

# CHEMISTRY

## GAMESS: Enabling GAMESS for Exascale Computing in Chemistry and Materials

Heterogeneous catalysis and the design of new catalysts is a grand challenge problem in computational chemistry that will require the capabilities of exascale computing. The GAMESS project is extending methods and algorithms based on chemical fragmentation methods and coupling these with high-fidelity Quantum Chemistry (QC) and Quantum Monte Carlo (QMC) simulations to solve this problem. Through computation on a well-defined representative heterogeneous catalysis problem comprising mesoporous silica nanoparticles, GAMESS will demonstrate the capability to model physical systems requiring chemical interactions that involve many thousands of atoms, indicating a new ability to model complex chemical processes.

To take full advantage of exascale architectures, it is critical that application software be developed that can exploit multiple layers of parallelism and take advantage of emerging low-power architectures that dramatically lower energy and power costs without significant deterioration of time-to-solution. This work will develop ab initio methods for GAMESS based on fragmentation methods that have been shown to scale beyond the petascale combined with QMC. To attain exascale performance, GAMESS will be refactored to take advantage of modern computer hardware and software, and the capabilities of the C++ libccchem code that is codeveloped with GAMESS will be greatly expanded. Concurrently, performance analyses will be conducted for the broad array of electronic structure methods in GAMESS on current and emerging architectures to assess their ability to decrease time-to-solution. The improved codes that are developed will be brought to bear on the heterogeneous catalysis problem, specifically using mesoporous silica nanoparticles (MSNs), requiring thousands of atoms, as a template.

MSNs are highly effective, selective heterogeneous catalysts for a wide variety of important reactions including the production of carbinoamine, which is a starter material for other structures. MSN selectivity is provided by “gatekeeper” groups that allow only desired reactants A to enter the pore, keeping undesirable species B from entering the pore. The presence of a solvent further complicates the computational problem of simulating the

heterogeneous catalysis. Accurate electronic structure calculations are needed to deduce the reaction mechanism(s), including the effects of various solvents, and to subsequently design even more effective catalysts. The narrow pores (3–5 nm) can create a diffusion problem that can prevent product molecules from exiting the pore. Therefore, in addition to elucidating the reaction mechanism, the dynamics of the reaction process should be studied, and a sufficiently realistic cross section of the pore must be included. Small models are commonly used to approximate this type of system, with the expectation that a small model might provide insight into the system it represents. However, a recent computational study of the MSN catalysis of carbinolamine formation demonstrated that small proxy models are inadequate, both qualitatively and quantitatively.

This project involves computing both energetics and dynamics on a model reaction with a representative MSN. An adequate representation of the MSN pore requires thousands of atoms with an appropriate basis set. For example, 5,000 heavy atoms with the aug-cc-pVTZ basis set requires more than 500,000 basis functions, not including the hydrogen atoms, the reacting molecules, and especially the solvent molecules.

The energy surface will be mapped via GAMESS calculations using the EFMO + resolution of identity (RI)-MP2 methodology, with refined calculations using the EFMO+CR-CC coupled cluster approach or GAMESS EFMO + QMC approach for accurate reaction rates. The pore selectivity dynamics will be computed with an MD approach requiring approximately 10,000 energetics-type calculations utilizing the GAMESS+FM0 code.

### Progress to date

- Developed and optimized the underlying RI-MP2 energy + gradient code for both closed and open shells to GPU architectures.
- Developed a preliminary GAMESS-HF (Hartree-Fock) proxy application based on a slightly modified SIMGMS module that utilizes the SIMINT and OED integral libraries.
- Evaluated the performance of the LIBCCHEM GPU implementations of HF, MP2, and RI-MP2 methods on NVIDIA P100 (Pascal) and V100 (Volta) GPUs using a set of input files for calculations on linear alkenes of increasing size.
- Validated GAMESS (E)FM0 methodology for fractional MSN systems and performed weak-scaling studies.

GAMESS will use new methods and algorithms to enable computations of chemical processes involving thousands of atoms that will lead to the solution of a grand challenge problem in computational chemistry using exascale computing.

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