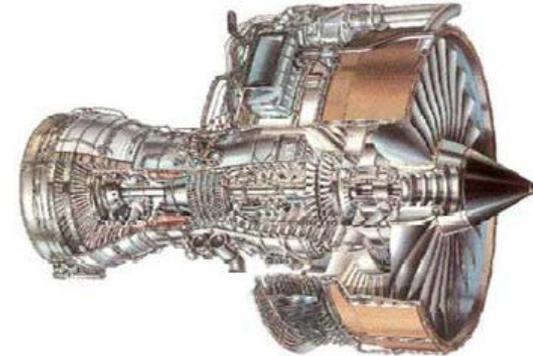
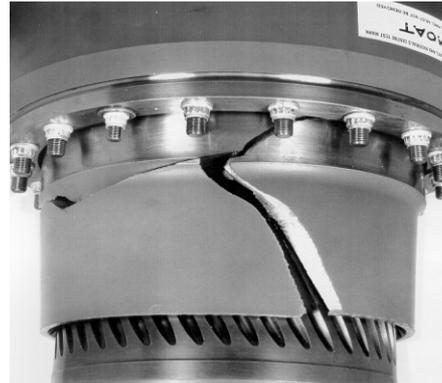
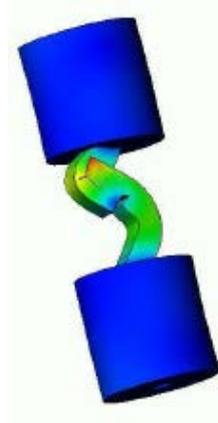


Exceptional service in the national interest

N=O=MAD
Research Institute



Development of Reactive Potentials for Molecular Dynamics Simulations

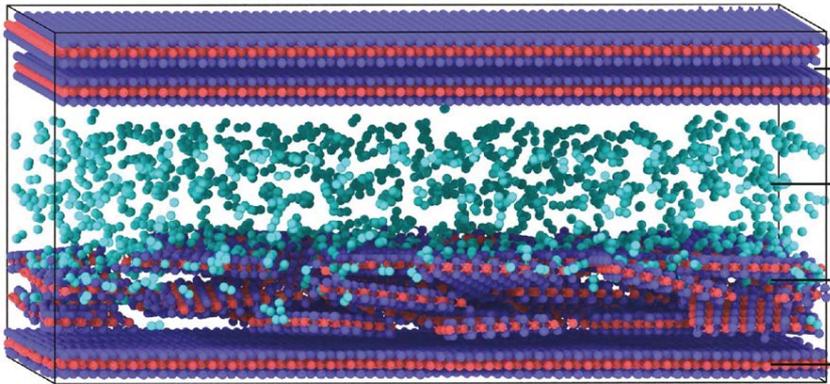
Students: Thomas Adams, Helen Cleaves

Mentors: Scott Grutzik, Normand Modine, Mark Wilson

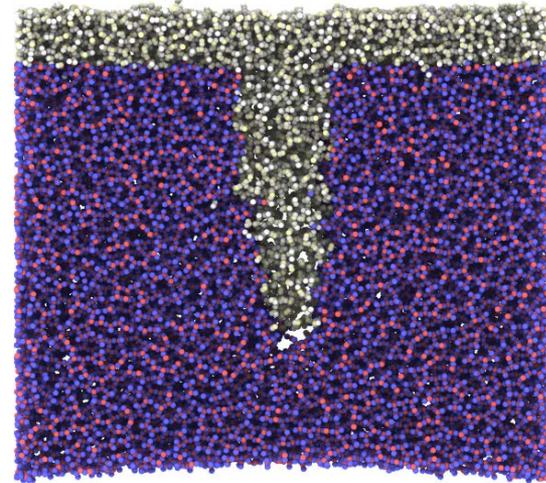
Computational Materials and Data Science (1864)

Component Science and Mechanics (1556)

