Chemical Physics Research

Portfolio Description

This activity supports experimental and theoretical investigations in the gas phase, condensed phase, and at interfaces aimed at elucidating the molecular-scale chemical and physical properties and interactions that govern chemical reactivity, solute/solvent structure, and transport. Also supported are new opportunities to attain predictive understanding of chemical reactivity, including structural and dynamical studies that emphasize a complete understanding of reactive chemistry at full quantum detail. These activities include the development and implementation of predictive computational modeling and simulation approaches, incorporating advanced theory and experimental validation, for scientific discovery across multiple scales. The impact on DOE missions is far reaching, including energy utilization, catalytic and separation processes, energy storage, and environmental chemical and transport processes.

The Chemical Physics portfolio comprises three program areas: (1) Gas Phase Chemical Physics, (2) Condensed Phase and Interfacial Molecular Science, and (3) Computational and Theoretical Chemistry. Each program area has a core focus, and there are significant synergies among them:

- *Gas Phase Chemical Physics (GPCP)* research emphasizes studies of the dynamics and rates of chemical reactions at energies characteristic of combustion, and the chemical and physical properties of key combustion intermediates. The overall aim is the development of a fundamental understanding of chemical reactivity enabling validated theories, models and computational tools for predicting rates, products, and dynamics of chemical processes involved in energy utilization by combustion devices. Important to this aim is also the development of experimental tools for discovery of fundamental dynamics and processes affecting chemical reactivity. Combustion models using this input are developed that incorporate complex chemistry with the turbulent flow and energy transport characteristics of real combustion processes.
- *Condensed Phase and Interfacial Molecular Science (CPIMS)* research emphasizes molecular understanding of energy-relevant chemical, physical, and electron-driven and photon-driven processes in aqueous media and at interfaces. Studies of reaction dynamics at well-characterized metal and metal-oxide surfaces and clusters lead to the development of theories on the molecular origins of surface-mediated catalysis and heterogeneous chemistry. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects and radiation-driven chemistry in nuclear fuel and waste environments. Studies of model condensed-phase systems target first-principles understandings of molecular reactivity and dynamical processes in solution and at interfaces. The approach confronts the transition from molecular-scale chemistry to collective phenomena in complex mesoscale systems, such as the effects of solvation on chemical structure and reactivity.
- *Computational and Theoretical Chemistry (CTC)* research emphasizes development and integration of new and existing theoretical and computational approaches for the accurate and efficient description of processes relevant to the BES energy mission. Of special interest is foundational research on computational design of molecular- to meso- scale materials and processes, and on next-generation simulation of processes that are so complex that efficient computational implementation must be accomplished in concert with development and testing of theories and algorithms. As such, supported efforts are tightly integrated with the

research and goals of the CPIMS and GPCP programs and many have wider crosscutting relevance, advancing goals of other BES chemistry, biochemistry and geochemistry programs. Common to all of these areas is the need for new approaches that go well beyond standard representations to address excited-state dynamics, low-energy diffusive effects, the inclusion of spin-dependent effects, the ability to model extremely anharmonic processes, and the ability to account for all types of energy exchange between matter and radiation in vacuum and in solvated environments.

Unique Aspects

The BES 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:

- Synergy among the three program areas is a hallmark of the Chemical Physics portfolio. Methods, tools, and knowledge developed in each area inform the others, and many supported efforts bridge the three program areas; this synergy is pronounced in concerted collocated efforts supported at Pacific Northwest and Lawrence Berkeley National Laboratories, and at the Combustion Research Facility (CRF).
- The program is uniquely positioned to undertake joint theoretical, computational and experimental efforts. Such a capability is essential for validating and improving models and methods used to design chemical processes, which are increasingly complex and data-intensive.
- The GPCP program is the principal supporter of high-temperature chemical kinetics and gas-phase chemical reaction dynamics in the nation. This activity also has oversight for several national laboratory programs, including the CRF, a unique, multi-investigator research laboratory that has a strong collaborative visitor program and that promotes synergism between BES-supported basic research and the applied science and technology programs supported the Office of Energy Efficiency and Renewable Energy (EERE) and industry.
- The CPIMS program is unique is its relevance to DOE mission areas, providing a fundamental basis for understanding chemical reactivity in complex systems, such as those encountered in catalysis, energy storage, separations, and the environmental contaminant transport in mineral and aqueous environments. This program is a major supporter of basic research on chemical reactivity of molecular species in the liquid phase, on metal clusters, and at solid-gas and solid-liquid interfaces.
- The CTC program is fully integrated with other BES research activities, contributing principally to the GPCP and CPIMS elements of the Chemical Physics portfolio, 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.

Relationship to Other Programs

Research under this activity complements research supported across the Office of Basic Energy Sciences and coordinates and leverages efforts with other agencies and facilities. These interactions include:

- *Gas Phase Chemical Physics:* The GPCP program and DOE EERE support coordinated combustion research efforts at the CRF and at Argonne National Laboratory (ANL). The GPCP program works with the Air Force Office of Scientific Research (AFOSR), Office of Naval Research (ONR), Army Research Office (ARO), National Aeronautics and Space Administration (NASA), National Institute of Standards and Technology (NIST), and the National Science Foundation (NSF) as an active member of the Multi-Agency Coordinating Committee on Combustion Research (MACCCR) to host an annual Fuels Research Review as well as combustion workshops. These linkages include common principal investigators and industry relationships in a number of programs, joint workshops, and coordination meetings. GPCP supports the Chemical Physics Beamline at the Advanced Light Source (ALS).
- *Condensed Phase and Interfacial Molecular Science:* There is a strong coupling between the CPIMS and Solar Photochemistry programs in the fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces. Support is provided for basic research to scientists at Pacific Northwest National Laboratory who utilize the William R. Riley Environmental Molecular Sciences Laboratory, a national user facility operated by the DOE/SC Office of Biological and Environmental Research. Experiments concerning ultrafast chemical imaging are supported at the Center for Nanoscale Materials at Argonne National Laboratory in coordination with the BES Scientific User Facilities Division. Support is provided for the Molecular Environmental Science Beamline at the ALS.
- *Computational and Theoretical Chemistry:* 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 to 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.

