EMSL

NWChem and Actinide Chemistry

ACTINIDE CHEMISTRY MEETS COMPUTATION

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

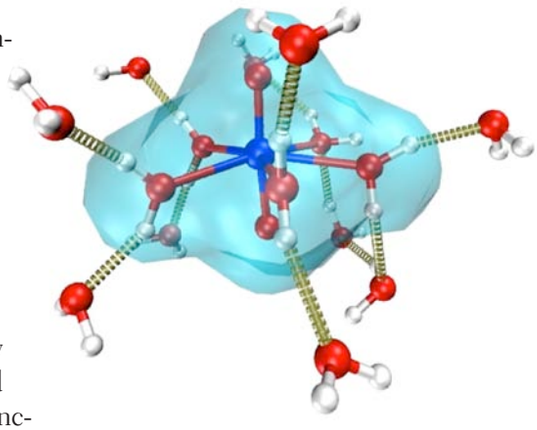
Capturing how contaminants migrate across groundwater-surface water interfaces is a challenge that researchers at the Department of Energy's EMSL—the Environmental Molecular Sciences Laboratory—are rising to. This challenge, a top priority for waste cleanup efforts at the Hanford Site in Richland, Washington, and other parts of the DOE weapons complex, is being addressed using NWChem, a computational chemistry package developed at EMSL that is designed to run on high-performance parallel supercomputers, such as EMSL's Chinook.

NWChem is enabling breakthrough discoveries in actinide behavior and chemistry, in part because it allows researchers to accurately model the dynamical formation, speciation, and redox chemistry of actinide complexes in realistic complex molecular environments. The knowledge about the molecular mechanisms gained from these simulations can then be applied to real-world, geochemical field-scale studies as well as subsurface contaminant behavior and transport problems.

Discoveries in actinide chemistry impact a wide range of radioactive waste and cleanup challenges and may lend to the design and operation of future nuclear facilities.

NWCHEM – MOLECULAR DETAIL

NWChem aims to be scalable both in its ability to treat large problems efficiently and in its use of available parallel computing resources. It offers a unique set of capabilities to model small molecules and large, extended, mixed solid phase-solution phase systems, including periodic boundary conditions, with relativistic effects such as spin-orbit corrections, which enable researchers to characterize redox chemistry in complex actinide systems. This capability is based on the spin-orbit zeroth order regular approximation (ZORA) methodology for both Gaussian and plane-wave density functional theory (DFT). Combined with Car-Parrinello DFT molecular dynamics, it allows researchers to model the dynamic environment. In addition, exact exchange and self-interaction correction (SIC) methodologies can describe localized charge distributions necessary to obtain accurate results.



NWChem, DOE's premier computational chemistry software, provides a major modeling and simulation capability for molecular actinide science.

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ABOUT EMSL

EMSL, a U.S. Department of Energy national scientific user facility located at Pacific Northwest National Laboratory, provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.

EMSL's distinctive focus on integrating computational and experimental capabilities as well as collaborating among disciplines yields a strong, synergistic scientific environment. Bringing together experts and an unparalleled collection of state-of-the-art instruments under one roof, EMSL has helped thousands of researchers use a multidisciplinary, collaborative approach to solve some of the most important and complex national scientific challenges in energy and environmental sciences.

Researchers from around the world are encouraged to submit a proposal to use EMSL's unique capabilities in combination with each other with an emphasis on merging computational and experimental instruments. To submit a proposal for use of EMSL or to learn more about the science conducted at EMSL and the instruments and expertise available to users, visit www.emsl.pnl.gov.

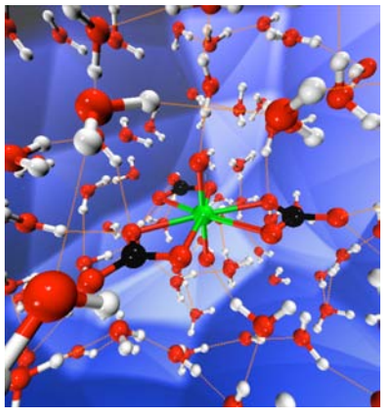
DOWNLOAD NWCHEM

EMSL invites the scientific community to apply its capabilities and expertise to their studies of molecular-scale properties of actinide-containing solutions and materials as well as the separation processes relevant to advanced nuclear energy systems.

NWChem software is free of charge, subject to the terms and conditions of the EMSL software user agreement. Download the software at http://www.emsl.pnl.gov/capabilities/computing/nwchem/.

STUDYING PLUTONIUM IONS IN SOLUTION

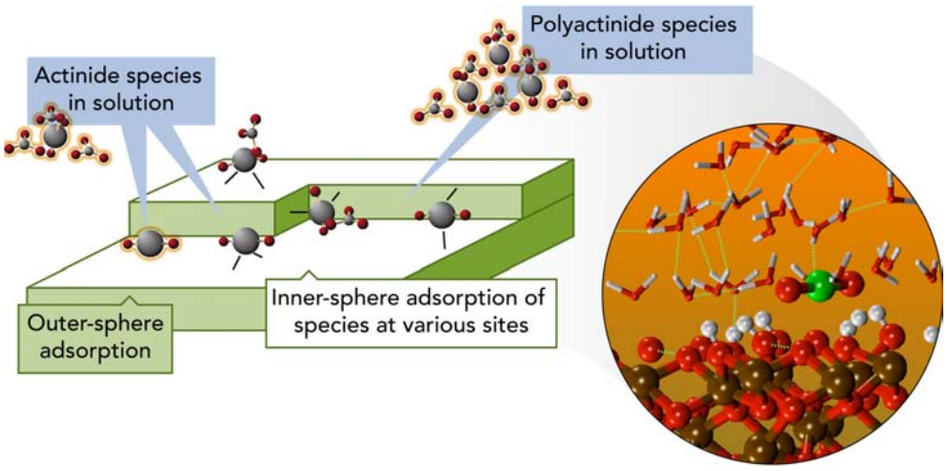
NWChem is used to model the oxidation states and redox chemistry of uranium and plutonium ions in complex solution environments. These studies require the proper inclusion of spin-orbit coupling to address more complex open-shell 5f occupations. To obtain reliable structural information, and to obtain accurate energetics for the formation and transformation of plutonium species, reliable NWChem-based computational chemistry methodologies are coupled with realistic solvation models, and include spin-orbit coupling from the outset. Results of simulations of uranyl in water showed excellent agreement with available experimental data. (*J. Chem. Phys.* 128 (12): 124507, 2008)



Ab initio dynamics simulation of actinyl ions complexing with carbonate ions in aqueous solution.

UNDERSTANDING THE INTERACTION OF ACTINIDES WITH INTERFACES

NWChem is used to model and compare the sorption processes and reduction mechanisms of uranium-based actinide species with ligands such as carbonate and hydroxyl on solvated iron-oxides surfaces as well as clay layers. Structural and spectroscopy data from these simulations can be used to interpret experimental extended x-ray absorption fine structure (EXAFS) data. Accurate energetics calculations allow researchers to investigate the effects of the solution/solid interface on the relative stability of oxidation states and redox energetics of the actinide ions in solution.



Complex solvated actinide species can adsorb through various mechanisms (left). At the surface the actinide can be reduced, and/or incorporated, or new species can be formed. Ab initio dynamics simulation of solvated actinide species on the hydroxylated iron-oxide surface (right) will provide molecular scale insight into these chemical processes.

September 2009
PNNL-SA-68530

Pacific Northwest NATIONAL LABORATORY

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