the Physical Behavior of Materials on theory of formation in the nanoscale, Experimental Condensed Matter Physics on single crystal and thin film growth, and Electron and Scanning Probe Microscopies for studies on the growth phenomena at the nanoscale.
- There are active interactions with the DOE Offices of Energy Efficiency and Renewable Energy (EERE) and Fusion Energy Sciences (FES) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Within the larger federal research enterprise, program coordination is through the Federal Interagency Materials Representatives (FIMaR), the Federal Interagency Chemistry Representatives (FICR), and the Interagency Coordination Committee on Ceramics Research and Development (ICCCRD).
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).
- There are particularly active interactions with the National Science Foundation (NSF) through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Experimental Condensed Matter Physics

Portfolio Description

The Experimental Condensed Matter Physics (ECMP) program supports research that will advance our fundamental understanding of the relationships between intrinsic electronic structure and properties of complex materials. The program focus is largely on systems whose behavior derives from electron correlation effects, competing or coherent quantum interactions, and effects of interfaces, defects, anisotropy, and reduced dimensionality. Scientific themes include unconventional superconductivity, magnetism, low-dimensional electron systems, topologically protected states and their spin dynamics, and nanoscale systems. The program also supports research that involves characterization of the electronic states and properties of materials under extreme conditions, such as ultra-low temperatures and ultra-high magnetic fields. Research is also supported on materials phenomena at interfaces with an emphasis on non-equilibrium electronic, structural, and magnetic states between dissimilar materials, as well as the development of experimental techniques that enable such studies. Support for the synthesis of materials required for the broader research activities is also provided. The program will continue to support research that will result in a fundamental understanding of unconventional superconductivity.

Scientific Challenges

The scientific challenges for this program are well summarized in the 2015 Basic Energy Sciences Advisory Committee report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* (all BES reports can be found at: <https://science.energy.gov/bes/community-resources/reports/>). Particularly relevant to ECMP are: 1) Mastering Hierarchical Architectures and Beyond-Equilibrium Matter; 2) Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces and Disorder; 3) Harnessing Coherence in Light and Matter. The following exemplify the relevance to ECMP in realizing emerging materials properties:

- Synthesize 1-, 2-, and 3-D mesoscale systems;
- Define the important length scales determining structural, charge, spin, and orbital ordering, and understand how they compete;
- Control interface and defect states and spatial and temporal disorder in materials; and
- Control long-range spatial coherence and temporal behavior in structural, charge, spin, and orbital interactions.

These address opportunities in the wide array of strongly correlated electron phenomena included in the program, such as superconductivity, magnetism, topological materials, and quantum effects associated with two-dimensional systems. These also apply directly to ongoing and emerging work in multiscale (nano, meso, and macro) physics in the program. Implied in the above is the development of synthesis and characterization tools required to realize these opportunities. Also implied is close collaboration with theory for guidance and insights in these endeavors.

Also important to this activity are the priority research directions identified in the follow-up BES report on *Basic Research Needs for Quantum Materials*.

Projected Evolution

This activity will include further work to advance our fundamental knowledge of highly correlated systems, including phenomena that occur at the nanoscale, at ultra-low temperatures, and in very high magnetic fields. The program will expand to investigate phenomena that occur in mesoscale structures, where electron confinement results in new materials properties in systems such as semiconducting quantum dots; metallic, magnetic, and ferroelectric nanocrystals; and lithographically patterned graphene sheets. The portfolio can be expected to continue thrusts in electronic structure, new materials, surfaces/interfaces, and development of experimental techniques to enable new physics. Efforts will continue to strengthen research in unconventional superconductivity, including the high-temperature cuprate and iron-based and other highly anisotropic superconductors. In the last few years, the program has increased support for spin physics and nanomagnetism, topological states of matter, and graphene-like materials. Continued growth in research support is expected in the area of quantum materials. Research on conventional superconductors is not a growth area.

Significant Accomplishments

The ECMP activity has a long history of accomplishments. Among these are the discovery of ion channeling and the development of the field of ion implantation, the discovery of metallic and strained-layer superlattices, the establishment of the field of thermoacoustics and thermoacoustic refrigeration and heating, the first observation of superconductivity in a magnetically doped semiconductor (platinum antimony [PtSb₂] with ~1% Yb), and design/construction of the 100 T multishot magnet (now operated by the National High Magnetic Field Laboratory). The 100 T magnet currently holds the world record for long pulse, high magnetic fields in a reusable magnet. In addition, the activity has supported much of the seminal work in the fields of high-temperature superconductors and quasicrystals, efforts now pursued worldwide.

Recent accomplishments in the program include:

- First observation of charge-neutral quasiparticles which may provide new insights into the mechanism responsible for high-temperature superconductivity.
- First demonstration of current-driven manipulation of magnetic skyrmions at room temperature in commonly used magnetic materials.
- The detailed nature of the hidden order parameter in the heavy-fermion superconductor (URu₂Si₂) was revealed, 30 years after it was first discovered.
- Direct observation of giant magnetic anisotropy in non-rare-earth-based materials.
- Demonstration of a very large coercivity enhancement in V₂O₃/Ni bilayers driven by nanoscale phase coexistence.

Unique Aspects

This activity continues to support research on electronically complex and quantum materials that impact a wide range of topics including unconventional superconductivity, magnetism, and low-dimensional electron systems. The research on magnetism and magnetic materials focuses on hard magnet materials, such as those used for permanent magnets and in motors; on spin-orbit and exchange coupling, important for information technologies; and on spin-polarized electron transport, particularly in nanometer-scale structures. The superconductivity portfolio comprises a concerted and comprehensive energy-related basic research program. Research on the

properties of materials in high magnetic fields utilizes the 100 Tesla multi-shot magnet (designed and built by BES), now located at the National High Magnetic Field Laboratory at Los Alamos National Laboratory. Internationally, this activity holds a position of world leadership in the areas of magnetism, superconductivity, materials characterization, two-dimensional electron gas materials, and nanoscale science. New, exciting areas launched within this activity include studies on interfacial effects in magnetism, topological insulators, skyrmions, and iron-based superconductors.

Mission Relevance

Improving the understanding of the electronic behavior of materials on the atomistic scale is relevant to the DOE mission in energy, as these structures offer enhanced properties and could lead to dramatic improvements in technologies for energy generation, conversion, storage, delivery, and use. Specifically, research efforts on the fundamental mechanisms of superconductivity, the physics of low-dimensional systems, and understanding charge-orbital-spin interactions provide the scientific underpinnings for a broad range of energy technologies. This activity also supports basic research in semiconductor and spin-based electronics of interest for the next-generation information technology and electronics industries.

Relationship to Other Programs

The research in this activity is aimed at building a fundamental understanding of the electronic behavior of materials as a foundation for future energy technologies. Improving the understanding of the physics of materials at the nanoscale will be technologically significant, as these structures offer enhanced properties and could lead to dramatic improvements in technologies for energy generation, conversion, delivery, and utilization. This activity also supports semiconductor and spintronics research of fundamental interest to the information technology and electronics industries.

These research efforts are closely coordinated with other core research activities in BES, including: Physical Behavior of Materials on superconductivity and magnetism; Synthesis and Processing Science on single crystal and thin film growth; X-ray and Neutron Scattering on advanced scattering techniques; and Theoretical Condensed Matter Physics on superconductors, nanostructures, and low-dimensional systems. This research activity also sponsors—jointly with other core research activities and the Energy Frontier Research Centers program, as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops.

The Program also works with agencies outside of BES.

- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).

- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).
- The program has also supported topical studies by the National Research Council (NRC) of the National Academies, including *Condensed-Matter Physics and Materials Physics: The Science of the World Around Us*, *Assessment of and Outlook for New Materials Synthesis and Crystal Growth*, *Optics and Photonics: Essential Technologies for our Nation*, and *High Magnetic Field Science*. The program is jointly supporting, with NSF, the NRC study *Frontiers of Materials Research: A Decadal Survey*. The 2020 assessment is expected to be complete by September, 2018.
- This program and the National Science Foundation (NSF) support the NRC Condensed Matter and Materials Research Committee (formerly the Solid State Sciences Committee), which is charged with assessing the state of the field and advising federal agencies on research priorities. Additional interactions with the NSF include joint support of National Academies studies in relevant areas and ongoing communication about research activities.
- The program also participates in interagency coordination groups such as the Interagency Coordination Committee on Ceramics Research and Development and the Federal Interagency Materials Representatives (FIMaR).

Theoretical Condensed Matter Physics

Portfolio Description

This program supports research in Theoretical Condensed Matter Physics with an emphasis on quantum materials, materials discovery, non-equilibrium transport and ultrafast response, and fundamental research in materials related to energy technologies. Suitable topics include strongly correlated electron systems, quantum phase transitions, magnetism, superconductivity, semiconductors, thermoelectric materials, optical response, neutron and photon scattering, theory of nanoscale and mesoscale systems, and computational and data-driven materials design. Approaches from purely analytical to computational are supported, as are methods that incorporate multiple length and time scales. Computational materials research may include development of validated, open-source codes and data analytics.

Scientific Challenges

The Theoretical Condensed Matter Physics activity explores and advances the frontiers in research through the application of the methods and principles of physics. Doing so requires addressing specific scientific challenges and opportunities, such as those identified in the BES reports: *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science*, *From Quanta to the Continuum: Opportunities for Mesoscale Science*, *Computational Materials Science and Chemistry*, and *Basic Research Needs Workshop on Quantum Materials for Energy Relevant Technology* (<http://science.energy.gov/bes/community-resources/reports/>).

Challenges and opportunities identified in these reports include research on high-temperature superconductivity and beyond, where continuing discoveries of complex phase behavior remain to be understood and related to their dynamics and non-equilibrium processes. Similarly, complex materials offer many opportunities for the study of quantum systems and emergent behavior.

Bridging length scales is a continuing major goal on which progress is ongoing. More than integrating atomic-level scales with the nanometer or mesoscale in materials, this also requires integrating the domain of quantum laws with classical laws of physics. Bridging time scales is similarly important with some of the most exciting advances coming from new theoretical methods implemented in a computational environment. Basic theory has challenges; for example, density functional theory is moving to a resolution of the long-standing problems of correlations and for correctly treating excited states. Treatment of non-equilibrium systems needs advances in non-equilibrium statistical mechanics. In the computational area, a variety of algorithms no longer scale to the tens of thousands of processors available now and will be faced with millions of processors in the future.

Projected Evolution

The program will continue to emphasize theory and computation that extend the understanding of quantum materials. These include strongly correlated materials, magnetic and superconducting materials, and transition metal oxides with targeted quantum properties, as well as exotic states of matter, for example those found in topological insulators, as well as Dirac and Weyl semimetals. The BES Basic Research Needs workshop report on *Quantum Materials for Energy*

Relevant Technology identified related topics. Predictive theory and modeling, as it relates to the Materials Genome Initiative, will become more important, as will advanced computational techniques such as the Quantum Monte Carlo method for predictive materials science. Time-dependent and non-equilibrium phenomena, especially at the femtosecond time scale and in electron transport, are important areas for future research.

Cold atom, soft matter and biomolecular physics, polymers, glassy systems, granular materials, ionic liquids, surface chemistry, and quantum computing are not current priorities in Theoretical Condensed Matter Physics.

Significant Accomplishments

The program has a history of enabling theoretical and computational advances that have contributed to the broad understanding of condensed matter physics. Examples include many-body perturbation theory as implemented in the GW method, which provided a first-principles theory of the band gap of semiconductors; the prediction of topological insulators; the theory and design of photonic band gap materials; the development of software to predict x-ray absorption in materials and its use to obtain atomic geometry; the understanding of the critical role of dissipation of vortices in superconductors; the prediction of the intensity of optical absorption in semiconducting nanoparticles; and advances in dynamical mean field theory, a widely used method for treating correlated electron materials, and its use to understand neutron scattering in actinides. Recent accomplishments include:

- Prediction of new topological states in materials including Dirac and Weyl semi-metals.
- Development of high throughput computational techniques for materials discovery including the Materials Project—an open database with more than 65,000 inorganic compounds and the largest collection of calculated elastic tensors.
- Improved quantum Monte Carlo techniques for strongly correlated materials including the ability to treat spin-orbit interactions.
- Methodological advances of the local density approximation combined with the Gutzwiller approximation to determine the structural properties of strongly correlated electron materials, including finite temperature effects.
- Microscopic model of silicon nanowire to help explain the voltage-tunable circular photogalvanic effect, i.e., a photocurrent with direction determined by the chirality of light.

Unique Aspects

Research in predictive theory and modeling has an emphasis on functional materials, excited states, and high-throughput computation. Novel, physics-based computational techniques are supported including quantum Monte Carlo, improvements to density functional theory, extensions of dynamical mean field theory, density matrix renormalization group, and self-consistent GW calculations (calculations based on many body perturbation theory which includes electron-electron and electron-hole interactions). The program will continue to emphasize basic research on matter at atomistic length scales, expanding to include properties at the mesoscale. Research supported by this program is motivated by recent developments in materials science, advancing the understanding of fundamental physics, and the potential for impact on energy technologies.

A unique component of this program is the support of theoretical efforts to understand experimental observations. This includes theory extracting basic physical insights from experiments at national scientific user facilities, such as the x-ray free electron laser at SLAC National Accelerator Laboratory, synchrotron light sources, and the Spallation Neutron Source.

Mission Relevance

The Theoretical Condensed Matter Physics program supports fundamental research on the principles of physics to understand, predict, and ultimately control matter and energy at the level of electrons, atoms, and molecules. This research provides the foundation for new materials that will underpin the future development of energy-relevant technologies including systems for energy storage, transformation, and utilization, with levels of performance superior to the current state of the art.

Relationship to Other Programs

This program maintains strong interactions with other research activities within BES, driven by the opportunity of stimulating theory through experimental discovery, and bringing solid theoretical foundations and understanding to new processes of interest to experimental and facilities programs. The program includes modeling and simulation efforts in support of the interagency Materials Genome Initiative (MGI) and research utilizing large-scale computational science with joint funding from DOE's Advanced Scientific Computing Research (ASCR) program. The MGI has added a component of *validated* theory and modeling, which includes data repositories aimed at increasing the rate of materials discovery. Because this program has oversight responsibility for a portion of the high-performance computing resources at the National Energy Research Supercomputer Center (NERSC), there is particular interest in opportunities for implementing complex theoretical methods as predictive tools in support of experimental science and the broader community.

- Within BES, this research activity sponsors—jointly with other BES core research activities as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops.
- These research efforts are closely coordinated with other core research activities in BES, including Experimental Condensed Matter Physics on superconductors, nanostructures, and low-dimensional systems.
- The program actively collaborates with ASCR on research opportunities in large-scale, advanced computational tools and resources through the Scientific Discovery through Advanced Computing (SciDAC) partnership.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office, which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology for the National Nanotechnology Initiative.
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies

through the NSTC Subcommittee on the Materials Genome Initiative (MGI).

- There are particularly active interactions with the National Science Foundation through the MGI PI meetings, workshops, and communication about research activities.

Physical Behavior of Materials

Portfolio Description

This activity supports basic research on the physical behavior of materials in response to electric fields, magnetic fields, electromagnetic fields, chemical environments, thermal excitation, size effects, and the proximity effects of surfaces and interfaces. Emphasis is on developing a fundamental understanding of processes taking place between charge carriers, photons, lattice vibrations, and other collective excitations in materials. Included within the activity is research to understand the role of crystal defects, phase equilibria and kinetics of reactions in materials in unusual environments, and diffusion and transport phenomena encountered in energy applications.

Scientific Challenges

The challenge in this area is to develop the scientific understanding of the mechanisms that control the behavior of materials and to use that understanding to design new materials with desired behaviors. The program encompasses efforts aimed at understanding the behavior of organic and inorganic electronic materials, magnetism and advanced magnetic materials, manipulation of light/photonic lattices, corrosion/electrochemical reactions, and high-temperature materials behavior through intimately connected experimental, theoretical, and modeling efforts leading to *a priori* design of new materials.

Specific scientific challenges and opportunities are identified by the BES Advisory Committee's reports (<https://science.energy.gov/bes/community-resources/reports/>), including *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* and *From Quanta to the Continuum: Opportunities for Mesoscale Science*, as well as the BES Basic Research Needs workshops.

Projected Evolution

The long-term goal of this program is to develop an atomistic understanding of the macroscopic physical behavior of materials. It is important to understand the relationship between a material's properties and its response to external stimuli. This can be achieved by determining structure-property relationships over multiple length scales, with emphasis at the atomic level, and by understanding the response of the nanometer and mesoscale features of the material to those external stimuli. This program seeks to foster theory, modeling, and simulation activities that address charge and energy transfer; electronic structure calculation; exciton dynamics and transport; and spin dynamics in energy relevant materials.

The program currently emphasizes electronic and magnetic behavior of materials. The program also supports corrosion and electrochemistry science, nanoscale phenomena, and multiscale modeling of materials behaviors. Increased investment in photon-matter interactions and plasmonics will be considered. In addition, research that is focused on theory and modeling of physical behavior of materials, especially in the area of defects in crystals and their influence on the structural properties of materials will be deemphasized.

Significant Accomplishments

This activity has had broad and significant impact in many classes of materials and phenomena.

Some of the recent accomplishments include:

- Invention of world's smallest transistor with 1-nanometer gate lengths using MoS₂ material, and a one-nanometer diameter single walled carbon nanotube as a gate electrode, achieving near ideal operational characteristics of a transistor.
- Discovery of near-unity photoluminescence quantum yield in MoS₂ material, achieved by a special surface treatment they developed, increasing the room temperature photoluminescence quantum yield from 0.6% to 95%. The treatment eliminates defect-mediated nonradiative recombination, yielding near-perfect properties that opens the door for the development of highly efficient light-emitting diodes, lasers, and solar cells based on two-dimensional (2D) materials.
- Discovery of thermally injected spin current in a metal that can be amplified 10-fold, when a one-nanometer thick antiferromagnetic layer (like NiO or CoO) is introduced between the source (Yttrium Iron Garnet) and the metal.
- Discovery of the first 2D material that supports both superconducting and topological states at the same time. Researcher demonstrated by first-principles theory, scanning tunneling spectroscopy, and angle-resolved photoemission spectroscopy that the (2D) superconductor of single-layer FeSe also exhibits one-dimensional topological edge states.
- Discovery of an anomalously low electronic thermal conductivity in metallic VO₂ material at temperatures above room temperature. Such anomalies where charge carriers not contributing to the heat conduction in materials has only been observed at extremely low temperatures before.
- Discovery of a B₁₂(CN)₁₂²⁻ molecule with colossal stability that may find potential use as a halogen-free electrolyte in batteries. State-of-the-art theoretical modelling studies discovered that CN ligand substitution for hydrogen in B₁₂H₁₂²⁻ increases the second electron binding energy from 0.9 eV to 5.3 eV and makes it an extremely stable molecule.

Unique Aspects

This program supports research to develop a fundamental understanding and identification of detailed mechanisms responsible for the physical behavior of materials, and the incorporation of this knowledge into predictive models. Unique activities of the program include the design and characterization of new materials and the manner in which they interact with electromagnetic fields. These range from photo-induced charge transport in novel semiconducting materials to the optical interactions with meta-materials resulting in phenomena that could not be observed in naturally occurring materials. The research supported includes investigations on novel methods to modify the bandgap energy of materials for photovoltaics and optoelectronics. The program also emphasizes research to understand influence of magnetic fields on materials. Within BES, the program uniquely supports research on the thermal behavior of materials, investigating thermoelectric and magnetocaloric effects.

