

Computational Design of New Materials for Energy and Environmental Applications
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Computational Resources Requested

Resource Type	SUs Requested	Maximum SUs allowed
MPI	3,050,000	3,200,000
SMP standard (default)	1,300,000	1,300,000
SMP specialty (high memory)	0	500,000
HTC	0	100,000
GPU	0	3,200,000

Project Description

We are requesting computational resources for three different research projects. Project 1 deals with developing nanoporous catalysts. Project 2 involves anhydrous proton transport on a functionalized graphane membranes. Project 3 is about capture, detection, and destruction of chemical warfare agents. The computational demands for each are estimated below.

Project 1: Nanoporous Catalysts

This project involves developing functional groups on linkers containing metal and non-metal catalytic sites, and modified secondary building units (SBUs) having open metal catalytic sites. The applications involve various catalytic reactions relating to energy and environmental applications. This project is funded by DOE. We are exploring a number of different metal organic frameworks (MOFs). We have carried out timing calculations on a prototypical MOF, UiO-66 and scaling plots are included below. This work involved the following types of calculations: geometry optimizations, ab initio molecular dynamics, climbing image nudged elastic band, frequency analysis. We primarily use CP2K to do these calculations.

Geometry optimization. Based on previous calculations on functionalized UiO-67 and similar MOFs we estimate that each optimization will require about 500 SUs. We plan to explore approximately 10 different materials with 6 different reacting species each, and each species will be optimized at about 10 different starting locations to map out for a total energy landscape. We estimate a total requirement of $500 \times 10 \times 6 \times 10 = 300,000$ SUs on MPI for the geometry optimizations. **Ab initio molecular dynamics (AIMD).** We estimate that a total time of 10 ps (with a 0.25 fs time step) is necessary for AIMD calculations to explore binding energies, proposed reaction mechanisms and explore configurational space. Each trajectory will require about 12,000 SUs so for 10 different materials with 6 different reacting species each, we require about **700,000 SUs on MPI** for the AIMD jobs. **CI-NEB.** We need to identify reaction pathways each of the reacting species. Each CI-NEB calculation will require about 12 images running on MPI, where we can have multiple cores per image. We need to make several CI-NEB runs by tuning the structure of each image in order to identify a single reaction to locate the correct transition state, with each NEB job taking about 8,000 to 9,000 SUs. In total, we estimate about $10 \times 6 \times 8,500 \sim 500,000$ SUs on MPI for the CI-NEB calculations for the MOFs we plan to explore.

Frequency analysis. CPU hours for performing the frequency analysis depends on the number of atoms in the system. The frequency calculation performs six displacements on each atom. The frequency analysis needs to be performed on reactants (R), transition states (TS), and products (P) for each reactions and also other configurations. We estimated the required SUs by

from calculations on the UiO-66-P-BF₂ system, at about 2,000 SUs per system for a total of about 2,000×10×6×3 ~**400,000 SUs on MPI** for frequency analysis.

Project 2: Anhydrous Proton Transport on a functionalized graphane membrane

Research Project 2 include computations involving a series of electronic band structure calculations, AIMD simulations, CI-NEB and phonon density of states calculations for the various systems and configurations of functionalized graphane. These system sizes are smaller than the previous projects, so we will run these calculations on SMP instead of MPI. We estimate that the electronic structure and phonon density of states calculations will require about **300,000 SUs on SMP**. AIMD calculations will be used to compute diffusivities for protons and for developing empirical potentials for an empirical valence bond approach for modeling proton transport. We have found that simulations at the temperatures of interest require a time step of 0.5 fs. We require at least 30 ps for diffusion calculations. We require at least 10 independent trajectories for each system. We plan to compute diffusivities at four different temperatures for each system. Each trajectory requires about 10,000 SUs, for a total of 400,000 SUs per system. We plan to investigate four different systems for a grand total of **1,600,000 SUs on SMP** for the AIMD jobs. CI-NEB calculations are required for identifying diffusion pathways near the ground state. These calculations can be run on MPI by putting different replicas on different nodes. We estimate a need for about **100,000 SUs on MPI**.

Project 3: Capture, Detection, and Destruction of CWAs

We are investigating stratified MOFs with embedded plasmonic nanoparticles for chemical warfare agent (CWA) capture, detection and destruction. This project involves calculations with MOFs that are fairly similar to those in Project 1, primarily using CP2K. We are screening interactions between various functionalized MOFs and CWA and CWA simulants in order to identify functional groups that will selectively bind the CWAs and simulants. We are also exploring diffusion of CWA and simulant molecules in various MOFs, primarily with model potentials, but DFT calculations will be used to parameterize potentials. We are also computing the reaction pathways for CWA and simulant molecules degrading at catalytic sites on the MOFs, requiring Growing String Method and CI-NEB calculations. The AIMD simulations, binding energy calculations, and reaction pathway searches are estimated to require **350,000 SUs on MPI**. In addition, we are doing calculations of Cu₂Se with VASP to explore the band structure as a function of defects (Cu_{2-x}Se) and thermal disorder. These calculations run more efficiently on the SMP cluster and we request **100,000 SUs on SMP**.