Significant Accomplishments

- Impacts in fundamental science include the development of molecular beams and ion imaging techniques that have spawned a generation of experiments in state-to-state chemical reaction dynamics and energy transfer, much of which has been supported by the chemical physics program. The capabilities have been extended to the development of molecular beam and laser sputtering techniques for the study of atomic clusters as prototypical models for catalysis.
- Ultrafast laser spectroscopy has provided important insights into hydrogen bonding and proton transport in water in nano-confined geometries. Support has yielded for the first time a conclusive link between the size of catalytic particles on a surface, the particle electronic properties, and the ability of particles to speed chemical reactions. Advances in high resolution time-resolved spectroscopy have yielded information on intermediates and product state distributions with unprecedented isomeric specificity.
- Recent advances in low-temperature scanning tunneling microscopy (STM) have been combined with temporally and spatially resolved spectroscopic tools such as ultrafast, two-photon photoemission, resulting in the discovery of long-lived electronic surface states that could lead to new ways to induce and control electronic excitation at surfaces, and have

yielded an unprecedented view of the coupling of electronic and vibrational motion within a single molecule.

- Advanced probes of combustion environments have also yielded recent discoveries, such as the direct observation of Criegee reaction kinetics important in combustion and atmospheric chemistry.
- Development of high-fidelity engine simulations has demonstrated the importance of molecular scale dynamics, e.g. quantum tunneling, on engine performance.
- 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.
- Development and application of new approaches to density functional and traditional wavefunction-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.

Mission Relevance

- The GPCP activity contributes strongly to the DOE mission in the area of 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 consequences. 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.
- The CPIMS activity impacts a variety of mission areas by providing a fundamental basis for understanding chemical reactivity in complex systems, such as those encountered in catalysis and environmental processes, along with activity that provides fundamental underpinnings relevant to energy production and storage. Surface-mediated chemistry research in this activity complements more directed efforts in heterogeneous catalysis. Condensed-phase and interfacial chemical physics research on dissolution, solvation, nucleation, separation, and reaction provides important fundamental knowledge relevant to the environmental contaminant 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.
- The CTC activity aims to advance the Chemical Physics goals just described and also advance mission areas across BES. For example, supported activities advance next-generation solar energy, sunlight-to-fuels, and energy storage concepts.

Scientific Challenges

Research in Chemical Physics 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. Specific opportunities include:

Gas Phase Chemical Physics

- Improve and expand experimental measurement of highly energetic, unstable molecules to diagnose complex reacting flows and, in more controlled environments, to determine molecular dynamics and reaction rates at elevated temperatures and pressures.
- Develop computational approaches of acceptable precision for the calculation of potential energy surfaces for ground and excited electronic states and their conical intersections for chemically important species including free radicals.
- Improve accuracy and throughput of methods for calculating chemical reaction rates from detailed chemical dynamics, including reactions without barriers for which statistical theories do not apply.
- Develop methods of uncertainty quantification and model reduction to enable high-fidelity predictive combustion models.
- Understanding the interaction of chemistry and fluid dynamics in turbulent combustion conditions.
- Role of multiphase chemistry in combustion, including fuel aerosols and soot particle formation and growth.

Condensed Phase and Interfacial Molecular Science

- 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 nano-confinement effects.
- Develop a structural basis for understanding gas/surface interactions, encouraging site-specific studies that measure local behavior at defined sites.
- Understand the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding and proton transport.
- Develop new experimental and theoretical tools that push the horizon of joint space-time resolution needed to probe chemical behavior selectively at interfaces and in solution.

Computational and Theoretical Chemistry

- 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

The focus of the chemical physics program is the development of a molecular-level understanding of gas-phase, condensed-phase, and interfacial chemical reactivity of importance to combustion, catalysis, energy conversion and storage, and environmental preservation. The desired evolution is to predictive capabilities that span the microscopic to macroscopic domains enabling the computation of individual molecular interactions as well as their role in complex, collective behavior in real-world devices. Currently, increased emphasis in gas-phase chemical physics is on validated theories and computational approaches for the structure, dynamics, and kinetics of open shell systems, experimental measurements of combustion reactions at high pressures, better insight into soot particle growth and an improved understanding of the interaction of chemistry with fluid dynamics. In surface chemistry, continued emphasis is on the development of a structural basis for gas/surface interactions, encouraging site-specific studies that measure local behavior at defined sites. At interfaces, emphasis is on aqueous systems and the role of solvents in mediating solute reactivity. Expanding into the future, plans are to enhance the use of computer-generated mechanisms and models in combustion science, broaden efforts to molecular building blocks of emerging fuels, probe the chemical physics of energy transfer in large molecules, to explore the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding, and to investigate temporally resolved interfacial chemical dynamics and charge transfer using advances in chemical imaging. Computational and theoretical efforts will continue to expand in scope, to span BES mission-relevant research in chemical sciences, geosciences and biosciences, while at the same time remaining tightly integrated with these efforts. A continuing emphasis on DOE mission impact will guide the selection of research opportunities and interactions with other programs and organizations.