Mission Relevance

The research supported by this activity is necessary for the discovery of novel material properties and improving materials performance and reliability in chemical, electrical, and electrochemical applications, including the ability to generate and store energy in materials. Materials in energy-relevant environments are increasingly being exposed to extreme temperatures, strong magnetic fields, and hostile chemical conditions. A detailed understanding of how the physical-properties behavior of materials is linked to these surroundings and this exposure history is critical to the

understanding of photovoltaics, fast-ion conducting electrolytes for batteries and fuel cells, corrosion, novel magnetic materials for low-magnetic-loss power generation, magnetocaloric materials for high-efficiency refrigeration, and new materials for high-temperature gasification.

Relationship to Other Programs

This activity closely interacts with other programs in BES as well as with other DOE activities and interagency coordination groups:

- Within BES, this research activity sponsors—jointly with other core research activities, the Energy Frontier Research Centers program, and the Joint Center for Energy Storage Research (JCESR), as appropriate—program reviews, principal investigators' (PI) meetings, and programmatic workshops.
- There are active interactions with the DOE Office of Energy Efficiency and Renewable Energy (EERE) through workshops, program reviews, PI meetings, and communication of research activities and highlights.
- Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center activities and reviews in the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordinating Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).
- The program also participates in interagency coordination groups such as the Interagency Coordination Committee on Hydrogen and the Federal Interagency Materials Representatives (FIMaR).
- There are particularly active interactions with the National Science Foundation (NSF) through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.

Mechanical Behavior and Radiation Effects

Portfolio Description

This activity supports basic research to understand defects in materials and their effects on properties such as strength, structure, deformation, and failure. Defect formation, growth, migration, and propagation are examined by coordinated experimental and modeling efforts over a wide range of spatial and temporal scales. The program supports research on deformation of ultra-fine-scale materials, fundamental studies of radiation resistance, and research that would lead to microstructural design for increased strength, formability, and fracture resistance in energy-relevant materials. In addition to traditional structural materials, it is also becoming increasingly important to understand deformation and failure mechanisms in other materials used in energy systems (e.g., membranes, coating materials, electrodes). Within these areas, research on topics such as driven systems, mesoscale science, and non-linear cooperative phenomena (multiple inputs, e.g., radiation + stress + corrosion) are of interest.

The long-term goal of this program is to develop the scientific underpinning of defect behavior that will allow the development of predictive models for the design of materials having superior mechanical properties and radiation resistance. Towards this goal, research will be emphasized that takes advantage of the new capabilities to fabricate and test tailored structures down to the nanoscale, as well as utilizing newly developed and more powerful parallel computational platforms and experimental tools to evaluate and measure behavior at a wide range of time and length scales.

Scientific Challenges

Irradiation and deformation can push materials out of equilibrium, creating a dynamic system that has unexpected behaviors. Examples include the type of severe plastic deformation that leads to non-equilibrium and highly radiation-resistant particles in oxide-dispersion-strengthened alloys, and 3-dimensional patterns and unexpected phase separations/morphologies developed by radiation damage. These are challenging to study because of the non-equilibrium nature, but can have profound influence on the development of new understanding and superior materials.

Cooperative phenomena: What is missed when observing or modeling individual defects or processes in a linear fashion? Often it is found that there are synergistic and system-level effects to mechanical behavior, as a number of deformation processes rely on cooperative movement of defects or microstructural components, or application of more than one driving force. These processes include strain hardening, stress corrosion cracking, grain boundary sliding, and chemo-mechanical response. Investigation of mechanical behavior emphasizing cooperative phenomena could yield greater insight into material behavior. It should be emphasized that complexity alone is not of interest, but rather synergy in behavior leading to unexpected phenomena.

Bridging the length and time scales, modeling, and measurement from atomic to continuum: The formation and motion of defects take place over a wide range of length and time scales. In order to fully understand response of the materials, it is necessary to successfully model and measure defect motion and interactions over this range of length (from sub-nanometer to millimeter) and time scales (picoseconds to seconds) in a unified manner. This includes not only improved

computational methods but also improved measurement techniques for full 3-dimensional analysis of microstructures.

Projected Evolution

Systems that are driven away from equilibrium, or studies that focus on dynamic equilibrium, are of increasing interest. Important characteristics to be understood, for example, are the complex behaviors of interfaces (e.g. diffuse, dynamically re-arranging). This can affect the response to being driven by stress and strain (grain boundary sliding, segregation, particle-dislocation interactions, strain transfer across boundaries) and the response of the material to irradiation. One can also imagine systems resistant to being driven from equilibrium, or utilizing new strategies to provide equilibrium structures.

In addition to traditional structural materials, it is also important to understand deformation and failure mechanisms in other materials used in energy systems (e.g., membranes, coating materials, and electrodes), so this is an area of potential growth.

Areas that are not part of the core program and are therefore not encouraged for future research are studies that focus on mechanics of materials rather than materials science, high-strain-rate deformation, and high-dose irradiation response.

Significant Accomplishments

The Mechanical Behavior and Radiation Effects activity has resulted in a variety of scientific accomplishments, including the discovery of new materials that resist radiation damage; the understanding of new, tough ceramic materials; and the discovery of new analytical techniques and test methods that have impacted a number of research projects. Recent accomplishments include:

- Developing an understanding of ionization-induced healing in irradiated structural ceramics;
- Use of experimental methods and atomistic modeling to elucidate the mechanisms by which radiation resistance in silicon carbide is influenced by the proximity of grain boundaries;
- Discovering and defining unexpectedly high chromium mobility and selective oxidation during grain-boundary corrosion in Ni-Cr alloys;
- Measuring of rare and potentially harmful microstructural features during abnormal grain growth, by refinement of an x-ray diffraction technique; and
- Gaining an overarching picture of nano-indentation response in small structures, including the influence of stochastic events at length scales intermediate between “nano” and “bulk” behavior.

Unique Aspects

This activity represents a major fraction of federal support for basic research in mechanical behavior and is the sole source of federal support for basic research in radiation damage. In the science of mechanical behavior, cutting-edge experimental and computational tools are bringing about a renaissance, such that researchers are now beginning to develop unified, first-principles models of deformation, fracture, and damage.

Mission Relevance

The ability to predict materials performance and reliability and to address service life extension issues are important to the DOE mission areas of robust energy storage systems; fossil, fusion, and nuclear energy conversion; radioactive waste storage; environmental cleanup; and defense programs. Among the key materials performance goals for these technologies are good load-bearing capacity, failure and fatigue resistance, fracture toughness and impact resistance, high-temperature strength and dimensional stability, ductility and deformability, and radiation tolerance. Since materials from large-scale nuclear reactor components to nanoscale electronic switches undergo mechanical stress and may be subjected to ionizing radiation, this activity provides the fundamental scientific underpinning to enable the advancement of high-efficiency and safe energy generation, use, and storage as well as transportation systems.

Relationship to Other Programs

The research in this activity has, at its heart, the influence of defects on properties of materials and as such underpins, or interacts with, a number of BES, DOE, and other Federal government programs. Particularly, through its focus on atomic-level understanding of defect-property relationships, it is complementary to the emphasis on behavior of complex materials in the BES Physical Behavior of Materials activity, and to Electron and Scanning Probe Microscopies research, whose focus is on the relationship of structure to physical properties.

- Within BES and DOE, this research activity sponsors—jointly with other core research activities and the Energy Frontier Research Centers program as appropriate—program reviews, principal investigators’ meetings, and programmatic workshops. Important links have been made with DOE research on nuclear energy, fusion energy, lightweight materials, defense programs, and radioactive waste storage.
- The program also participates in interagency coordination groups such the Interagency Coordination Committee on Ceramics Research and Development and the Federal Interagency Materials Representatives (FIMaR).
- Some nanoscience-related projects in this activity are performed using capabilities in the Nanoscale Science Research Centers managed by the BES Scientific User Facilities Division. BES further coordinates nanoscience activities with other federal agencies through the National Nanotechnology Coordination Office (NNCO), which provides technical and administrative support to the National Science and Technology Council (NSTC) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) for the National Nanotechnology Initiative (NNI).
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the NSTC Subcommittee on the Materials Genome Initiative (MGI).

X-ray Scattering

Portfolio Description

This activity supports basic research on the fundamental interactions of photons with matter to achieve an understanding of atomic, electronic, and magnetic structures and excitations and their relationships to materials properties. The main emphasis is on x-ray scattering, spectroscopy, and imaging research, primarily at major BES-supported user facilities. Instrumentation development and experimental research in time-resolved and ultrafast materials science are an integral part of the portfolio.

Scientific Challenges

Ultrafast excitation and exploration of dynamic pathways to metastable states provides another path to explore the subtle energetic phase space of correlated electron materials (much like ultra-high-pressure techniques access new states along that not-fully-explored dimension). Optical, IR, and THz pumped probes can excite materials away from equilibrium through different mechanisms; and ultrafast probe measurements are capable of capturing the short-lived and elusive physics in a unique regime of matter. Recent and foreseeable advances in high-brightness x-ray sources create an unprecedented opportunity to image interactions at nanometer spatial dimensions and ultrafast time scales. Understanding how ultrafast coherent radiation can manipulate condensed matter and how matter relaxes back to its unperturbed state may ultimately lead to novel materials synthesis techniques, especially at the nanoscale.

Recent advances in both sources and instrumentation have yielded gains in intensity on samples, facilitating rapid experiments and in-place configurations. Smaller samples can be probed with unprecedented temporal and spatial resolution, accuracy, and sensitivity under various parametric conditions. Such information aids the development of novel processing techniques and the search for new exotic materials. In-place studies are entering the ultrafast time domain by coupling laser pumped ultrafast electronic excitations to atomic strain-driven processes. There also exists the possibility of selectively studying the dynamics of such phenomena through designed and driven excitations of quasi-particles and metastable states that would not necessarily be thermally accessible.

Projected Evolution

Advances in x-ray scattering and ultrafast sciences will continue to be driven by scientific opportunities presented by improved source performance and optimized instrumentation. The x-ray scattering activity will continue to fully develop the capabilities at the DOE facilities by supporting research that pushes instrumentation and technique development to address frontier scientific challenges. A continuing theme will be the integration and support of materials preparation and complex data analysis development, as these are vital to carrying out and understanding careful x-ray structural measurements related to materials properties. New investments in ultrafast science will focus on research that develops and uses radiation sources associated with BES facilities and beam lines, but also includes ultra-short-pulse x-ray and THz radiation probes created by conventional tabletop laser sources. The program does not support research considered “mature use” of existing x-ray or ultrafast techniques.

Significant Accomplishments

This program supports groups that have contributed to the development of such powerful techniques as inelastic x-ray scattering, x-ray absorption structural spectroscopy, x-ray microscopy and coherent diffraction imaging, nanoscale focused beam diffraction, time-resolved spectroscopy, and resonant x-ray scattering providing specific chemical, magnetic, and excitation contrast.

Recent accomplishments include:

- Sensitive measurements of surface-segregated atomic and electronic structure in new catalysis alloys and nano-particles were made, as well as measurements of distortions in the atomic ordering resulting from the interfacial constraints on perovskite oxide films that exhibit unique magnetic and electron-transport behavior.
- Progress in understanding the rich magnetic and electronic structure of correlated electron materials continues in terms of mapping out phase boundaries and determining the nature of the competing quantum interactions behind transitions in physical properties.
- Refined *in situ* techniques have become more adept at probing small samples, surfaces, and interfaces under extreme processing environments of temperature, pressure, and reactive gases.
- When a material is excited by light or thermal energy to non-equilibrium states, different pathways back to equilibrium often have different time scales. Recent experiments in ultrafast science have employed multiple probes with different sensitivity to various relaxation mechanisms. Fresh results are beginning to tease out the faster dynamics of electronic structure from the slower recovery of atomic motion and lattice strain.

Unique Aspects

The DOE history and mission have played important roles in BES' current position as the nation's steward of major x-ray facilities. As part of its stewardship, BES maintains strong fundamental research programs at these facilities in materials and related disciplines. This includes the research that has motivated the BES-supported construction of the Linac Coherent Light Source (LCLS) and National Synchrotron Light Source-II (NSLS-II). The unique properties of synchrotron and free electron laser radiation—high flux and brightness, tunability, polarizability, and high spatial and temporal coherence, along with the pulsed nature of the beam—afford a wide variety of experimental techniques whose development and early application to materials science are supported by this program.

Ultrafast materials science involves time-domain investigations examining, for example, the early stages of materials transformation through electronic structure excitation, and subsequent energy transfer through various quantum-mechanical structural pathways involving competing modes of ordering and energy dissipation. The aim of such ultrafast research is to investigate the details of dynamic events at the most fundamental time scales, leading to the understanding of emergent phenomena such as phase transformations and the nucleation of defects in materials that result in the degradation of their properties. Time-resolved fundamental investigations of the dynamic shifts in electronic structure and the flow of energy in new materials, such as two-dimensional films and surface states on topologically constrained quantum materials with strong

spin-orbit coupling, are supported by this activity. Potential applications involve coherent control of surface chemical reactions and structures, creation of non-equilibrium phonon distributions with ultra-short lifetimes or transient and metastable phase structures, dynamic control of magnetic spin physics and ferroelectric polarization ordering, and excitation driven separation of degeneracies in materials with competing states of quantum ordering.

Mission Relevance

The increasing complexity of DOE mission-relevant materials such as superconductors, semiconductors, and magnets requires ever more sophisticated scattering techniques to extract useful knowledge and to develop new theories for the behavior of these materials. X-ray scattering probes are among the primary tools for characterizing the atomic, electronic, and magnetic structures of materials in relevant processing and energy-conversion environments.

Relationship to Other Programs

Within the various DOE science and technology programs, x-ray techniques play a key role in the investigation of materials and processes related to energy conversion and use by providing atomic- and molecular-level information on the structure of nano-particles, layered hetero-structures, and catalytic surfaces under realistic chemical environments and in actual engineering designs such as those found in batteries and electronic devices. Extending into the ultrafast regime, there is the promise of expanding understanding across the full range of chemistry and materials sciences by allowing femtosecond stroboscopic investigations of the earliest stages of dynamic phenomena critical to energy conversion.

The x-ray scattering portfolio contributes to other program elements as they seek to understand atom and electron structural behavior relevant to the unique materials configurations supported by those programs. This is particularly true of the Experimental and Theoretical Condensed Matter Physics programs in BES because charge, spin, orbital and atomic structure and dynamics determination play a critical role in understanding materials behavior at the level of strong quantum interactions and emergent quantum coherence. There is close coordination with the BES Scientific User Facilities Division and with other agencies, including the National Science Foundation.

Within the larger federal research enterprise, program coordination is through the Federal Interagency Materials Representatives (FIMaR).

Neutron Scattering

Portfolio Description

This activity supports basic research on the fundamental interactions of neutrons with matter to achieve an understanding of the atomic, electronic, and magnetic structures and excitations of materials and their relationship to materials properties. Emphasis will be on the application of neutron scattering and spectroscopy as major tools for materials research primarily at BES-supported user facilities. Development of next-generation instrumentation concepts, software tools for data analysis and modeling, and novel applications of polarized neutrons are important elements of this activity.

Scientific Challenges

Quantum Materials – Quantitative understanding of the new states of matter such as spin liquids, topological insulators, topological magnon insulators, magnetic monopoles and skyrmions, and the collective mesoscale phenomena emerging from the interplay between charge, spin, orbital and lattice degrees of freedom in materials, including high temperature superconductors, multiferroics, thermoelectrics, ferroelectrics, spintronics and quantum magnets, remains a major challenge. Inelastic neutron scattering, diffraction and reflectometry will play major roles in the studies of these materials.

Matter Under Extreme Conditions – Extreme temperature (both ultrahigh and ultralow), high pressure, magnetic and electric fields, shear and combinations thereof are important parameters for material design and synthesis as well as for tuning material properties. Highly optimized neutron scattering spectrometers with novel sample environments will enable *in situ* studies at conditions relevant to understanding the mesoscopic behavior of materials. Similarly, scattering experiments at high magnetic fields can be used to study materials during phase transitions, allowing separation of magnetic field effects as well as to simulate effects normally observed via doping.

Multi-component Complex Materials – Interfaces play strong roles in the behavior of multi-component systems and thin films of hybrid materials. The role of the structure and dynamics of individual constituents on the emergent behavior in the materials can be readily probed by exploiting the unique contrast variation with isotopes and polarized neutrons using neutron scattering and reflectometry. Highly optimized instruments at the Spallation Neutron Source (SNS) will enable science requiring smaller samples with unprecedented resolution, accuracy, and sensitivity under relevant parametric conditions.

Projected Evolution

The Neutron Scattering activity will continue its stewardship role in fostering growth of U.S. neutron scattering community in the development of innovative time-of-flight neutron scattering and imaging instrumentation concepts and their effective utilization for transformational research. Topics that will be emphasized are new states of matter and phenomena in hard and soft condensed matter, spintronics, self-assembly, design principles and collective behavior of multicomponent systems, interfacial science, and mesoscale science where macroscopic properties are manifested. A continuing theme is fostering strong interaction between synthesis,

neutron scattering experiments, theory, and high performance computation to accelerate the fundamental understanding needed for predictive design of advanced materials for future energy needs. Areas that are not a high priority are those with a major focus on conventional and high temperature superconductivity and organic photovoltaics.

Significant Accomplishments

BES supported the pioneering research of Clifford G. Shull in the development of the neutron diffraction technique at Oak Ridge National Laboratory that led to the 1994 Nobel Prize in Physics. Shull's work launched the field of neutron scattering, which has proven to be among the most important techniques for elucidating the structure and dynamics of solids, superconductors, fluids, soft matter and magnetic materials.

Neutron scattering groups supported by this activity at the DOE national laboratories provided the leadership and expertise in the pioneering design and development of virtually all the current highly optimized time-of-flight instruments and techniques in neutron scattering and spectroscopy at the SNS. Recent scientific accomplishments include:

- First realization of a novel material that can conduct magnetic waves on its edge, but not within its bulk;
- Demonstration of the tunability of defects in the bulk to control the surface electronic properties of a canonical topological insulator;
- Established the wave-like properties of metallic magnetism and the itinerant character of magnetism in iron-based superconductors;
- Showed that the unconventional superconductivity can be continuously tuned towards a Mott insulator in an iron-based superconductor, indicating the similarity with cuprates that exhibit unconventional superconductivity driven by strong electronic correlations;
- Established evidence for the propagation of magnetic monopoles in a well-known quantum spin ice material and measured their mass;
- First direct observation of the Skyrmion Hall Effect;
- Discovered that the interactions of electrons and atom vibrations responsible for the thermal conductivity and electrical conductivity in materials can be altered with high temperature, a behavior well known to be controlled with high pressures;
- Established a key correlation between the properties of the high-temperature liquid dynamics and the arrested glassy state properties in three prominent classes of glass-formers: metallic, molecular, and network; and
- Developed a novel process known as dopant induced solubility control (DISC) that allows patterning of organic features with unprecedented small sizes.