Scaling

We have computed the speedup as a function of the number of nodes using 1, 2, 4, 8, and 16 nodes, corresponding to 56, 112, 224, and 448 cores, respectively, for a system consisting of a MOF supercell having 912 atoms. The CPU time is for 120 SCF steps in each case. The speedup is defined as the wall time for the smallest number of cores divided by the wall time required for a larger number of cores. Three different energy cutoff values were used for the calculations, 360, 450, and 600 Ry. For all but the most accurate requirements, a cutoff of 360 Ry is

considered sufficient. The results are plotted in Figure 1. We observe good scaling for 4 nodes (112 cores) for all values of the energy cutoff compared with ideal scaling shown as the black line. The scaling is acceptably good for 8 nodes for the 360 Ry and 450 Ry cutoff values. The efficiency of the run is significantly degraded for all runs for 16 nodes. Thus, we conclude that we can efficiently use up to 112 cores (4 nodes) on MPI.

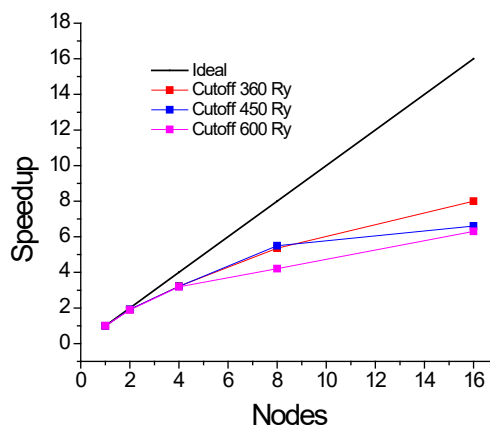


Figure 1: CP2K scaling (speedup) with number of cores as a function of planewave cutoff. The 360 Ry cutoff is typically sufficient for most calculations.

We have computed the scaling of the CP2K code with system size by comparing time required for 120 SCF iterations as a function of the number of atoms in the system holding the number of cores constant. We performed calculations using both 1 node (28 cores) and 4 nodes (112 cores). We used system sizes containing 1, 2, 4, and 8 unit cells of the UiO-66 framework, with 114, 228, 456, and 912 atoms, respectively. These results are plotted in Figure 2. We see from Figure 2 that CP2K scales remarkably well with system size, both for 1 and 4 nodes. In fact, the scaling for 4 nodes is better than linear, which is counterintuitive. This remarkably good scaling with system size is an artifact of the very bad parallelization for the smallest system size of 114 atoms. Thus, for 4 nodes the improvement in communications efficiency improves the CPU faster than the increase in computational effort due to the inherent scaling of DFT. Linear scaling on the plot in Figure 2 is shown by the black line. This linear scaling was computed for the 1 node case. Thus, we see that for 1 node the scaling with system size is superlinear, but even at the largest system size the scaling is actually very good (about a factor of 2 larger than linear). For the 4 node calculations the scaling is even better than linear (slope of line < 1). Again, this is an artifact of poor efficiency with the number of nodes for the small system sizes.

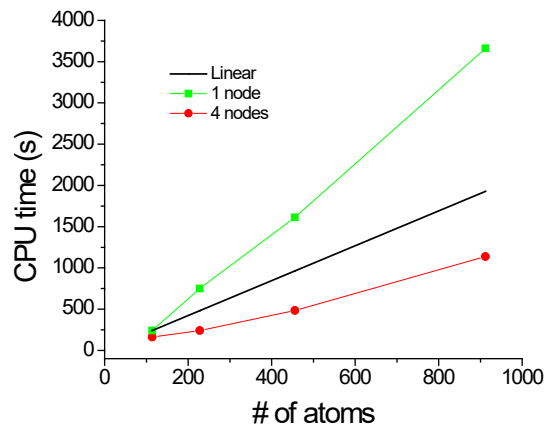


Figure 2: Computational scaling of CP2K with system size per 120 SCF iterations. Timing calculations were performed using either 1 or 4 nodes (28 or 112 cores) for each job.

