# 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 5*f* 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 5*f* 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 5*f* 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 5*f* 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 5*f* and 6*d* electrons leads to a better quantum-mechanical understanding of all bonding as these molecules containing elements

---

[1] https://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 wasteforms, 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.