Unique Aspects

The DOE history and mission have played important roles in shaping BES' current position as the nation's steward of major neutron facilities. Historically, neutron sources descended from the nuclear reactors that were constructed in the early 1940s as part of the U.S. Atomic Energy Program. This activity has evolved from the pioneering, Nobel prize-winning efforts of Clifford G. Shull in materials science to the current program that encompasses multiple techniques and disciplines. BES is a principal supporter of both research and instrumentation development at DOE's major U.S. neutron scattering facilities. It maintains strong fundamental research

programs in materials and related disciplines at these facilities that serve to drive advancements in both the techniques and instrumentation. High impact science from this activity provided the scientific case to motivate the construction of the SNS, the BES facility with the highest pulsed neutron flux in the world and a range of optimized neutron scattering instruments.

Mission Relevance

The increasing complexity of DOE mission-relevant materials including superconductors, magnets, magnetoelectric materials, energy storage devices, photovoltaics, thermoelectrics, materials for gas separation, metallic alloys, organic/inorganic hybrid materials and polymer nanocomposites requires ever more sophisticated scattering techniques to investigate the structure and dynamics at relevant length and time scales and to develop theories which can predict the behavior of these materials. Neutron scattering probes are among the essential tools for characterizing the atomic, electronic, and magnetic structures of materials. The activity is relevant to the behavior of matter in extreme environments including high and ultralow temperature, high pressure, shear, magnetic fields and combinations thereof.

Relationship to Other Programs

This activity interacts closely with the BES Scientific User Facilities Division in the development of new instrumentation concepts and sophisticated software tools for data analysis and coordination on complementary scientific portfolios. It supports focused research in the areas of superconductivity, magnetism, thermoelectrics, materials under extreme conditions, interfacial structure and dynamics for energy storage, hydrogen storage, gas separation, carbon sequestration, and catalysis. Nanoscience-related projects in this activity are coordinated with the Nanoscale Science Research Center user facilities and reviews in the BES Scientific User Facilities Division. In addition, there are coordination activities with other federal agencies:

- Coordination with the National Institute of Standards and Technology's Center for Neutron Research helps to ensure development of instrumentation and capabilities that best serve the broad neutron scattering user community.
- Predictive materials sciences activities and the associated theory, modeling, characterization, and synthesis research are coordinated with other federal agencies through the National Science and Technology Council Subcommittee on the Materials Genome Initiative.
- Active interactions with the National Science Foundation through workshops, joint support of National Academy studies in relevant areas, and communication about research activities.
- Coordination with National Science Foundation on research instrumentation infrastructure for such activities as crystal growth and characterization.
- Within the larger federal research enterprise, program coordination is through meetings of the Federal Interagency Materials Representatives (FIMaR).

Electron and Scanning Probe Microscopies

Portfolio Description

This activity supports basic research in materials sciences using advanced electron and scanning probe microscopies and related spectroscopy techniques to understand the atomic, electronic, and magnetic structures and properties of materials. This activity also supports the development of new instrumentation concepts and quantitative techniques, including ultrafast electron diffraction and imaging techniques, to advance basic science and materials characterizations for energy applications. The goal is to develop a fundamental understanding of materials through advanced microscopy and spectroscopy.

Scientific Challenges

There are major scientific challenges in understanding quantum materials in order to harness their rich technological potential. Advanced, innovative imaging and spectroscopy are needed to solve forefront scientific problems in understanding materials properties and functionality, including quantum phase transitions, order and disorder in quantum materials, new types of topological order, spin transport and dynamics, and nano-structuring as a means of controlling relevant parameters of quantum materials systems. Relevant research challenges include: imaging functionality at the near-atomic to the mesoscale; development of a fundamental understanding of electron scattering and nanoscale ordering phenomena in matter; utilization of high-resolution, quantitative analysis of nano- and mesoscale materials to understand the origin of macroscopic properties and enable the design of high-performance materials; understanding the electronic structure, spin dynamics, magnetism, and transport properties from atomistic to mesoscopic scales; understanding the interplay between charge, orbital, spin, and lattice structures in complex materials; determination of interface structures and understanding the link between surface/interface/defect structures and materials properties; correlation of structure and properties of nano- and meso-structured materials for energy applications with quantitative *in situ* analysis capabilities; development of time-resolved microscopy with high spatial, temporal, and energy resolutions to understand and potentially control emergent phenomena at their natural time and length scales, under equilibrium and/or extreme conditions; and the application of first-principles theory to understand the data obtained from microscopy instrumentation and how to use this information to predict the structures of real materials.

Projected Evolution

This program emphasizes basic research for the fundamental understanding of materials using advanced microscopy and spectroscopy techniques. The program will use currently available electron and scanning probe microscopy capabilities; develop new, innovative instrumentation and techniques; and use advanced scattering, imaging, and spectroscopy methods to understand functionality, fundamental processes, and dynamics of materials at the near-atomic to mesoscopic length scales.

To address forefront scientific challenges, new state-of-the-art experimental and theoretical techniques need to be developed. This activity will continue to support the development and use of advanced microscopy instrumentation/techniques, and the associated theoretical tools to understand the experiments, for research on imaging materials functionality and understanding the properties of materials. A growing area in recent years is imaging functionality and correlating structure and properties at the atomic or nanometer scale. In addition to the high

spatial and energy resolutions, recent research efforts also include ultrafast electron diffraction, spectroscopy, and imaging to understand the dynamics and behavior of matter under conditions far from equilibrium. The combination of multiple probes in a single experiment is expected to address complex and challenging materials science problems. Significant improvements in resolution and sensitivity in microscopy and related spectroscopy techniques will provide an array of opportunities for groundbreaking science. Research that is deemed “mature use” of microscopy techniques is not a programmatic priority.

Significant Accomplishments

This program has been a major U.S. supporter of microscopy research for developing a fundamental understanding of materials. Scientific achievements in this program include the development of leading U.S. capabilities for materials characterization at sub-angstrom length scales that are coupled with advances in detectability limits and precision quantitative analytical measurement. Historical accomplishments include: the development of the Embedded Atom Method to study defects in materials, which revolutionized computational materials science by permitting large-scale simulations of materials structure and evolution; the successful correction of electron microscope lens aberrations that allowed the first spectroscopic imaging of single atoms within a solid; the development of dynamic transmission electron microscopy, which couples high time resolution (~nanoseconds) with high spatial resolution (~nanometers), providing a unique tool for probing and understanding materials dynamics; and the visualization of electronic structure at the nanometer and atomic scale by spectroscopic imaging scanning tunneling microscopy, which contributed to the understanding of the electronic transport mechanisms for superconductivity. Investigations by local probes have revealed new physics in two-dimensional materials, including an electron-hole asymmetric sequence of fractional quantum Hall states in bilayer graphene afforded via electronic compressibility measurements using a scanning single-electron transistor.

Recent accomplishments include:

- Precision measurements of the heavy-fermion band structure using quasiparticle interference imaging scanning tunneling microscopy, in combination with theory, shows that the mechanism of Cooper pair formation (and thus superconductivity) is magnetic interactions between the spins on the Ce atomic sites in a heavy fermion superconductor CeCoIn₅. This is the first direct verification for a magnetic Cooper pairing in a material.
- With improved energy resolution, vibrational spectroscopy is performed for the first time in an electron microscope with a subnanometer focused electron beam.
- Magnetoelectric Force Microscopy is developed to detect the local cross-coupling between magnetic and electric dipoles. Combined experimental observation and theoretical modeling provide understanding on how a bulk linear magnetoelectric effect can be realized in a new family of materials.
- Precise determination of the 3D coordinates of thousands of individual atoms in a material allows direct measurements of the atomic displacement and full strain tensor through advanced electron tomography.
- Femtosecond optical doping and electron crystallography reveal metastable and hidden phases in correlated electron crystals.
- Through the development of atomically resolved secondary electron imaging method, the

atomic structure of the surface of a material is resolved in addition to its bulk atomic structure.

- Elastic softening phenomena associated with the lattice instability at ferroelectric phase transitions are revealed at length scales of ~10 nm. A giant elastic tunability of stiffness (>30%) was discovered in BiFeO₃ epitaxial thin films through an atomic force microscopy study utilizing band-excitation piezoresponse spectroscopy.
- Direct imaging by electron microscopy shows that amphiphilic peptoid molecules form tubes with radii of about 4 nm wherein both hydrophilic and hydrophobic groups are exposed to water, revealing another design principle for building nanostructures in soft matter.
- One-dimensional conductive edges and characteristic flaws are revealed in atomically thin transistors using near-field microwave microscopy.

Unique Aspects

Materials properties at macroscopic scale originate from microscopic details, via a hierarchy of length scales. This activity is driven by the need for quantitative characterization and understanding of the structure, chemistry, and physical properties of materials at near-atomic length scales. High spatial resolution in electron and scanning probe microscopies and spectroscopy provides unique opportunities to characterize atomic and mesoscale structures in technologically important materials. This activity supports comprehensive microscopy research in the development, implementation, and exploitation of a variety of electron beam and scanning probe techniques for fundamental understanding, characterization, and analysis of materials. These microscopy and spectroscopy tools have the highest spatial, energy, and time resolutions to address the forefront scientific questions in materials. Research results are increasingly coupled with first-principles theory, which offers quantitative insights on the atomic origins of materials properties.

Mission Relevance

This activity is relevant to materials research and energy technologies through the determination of structure and properties of mesostructured materials for a wide range of energy generation and use technologies. The nation's long-term energy needs present many fundamental challenges that require new materials and characterization tools such as electron beam and scanning probes. A recent report from the Basic Energy Sciences Advisory Committee has identified "Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales" as a transformative opportunity for discovery science. Performance improvements for environmentally acceptable energy generation, transmission, storage, and conversion technologies depend on a detailed understanding of the atomic, electronic, and magnetic structures found in advanced materials; electron and scanning probe microscopies and associated spectroscopy are among the primary tools for characterization of these structures. Analysis of the surface and interior of nano- or meso-scale structures related to the functionality of materials often require multimodal or multiple-probe *in situ* and *in operando* microscopy techniques under various environments. Design and development of revolutionary tools and techniques are needed to accelerate discovery and technological deployment of advanced materials.

Relationship to Other Programs

This activity interfaces with other research programs in BES, including X-Ray and Neutron

Scattering, Condensed Matter Physics, Synthesis and Processing Science, Materials Chemistry, and Catalysis Science. In addition,

- BES Nanoscale Science Research Centers (NSRCs) user facilities have thrust areas that provide unique capabilities for electron and scanning probe microscopy.
- This activity produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy (EERE).
- Within the larger federal research enterprise, program coordination is through meetings of the Federal Interagency Materials Representatives (FIMaR).

X-ray Light Source Facilities

Portfolio Description

This activity supports the operation of five x-ray light sources. Four of the light sources are storage ring-based sources: the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), the National Synchrotron Light Source-II (NSLS-II) at Brookhaven National Laboratory (BNL), and the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory (SLAC). The fifth light source, the Linac Coherent Light Source (LCLS) at SLAC, is a free-electron laser that provides laser-like radiation in the x-ray region of the spectrum, with 10 orders of magnitude greater peak power and brightness than the most powerful storage ring-based light sources. The newly constructed NSLS-II, which has replaced NSLS, started operation in FY 2015 to enable the study of material properties and functions at the nanoscale level and to provide the world's finest x-ray imaging capabilities.

Scientific Challenges

First, the facilities must be operated optimally, which means optimizing instrument-hours of operation, not just accelerator-hours of operation, and making the instruments widely available to the general user community. Second, optimal utilization of the LCLS coherent short-wavelength x-ray source will require continued development of new capabilities and advanced optics, instruments, and detectors.

Projected Evolution

X-ray scattering will continue to play a central role in the growth of BES programmatic science. The facilities will need continuous growth and advancement in terms of upgrades, new instruments, and increased availability of user time. The set of instruments associated with these facilities provides unique scientific and technical capabilities, rarely available in other parts of the world. These facilities need to be kept in an optimal operational condition in order to maintain and increase the tremendous scientific achievements they have facilitated.

The LCLS has properties vastly exceeding those of storage ring-based light sources in three key areas: peak brightness, coherence, and ultrashort pulses. The peak brightness of the LCLS is 10 orders of magnitude greater than current synchrotrons; the light is coherent or "laser like" enabling many new types of experiments; and the pulses are short (~50 femtoseconds in standard operation with improvements that can further reduce the pulse length to <5 femtoseconds), enabling studies of fast chemical and physical processes. These characteristics open new realms of scientific applications in the chemical, material, and biological sciences including fundamental studies of the interaction of intense x-ray pulses with simple atomic systems, structural studies on single nanoscale particles and biomolecules, ultrafast dynamics in chemistry and solid-state physics, studies of nanoscale structure and dynamics in condensed matter, and use of the LCLS to create plasmas.

Significant Accomplishments

During the past three decades, BES has been the nation's major supporter of x-ray light sources. BES support pioneered new storage ring lattices for improved beam stability and brightness; developed insertion devices that provide 10 to 12 orders of magnitude greater brightness than the best conventional x-ray sources; and discovered or developed such powerful experimental techniques as magnetic x-ray scattering, microbeam diffraction, x-ray microscopy, photoelectron spectroscopy and holography, x-ray nanoprobe, full-field and

diffraction imaging, synchrotron x-ray scanning tunneling microscopy, rapid acquisition pair distribution function, inelastic x-ray scattering using nuclear resonances, extended x-ray absorption fine structure, and near-edge x-ray absorption fine structure. The newly constructed light source, NSLS-II, has successfully commissioned and delivered x-rays to general users through routine top-off operation.

Recent accomplishments at the light source facilities include:

- At the Stanford Synchrotron Radiation Lightsource, researchers developed a new fabrication method to produce advanced x-ray diffractive nanostructured devices for high-resolution, high-efficiency manipulation of hard x-rays. At the Advanced Photon Source, scientists developed a new multilayer grating interferometer that was used to produce high-quality x-ray phase-contrast images. These new optical devices have significantly enhanced the imaging quality at the BES light sources.
- A new resonant soft x-ray scattering technique was developed at Lawrence Berkeley National Laboratory's Advanced Light Source to determine the 3-D structure and chemical composition of novel polymer films formed by directed self-assembly. The results of these new measurements will guide improvements in the directed self-assembly process to assist the semiconductor industry in the development of high-volume, cost-effective semiconductor manufacturing at the nanoscale.
- Time-resolved soft x-ray transmission microscopy measurements revealed the strength and duration of trains of electric and magnetic pulses affecting the circulation of a magnetic vortex that may lead to the possibility of magnetic memory bits with four states instead of two, improving storage capacity as well as energy efficiency.
- Scientists at NSLS-II developed a hard x-ray scanning microscope employing novel nanofocusing optics that produces a tiny x-ray beam with unprecedented spatial resolution. The microscope provides researchers a unique capability that opens up new scientific frontiers of high-resolution x-ray imaging, taking full advantage of the brightness of NSLS-II. This development won a 2016 Microscopy Today Innovation Award and a 2016 R&D 100 award.

Unique Aspects

The BES light sources are the most advanced facilities of their kind in the world. Together, they served over 11,000 users in FY 2016 from academia, Department of Energy (DOE) national laboratories, and industry, a number that has increased at a very fast pace in the past decade. As current facilities and those under construction are fully instrumented, this number could continue to grow at this fast rate in the next decade. These light sources represent the largest collection of such facilities operated by a single organization in the world. Conception, design, construction, and operation of these facilities are among the core competencies of the BES program.

Mission Relevance

These facilities were born from the most fundamental of needs, i.e., the need to characterize materials at the atomic and molecular level. In order to understand, predict, and ultimately control materials properties, it is necessary to determine the atomic constituents of materials, the positions of the atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, magnetic or electric field, and chemical change. A large number of experimental and theoretical tools are used to achieve these ends. In the last two decades, the experimental demands have motivated the development of large-scale powerful facilities that are too complex and expensive to develop, construct, and operate by individual institutions and/or companies. Such highly sophisticated tools are by their nature centralized and

staffed with specialists who provide expertise to the user community to optimize the scientific use of the facility. The development, construction, and operation of these facilities are one of the most important missions and core competencies of BES. The scientific accomplishments of these facilities are reflected in the large number of publications appearing annually in the most important scientific journals.

Relationship to Other Programs

- This activity has very strong interactions with all BES programmatic research that uses x-ray light sources. This includes research in atomic physics, condensed matter and materials physics, chemical dynamics, catalysis, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and much more.
- Interaction also exists with other parts of the Office of Science, notably the Office of Biological and Environmental Research and the Office of Fusion Energy Sciences, and with other areas of DOE, notably the National Nuclear Security Administration, the Office of Energy Efficiency and Renewable Energy, Office of Nuclear Energy, and the Office of Environmental Management.
- There are frequent contacts with other federal agencies in order to better coordinate efforts in optimizing beamlines and instruments. This activity is establishing more frequent contacts with international user facilities such as the European Synchrotron Radiation Facility (ESRF) in France, European X-Ray Free Electron Laser (XFEL) in Germany, Super Photon Ring-8 GeV (Spring-8) in Japan, Positron Elektron Tandem Ring Anlage III (PETRA III) in Germany, and others. The objectives are to share experiences and to make optimal use of present facilities.

Neutron Scattering Facilities

Portfolio Description

This activity supports the operation of two neutron scattering facilities: the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL), which is a high flux research reactor; and the Spallation Neutron Source (SNS) at ORNL, which is the most powerful pulsed spallation neutron source in the world.

Scientific Challenges

As new areas of science open up that are impacted by neutron scattering research, new instrumentation capabilities must be developed at the neutron scattering facilities and existing instrumentation must undergo a continual upgrade and refinement process to provide optimal capabilities for the user program and to enable world-class scientific research. Many of the current and future developments focus on increased effective intensity using new detector technology and focusing optics, increased resolution using long-wavelength neutron beams, and new sample environment capabilities.

Projected Evolution

Neutron scattering will continue to play a central role in the growth of BES programmatic science. The set of instruments associated with these facilities provides unique scientific and technical capabilities that serve the needs of the scientific community. These facilities necessarily must be kept in an optimal operational condition with increasing availability of user time in order to maintain and increase the tremendous scientific achievements they have facilitated.

Significant Accomplishments

Since the late 1940s, BES and its predecessors have been the major supporter of neutron science in the United States, from the earliest work of Clifford Shull and E. O. Wollan at ORNL's Graphite Reactor in the 1940s to the Nobel Prize in Physics shared by Clifford Shull and Bertram Brockhouse in 1994 for their work on neutron scattering. DOE has developed research reactors and spallation sources as high-flux neutron sources for neutron scattering research, including diffraction, inelastic scattering (spectroscopy), reflectivity, and imaging, and has helped pioneer virtually all the instruments and techniques used at these facilities world-wide. Because of the neutral charge and magnetic moment of the neutron, neutrons penetrate most materials with minimum absorption and, via their scattering from both the nuclei and the magnetic electrons, three-dimensional atomic and magnetic structures can be obtained. In addition, thermal neutrons have energies comparable to phonon and magnon excitations in solids, and thus can provide dynamic information via inelastic scattering. Neutrons possess other unique properties including sensitivity to light elements, which is invaluable to polymer, biological, and pharmaceutical research.

Neutron scattering studies have been crucial to a detailed understanding of many materials and properties including:

- The structure and dynamics of new classes of high-temperature superconductors,
- The structure of proteins utilizing the sensitivity of the technique to light elements in concert with light source data,
- The study of interfacial effects in magnetic thin films and superlattices using neutron reflectivity,
- The determination of complex polymer structures,

- Examination of porous materials including oil-bearing shales, and
- Non-destructive property measurements of automotive gears, brake disks, airplane wings, engines, and turbine blades utilizing the high penetrating power of neutrons for industrial applications.