Motivation: Materials Modeling with Chemical Accuracy



ReaxFF: Permeation of AO and O_2 gas in MoS_2 solid lubricant



ReaxFF: Impact of water in fracture of silica glass

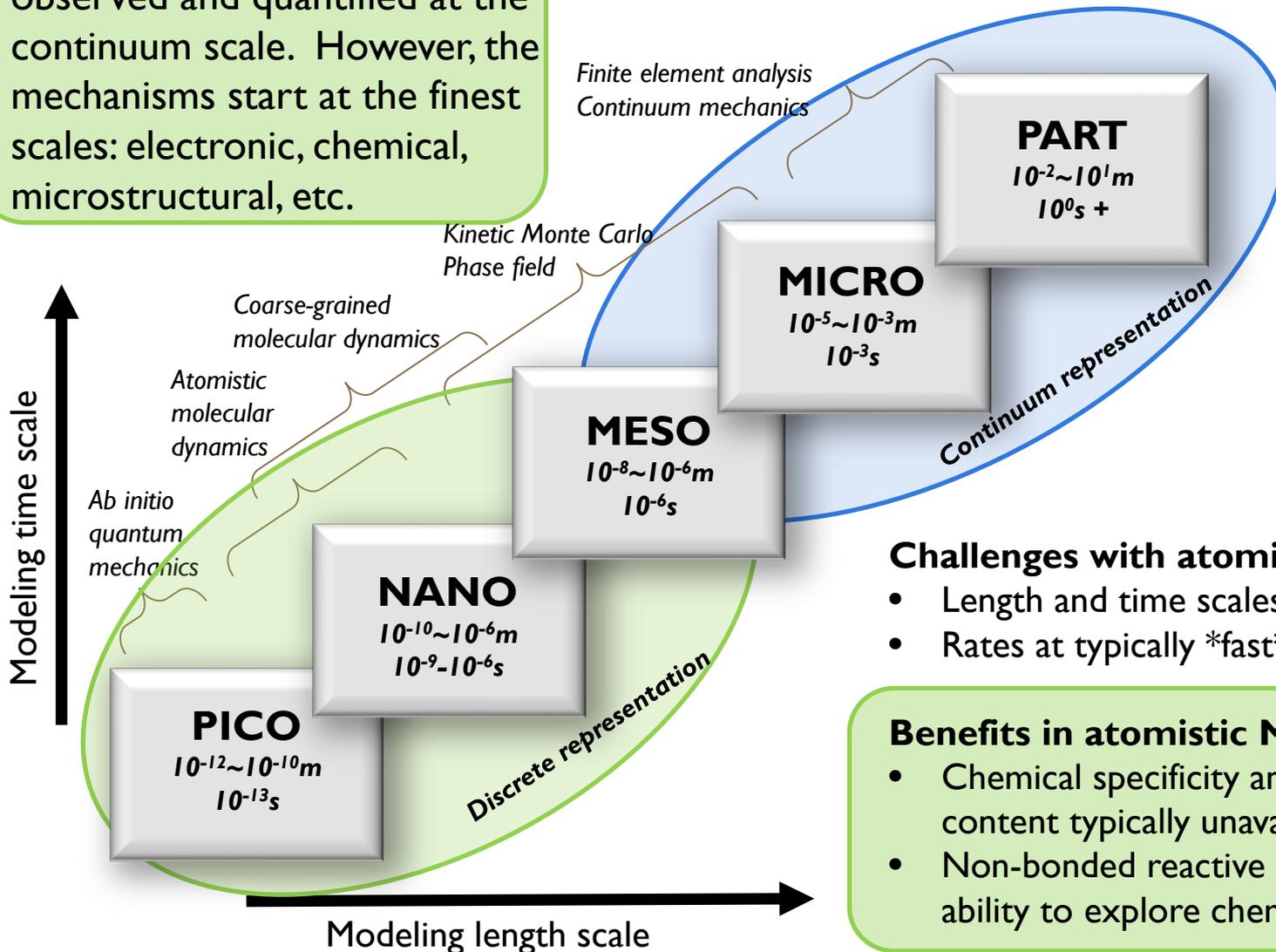
Images courtesy of Mark Wilson

- Reactive potentials are at the scientific cutting edge for atomistic modeling
- Lack of physical connections between atoms
- Charge equilibration- partial charges
- Estimates of bond orders – allows for modeling of chemical reactions

Length/Time Scales



Material performance is often observed and quantified at the continuum scale. However, the mechanisms start at the finest scales: electronic, chemical, microstructural, etc.