Funding Sources

Koblar Alan Jackson (Central Michigan University), PI. J.K. Johnson Co-PI (with others), “FLO-SIC: Efficient Density Functional Theory Calculations Without Self-Interactions”
 DOE BES DE-SC0018331
 \$4,799,997.00 total. Pitt share: \$1,175,701 JKJ share: \$559,641
 09/01/2017—08/31/2021

Person-months per year: 0.1

J. K. Johnson, PI, "Fundamentals of Anhydrous Proton Transport on the Surface of Functionalized Graphane"

NSF PD 16-1403

\$300,000

08/01/17—07/31/20

Person-months per year:1.0

J. K. Johnson, PI, with Co-PIs: N. Rosi (Pitt, Chemistry), J. Millstone (Pitt, Chemistry), E. Borguet (Temple University)

"Design, Synthesis and Characterization of Hybrid Stratified MOF-Plasmonic Nanoparticle Materials for Detection and Destruction of Chemical Agents"

DTRA

\$2,500,000 total, Pitt share: \$1,895,355.00 (Johnson, Rosi, Millstone)

Person-months per year: 0.5

Involvement of CRC Consultants

All consultants have been involved through addressing issues through help tickets. Barry Moore has been involved in getting codes working and optimizing performance of codes. We expect that Leonardo will be helpful we optimizing and installing codes in the future.

Publications acknowledging use of CRC (or SaM) resources over the past year

1. Abhishek Bagusetty, J. Karl Johnson, "Unraveling Anhydrous Proton Conduction in Hydroxygraphane", *Journal of Physical Chemistry Letters*, **10**, 518-523 (2019). [DOI:10.1021/acs.jpcelett.8b03627](https://doi.org/10.1021/acs.jpcelett.8b03627)
2. Tianyi Cai, J. Karl Johnson, Ye Wu, Xiaoping Chen, "Toward Understanding the Kinetics of CO₂ Capture on Sodium Carbonate", *Applied Materials & Interfaces*, **11**, 9033-9041 (2019). [DOI: 10.1021/acsami.8b20000](https://doi.org/10.1021/acsami.8b20000)
3. Lin Li, Sen Zhang, Jonathan P. Ruffley, J. Karl Johnson, "Energy Efficient Formaldehyde Synthesis by Direct Hydrogenation of Carbon Monoxide in Functionalized Metal Organic Frameworks", *ACS Sustainable Chemistry & Engineering*, **7**, 2508-2515 (2019). [DOI: 10.1021/acssuschemeng.8b05413](https://doi.org/10.1021/acssuschemeng.8b05413)
4. Abhishek Bagusetty, Joshua Livingston, J. Karl Johnson, "Graphamine: Amine Functionalized Graphane for Intrinsic Anhydrous Proton Conduction", *Journal of Physical Chemistry C*, **123**, 1566-1571 (2019). [DOI: 10.1021/acs.jpcc.8b09001](https://doi.org/10.1021/acs.jpcc.8b09001)
5. Kamal Sharkas, Lin Li, Kai Trepte, Kushantha P. K. Withanage, Rajendra P. Joshi, Rajendra R. Zope, Tunna Baruah, J. Karl Johnson, Koblar A. Jackson, and Juan E. Peralta "Benchmarking the Fermi-Löwdin Orbital Self-Interaction Correction Method: The SIE4×4 and SIE11 Test Sets", *Journal of Chemical Theory and Computation*, **122**, 9307-9315, (2018). [DOI: 10.1021/acs.jpca.8b09940](https://doi.org/10.1021/acs.jpca.8b09940)
6. Jingyun Ye, Lin Li, and J. Karl Johnson, "The Effect of Topology in Lewis Pair Functionalized Metal Organic Frameworks on CO₂ Adsorption and Hydrogenation", *Catalysis Science & Technology*, **8**, 4609-4618 (2018). [DOI: 10.1039/c8cy01018h](https://doi.org/10.1039/c8cy01018h)

Minh Nguyen Vo, Yasemin Basdogan, Bridget S. Derksen, Nico Proust, G. Adam Cox,

- Cliff Kowall, John A. Keith, and J. Karl Johnson, "The Mechanism of Isobutylene Polymerization: Quantum Chemical Insight into AlCl₃/H₂O-Catalyzed Reactions", *ACS Catalysis*, **8**, 8006-8013 (2018). DOI: [10.1021/acscatal.8b01494](https://doi.org/10.1021/acscatal.8b01494)
7. Ashish Bhatnagar, J. Karl Johnson, M.A. Shaz, and O.N. Srivastava, "TiH₂ as a Dynamic Additive for Improving the De/Re-hydrogenation Properties of MgH₂: A Combined Experimental and Theoretical Mechanistic Investigation", *Journal of Physical Chemistry C*, **122**, 21248-21261 (2018). DOI: [10.1021/acs.jpcc.8b07640](https://doi.org/10.1021/acs.jpcc.8b07640)