Unique Aspects

The DOE neutron scattering facilities are the most advanced facilities of their kind in the world. Together, they serve over 1,300 users annually from academia, Department of Energy (DOE) national laboratories, and industry. These neutron scattering sources represent the largest collection of such facilities operated by a single organization. Conception, design, construction, and operation of these facilities are among the core competencies of the BES program.

Mission Relevance

These facilities were born from the most fundamental of needs, i.e., the need to characterize materials at the atomic and molecular level. In order to understand, predict, and ultimately control materials properties, it is necessary to determine the atomic constituents of materials, the positions of atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, magnetic or electric field, and chemical change. A large number of experimental and theoretical tools are used to achieve these ends. In the last two decades, the experimental demands have motivated the development of large-scale powerful user facilities that are too complex and expensive to develop, construct, and operate by individual institutions and/or companies. Such highly sophisticated tools are by their nature centralized and staffed with specialists who provide expertise to the user community to optimize the scientific benefit of the facility. The development, construction, and operation of these facilities are one of the most important missions and core competencies of BES. The scientific accomplishments of these facilities are reflected in the large number of publications appearing annually in the most important scientific journals.

Relationship to Other Programs

- This activity has very strong interactions with many areas of BES programmatic research. This includes research in condensed matter and materials physics, chemistry, soft matter materials, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and many other disciplines.
- Interaction also exists with other parts of the Office of Science, notably the Office of Biological and Environmental Research and the Office of Nuclear Physics, and with other areas of DOE, notably the National Nuclear Security Administration and the Office of Energy Efficiency and Renewable Energy.
- There are frequent contacts with other federal agencies in order to better coordinate efforts in optimizing beamlines and instruments. This also includes national and international user facilities such as the National Institute of Standards and Technology (NIST) Center for Neutron Research, Institut Laue-Langevin (ILL) in France, ISIS in the United Kingdom, Japan Proton Accelerator Research Complex (J-PARC) in Japan, and the future European Spallation Source (ESS) in Sweden. The objectives are to share experiences and to make optimal use of present facilities.
- In addition to scattering research, HFIR has ongoing programs for the production of important medical and industrial isotopes and for studying the effects of neutron irradiation on nuclear materials for fission and fusion reactors

Nanoscale Science Research Centers

Portfolio Description

The Nanoscale Science Research Centers (NSRCs) are DOE's premier user facilities for interdisciplinary research to understand and control matter at the nanoscale, serving as the basis for a national program that encompasses new science, new tools, and new computing capabilities. NSRCs provide critical infrastructure to support the national nanoscience research effort in energy and are the single largest investment of the National Nanotechnology Initiative. Each center has particular expertise and capabilities in selected theme areas such as electronic and photonic nanomaterials synthesis, electron microscopy, quantum structures, nanostructure characterization, catalysis, theory/modeling/simulation, soft and biological materials, imaging and spectroscopy, nanofabrication, and nanoscale integration. The centers are housed in custom-designed laboratory buildings located near major BES facilities for x-ray or neutron scattering, which complement and leverage the capabilities of the NSRCs. These laboratories contain clean rooms, nanofabrication resources, one-of-a-kind signature instruments, and other world-class instruments not generally available except at major user facilities. NSRCs are knowledge-based facilities which, in addition to instrumentation capabilities, offer optional collaborative research with expert scientists in their fields. These facilities are routinely made available on a scientific-merit basis to the broad research community. The five NSRCs are:

- Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory
- Center for Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory and Sandia National Laboratories
- Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory
- Center for Nanoscale Materials (CNM) at Argonne National Laboratory
- The Molecular Foundry (TMF) at Lawrence Berkeley National Laboratory

Scientific Challenges

Strategic investments in scientific areas of opportunity are necessary to help our nation develop a balanced research and development infrastructure, advance critical research areas, and nurture the scientific and technical workforce of the 21st century. Nanotechnology R&D is a top federal priority with broad potential implications for the nation's competitiveness. DOE's participation in this effort includes the development and operation of the NSRCs, whose goals include: (1) to attain a fundamental scientific understanding of nanoscale phenomena, particularly collective phenomena; (2) to achieve the ability to design and synthesize materials at the atomic level to produce materials with desired properties and functions; (3) to develop experimental characterization techniques and theory/modeling/simulation tools necessary to drive the nanoscale revolution; and (4) to take full advantage of synergies with other existing major user facilities.

There are a large number of specific scientific challenges, many of which benefit from the co-location of disparate disciplines in order to fabricate, assemble, and manipulate nanosized components into complex macroscopic 3D structures having functionality at nanoscale dimensions. One of the most challenging scientific problems is interfacing hard and soft matter, e.g., the world of electronic and structural materials with the world of biomaterials. These centers employ advanced experimental and theoretical tools to tailor and control the functionality, compatibility, performance, and integration of materials at such interfaces towards realizing systems that benefit society. These facilities must be kept in optimal operation to serve the ever-increasing number of users.

Projected Evolution

The NSRCs have established significant major capabilities and scientific leadership in several areas of nanoscience and work effectively with the large user community and their co-located facilities. The NSRC Triennial Reviews in CY 2016 showed that they have very high scientific productivity and serving a record 3,200 Users. The number of user proposals has steadily increased and acceptance rates have begun to decrease, indicating that the Centers are at capacity. Publication productivity in high-impact journals and the increasing user demand are signs that the NSRCs have been effectively assimilated into the national scientific infrastructure. The NSRCs are expected to perform as world-leading institutions, excelling both in scientific impact and productivity and in working with users. As they evolve, they will continue to develop new and unique world-leading capabilities in nanomaterials synthesis, characterization, nanofabrication, theory, and computation to serve the scientific community. Scientific themes are evolving synergistically into the physical biosciences and chemistry disciplines. With comprehensive capabilities and a collaborative research model, NSRCs accelerate the best research with users in a cost-effective way and assist in the translation of basic science with industry users in the area of manufacturing science.

Significant Accomplishments

All five NSRC facilities entered full user operations between FY 2006 and FY 2008. In the operations phase of the NSRCs, user activity has increased substantially from four operational centers with nearly 800 unique users in FY 2007 to the present five operating centers serving over 3,200 users in FY 2016. In FY 2015, the Electron Beam Microcharacterization Centers were merged with their co-located NSRCs, increasing the world-class capabilities available to NSRC users. Since their inception the NSRCs have served over 27,000 users, and they are essentially at capacity. Many new and exciting capabilities and scientific discoveries have emerged in a wide range of nanoscience areas. Research highlights include:

- The electron-beam-directed assembly of polymers with features relevant to terabit-per-square inch magnetic storage media was achieved.
- Novel metamaterials for next-generation terahertz flat optics were developed.
- World record atomic-scale electron tomography measurement capability was developed to determine positions of atoms (22 picometer accuracy).
- Unprecedented-spatial-resolution hard x-ray optics for nanotomography implemented.
- Precision polymer deuteration chemical processes were developed for enhancing neutron-beam probing of soft-material folding behavior.
- Lubricants composed of nanodiamonds and graphene that exhibit near-zero friction were invented.
- A new spectroscopic optical scanning probe for characterizing surface chemistry at the nanoscale was invented and is being commercialized.
- The first 3D crystalline nanoparticle superlattice assembly using a novel solution-based self-assembly approach was achieved.
- Successful synthesis of new 2D materials for quantum sensing and computing was demonstrated.
- New atmospheric pressure *in operando* x-ray characterization capabilities established for catalysis studies.

Unique Aspects

NSRCs are unique in that they provide capabilities and expert resources to the scientific user community to discover, understand, and synthesize nanomaterials and nanostructures, and facilitate access to other co-located major facilities including synchrotron radiation light sources,

neutron scattering centers, high-performance computing, and microfabrication facilities. The NSRC model accelerates cycles of learning and leverages investments in university, government and industry research projects. The NSRCs offer a broad range of capabilities and are accessible without usage fees for non-proprietary work, with instrument time and staff support allocated on the basis of peer-reviewed proposals. The purposes of the NSRCs are as follows:

- Advance the fundamental understanding and control of phenomena and materials at the nanoscale regime.
- Provide an environment to support interdisciplinary research of a scope, complexity, and disciplinary breadth not possible under traditional individual-investigator or small-group efforts.
- Provide the foundation for the development of nanotechnologies important to DOE.
- Provide unique and state-of-the-art tools to university, laboratory, and industry researchers and leverage the capabilities of other national user facilities for materials characterization employing photons and neutrons.
- Provide a formal mechanism for both short- and long-term collaborations and partnerships among DOE laboratory, academic, and industrial researchers.
- Provide training for graduate students and postdoctoral associates in interdisciplinary nanoscale science, engineering, and technology research.

Mission Relevance

A part of the mission of the Office of Science is to "deliver the premier tools of science to our Nation's research enterprise." The NSRCs join the suite of major DOE user facilities that fulfill this objective. A seminal DOE-BES workshop and subsequent report on *Basic Research Needs to Assure a Secure Energy Future* ([report link](#)) cited nanoscience as a critical cross-cutting theme, and this has been reiterated in numerous follow-up reports on Basic Research Needs for specific focused aspects of energy research, such as the hydrogen economy ([report link](#)), solar energy utilization ([report link](#)), and solid-state lighting ([report link](#)). The most recent BES Advisory Committee (BESAC) report *Challenges and Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* ([report link](#)) further emphasizes the importance of nanoscience to achieving breakthroughs at these frontiers. In addition, BES and the National Science and Technology Council co-sponsored a major workshop and report on *Nanoscience Research for Energy Needs* ([report link](#)) that identified key research targets and foundational themes for energy-related nanoscience. As stated in the Executive Summary of that report, "At the root of the opportunities provided by nanoscience to enhance our energy security is the fact that all of the elementary steps of energy conversion (e.g., charge transfer, molecular rearrangement, chemical reactions, etc.) take place on the nanoscale."

Relationship to Other Programs

- The fundamental science being carried out at the NSRCs is closely related to BES programmatic research spanning nanometer through mesoscales at universities, national laboratories and companies. Over 30% of BES-supported principal investigators are NSRC users. NSRCs strongly support the DOE Energy Innovation Hubs and Energy Frontier Research Centers.
- Researchers supported by other parts of the Office of Science, other parts of DOE, and other federal agencies are part of the overall NSRC user community.
- BES coordinates nanoscience activities with other federal agencies through the National Science and Technology Council (NSTC) Nanoscale Science, Engineering, and Technology (NSET) subcommittee, which leads the National Nanotechnology Initiative.

Accelerator and Detector Research

Portfolio Description

This activity supports basic research in accelerator physics, x-ray and neutron detectors, and advanced x-ray optics instrumentation. Accelerator research is the cornerstone for the development of new technologies that will improve the performance of light sources and neutron spallation facilities. The research explores new areas of science and technologies that will facilitate the construction of next-generation accelerator-based user facilities. The program is investing in research leading to a new and more efficient generation of photon and neutron detectors and in x-ray optics which are crucial components in the optimal utilization of the neutron or photon beams. Research includes studies on creating, manipulating, transporting, and diagnosing ultra-high-brightness electron beam behavior from its origin at a photocathode to propagation through undulators, and on transporting, analyzing, and detecting x-ray beams. Studies on achieving sub-femtosecond free-electron laser (FEL) pulses are also undertaken. Demonstration experiments are being pursued in advanced FEL seeding techniques, the study of methods to control the spectral properties of an x-ray self-amplified spontaneous emission (SASE) FEL using amplitude and phase mixing, and other optical manipulations to reduce the cost and complexity of seeding harmonic generation FELs. High-precision timing techniques for synchronization of accelerator and laser systems and for high-resolution measurements of electron- and photon-beam pulse duration and timing are being explored. Experimental tests of beam phase-space distributions are being conducted to demonstrate loss-control mechanisms for very high proton beam currents at neutron sources. Theoretical and experimental studies on collective electron effects are also supported.

Scientific Challenges

The Accelerator and Detector Research Program supports work toward the development of:

- New accelerator concepts crucial to the design and upgrade of synchrotron light sources and neutron scattering facilities.
- High-repetition-rate, ultra-bright, transform-limited, femtosecond x-ray pulses over a broad photon energy range with full spatial and temporal coherence.
- New electron sources to optimize the performance of FEL facilities, which are presently limited in x-ray power and spectrum coverage due to the unavailability of suitable injectors. Ultra-fast and ultra-bright electron sources are also required for advances in ultrafast electron diffraction and future ultrafast electron microscopy.
- Components suitable for diffraction-limited storage rings with beamlines, optics, and detectors compatible with the increase in brightness afforded by upgraded storage rings.
- New detectors that are capable of using the high data rates associated with high-brightness sources, thus increasing beamline efficiencies and user throughput.
- Low-background, high-spatial-resolution neutron detectors, and replacement of Helium-3-based detectors.
- X-ray optics instrumentation that can compensate for detector limitations to enhance the combined spatial, temporal, and energy resolution of experimental data.
- Special emphasis on R&D leading to more energy-efficient machines and devices that go beyond the most common methods of particle acceleration.

Projected Evolution

X-ray and neutron scattering will continue to play a central role in the growth of Basic Energy Sciences (BES) programmatic science. The Spallation Neutron Source (SNS) will be the most

powerful neutron spallation source in the world for years to come. Future FEL light sources are expected to provide high-repetition-rate, ultra-bright, transform-limited, femtosecond x-ray pulses over a broad photon energy range, with full spatial and temporal coherence.

Two major components will be required for the advancement of material science: the production of photon beams with increased average flux and brightness, and the detection tools capable of responding to the high photon-beam intensity. The first component will require higher repetition-rate photocathode guns and radiofrequency systems, and photon beams of enhanced temporal coherence, such as produced by improved seeding techniques or x-ray oscillators in the case of FELs. Secondly, detectors will require higher computational capabilities per pixel, improved readout rates, radiation hardness, and better energy and temporal resolutions. Additionally, R&D will be required to produce ultrafast beam instrumentation capable of measuring accurately femto- and attosecond bunch lengths. Higher neutron-flux capabilities at the SNS will demand high-intensity hydrogen negative ion currents, possibly provided by the development of high-power and high-frequency lasers, and detectors designed for advanced neutron imaging with very high throughput. Finally, R&D emphasizing energy-efficient machines and strong collaborations among the national laboratories and universities will allow a cost-effective, coordinated, and interdisciplinary approach to research and development in accelerators, detectors, and x-ray instrumentation.

Significant Accomplishments

- This activity was a major supporter of theoretical and experimental studies that led to realization of the Linac Coherent Light Source (LCLS). Theoretical and simulation studies addressed many of the fundamental physics questions concerning SASE FELs and high-brightness beams, leading to successful experiments.
- A novel concept to generate multiple simultaneous spikes, or multi-color, x-ray FEL pulses with unprecedented performance in terms of power and pulse-delay control was demonstrated. The novel scheme outperforms existing techniques at soft x-ray wavelengths, and produces high-power, femtosecond pulses flexible color separation. The development opens the way to new forms of spectroscopy.
- An innovative *in situ* and *in operando* x-ray analysis system was developed to fully explore and analyze the physics and chemistry of photo-cathode materials.
- A program that explores the application of 3D techniques to the difficult problem of integrating x-ray sensors of high-resistivity silicon and readout application-specific integrated circuits of low-resistivity silicon has achieved the first successful three-dimensionally integrated chip for photon science. When fully developed, these sensors will be capable of handling synchrotron radiation at energies up to 100 keV.
- A new imaging pixel array detector was developed that can acquire successive high-dynamic-range x-ray images at rates of up to 10 million frames per second, allowing acquisitions of real-time x-ray “movies” of structural changes in matter.
- A tool that provides a powerful pulse-by-pulse diagnostic with femtosecond resolution allows scientists to directly measure the x-ray power profile and to obtain a much more detailed view of the individual pulses that interact with their samples. For the first time, scientists can directly measure the x-ray power profile on a shot-by-shot basis with femtosecond resolution, providing a noninvasive diagnostic tool for photon experiments and new insight into lasing dynamic.
- A suite of tools for analysis and management of scattering data obtained in materials experiments at BES facilities was developed. This collaboration with the Office of Advanced Scientific Computing Research was driven by the increasing data and

computational requirements of handling and using data in diffuse scattering analysis of materials and their structural characterization.

- An ultrafast electron diffraction system developed to complement the capabilities of x-ray FELs has achieved unprecedented detection sensitivities and has demonstrated the highest combined spatial and temporal resolutions of similar existing systems. The system was used to detect the temporal evolution of non-equilibrium phonons in femtosecond laser-excited ultrathin single-crystalline gold films, establishing the usefulness of high-energy UED for dynamic momentum resolved phonon studies.

Unique Aspects

Technological advances require new materials and chemical processes for novel and improved sources of energy. The necessary tools enabling control and observation of the temporal evolution of electrons, atoms, and chemical reactions demand machines capable of producing high brightness, high duty factor, and short beam pulses. The accelerator and detector research carried out by the program aims to improve the output and capabilities of synchrotron radiation light sources and the neutron scattering experiments at facilities that are the most advanced of their kind in the world. These light sources and neutron scattering sources represent the largest collection of such facilities operated by a single organization in the world.

Mission Relevance

The Accelerator and Detector Research program supports the most fundamental of research needs to characterize and control materials at the atomic and molecular level. In order to understand, predict, and ultimately control materials properties, it is necessary to determine the atomic constituents of materials, the positions of the atoms in materials, and how the materials behave under the influence of external perturbations such as temperature, pressure, chemical attack, and excitation by photons, electrons, and other particles. The activity seeks to develop new concepts in accelerator science to be used in the design of accelerator facilities for synchrotron radiation and spallation neutron sources that will provide the means necessary to achieve a fundamental understanding of the behavior of materials. Also supported is the development of higher-precision, more efficient detectors capable of acquiring data several orders of magnitude faster than state-of-the-art detectors, and advanced x-ray optics that offers higher precision and higher accuracy in order to fully exploit the high fluxes delivered by the new facilities.

Relationship to Other Programs

- This activity has very strong interactions with all BES programmatic research that uses synchrotron and neutron sources. This includes research in atomic physics, condensed matter and materials physics, chemical dynamics, catalysis, geosciences, high-pressure science, environmental sciences, engineering, biosciences, and much more.
- This activity is a stakeholder of the Office of High Energy Physics Accelerator Stewardship subprogram, established to support use-inspired basic research in accelerator science and technology.
- There is an ongoing collaboration with the Advanced Scientific Computing Research program to support code development relevant to beam dynamics and to develop tools and codes addressing the exponential growth of experimental data at the BES facilities.
- This activity also interacts with other DOE offices, especially in the funding of capabilities whose cost and complexity require shared support.
- There are ongoing industrial interactions through the DOE Small Business Innovation Research and Small Business Technology Transfer programs for the development of advanced accelerator technology, detectors, and x-ray optics instrumentation.

Atomic, Molecular, and Optical Sciences

Portfolio Description

This program supports basic experimental and theoretical research aimed at understanding the structural and dynamical properties of atomic and molecular systems. The research focuses on fundamental interactions of these systems with photons and electrons to characterize and control their behavior. The goal is to develop accurate quantum-mechanical descriptions of dynamical processes such as chemical bond breaking and forming, interactions in strong fields, and electron correlation. Topics of interest include the development and application of novel, ultrafast probes of matter; the interactions of atoms and molecules with intense electromagnetic fields; and quantum control of atomic and molecular systems.