Challenges with atomistic MD modeling:

- Length and time scales
- Rates at typically *fast*

Benefits in atomistic MD modeling:

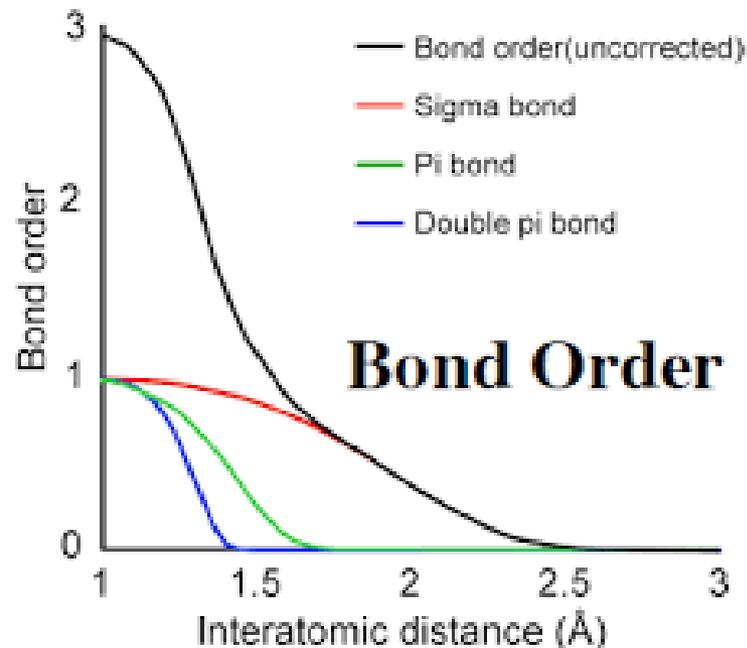
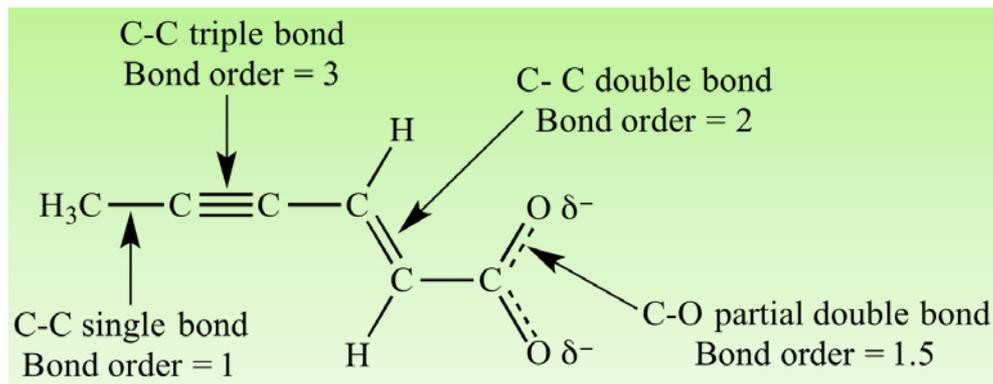
- Chemical specificity and microstructural content typically unavailable to other scales
- Non-bonded reactive potentials offer the ability to explore chemistry

What are Reactive Potentials?



Incorporate physics not typically accounted for in classical MD

- As a consequence are more computationally expensive
- ReaxFF treats bond order as a continuous function of interatomic distance
- **BOND ORDER** is the number of covalent bonds between two atoms