Scientific Challenges

In recent years, atomic, molecular, and optical science (AMOS) has transformed from a field in which the fundamental interactions of atoms, molecules, photons, and electrons are probed to one in which they are controlled. Systems studied are increasingly complex, and exhibit highly correlated, non-perturbative interactions. Scientists can shape the quantum-mechanical wave functions of atoms and small molecules using controllable laser fields, create nanoscale structures that manifest novel light-matter interactions and properties, and drive electrons coherently to generate ultrafast x-ray pulses. Theoretical advances are enabling modeling and simulation of increasingly complex systems to provide interpretation of existing data, and predictions for new experiments. These capabilities create opportunities to investigate chemical processes under conditions that are far from equilibrium, where complex phenomena are predominant and controllable, and on ultrafast timescales commensurate with the motions of atoms and electrons. Research in AMOS is fundamental to meeting the grand challenges for basic energy sciences, as identified in the 2007 report from the Basic Energy Sciences Advisory Committee, *Directing Matter and Energy: Five Challenges for Science and the Imagination*, and reiterated in the 2015 report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* (<https://science.energy.gov/bes/community-resources/reports/>).

Projected Evolution

The program emphasizes ultrafast, strong-field, short-wavelength science, and correlated dynamics in atoms and molecules. The AMOS program will continue to have a prominent role at Basic Energy Sciences (BES) facilities in understanding and controlling the interaction of intense, ultrafast extreme ultraviolet and x-ray pulses with matter. Examples include the use of high-harmonic generation or its variants as soft x-ray sources; intense, ultrafast x-ray science at the Linac Coherent Light Source (LCLS); and development and characterization of femtosecond and attosecond pulses of x-rays at accelerator-based and table-top sources. Applications at these light sources include ultrafast imaging of chemical reactions, diffraction and harmonic generation from aligned molecules, and inner-shell photoionization of atoms and molecules. Coherent control of nonlinear optical processes and tailoring of quantum-mechanical wave functions with lasers will continue to be of interest, particularly in molecular systems. Experimental and theoretical tools will be used to study low-energy electron-molecule interactions in the gas and condensed phases. Key targets for greater investment include

attosecond science, ultrafast x-ray science, and ultrafast electron diffraction from molecular systems.

The AMOS program is not accepting applications in the areas of quantum information science, nanoscience, bioscience, and science of ultracold systems.

Significant Accomplishments

The AMOS program has been a major supporter of experimental and theoretical studies of the fundamental properties of atoms, ions, and small molecules and their interactions with photons and electrons. This activity has produced a vast knowledge base, with a broad impact on science and technology. It has led to the development of powerful new methods for momentum imaging of collision fragments that have seen wide application in atomic, molecular, and chemical physics. This knowledge is being used to control the quantum behavior of atoms and molecules and has propelled further development and scientific applications of ultrafast x-ray sources using table-top lasers and third-generation synchrotrons (i.e., the Advanced Light Source and the Advanced Photon Source). Enhanced high-harmonic generation and fundamental interactions of intense controlled laser fields with atoms and small molecules leading to ionization and fragmentation have been explored in great detail. Efforts involving high-field interactions, ultrafast processes, and ultrashort x-ray pulses continue to build the science foundation required for research at x-ray free-electron lasers such as the LCLS. X-ray pulses with durations of femtoseconds can produce stop-action pictures of the motion of atoms during molecular transformations. New sources, producing attosecond-duration pulses, enable imaging of the real-time motion of electrons during the course of chemical reactions.

Recent accomplishments in the program include:

- Generation of ultrashort x-ray pulses from table-top, laser-based sources to provide complementary capabilities to x-ray free-electron lasers.
- High-harmonic generation in gases and solids has been used to shift laser light from the infrared or visible to extreme-ultraviolet and soft x-ray wavelengths.
- Optical manipulation of the harmonic-generation process has been used to produce isolated extreme ultraviolet pulses with linear or circular polarization and with pulse durations shorter than 100 attoseconds.
- New sources and methods have been developed to use ultrafast electron diffraction for three-dimensional imaging of gas-phase species, providing sub-angstrom spatial resolution and femtosecond time resolution.
- AMOS scientists were deeply involved in commissioning and early experiments at the LCLS and have continued to lead and contribute to many ground-breaking experiments. In addition to leading development of an x-ray split-and-delay instrument and the imaging end-station, AMOS researchers have led pioneering experiments to develop a fundamental, quantitative understanding of the complex molecular dynamics induced by very-high-intensity ultrafast x-ray pulses. Results at this facility also include single-particle imaging of nanoparticles, inner-shell lasing, and non-linear x-ray spectroscopy. AMOS scientists continue today to set the stage for new breakthroughs to exploit next-generation capabilities that will be available when the LCLS-II construction project is completed.
- Pump-probe techniques using ultrafast x-rays have enabled ultrafast chemical dynamics measurements with atomic specificity and femtosecond time resolution.

Unique Aspects

The knowledge and techniques developed by investigators in the AMOS program are critical components of the fundamental science effort of the Department of Energy (DOE) and research conducted at BES user facilities. The results of this research have applicability in a wide array of science and technology. The AMOS activity provides new ways to control and probe interactions in the gas and condensed phases, enhances our ability to understand materials, and enables full exploitation of the BES x-ray light sources. This enabling aspect will continue to be emphasized, particularly with respect to research involving the generation and application of ultrafast, intense x-ray and extreme ultraviolet light pulses using the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL), the Advanced Photon Source at Argonne National Laboratory, and the LCLS and the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory (SLAC). This area of research benefits from research efforts in the Ultrafast X-ray Science Laboratory at LBNL and the PULSE Institute for Ultrafast Energy Science at SLAC. The AMOS program is a major supporter of synchrotron-based and x-ray free-electron-laser-based atomic, molecular, and optical science in the United States.

Mission Relevance

The knowledge and techniques produced by this activity form a science base that underpins several aspects of the DOE mission. New methods for using photons, electrons, and ions to probe matter lead to more effective use of BES synchrotron, free-electron laser, and ultrafast electron diffraction facilities. Similarly, studies of formation and evolution of highly-excited states of atoms, molecules, and nanostructures provide a fundamental basis for understanding elementary processes in solar energy conversion and radiation-induced chemistry.

Relationship to Other Programs

- The program supports experiments involving ultrafast x-ray characterization and AMOS at the LCLS at SLAC, in coordination with the BES Scientific User Facilities Division.
- Numerous complementary relationships exist between the AMOS program and other core research activities across the BES Chemical Sciences, Geosciences, and Biosciences Division in the development and application of ultrafast methods to elucidate and control molecular dynamics and charge transport important for photochemical reactions and light-harvesting applications.
- A close working relationship exists with the National Science Foundation (NSF) Atomic Molecular and Optical Physics program. AMOS and NSF have co-funded the National Academies' activities sponsored by the Committee on Atomic, Molecular, and Optical Sciences.

Gas Phase Chemical Physics Research

Portfolio Description

This program supports research on gas-phase chemical processes important in energy applications. In the past, clean and efficient use of chemical energy was the major focus, such as in combustion processes, and it continues to be a significant driver. The overall goal of this program is to understand energy flow and reaction mechanisms in complex, nonequilibrium, gas-phase environments in which the coupling of chemical and transport processes is poorly understood, such as those encountered in combustion. The program may be divided into four basic science research thrusts described below.

1. *Light-Matter Interactions.* This thrust consists of research in molecular spectroscopy and diagnostics development to probe molecular structure, dynamics and interactions in complex gas-phase systems. This research is expected to provide approaches for chemical and physical analysis of heterogeneous and dynamic gas-phase environments.
2. *Chemical Reactivity.* This thrust includes chemical kinetics and mechanisms, chemical dynamics, collisional energy transfer, and construction of, and calculations on, molecular potential energy surfaces. This research is expected to develop fundamental understanding of energy flows and chemical reactions, which is the basis for determining accurate rate constants and predictive chemical mechanisms, and to develop and validate new theoretical methods to improve accuracy of theoretical chemical kinetics.
3. *Chemistry-Transport Interactions.* This thrust consists of multidimensional, multi-scalar measurements in reacting flows and direct numerical simulation and large eddy simulation modeling of turbulent reacting flows. Research in this area is expected to lead to the development of multiplexed diagnostics that measure many variables simultaneously to overcome irreproducibility associated with turbulence and a better understanding of turbulence-chemistry interactions.
4. *Gas-Particle Interconversions.* This thrusts consists of research on the formation, growth and evaporation of small particulates and aerosols and the transition to supercritical fluids at high pressures. This research is expected to lead to the development of mechanistic models of particle formation and growth, as well as a better understanding of particle evaporation.

Scientific Challenges

Several challenges for the gas phase chemical physics (GPCP) community voiced at research meetings, workshops, and strategic planning sessions are listed below.

- Develop artificial intelligence methodologies to automate gas phase chemical physics modeling and calculations.
- Develop experimental and computational methods that can handle more complex molecules, multi-species, and multi-reaction systems.
- Understand kinetics at high pressures where collisions do not occur as isolated binary events.
- Understand the role of non-thermal kinetics, i.e., the effect of reactions occurring during the thermalization process.
- Understand the transition between gas and condensed phase including transitions from polycyclic aromatic hydrocarbons to stacked polymers and evaporation to sprays.

- Develop experimental and computational methods to characterize rare events and stochastic processes by understanding the critical roles of heterogeneity, non-ideality, and disorder.
- Understand and control the complexity of interacting chemistry and physics via revolutionary advances in models, algorithms and computing.
- Interrogate the relationship of reaction processes across time and length scales via transformative advances in imaging capabilities.

Projected Evolution

Major thrust areas supported by the Gas Phase Chemical Physics program include quantum chemistry, reactive molecular dynamics, chemical kinetics, spectroscopy, predictive combustion models, combustion diagnostics, and soot formation and growth. Currently, increased emphasis in gas-phase chemical physics is on validated theories and computational approaches investigating the effect of non-thermal initial distributions on the reactions of radicals, experimental investigations of radical-radical reactions, better insight into chemical reactions at high pressures, and improved understanding of the interaction of chemistry with fluid dynamics and stochastic in-cylinder processes.

The Gas Phase Chemical Physics program does not support research in non-reacting fluid dynamics and spray dynamics, data-sharing software development, end-use combustion device development, and characterization or optimization of end-use combustion devices.

Significant Accomplishments

Recent accomplishments in the Gas Phase Chemical Physics program include the following:

- Development of new spectroscopic techniques as well as an improved understanding and interpretation of complicated spectra has resulted in a number of significant breakthroughs including the direct observation and kinetics of important intermediates in combustion and atmospheric chemistry including the Criegee intermediate and hydroperoxy alkyl radical (QOOH), and the direct determination of isomerization transition state energy barriers.
- Direct confirmation of the role of hydrogen-abstraction and acetylene-addition processes in the soot formation mechanism was achieved by use of a hot nozzle coupled to a synchrotron (Advanced Light Source).
- Development of single shot multi-species detection was achieved via Raman scattering measurements of 12 species in a dimethyl ether flame.
- Inclusion of the prompt dissociation of HCO, prior to achieving thermal equilibrium, in chemical kinetic modeling has been shown to influence the combustion of important fuels.

Unique Aspects

The Basic Energy Sciences (BES) Gas Phase Chemical Physics research activity is unique in its long-term support of a number of fundamental chemical science areas, and in its integration of capabilities from research universities and DOE national laboratories, enabling long-term progress in difficult scientific areas as well as effective coupling to DOE missions. This activity also has oversight for several national laboratory programs, including the Combustion Research Facility (CRF), a unique, multi-investigator research laboratory that has a strong collaborative visitor program that promotes synergy between BES-supported basic research and the applied science and technology programs supported by the Office of Energy Efficiency and Renewable Energy (EERE) and industry.

Mission Relevance

The GPCP activity contributes strongly to the DOE mission in the efficient and clean combustion of fuels. The coupling of complex chemistry and turbulent flow has long challenged predictive combustion modeling. Truly predictive combustion models enable the design of new combustion devices (such as internal combustion engines, burners, and turbines) with maximum energy efficiency and minimal environmental impacts. In transportation, the changing composition of fuels, from those derived from light, sweet crude oil to biofuels and fuels from alternative fossil feedstocks, puts increasing emphasis on the need for science-based design of modern engines.

Relationship to Other Programs

Research under this activity complements research supported across BES and coordinates and leverages efforts with other agencies and facilities. Strong ties exist between the GPCP program and other programs in the BES Chemical Sciences, Geosciences, and Biosciences Division. Development of computational methods for potential energy surfaces are carried out by investigators supported by both the GPCP program and the Computational and Theoretical Chemistry program. The Condensed Phase and Interfacial Molecular Science program and the GPCP program support research in high pressure gas-liquid interfaces. The Atomic Molecular and Optical Sciences program and the GPCP program use several of the same DOE facilities and leverage experimental techniques developed in the programs. The GPCP program and DOE EERE support coordinated combustion research efforts at the CRF and at Argonne National Laboratory. The GPCP program works with several federal research agencies as an active member of the Multi-Agency Coordinating Committee on Combustion Research to host an annual Fuels Research Review.

Condensed Phase and Interfacial Molecular Science

Portfolio Description

The Condensed Phase and Interfacial Molecular Science (CPIMS) program emphasizes basic research at the boundary of chemistry and physics, pursuing a molecular-level understanding of chemical, physical, and electron- and photon-driven processes in liquids and at interfaces. With its foundation in chemical physics, the impact of this crosscutting program on DOE missions is far-reaching, including energy utilization, catalytic and separation processes, chemical synthesis, energy storage, and subsurface chemical and transport processes. Experimental and theoretical investigations in the condensed phase and at interfaces aim to elucidate the molecular-scale chemical and physical properties and interactions that govern chemical reactivity, solute/solvent structure and transport. Studies of reaction dynamics at well-characterized surfaces and clusters lead to the development of theories on the molecular origins of surface-mediated catalysis and heterogeneous chemistry. Studies of model condensed-phase systems target first-principles understanding of molecular reactivity and dynamical processes in solution and at interfaces. Studies across scales confront the transition from molecular-scale chemistry to collective phenomena in complex systems. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiation-driven chemistry in nuclear fuel and waste environments.

Scientific Challenges

Research in Condensed Phase and Interfacial Molecular Science is fundamental to meeting the grand challenges for basic energy sciences, as identified in the report *Directing Matter and Energy: Five Challenges for Science and the Imagination* ([report link](#)). Specific opportunities include: develop and apply new experimental methods for characterizing chemically active molecular-scale structures and reaction mechanisms at interfaces; characterize high-energy electron- and photon-stimulated processes at complex interfaces; design quantitative models for condensed-phase solvation that include polarization, charge-transfer, and confinement effects; develop a structural basis for understanding gas/surface interactions, encouraging site-specific studies that measure local behavior at both defined sites and transient, complex environments; and understand the molecular origins of condensed-phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding and proton transport.

Projected Evolution

The program will continue to support research using new experimental and theoretical tools that push the horizon of spatial and temporal resolution needed to probe chemical behavior selectively at interfaces and in solution, enabling studies of composition, structure, bonding, and reactivity at the molecular level. The transition from molecular-scale chemistry to collective phenomena in complex systems is also of interest, including the effects of solvation on chemical structure and reactivity, in both aqueous and non-aqueous media. In this manner, the desired evolution for supported research is toward predictive capabilities that span the microscopic to mesoscale domains, enabling the computation of individual molecular interactions as well as their role in complex, collective behavior in the real world. Key targets for greater investment in the near future include a shift away from ideal, perfectly ordered interfaces toward more complex interfaces, including those created with amorphous materials; systems with novel solvents and mixed solvent systems; and experimental and computational studies that extend

molecular-level insight across a range of scales. These new directions are described further in the recent reports entitled *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* ([report link](#)) and *From Quanta to the Continuum: Opportunities for Mesoscale Science* ([report link](#)).

The Condensed Phase and Interfacial Molecular Science program does not fund research in continuum fluid mechanics or fluid dynamics, applications such as the development of micro-scale devices, and research that is of principal importance to medical sciences and applications.

Significant Accomplishments

Recent accomplishments in the Gas Phase Chemical Physics program include the following:

- The pursuit of substrates needed for chemical imaging experiments has led to the first demonstration of borophene.
- Novel multidimensional coherent spectroscopy has enabled the first observation of transient excitons in metals.
- The interfacial radioactive transformation of iodine-125 to an isotope of tellurium in gold layers was demonstrated for the first time, providing a new means to study radiation-driven reactions at liquid/metal interfaces.
- Single atom alloy catalysts were demonstrated on surfaces and as nanoparticle catalysts for hydrogenation reactions, showing high carbon monoxide tolerance.
- A new technique has been invented, in which a single carbon monoxide molecule is attached to the tip of a scanning tunneling microscope, enabling the relationship of the structure and function of single molecules to be further clarified.
- A new, ultrafast mid-infrared spectrometer with unusually broad frequency span (allowing monitoring of stretches and bends simultaneously) led to the discovery of the dominant structure that results when liquid water accommodates extra protons. In a related effort, a cluster of water molecules was shown to incorporate an extra proton in the formation of an aqueous acid, with the extra proton residing on the surface of a cage structure formed by 21 water molecules.
- In a vital insight for tailoring catalytic activity for energy storage, two types of intermediates for the water oxidation reaction, arranged perpendicular and parallel to the surface, were found to be stabilized by water molecules in the electrolyte that reorganize to accommodate them.

Unique Aspects

The CPIMS activity is unique in its long-term support of fundamental chemical science in the condensed phase and at interfaces that is fully integrated with many other BES research activities, and in its integration of capabilities from research universities and DOE national laboratories and user facilities. This enables long-term progress in difficult scientific areas as well as effective coupling to DOE missions. The CPIMS activity emphasizes basic, discovery science rather than use-inspired activities.

Mission Relevance

The CPIMS activity impacts a variety of mission areas by providing a fundamental basis for understanding chemical reactivity and dynamics in transient, complex systems, such as those encountered in energy production and storage. Condensed-phase and interfacial chemical physics

research on dissolution, solvation, nucleation, separation, and reaction provides important fundamental knowledge relevant to transport in mineral and aqueous environments. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects in nuclear fuel and waste environments.

Relationship to Other Programs

Research under this activity complements research supported across BES and coordinates and leverages efforts with other agencies and facilities. There is a strong interaction with other BES programs, including the Solar Photochemistry program (fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces), the Computational and Theoretical Chemistry program (extension of computational methods to larger, more complex chemical systems in solution and at complex interfaces), the Atomic, Molecular, and Optical Sciences program (ultrafast spectroscopies in solution and at interfaces), the Geosciences program (extension of multiscale chemical dynamics imaging for complex, subsurface flows), the Catalysis program (surface chemistry and synthesis in catalysis science), and the Synthesis and Processing Science program (chemical dynamical processes in synthesis and collective effects on reactivity during nanoparticle synthesis). The interaction with BES Nanoscale Science Research Centers (in coordination with the BES Scientific User Facilities Division) is significant, including support for novel interfaces needed in chemical imaging science, studies of novel solvents and electrolytes, and examinations of catalytic water reactions at electrode interfaces. CPIMS-supported scientists include users of the Advanced Photon Source at Argonne National Laboratory, the Linac Coherent Light Source at SLAC National Accelerator Laboratory, and the Advanced Light Source at Lawrence Berkeley National Laboratory.

Computational and Theoretical Chemistry

Portfolio Description

The Computational and Theoretical Chemistry (CTC) program supports development, improvement, and integration of new and existing theoretical and massively parallel computational or data-driven strategies for the accurate and efficient prediction or simulation of processes and mechanisms relevant to the Basic Energy Sciences (BES) mission. Focus is on non-empirical next-generation simulation of complex processes that require simultaneous computational implementation, testing, and development of new theories and algorithms. Efforts should provide fundamental solutions to problems associated with efficient conversion to clean, sustainable, renewable, novel or highly efficient energy use. Efforts must, directly or as part of multi-scale simulation methods, improve the ability to simulate processes at the molecular- and nanoscales. This includes computational and theoretical tools that enhance analysis of spectroscopic measurements or efforts aimed at enhancing accuracy, precision, applicability, scalability, or the fundamental basis of all variants of quantum-mechanical simulation methods. Developments of spatial and temporal multi-scale/multistage methodologies that allow for time-dependent simulations of resonant, non-resonant, and dissipative processes as well as rare events are encouraged. Developments of capabilities for simulation of light-matter interactions, bond breaking, conversion of light to chemical energy or electricity, and the ability to model and control externally driven electronic, magnetic, and spin-dependent transport processes in laboratory or natural/solvated environments are encouraged.

Scientific Challenges

Research in Computation and Theoretical Chemistry is fundamental to meeting the grand challenges for basic energy sciences, as identified in the recent report on this topic from the Basic Energy Sciences Advisory Committee, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* (<https://science.energy.gov/bes/community-resources/reports/>). Specific opportunities include:

- Improve efficiency for quantum-mechanical based simulations of chemical and molecular processes that impact the BES mission. Such improvements are achieved through multi-scale coupling, melding of chemical, physical and mathematical methods, or improved parallelization.
- Develop new theoretical time-domain and frequency-domain simulation tools for computing structural, transport, and optical properties of nanoscale systems in polarizable environments.
- Develop methods to computationally determine how to externally control both resonant and non-resonant energy, charge, spin and matter transfer processes in chemical and molecular systems with low-energy sources of radiation or applied fields, small thermal swings, and/or relatively minor changes in the external environment.

Projected Evolution

Topics of interest include practical predictive methods for (1) excited-state or collective phenomena in complex molecular systems, (2) nontraditional or novel basis sets, meshes or representation of quantum-mechanical degrees of freedom, and (3) simulation and coupling of all interactions/scales that depend upon electronic, vibrational and atomistic structure to improve descriptions of dissipative interactions due to weak and strong interactions among matter, radiation, fields, environment, and solvents.

Methods for, or applications to, systems that do not explicitly consider rearrangements of quantum-mechanical degrees of freedom are not supported.

Significant Accomplishments

This activity has played a major role in the development of quantum chemistry methodologies for accurate predictions of chemical properties. These developments have led to theories and computer codes for the calculation of thermodynamic properties and chemical reaction rates in the gas phase as well as the properties of complex molecular systems in the condensed phase. Accomplishments include the development and application of new approaches to density functional and traditional wave-function-based methods for predicting energetic processes involving ground- and excited-electronic states. These developments allow BES researchers to predict excited states in large light-harvesting complexes, address thermal and electronic transport through molecules, quantify dynamics associated with multiple carrier generation, investigate conversion of visible light into chemical energy and address plasmon-driven chemical reactions. They have also led to new approaches for non-destructive spectroscopic evaluation and interrogation of chemical conversion and separation systems and for unprecedented approaches to probing potential energy surfaces in mesoscale systems such as metal-organic frameworks.

Unique Aspects

The CTC activity is unique in its long term support of a number of fundamental chemical science areas, and in its integration of capabilities from research universities and DOE national laboratories, enabling long-term progress in difficult scientific areas as well as effective coupling to DOE missions. The CTC program is fully integrated with other BES research activities, contributing principally to the Gas Phase Chemical Physics and Condensed Phase and Interfacial Molecular Science programs, but also providing significant support to efforts spanning BES chemistry, biochemistry and geochemistry research. A unique component of this program is its support for extremely complex research that requires simultaneous development of theoretical and massively parallel computational implementation.

Mission Relevance

The CTC activity aims to advance the chemical physics goals described above and also advance mission areas across BES. For example, supported activities advance next-generation solar energy, sunlight-to-fuels, and energy storage concepts.

Relationship to Other Programs

Research under this activity complements research supported across BES and coordinates and leverages efforts with other agencies and facilities. The CTC program co-funds efforts with the Office of Advanced Scientific Computing Research (ASCR) where appropriate for the BES and ASCR missions, and has supported and participated in efforts with the technical community and other agencies to foster advanced approaches for the design of materials and chemistry. These efforts have included workshops on BES-relevant Scientific Discovery through Advanced Computing, workshops on materials and chemistry by design, and workshops aimed at understanding the increasing role of computational chemistry in industry.

Solar Photochemistry

Portfolio Description

This program supports fundamental, molecular-level research on solar energy capture and conversion in the condensed phase and at interfaces. These investigations of solar photochemical energy conversion focus on the elementary steps of light absorption, charge separation, and charge transport within a number of chemical systems, including those with significant nanostructured composition. Supported research areas include organic and inorganic photochemistry, catalysis and photocatalysis, photoinduced electron and energy transfer in the condensed phase and across interfaces, photoelectrochemistry, and artificial assemblies for charge separation and transport that mimic natural photosynthetic systems. Enhanced theory and modeling efforts form an integral part of the rational design of these artificial solar conversion systems.

Scientific Challenges

The major challenges in solar photoconversion have been outlined in a BES workshop on *Basic Research Needs for Solar Energy Utilization* ([report link](#)). Among these challenges, knowledge gained in charge separation and transport needs to be applied to activation of small molecules such as CO₂ and H₂O via photocatalytic cycles to transform them into fuels. The principles of this research are being extended to the problem of nitrogen fixation. The major scientific challenge for photoelectrochemical energy conversion is that semiconductors capable of absorbing solar photons are susceptible to oxidative degradation in water, whereas oxide semiconductors resistant to oxidative degradation absorb too little of the solar spectrum. Ongoing research activities include photosensitized nanoparticulate solids and the study of multiple exciton generation within nanoparticles and structured organic complexes. Experimental and theoretical studies on quantum coherence in light antenna complexes should lead to efficient and robust artificial light-collecting molecular assemblies. Computational chemistry methods should be developed and applied in design of photocatalysts and molecular dynamics simulations in artificial photosynthesis. There are also challenges in fundamental understanding of energy transfer and the generation, separation, and recombination of charge carriers in organic-based molecular semiconductors, which can lead to a new type of inexpensive and flexible solar cell. A workshop on *Basic Research Needs for Advanced Nuclear Energy Systems* ([report link](#)) identified new directions, connections, and roles for radiation chemistry in the nuclear energy systems of the future. A common theme is the need to explore radiolytic processes that occur across solid-liquid and solid-gas interfaces, where surface chemistry can be activated and changed by radiolysis. These interfaces abound in nuclear reactors and high-level radioactive wastes. A more fundamental understanding of radiolytic reactions in heterogeneous media is needed in order to predict and control radiation-chemical transformations in complex environmental systems.

Projected Evolution

Advancing the science underpinning solar fuels production will require new semiconductor and molecular systems for photoconversion. Of emphasis are new hybrid systems that feature molecular catalysis at surfaces and new nanoscale structures for the photochemical generation of fuels. Novel quantum-size structures, such as hybrid semiconductor/carbon-nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites,

must be examined. Unresolved basic science issues in photocatalysis will be explored in coupling photoinduced charge separation to multielectron, energetically uphill redox reactions. Photoconversion systems will be investigated that are based on organic semiconductors and conducting polymers, which are inexpensive and easy to manufacture.

The Solar Photochemistry program does not fund research on device development or optimization.

Significant Accomplishments

Significant advances in this program follow from the understanding and control of the fundamental processes for harvesting energy from sunlight. These include the light harvesting of solar photons, the subsequent separation of charge through electron transfer to produce current, which can be directed to catalysis of chemical reactions for energy storage.

- Researchers discovered unexpected quantum coherence in energy transfer within the light-absorbing antenna complexes of natural photosynthetic systems, which enables the absorbed light to spread out and sample the physical space of the chromophores and find the right place for electron transfer and charge separation.
- In research on quantum dot nanoparticles and organic dyes, scientists predicted and confirmed the generation of two electron-hole pairs through absorption of a single photon. A new generation of solar cells is envisioned, labeled “third generation,” that will exceed the Shockley-Queisser limit on present solar-cell efficiencies.
- In systems for artificial photosynthesis, investigators developed molecular models for light-to-chemical energy conversion. This work refined the models of electron transfer and charge transport in organic complexes that are the backbone of advances in organic and polymeric “plastic” solar cells.
- Advances in homogeneous catalysis of photo-induced water splitting led to the synthesis of many thousands of inorganic catalysts within the past several years. A new field in photochemistry has been created with the study of molecules located at solid surfaces where new pathways exist for charge-transfer-induced catalysis for chemical energy storage.
- Many novel nanostructures of semiconductor electrodes were developed for the photoelectrolysis of water and reduction of CO₂ to multi-carbon compounds. This research in Solar Photochemistry formed the basis of the Joint Center for Artificial Photosynthesis Energy Innovation Hub and a number of Energy Frontier Research Centers focused on the science of solar photoconversion.

Unique Aspects

This activity is the dominant supporter of solar photochemistry research in the United States. The research explores the fundamental science of solar photochemical energy conversion, which is an important long-range option for meeting future energy needs. An attractive alternative to semiconductor photovoltaic cells, solar photochemical and photoelectrochemical conversion processes create the potential to produce fuels, chemicals, and electricity with minimal environmental impact and with closed renewable energy cycles. Artificial photosynthesis can be coupled to chemical reactions for energy storage in the form of hydrogen, methane, or complex hydrocarbons. The activity also provides unique support for radiation science, investigating fundamental physical and chemical effects produced by the absorption of energy from ionizing radiation. Fundamental studies of radiation science are of importance in understanding chemical reactions that occur in radiation fields of nuclear reactors, including in their fuel and coolants,

and in the processing, storage, and remediation of nuclear waste. This research is required for effective nuclear waste remediation, fuel-cycle separation, and design of next-generation nuclear reactors.

Mission Relevance

The research supported by this program produces fundamental knowledge that underpins DOE missions in energy production and environmental management. Solar photochemical energy conversion is an important option for generating electricity and chemical fuels and therefore plays a vital role in DOE's development of solar energy as a viable component of the nation's energy supply. Photoelectrochemistry provides an alternative to semiconductor photovoltaic cells for electricity generation from sunlight using closed, renewable energy cycles. Solar photocatalysis, achieved by coupling artificial photosynthetic systems for light harvesting and charge transport with the appropriate electrochemistry, provides a direct route to the generation of fuels such as hydrogen, methane, and complex hydrocarbons. Radiation chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy.

Relationship to Other Programs

The Solar Photochemistry research effort interfaces with several activities in BES as well as within DOE.

- Within BES, research efforts are coordinated with Photosynthetic Systems and Physical Biosciences activities in bio-inspired and biomimetic systems and components, Catalysis Science in aspects of catalysis and photocatalysis and the Materials Sciences and Engineering Division efforts in fundamental photovoltaics research.
- This research activity sponsors—jointly with other BES research activities as appropriate—program reviews, principal investigators' meetings, and programmatic workshops.
- Many projects within solar photochemistry coordinate efforts with the Joint Center for Artificial Photosynthesis Energy Innovation Hub, as well as with the relevant Energy Frontier Research Centers active in solar energy research.
- The work of solar photochemistry is relevant to the DOE Office of Energy Efficiency and Renewable Energy (EERE) activities in its Solar Energy Technologies program on photovoltaics and its Fuel Cell Technologies program.
- The radiation sciences activity in the Solar Photochemistry program is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences program in the physical and chemical aspects of radiolysis.
- There are also important interfaces between the radiation sciences activity and the DOE Office of Environmental Management activities in waste remediation and Office of Nuclear Energy activities on nuclear reactors and on nuclear waste processing and storage.

Photosynthetic Systems

Portfolio Description

This program supports basic research on natural photosynthesis—the capture of solar energy and its conversion to and storage as chemical energy in plants, algae, and photosynthetic prokaryotes. Natural photosynthesis encompasses a great diversity of energy-conversion biochemistry that is, as a rule, highly efficient. Understanding the mechanisms of this biochemistry is the overarching goal of the Photosynthetic Systems program. Research topics supported include, but are not limited to, light harvesting, photosynthetic electron and proton transport, photosynthetic uptake and reduction of carbon dioxide, and mechanisms of self-assembly, self-regulation, and self-repair exhibited by the proteins, membranes and cellular compartments that perform natural photosynthesis. A goal of the program is to foster greater fundamental knowledge of the structure and function of the diverse photosynthetic systems found in nature.

Scientific Challenges

Understanding the diverse and highly efficient chemical mechanisms by which natural photosynthesis converts sunlight into chemical energy remains a grand challenge for increasing solar energy utilization and enhancing biological and biomimetic reduction of carbon dioxide into carbon-based fuels. For example, despite the strong limitation on photosynthetic efficiency, the mechanisms by which the carboxylating enzymes of photosynthesis take carbon dioxide from air and incorporate it into carbohydrates are not completely defined. Similarly, cryptic pathways of electron transport within and between proteins of the photosynthetic electron transport system are poorly understood or, in some cases, unknown, despite their importance for regulating photosynthesis in response to variations in light and temperature. Molecular, biochemical, and biophysical studies of the mechanisms of the photosynthetic apparatus continue to be much needed, particularly pertaining to light harvesting and energy transduction as well as to the maintenance of the biological integrity of these systems including defect tolerance and self-repair. Increased understanding of the temporal and spatial dynamics and regulation of photosynthesis continues to be a critical research need. The chemistry and chemical physics of highly efficient, long distance transfer of photon energy between pigments in photosynthetic antenna complexes is also an important topic of study.

Projected Evolution

Advances in laser spectroscopy and chemical imaging will allow an unprecedented fundamental understanding of photosynthesis at the nanometer scale. The Photosynthetic Systems program will continue to emphasize basic research to understand the structural and mechanistic features of photosynthetic complexes, determine the mechanisms behind photon capture and charge transfer, characterize and control the weak intermolecular forces governing molecular assembly in protein complexes of photosynthesis, understand the biological machinery for cofactor insertion into proteins and protein subunit assemblies, uncover the biochemical mechanisms that can enhance energy conversion in photosynthetic systems, and determine the physical and chemical rules that underlie biological mechanisms of photo-protection and self-repair.

The Photosynthetic Systems program does not fund: 1) development or optimization of devices or processes; 2) development or optimization of microbial strains or plant varieties for biofuel or biomass production; 3) phenotype analyses that do not test specific hypotheses relevant to the

program; 4) genomic or other “omic” data acquisition that does not test specific hypotheses relevant to the program; 5) theory or modeling projects that lack empirical testing.

Significant Accomplishments

Research supported by the Photosynthetic Systems program has made significant advances in fundamental understanding of natural photosynthesis.

- Analysis of the diverse paths of photosynthetic electron transport in plants led to a new paradigm for how cyclic electron transport regulates photosynthesis for optimal plant growth under changing conditions of light and temperature.
- Ultra-fast lasers and x-ray crystallography facilities at DOE national laboratories were used to generate better structural models for how oxygen is produced by photosynthesis. Understanding the chemistry of photosynthetic oxygen evolution can inform the design of efficient catalysts that can generate hydrogen or carbon-based fuels from water, air, and sunlight.
- Significant progress was made in understanding the biochemical mechanisms by which plants and algae protect themselves from bleaching by sunlight. These findings also involved the use of ultra-fast lasers and X-ray crystallography facilities at DOE national laboratories.
- An innovative plant phenotyping approach was used to generate hundreds of thousands of outdoor photosynthesis measurements from around the world. Machine learning applied to the resulting data revealed how to predict plant productivity under diverse conditions from these measurements of photosynthesis.
- Studies of hydrogen production by photosynthetic organisms have led to new understanding of the chemistry of hydrogenase enzymes and creation of a novel biohybrid system that generates hydrogen fuel from water and sunlight.

Unique Aspects

The Photosynthetic Systems program is distinctive for its focus on the biochemistry and chemistry of natural photosynthesis and for the diversity of methodological approaches taken to understanding it. Basic research funded by Photosynthetic Systems combines biochemistry, biophysics, molecular biology, and computational science to generate a mechanistic knowledge of the biological capture of sunlight and its conversion to and storage as chemical energy. This multidisciplinary approach is a key strength of Photosynthetic Systems that enables a multidimensional fundamental understanding of natural photosynthesis. The broad portfolio of research projects supported by Photosynthetic Systems at universities and DOE national laboratories also generates a scientific knowledge base and technical capabilities relevant to understanding light-driven chemical systems of many kinds. Such fundamental understanding provides insights for future development of bioinspired, bio-hybrid, and biomimetic energy systems and informs strategies for improvement of biological photosynthesis.

Mission Relevance

The basic research supported by this program uncovers the underlying structure-function relationships and dynamic processes of natural photosynthesis. This fundamental knowledge can inspire and inform the engineering of bio-hybrid and biomimetic energy systems for conversion of sunlight into chemical fuels or electricity and can guide the genetic improvement of natural photosynthesis in plants which can enhance production of biofuels and other useful products.

Relationship to Other Programs

The Photosynthetic Systems program coordinates with other programs in BES as well as across the DOE and in other Federal agencies.

- Within the BES Chemical Sciences, Geosciences, and Biosciences (CSGB) Division, Photosynthetic Systems coordinates with the Physical Biosciences program in the areas of biological electron transport mechanisms and carbon dioxide fixation and with the Solar Photochemistry program in the areas of natural and artificial photosynthesis. Photosynthetic Systems also interacts with the Catalysis Science program in CSGB and the Biomolecular Materials program in the BES Materials Science and Engineering Division in areas such as biocatalysis and bioinspired and biomimetic photochemical systems and their components.
- This research activity sponsors—jointly with other core research activities and the Energy Frontier Research Centers program as appropriate—program reviews, principal investigators' meetings, and programmatic workshops.
- The basic research supported by the program complements the genomics- and biotechnology-related programs in the DOE Office of Biological and Environmental Research, the DOE Office of Energy Efficiency and Renewable Energy, and the DOE Advanced Research Projects Agency-Energy.
- Outside the DOE, the program collaborates and coordinates its activities with the National Science Foundation, U. S. Department of Agriculture, and National Institutes of Health in areas of mutual interest where there are multiple benefits.