General Goals of the Project

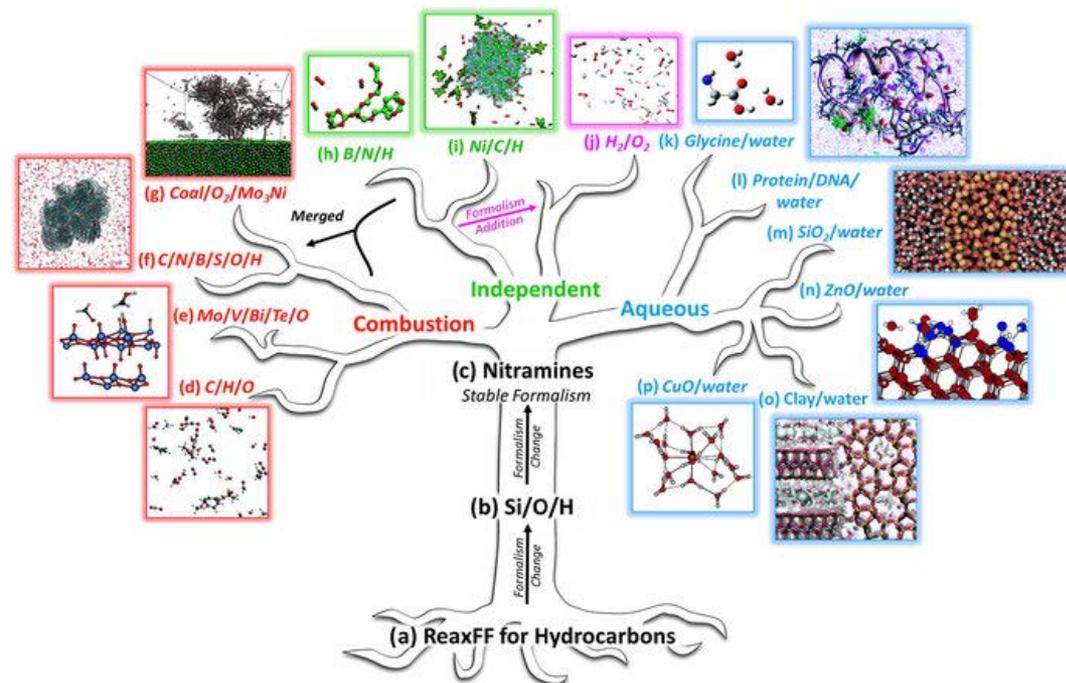


Challenge: As a user of reactive potentials, we are often limited by the available elemental constituents within a given potential

Goal: Develop the framework necessary to modify, create, and expand either existing or novel reactive potentials

Specific: Add BaSiO glasses potential

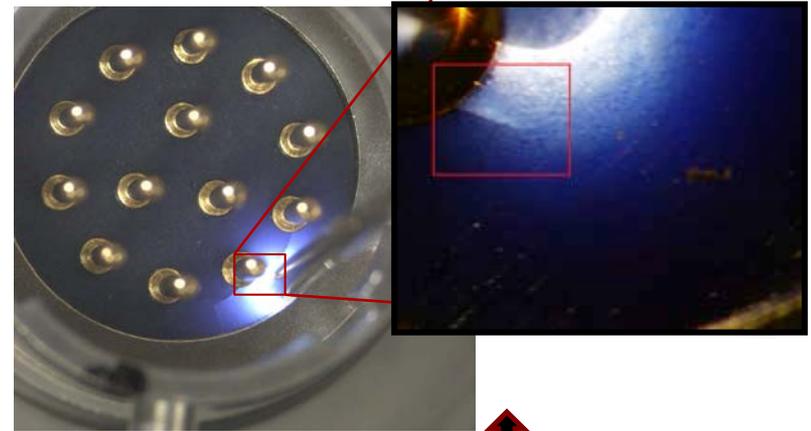
Approach: Utilize Dakota as an optimization engine to run multiple, small MD simulations designed to extract a single quantity of interest



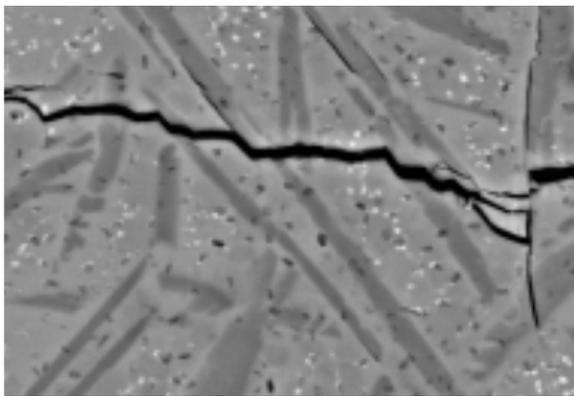
Why BaSiO Glasses?



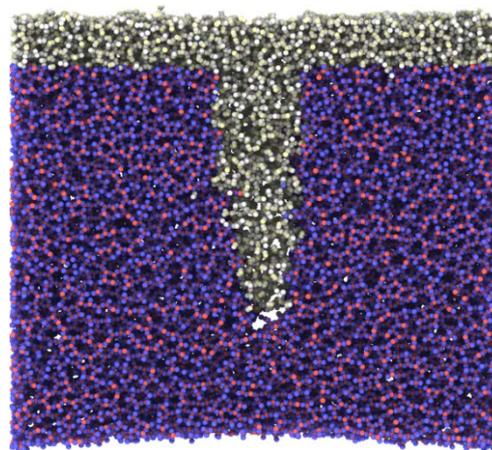
- Brittle materials are used throughout the stockpile. Examples include all headers, electronic connectors, and strong links
- Challenge: Make 30 year lifespan reliability predictions for components containing brittle materials. This requires predictive modeling