Physical Biosciences

Portfolio Description

This program supports basic research that combines physical science techniques with biochemical, chemical, and molecular biological approaches to discover the underlying physical and chemical principles that govern how plants and non-medical microbes capture, convert, and store energy. Fundamental research supported by the program includes studies that will provide a better understanding of the structure/function, mechanistic and electrochemical properties of enzymes that catalyze complex multielectron redox reactions (especially those involved in the interconversion of CO_2/CH_4 , N_2/NH_3 , and H^+/H_2), determine how the complex metallocofactors at the active sites of these enzymes are synthesized, and understand how the potential of these cofactors can be “tuned” using ligand coordination to reduce overpotential and better enable catalysis using earth-abundant metals. The program also funds mechanistic studies on electron bifurcation and catalytic bias in enzyme systems, and identifies the factors that direct and regulate the flow of electrons through energy-relevant metabolic pathways on larger spatial and temporal scales. Limited support is provided for basic research on the biosynthesis and structure of important electron stores in biological systems (such as plant cell walls, lipids, and terpenes), as well as for studies that will provide insight into the self-assembly and maintenance of biological energy transduction systems.

Scientific Challenges

The application of physical science and, increasingly, computational tools to understand at a fundamental level biological energy capture, conversion, and storage systems will provide important new insights that help address BES Grand Challenges (<https://science.energy.gov/bes/community-resources/reports/>). Analysis and control of electron flow in biological systems across a wide range of spatial and temporal scales is a significant scientific challenge, and can only be addressed with state-of-the-art techniques contributed from a wide variety of scientific disciplines. In this regard, the use of advanced molecular imaging, light sources, or neutron scattering methods will likely provide new and essential insights into enzyme catalysis and metabolic electron flux, as well as other ways that biological systems manage to efficiently meet their energy needs via mastery of several of the BES grand challenges. These scientific challenges require researchers to be trained in diverse disciplines; substantial progress has been made in developing the next generation of scientists with multidisciplinary expertise precisely because this activity is not defined by scientific discipline but rather by the nature of the problem to be solved. As such, this activity provides the unique opportunity for investigators with diverse backgrounds in chemistry, physics, microbiology, plant biology, and other fields to effectively and synergistically collaborate to solve these challenges for societal benefit.

Projected Evolution

Future impact is, in general, envisioned through increased integration of physical science and computational tools (e.g. ultrafast laser spectroscopy, current and future x-ray light sources, and theory and modeling techniques) to probe structural, functional, and mechanistic properties of enzymes, enzyme systems, and energy-relevant biological reactions and pathways related to energy capture, conversion, and storage. These studies will identify principles that will provide a basis for the design and synthesis of highly selective and efficient bioinspired catalysts, allow us to carefully control the flow of electrons in biological systems to achieve desired metabolic outcomes (e.g. enhance lipid or terpene production), and give us an unprecedented architectural

and mechanistic understanding of such systems. Investment in research on the plant cell wall biosynthesis and structure research is being deemphasized and the program is not considering new projects in this area at this time.

Physical Biosciences does not fund research in: 1) animal systems; 2) prokaryotic systems related to human/animal health or disease; 3) development and/or optimization of devices and/or processes; 4) development and/or optimization of microbial strains or plant varieties for biofuel/biomass production; 5) cell wall breakdown or deconstruction; 6) transcriptional or translational regulatory mechanisms and/or processes mediated by plant hormones; 7) environmental remediation and/or identification of environmental hazards. Projects should ideally be hypothesis-driven; projects that develop or rely primarily on high-throughput screening approaches will not be supported nor will theory/modeling projects that lack experimental verification.

Significant Accomplishments

The Physical Biosciences program has a strong record of scientific impact as exemplified by its support of research that was instrumental in defining *Archaea* as the third kingdom of life. Recent significant accomplishments of the program include:

- The determination that the final step of anoxygenic methane biosynthesis occurs via a methyl radical intermediate, which could provide the information needed to design energy-efficient catalysts and enable the cost-effective capture and use of stranded methane.
- Studies of hydrogenase and nitrogenase structure, function, and biosynthesis have provided a wealth of information on the assembly and mode of action of complex metal-organic cofactors and gated electron flow that are critical for the production of hydrogen and reduction of nitrogen in biological systems. Such foundational knowledge can help enable the design of more selective and efficient catalysts and processes aligned with achieving BES objectives.
- Studies of plant lipid biosynthesis and degradation have revealed new details of the biochemical pathways involved in conversion of carbon dioxide into fatty acids, storage of fatty acids as oil, and breakdown of oil in leaves. As a result of this research, plants were generated that had approximately a 150-fold increase in leaf oil content, providing a possible new approach for sustainable fuel production.
- The determination of the detailed structures of many of the complex polysaccharide components of the plant cell wall, as well as many important aspects of its supramolecular structure, have guided strategies aimed at improving the conversion efficiencies of plant biomass to fuel molecules.

Unique Aspects

Physical Biosciences is a unique federal program that lies at the interface of the biological, chemical, and physical sciences. A significant fraction of the supported research directly addresses BES Grand Challenges, especially the challenges of “controlling processes at the level of electrons”, “designing and perfecting atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties”, and “creating new technologies with capabilities rivaling those of living things.” The program is not strictly defined by scientific discipline and is unique in promoting multi- and cross-disciplinary approaches that provide the foundational scientific knowledge required for the development of bioinspired energy-relevant technologies and processes.

Mission Relevance

The research provides basic structure/function and mechanistic information necessary to accomplish bioinspired rational design of catalysts and more efficient biological energy transduction and storage. This impacts numerous DOE interests, including improved biochemical pathways for biofuel production, next-generation energy conversion/storage devices, and efficient, environmentally-benign catalysts.

Relationship to Other Programs

This research activity interfaces with several complementary activities within BES as well as within DOE and other federal agencies.

- Within BES, research efforts are closely coordinated with the Photosynthetic Systems program in the areas of natural photosynthesis, carbon fixation, and the organizational and structural principles of the cellular machinery; with the Solar Photochemistry and Catalysis Science programs in the areas of gating and control of electron flow, proton-coupled electron transport, and enzyme and biomimetic catalysis; and with the Separations and Analysis program in the area of analytical tool and technology development. To a more limited extent, Physical Biosciences coordinates with the Condensed Phase and Interfacial Molecular Science (CPIMS) and Computational and Theoretical Chemistry (CTC) programs.
- This research activity sponsors—jointly with other core research activities and the Energy Frontier Research Centers program as appropriate—program reviews, principal investigators' meetings, roundtables, and programmatically-relevant workshops.
- The more chemistry- and physics-oriented projects supported by this activity are synergistic with, and complementary to, the more genomics- and systems biology-oriented activities supported by the DOE Office of Biological and Environmental Research (BER). Communication and coordination with BER, as well as the DOE Office of Energy Efficiency and Renewable Energy and the Advanced Research Projects Agency-Energy, is achieved through quarterly meetings to ensure the effective and efficient use of DOE resources.
- The program collaborates and coordinates its activities with the National Science Foundation, U. S. Department of Agriculture, and National Institutes of Health in areas of mutual interest where there are multiple benefits.

Catalysis Science

Portfolio Description

This activity develops the fundamental principles behind the rational design of catalysts, and the deliberate and informed control of chemical transformations. Emphasis is on the understanding of the reaction mechanisms, enabling precise identification and control of catalytic active sites. The chemistry of most interest is the sustainable conversion of energy resources and the mitigation of environmental impacts of energy production and use; other areas outside DOE's missions are not considered. Research includes the elucidation of catalytic reaction kinetics and mechanisms. As part of such mechanistic studies, the program supports the synthesis of catalytic sites, molecular ligands, metal clusters, and reaction environments designed to tune catalytic activity and selectivity; the study of structure-reactivity relationships of inorganic, organometallic, or hybrid catalytic materials in solution or supported on solids; the dynamics of catalyst structure relevant to catalyst activity and stability; the experimental determination of potential energy landscapes for catalytic reactions; the development of novel spectroscopic techniques and structural probes for *in situ* or *in operando* characterization of catalytic processes; and the development of theory, modeling, and simulation specific to catalytic pathways.

Scientific Challenges

The unique challenge for Catalysis Science outlined in a BES workshop on *Basic Research Needs: Catalysis for Energy*¹ is to understand mechanisms and dynamics of catalyzed reactions in order to design new and more efficient pathways for the conversion of natural or artificial resources to fuels and chemicals. A special focus is the identification of catalytic carbon-neutral routes to long-term energy sustainability. For that purpose, new catalytic systems are needed that might involve novel hybrid organometallic-inorganic porous catalysts with multifunctional active sites required for new challenging reaction environments. To synthesize such catalysts, traditional surface chemistry, aqueous-solution chemistry, and high-temperature chemistry are complemented by softer routes, such as surface-functionalization of nanoparticles with coordination compounds. Organic or biological strategies may then be used to achieve unique molecular recognition properties (for example, size, shape, chirality, and hydrophobicity). The interfacial interactions induced by ligands, supports, and solvent spheres generate ways of tuning the reactivity and stability of catalytic materials. Indeed, one of the grand challenge identified by a recent report from the Basic Energy Sciences Advisory Committee on the *Challenges at the Frontiers of Matter and Energy*² focused on the design of revolutionary new forms of matter with tailored properties.

The characterization of synthetic catalysts demands spatial and temporal resolution under *ex situ* and *in situ* conditions. Both electronic and atomic structures must be correlated with secondary and macrostructure and their time-resolved evolution. The kinetically significant intermediates must be discriminated from those that are mere spectators. In particular, characterization of the reaction intermediates and pathways typically resorts to labeling, trapping, and molecular-probe experiments complemented with time-resolved, *in situ* spectroscopy in order to acquire information on bonding dynamics. The development of chemo-, regio-, and stereo-selective

¹ https://science.energy.gov/~media/bes/pdf/reports/files/cat_rpt.pdf

² https://science.energy.gov/~media/bes/besac/pdf/Reports/Challenges_at_the_Frontiers_of_Matter_and_Energy_rpt.pdf

reactions is challenging, particularly with heterogeneous or hybrid catalysts, sometimes requiring the use of cascade or tandem reactions. For this, appropriately accounting for weaker forces (including van der Waals interactions) on catalytic chemistry has become recognized as an essential element of the science. For homogeneous catalysis, one of the long-term challenges is to carry out these selective reactions under solvent-less conditions or in supercritical media or ionic liquids, while maintaining catalyst stability. For heterogeneous catalysis, the challenge is to work at extremely high temperature with high selectivity, or extremely low temperature with high activity.

Projected Evolution

The science of catalytic chemistry is still emerging. Much experimental information has been accumulated relating catalytic structure, activity, selectivity, and reaction mechanisms. Phenomenological catalysis is, however, evolving into predictive catalysis via integration of experiment and theory, reproducible synthesis of single-site catalysts, and thorough and precise characterization of catalysts and reaction mechanisms. The convergence of heterogeneous, homogeneous, electro-, photo-, and bio-catalysis is progressing. Examples are the use of long-range or secondary structure and structural flexibility to affect both activity and selectivity of inorganic catalysts, or the use of non-thermal activation, such as electrochemical and photochemical activation. At present, research is leading to identification of catalytic carbon-neutral routes to long-term energy sustainability, such as thermocatalytic production of H₂, NH₃ (outlined recently by a panel of experts in a report, *Sustainable Ammonia Synthesis*³), and other chemicals without secondary greenhouse gas emissions; selective and low-temperature activation of lower or higher alkanes or multifunctional molecules using non-precious or non-metallic catalysts; catalytic reaction mechanisms influenced by weak forces in confined or open catalytic environments; electrochemical and photo-electrochemical conversion of natural compounds or secondary products into chemicals and fuels; reactions in water, ionic liquids, and under extreme conditions; and quantitative and reproducible determination of kinetics and mechanisms, open source computational approaches, and shared databases leading to benchmarks for catalytic properties.

The Catalysis Science program does not fund research on: (1) synthesis of pharmaceuticals or, more generally, fine chemicals unrelated to energy applications; (2) cellular or organismal catalyzed reactions; (3) non-catalytic reactions; and (4) process or reactor design and optimization.

Significant Accomplishments

Over the last 20 years, the Catalysis Science program has advanced the molecular-level understanding of catalytic processes that underpin energy resource conversion and utilization. Significant accomplishments in this program include the design and controlled synthesis of catalyst active-site environments, characterization tools to unravel catalyst-structure relationships, and computational methods integrated with experimental design to predict system behavior. Examples are given below:

³<https://science.energy.gov/~media/bes/pdf/reports/2016/SustainableAmmoniaReport.pdf>

- In the theory of heterogeneous catalysis, scientists identified the most important parameters determining the catalytic properties of transition metal surface catalyzed processes leading to a set of catalyst design rules.
- Advanced tools and methods for operando-structural characterization have significantly improved the ability to investigate structure-function relationships in catalysis with sufficient detail and precision to enable catalyst improvement.
- In the field of advanced synthesis, researchers developed new methods for molecular control of single-site and multi-functional catalysts enabling new chemical pathways and tandem catalysis.
- Comprehensive studies were completed on selective oil reforming and hydroprocessing pathways utilizing new families of synthetic zeolites, noble metal alloys, and mixed sulfides and phosphides.
- New pathways were developed for selective oxidation of hydrocarbons leading to synthetic fuels and commodity and specialty chemicals, utilizing novel mixed metal oxides and supported metal nanoparticles.
- High-yield metathesis of unsaturated compounds with new organometallic transition metal complexes has led to novel routes to specialty and commodity chemicals.
- Polymerization of alkanes and alkenes with novel single-site metallocene catalysis is responsible for a large fraction of all oil-derived and biomass-derived industrial polymers.
- Selective and high-yield rearrangement of C-C, C-O, and C-H bonds in organic molecules was made possible by atomic-level control of nanoparticle composition, support interface, and reconstruction, areas that evolved from classical surface science.
- Low-temperature dinitrogen reduction and CO activation with novel organometallic complexes and heterogeneous catalysts has been advanced. Dinitrogen reduction is the essential step in the synthesis of ammonia and fertilizers, and water-gas shift via CO oxidation with water is responsible for the synthesis of most industrial hydrogen. Ammonia and hydrogen production account for over 5% of the world's energy use.

Unique Aspects

This activity is the largest single source of Federal funding for basic research in catalysis science that is focused on novel energy-relevant chemical transformations. An important element of this activity is the emphasis on maximizing atom and energy efficiency, which usually demands the discovery of new chemical pathways. Directing reactions along those pathways requires new catalytic processes developed specifically for the type of feedstock, energy source, and desired product. While advanced materials synthesis, molecular-level theory and new *in situ* instrumentation are key to designing new catalysts, they are not sufficient for the discovery of more efficient and sustainable chemical transformations. To specifically pursue efficiency, researchers in this program synergistically combine approaches used in heterogeneous, homogeneous, bio-, electro-, and photo-catalysis, as well as reaction engineering and computational chemistry. For *in operando* and *in situ* characterization of working reactions and for simulation of reaction pathways, catalysis researchers must increasingly resort to techniques with high spatial and temporal resolution and molecular-level sensitivity, as well as methods of theoretical and computational chemistry, many times contributing to the advancement of such methods. They extensively use laboratory scale instrumentation as well as DOE scientific user facilities.

Mission Relevance

Advances in the science of catalytic transformations impact a wide range of DOE mission areas. Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources, such as the conversion of crude petroleum and biomass into clean-burning fuels, chemicals, and materials. Catalysts are used in fuel cells and batteries as well as photocells for the production, storage, and utilization of chemical energy. Catalysts are essential for energy-efficient and sustainable routes for the production of basic chemical feedstocks and value-added chemicals, as well as for minimizing the production of unwanted byproducts.

Relationship to Other DOE Programs

- BES synchrotron facilities have customized and dedicated beamlines for catalysis science researchers. The Synchrotron Catalysis Consortium (SCC) funded by this program has been the first of its kind in the United States with a mission to promote the utilization of synchrotron techniques for cutting-edge catalysis research under *in situ* conditions.
- Within BES, other programs support research that is synergistic with the Catalysis Science program efforts, which is coordinated when appropriate:
 - Condensed Phase and Interfacial Molecular Science program and the Computational and Theoretical Chemistry program cover interfacial science, surface and solution chemistry, quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena.
 - The Solar Photochemistry activity supports photocatalysis and photoelectrocatalysis, while the Physical Biosciences and Photosynthetic Systems programs do so for enzymatic catalysis providing foundational knowledge for the design of biomimetic catalysts.
 - The Separations and Analysis activity and the BES Materials Discovery, Design and Synthesis team in the Materials Sciences and Engineering Division support the synthesis of organic, inorganic and hybrid materials that are often relevant for catalysis.
 - BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.
 - The Joint Center for Advanced Photosynthesis (JCAP) is an energy innovation hub whose scope encompasses the discovery and development of photocatalyst materials and processes for water splitting and CO₂ reduction.
 - Several Energy Frontier Research Centers (EFRCs) study and utilize catalysts and catalytic approaches while pursuing their specific research goals.
- The Catalysis Science activity produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy and the Office of Fossil Energy. Other federal agencies also support catalysis research: National Science Foundation (NSF), National Institutes of Health (NIH), Environmental Protection Agency (EPA), and the Defense Department agencies.

Heavy Element Chemistry

Portfolio Description

This activity supports basic research on the fundamental chemistry of the actinide and transactinide elements with the goal to understand the underlying chemical and physical principles that determine their behavior. The unique molecular bonding of the heavy elements is explored using theory and experiment to elucidate electronic and molecular structure as well as reaction thermodynamics. Emphasis is placed on: the chemical and physical properties of these elements to determine their bonding and reactivity in solution, at the interface, and in the solid-state; on the fundamental transactinide chemical properties; and on the overarching goal of resolving the *f*-electron challenge. The *f*-electron challenge refers to the inadequacy of current electronic structure methods to accurately describe the behavior of *f*-electrons, in particular: strong correlation, spin-orbit coupling, multiplet complexity, and associated relativistic effects. While the majority of the research supported by this activity is experimental, theoretical proposals are considered that integrate closely with existing experimental research. Synthetic and spectroscopic research is pursued within this activity on molecules that contain heavy elements and on how ligands interact with these elements.

Scientific Challenges

The role of *5f* electrons in bond formation remains the fundamental topic in actinide chemistry and is an overarching emphasis for this program. Resolving the role of the *f*-electrons is one of the three grand challenges identified in the report *Basic Research Needs for Advanced Nuclear Energy Systems* (2006)¹ and echoed in the report from the Basic Energy Sciences Advisory Committee, *Science for Energy Technology: Strengthening the Link between Basic Research and Industry* (2010)². The *5f* orbitals participate in the band structure of metallic and ceramic materials that contain the actinides and the nature of this participation down the actinide series is an area of active research. Theory and experiment show that *5f* orbitals participate significantly in molecular actinide compounds, for example, compounds required for advanced nuclear energy systems. The majority of this activity is pursued at the national laboratories or coordinated directly with them because of the infrastructure needed to handle these materials safely. Research in heavy element chemistry at universities through single-investigator grants is supported, encouraging collaborations between university and laboratory projects. Sophisticated quantum-mechanical calculations that treat spin-orbit interactions accurately need further development to predict the properties of molecules that contain actinides and predict the migration of radioactive species. Experimental validation of the theoretical properties of models will be key to understanding the role of the *5f* electrons.

Projected Evolution

The heaviest elements are the elements that we know the least about. This is due partly to the challenges posed by doing chemistry with molecules containing radioactive isotopes, and partly due to the fact that most of these elements were not even discovered until recently. Support of research to understand the chemical bonding of elements that have *5f* and *6d* electrons leads to a better quantum-mechanical understanding of all bonding as these molecules containing elements

¹https://science.energy.gov/~media/bes/pdf/reports/files/Basic_Research_Needs_for_Advanced_Nuclear_Energy_Systems_rpt.pdf

² https://science.energy.gov/~media/bes/pdf/reports/files/Science_for_Energy_Technology_rpt.pdf

at the extreme end of the periodic table pose an extreme test of our theoretical understanding of bonding. Sophisticated quantum mechanical theory that takes into account both spin-orbit and relativistic effects of actinide compounds and actinide species in industrially-relevant environments needs to be developed. We are still a long ways from being able to model and predict the chemical behavior of these elements where relativistic effects can dominate. Toward this end, more experimental physical-chemistry research will be pursued to explore the electronic structure of molecules containing the heaviest elements, especially those experiments that can directly probe electronic structure. Organic and inorganic chemical synthesis of ligands and heavy-element-containing molecules without an underlying hypothesis of chemical behavior that is being tested (and thus an indirect electronic probe) is not well-aligned with the future direction of the Heavy Element Chemistry program.

Based on programmatic priorities, the Heavy Element Chemistry program does not fund research on: the processes affecting the transport of subsurface contaminants, the form and mobility of contaminants including wastefoms, projects focused on the use of heavy-element surrogates, projects aimed at optimization of materials properties including radiation damage, device fabrication, or biological systems, which are all more appropriately supported through other DOE programs. Research that is focused primarily on separations and does not address the unique properties of the heavy elements would be better aligned with the BES Separations and Analysis program.

Significant Accomplishments

Early goals of this activity were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments, similar to the techniques that are still used for the heaviest of elements due to their low production rate. For the elements heavier than einsteinium in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out to determine chemical properties. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds. Continual progress has been made on elucidating the novel and unique chemistry of the elements directly relevant to energy production (the major actinides).

Unique Aspects

This activity represents the only Federal fundamental research program focused primarily on developing an understanding of the chemistry of heavy elements. All of the research sponsored through this activity is peer-reviewed and unclassified. The elements beyond uranium were unknown before the Manhattan Project and since that defining moment, this activity has been continuously supported in some manifestation throughout the Atomic Energy Commission years up to the present-day Department of Energy due to its underlying support of DOE's mission in Energy, Environment, and National Security. This long-term support of heavy element chemistry to researchers investigating the fundamental properties of actinides has been crucial to maintain U.S. leadership in this critical field. Although other Federal programs (such as the National Science Foundation and Department of Defense) provide support for actinide research, the Heavy Element Chemistry program is unique in identifying fundamental heavy element chemistry as a research thrust.

Mission Relevance

Knowledge of the chemical characteristics of the heavy elements under realistic conditions provides a basis for advanced fission fuel cycles. Fundamental understanding of the chemistry of these long-lived radioactive species is required to accurately predict and mitigate their transport and fate in the environment. Knowledge of the physical properties of defense-relevant elements is required to develop technologies to counter proliferation of weapon-useable nuclear material. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces is motivated by improving the separation processes that are essential for improved nuclear fuel cycles and final disposition of nuclear effluent.

Relationship to Other Programs

- Improved knowledge of the fundamental properties of the heavy elements has a direct, positive impact on many other Department of Energy missions, including but not limited to advanced nuclear energy, nuclear proliferation detection, defense program stewardship, and environmental remediation.
- This activity uniquely supports unclassified basic research on all the actinide and transactinide elements, while the more applied programs (nuclear energy, environmental, nuclear forensics, stockpile stewardship) limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest.
- This activity has a close relationship to the BES Separations and Analysis program on separations involving heavy elements, and is highly synergistic with applied nuclear programs, such as Nuclear Fuel Cycle research funded through the Office of Nuclear Energy.
- This activity sponsors research that is performed at many BES user facilities, such as the Advanced Light Source, the Stanford Synchrotron Radiation Lightsource, the Advanced Photon Source, as well as the Office of Advanced Scientific Computing Research user facilities.
- The Heavy Element Chemistry program provides fundamental knowledge that is foundational for national security-focused actinide research. Research of a more applied nature is pursued within the Office of Nonproliferation R&D of the National Nuclear Security Administration, the Basic Research program of the Defense Threat Reduction Agency, and at the National Technical Nuclear Forensics Center of the Department of Homeland Security.

Separations and Analysis

Portfolio Description

This research area supports fundamental separation science, broadly covering a variety of separation methodologies, including, for example, membrane processes, extraction under extreme conditions, ion exchange, and complexation. Also supported is work to improve the sensitivity, reliability, and productivity of analytical determinations in support of separation science and to pursue innovative principles that will enable chemical analysis of complex separations environments, including methods that radically improve chemical selectivity and spatial resolution in dynamic systems. The overall goal is to obtain a thorough understanding at the molecular, nano, and meso-scales of basic chemical and physical principles leading to novel separations and analytical methods.

Separations are essential to nearly all operations in processing industries and fundamental separation science research is particularly critical to address contemporary issues of fuel, feedstock, and effluent processing in all phases. Toward this aim, this portfolio includes fundamental research on selective extraction with a focus on underlying separation motifs that are broadly applicable beyond a narrowly focused process. Notably, the fundamental research pursued in this portfolio underpins DOE's nuclear stewardship responsibility; therefore, separation and analysis of transuranic fission and decay products are important components of the portfolio. Knowledge of molecular-level separations phenomena is required to characterize and process complex radioactive mixtures for final disposition.

Scientific Challenges

Currently, there is a special emphasis placed on inorganic and organic/hybrid membrane science: soft, hard or hybrid membranes; ultraselective separations under extreme chemical environments (acid/base, saline, high temperature); chiral resolution of enantiomers; molecular trapping and controlled/dynamic release of various types of isomers (constitutional, stereoisomers, isotomers, topoisomers, spin isomers, etc.); reactive separations; and complex mixture separations (such as mentioned in the *Basic Research Needs for Environmental Management* report¹). The development of fundamental principles to guide design and synthesis of ligands, adsorbents, and self-assembled complexants and membranes are also required. Significant challenges are posed by elucidation of principles and novel theoretical and computational approaches underlying complex fluids and aqueous interfaces, and, in general, molecular recognition, interfacial, ionic and weak interactions. Understanding separation phenomena at the atomic and molecular level is pursued to extend that understanding to the nanoscale, mesoscale, and macroscale phenomena to ultimately predict the thermodynamics, kinetics, and dynamics of separations processes.

Projected Evolution

Separations research will continue to advance the understanding and control of the atomic and molecular interactions between target species and separation media, and the resulting molecular structures, dynamics, kinetics, and transport properties resulting in desired meso- and macroscopic functionalities. Particular current interests include such topics as supramolecular recognition, synthesis of new porous materials, interfacial properties at the nanoscale, ligand design and synthesis of extractant molecules, mechanisms of transport and fouling in polymer and inorganic membranes, and solvation in fluids and their interfaces. This fundamental research is motivated by a desire to advance discovery and predictive design of future chemical

¹ https://science.energy.gov/~media/bes/pdf/reports/2016/BRNEM_rpt.pdf

separations concepts enabling efficient and multifunctional capabilities for a broad range of processes. Examples include membrane processes, complexation, extraction under both standard and supercritical conditions, ionic liquids, selective adsorption and efficient release, and limited fundamental aspects of chromatography. This program actively pursues better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces to improve separations processes that are essential for efficient future nuclear fuel utilization, as well as those that are broadly applicable to energy and chemical technologies.

This program pursues analytical research only in support of separations science. In particular, it will seek to understand the principles that enable chemical analysis of complex separations environments, where chemical specificity, spatial resolution, and temporal resolution are critical. However, it does not support the development of analytical instruments or methods.

Additional evolution of the program is anticipated from the growing emphasis on advanced energy sources, environmental management, and on exploiting the nanoscale revolution for scientific discovery and mission applications. Based on programmatic priorities, this activity does not support areas directly overlapping those supported by complementary programs in DOE or other agencies, including any engineering scale-up or development of narrowly defined processes, devices, or sensors; microfluidics; research that is directed toward medical applications; research on the transport of subsurface contaminants; or the form and mobility of contaminants including wastefoms.

Significant Accomplishments

This activity is responsible for such notable contributions as the concept of host-guest complexation; the use of the inductively coupled plasma for emission and mass spectrometry; the development of the TRUEX process based upon fundamental research on ligand design; and the development of SIMION, a program to simulate the motion of ions in fields that has become the standard tool internationally for development of ion lens.

More recent accomplishments include:

- A new calixarene ligand-based separations process that complexes Cs⁺ to clean up nuclear waste tanks.
- Significant contributions to the discovery of metal-organic framework materials for carbon capture and other gas separations.
- New approaches to ion separations that have impacted related applications (e.g. patents applicable to desalination).

Unique Aspects

The research supported by this activity is characterized by a unique emphasis on underlying chemical and physical principles, as opposed to the development of methods, materials, and processes for specific applications. The outcome from this research will significantly affect the energy use of a wide range of chemical processes.

Mission Relevance

Basic Energy Sciences (BES) supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels in order to provide the foundations for new energy technologies and to support DOE missions in energy, environment, and national security. The Separations and Analysis program is an important component of this effort, particularly to the DOE missions in energy and environment. Nuclear defense work left a

substantial amount of legacy waste, and this program pursues fundamental research that underpins technologies to enable eventual permanent disposition. Improved efficacy and energy efficiency in industrial chemical and energy production as well as the growing emphasis on alternative energy sources make the Separations and Analysis program directly relevant to the DOE's energy mission.

Relationship to Other Programs

- This activity coordinates with the Heavy Element Chemistry program, which supports research focused on understanding the fundamental chemistry of transuranium elements or fission products.
- This activity maintains a distinct portfolio from other BES activities, such as the Computational and Theoretical Chemistry, Catalysis Science, Condensed-Phase and Interfacial Molecular Science (CPIMS), Geosciences and Materials Chemistry Programs. The analysis research, in particular, is coordinated with a broad range of BES programs, and only research that is aligned specifically with the goals of the Separations and Analysis program is supported.
- A number of BES Energy Innovation Hubs and Energy Frontier Research Centers support investigators and topics of relevance to this activity.
- Other federal agencies support investigators and topics that are mutually complementary. Participation in program management working groups assures coordination across the DOE in related areas such as chemical and energy processes.

Geosciences

Portfolio Description

The geosciences program supports basic research in geology, geochemistry, and geophysics. Geochemical research emphasizes fundamental mechanistic understanding of reactions in earth materials including aqueous solutions, minerals, and organic matter, with particular emphasis on interfacial systems. Geophysical research focuses on the coupled thermo-hydrological-mechanical-chemical (THMC) properties of earth materials across multiple length and time scales with particular emphasis on brittle failure and fracture evolution. Geological research is focused on the development and implementation of methods to investigate long-time-scale geological processes with the highest possible accuracy and at the finest possible time resolution, as well as on fundamental understanding of the occurrence, extraction, and depletion of critical energy materials in the earth's subsurface.

Scientific Challenges

Understanding the natural heterogeneity of geochemical and geophysical properties and processes is critical to managing improved production of the earth's energy resources and safe disposal of energy-related wastes. Improved imaging and tracking of geochemical processes at the atomic scale using synchrotron x-rays and neutrons is critical for progress in understanding geochemical systems. New investigations are needed at the smallest scales to study reactivity, solute properties, and isotopic distributions in geological materials. Understanding pristine natural systems and DOE-specific sites requires improving our capabilities to make and understand high-resolution geochemical and geophysical measurements experimentally and in the field, and to model them and put them into the context of long-time-scale geological processes. Understanding mineral surface-particle-fluid interactions is key to predicting the fates of contaminants in the environment or predicting nuclear waste-site performance. Improved high-resolution geophysical process modeling will underlie new resource recovery, tracking of contaminants, and predicting and tracking repository performance, whether for nuclear or energy-related wastes (such as CO₂). Even with new, improved analytical equipment, technical challenges will continue in mastering data-fusion approaches to multiple-technique measurements, such as combined x-ray and neutron probes. Computational capabilities enabled by new high-performance computing architectures will be important contributors to molecular and geomechanical modeling techniques and will provide unique support to experimental analysis.

Projected Evolution

In the near term, geosciences research continues its focus on geomaterial properties; hydrogeomechanical modeling; and analytical, theoretical, and experimental geochemistry. It continues national laboratory and university projects focusing on understanding, at the finest possible resolution, the significance of fluid-rock interactions and how they contribute to mineral-fluid reactivity and chemical migration. Program activities will continue to investigate uses of synchrotron and neutron imaging in geosciences.

In the mid-term, the activity initiates research efforts aimed at discovering new earth processes. This discovery focuses on both small-scale, high-frequency processes (using pulsed x-rays, neutron sources, high-resolution mass spectrometry, and computational molecular modeling) and

large-scale, long-time processes (using THMC modeling and imaging of the dynamic response of earth materials to perturbations). Activities continue to drive improvements in subsurface access and in manipulation of processes to optimize subsurface response.

In the longer term, Geosciences activities will link analytical capabilities with computational capabilities at the micro-, meso-, and macro-scales to provide understanding of geological processes occurring at natural time and length scales and to test this understanding with increasingly accurate and fine-scale indicators of geologic history. Geosciences activities will provide robust understanding of the connection between chemical and mechanical coupling in earth materials across multiple length and time scales.

The BES Geosciences program does not fund research focused on single application areas such as, for example, CO₂ sequestration or geothermal energy production, or on topics such as signal processing and applied geophysics. Investigators proposing research in these areas should contact the appropriate technology office.

Significant Accomplishments

Over the last two decades, major accomplishments have been made in aqueous solution thermodynamics, nanogeoscience, high-resolution isotope geochemistry, reactive transport modeling, geomaterials rheology and stress response, and fracture network dynamics. Some recent examples include:

- Research on redox-driven interfacial processes occurring in highly insoluble subsurface iron oxides has revealed an unexpected highly dynamic, rapidly overturning interface driven by transfer of ferrous iron from solution into the predominantly ferric iron oxide. Such processes have implications for contaminant transport, which is often governed by redox transformations, and also for the ability of iron oxides to act as records of geologic processes over long time scales.
- Imaging of crystal growth dynamics on low-temperature, insoluble oxides and biominerals has led to the realization that crystallization proceeds not only via atom-by-atom processes but also by aggregation of preformed crystallites of the dimensions of nanometers. This work has implications for the design of toughened, fracture resistant materials.
- Construction of the first nuclear magnetic resonance probes capable of operating at gigapascal (10,000 atmosphere) pressures. This work gives new mechanistic insights into aqueous reaction mechanisms by subjecting reacting species to high pressures.
- Development of the first secondary-ion mass spectrometry capability for resolving isotope variations at 1 micron resolution. This work allows reconstruction of unprecedented detail in the chemical evolution of shales from burial to lithification and hydrocarbon generation.
- Development of new techniques for dating the evolution of fracture networks forming from dehydration and hydrocarbon release during sedimentary basin evolution. This work provides insight into pathways of hydrocarbon migration and accumulation.

Unique Aspects

Society and industry rely on the earth to provide both energy resources and the raw materials to synthesize energy production systems. As the easily-extracted energy resources are consumed, increasing demands are placed on subsurface science to provide novel ways of accessing new

types of resources and to do this in a high-yield, safe, and cost-effective manner. The earth must also be the ultimate repository of energy wastes. Intelligent waste management strategies rely on understanding, and planning for, a myriad of possible THMC processes, operating in the earth's crust on a wide range of time scales, many of which have not yet even been identified. Program activities provide basic knowledge needed for the solution of earth science-related problems in multiple DOE mission areas.

The defining aspects of the program are based on DOE capabilities in high performance computing, x-ray science, and neutron science. The BES Geosciences program plays a pioneering role in two major areas of geoscience research:

- 1) Molecular geochemistry, combining x-ray and neutron scattering observations with computational chemistry to reveal mineral-water interfacial structure and dynamics at the molecular level.
- 2) Geophysical process imaging, combining inversion of seismic, electromagnetic, and remote sensing data with THMC forward modeling codes to discover new geophysical processes operating in the shallow crust.

These areas define the BES Geosciences program relative to other federal funding agencies supporting geosciences research, such as the National Science Foundation and the United States Geological Survey. Examples of applications of these focus areas include (but are not limited to): (i) fundamental reaction mechanisms at mineral-water interfaces at the atomic/molecular level to better understand contaminant migration; (ii) reactive fluid-flow studies to better understand hydrocarbon transport, contaminant transport and remediation, and geothermal energy production; (iii) coupled THMC reactive transport modeling to increase the reliability of geological repository performance assessments.

Mission Relevance

Basic research in geosciences underpins knowledge behind improved access to the earth's subsurface and fosters a better understanding of the terrestrial impacts and limitations of energy technologies. This research informs the nation's strategy for optimizing access and mitigating impacts in a safe and cost-effective manner.

Performance assessments of energy production and disposal systems cannot be tested with any usual engineering approach. They have to rely upon conceptual and computational predictions of those systems over long temporal (decades to centuries to millennia) and spatial (kilometers) scales, based on geological observations. BES Geosciences program activities develop a fundamental understanding of geological processes relevant to energy materials production and to geological disposal options for byproducts from multiple energy technologies.

This new knowledge is critical to monitoring, verification, and accounting metrics associated with the development of new energy technologies, serving as a foundation for consent-based energy extraction and waste disposal activities. Knowledge of subsurface geochemical processes, operating both now and in the geologic past, is essential to determining the fate and transport properties of harmful elements from possible nuclear or other waste releases and to assessing the distribution and availability of critical energy materials in the earth's subsurface. Geophysical

modeling methods are needed to predict the response of subsurface reservoirs for energy materials extraction and waste storage.

Relationship to Other Programs

- With its focus on molecular interfacial geochemistry, the Geosciences program has strong connections to other BES Chemical Sciences, Geosciences, and Biosciences Division programs, including Condensed Phase and Interfacial Molecular Science, Chemical Theory and Computation, Heavy Element Chemistry, Solar Photochemistry, and Catalysis. In interactions with these programs, Geoscience provides expertise on interfacial processes occurring in chemically complex earth-abundant natural phases and receives input on innovative new theoretical and computational techniques perfected and validated on more idealized synthetic systems.
- Geosciences researchers also participate in Energy Frontier Research Centers.
- DOE user facilities, particularly synchrotron x-ray beamlines, are available to all of the geosciences community within the United States. BES research activities provide examples of innovative use of these user facilities focused on physical and chemical properties of geological systems.
- BES Geosciences activities are coordinated with applied programs within the Office of Fossil Energy (FE) and on Geothermal Energy within the Office of Energy Efficiency and Renewable Energy (EERE-GTO), and other DOE mission programs such as Environmental Management (EM) and Legacy Management. The BES program provides fundamental understanding of geochemical reactivity, the coupling of subsurface flow to geomechanical behavior of earth materials, and high-resolution geophysical process modeling that provides the foundation for predicting the long-term reliability of geological CO₂ sequestration (FE), devising approaches for utilizing geothermal energy (EERE-GTO), and understanding contaminant fate and transport in subsurface environments (EM).¹

¹ See Basic Research Needs for Geosciences

(https://science.energy.gov/~media/bes/pdf/reports/files/Basic_Research_Needs_for_Geosciences_rpt.pdf) and Subsurface Science, Technology, and Engineering Research and Development (SubTER) Roundtable Report (https://science.energy.gov/~media/bes/pdf/reports/2015/Controlling_Subsurface_Fractures_and_Fluid_Flow_rpt.pdf)