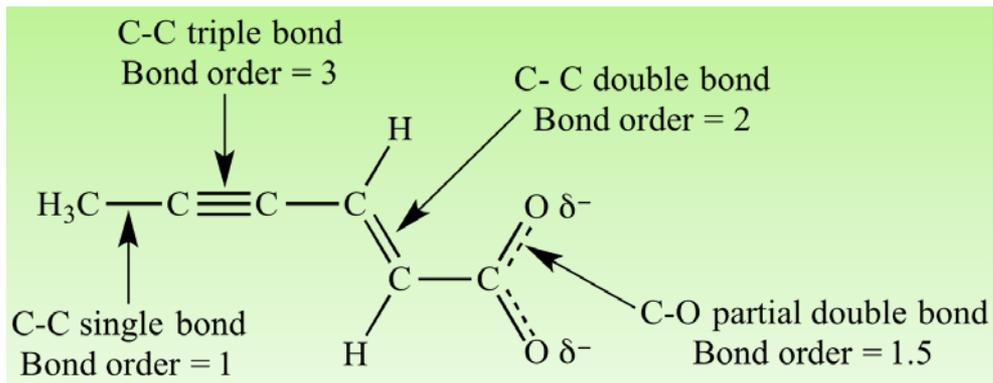
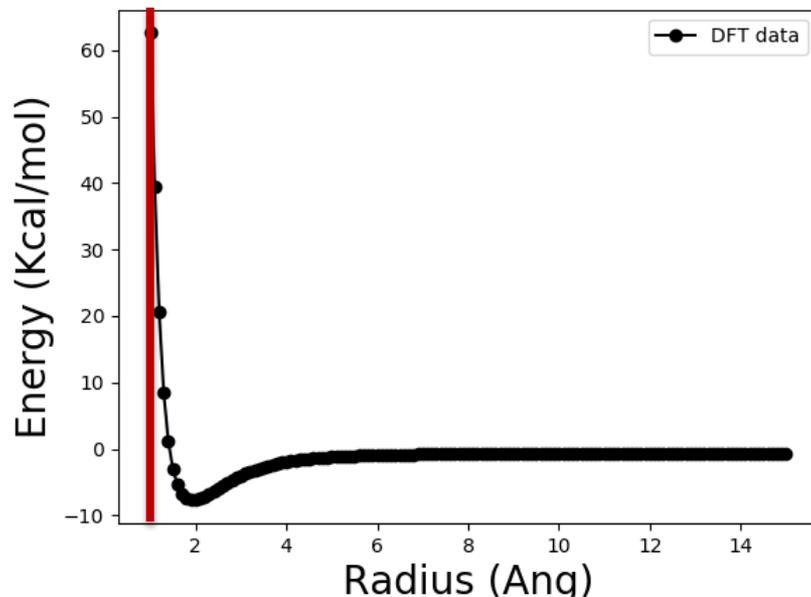
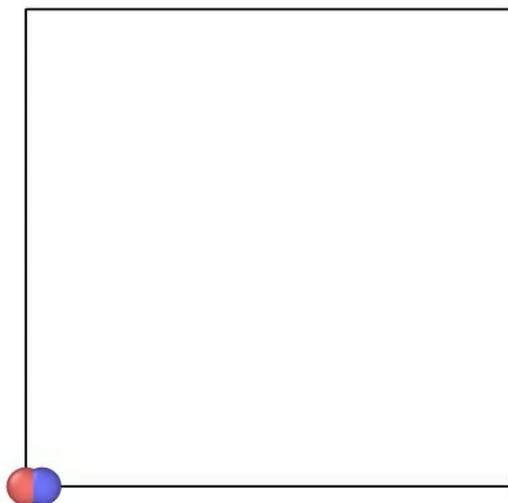
Glass to metal seals



Glass-ceramics ↑



The Training Data



What is a parameterization?

8



$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{trip} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdW} + E_{coulomb}$$

$$E_{bond} = -D_e \sigma BO_{ij}^\sigma * \exp[p_{bel} * (1 - BO_{ij}^\sigma)^{p_{bez}}]$$

$$E_{lp} = \frac{p_{lp2} * \Delta_i^{lp}}{1 + \exp[-75 * \Delta_i^{lp}]}$$

$$E_{over} = \frac{\sum_{j=1}^{nbond} p_{ovun1} * D_e^\sigma * BO_{ij} * \Delta_i^{lpcor}}{\Delta_i^{lpcor} + val_i} * \Delta_i^{lpcor} * \left[\frac{1}{1 + \exp(p_{ovun2} * \Delta_i^{lpcor})} \right]$$

$$E_{under} = -p_{under} * \frac{1 - \exp[p_{ovun6} * \Delta_i^{lpcor}]}{1 + \exp[-p_{ovun2} * \Delta_i^{lpcor}]} * f_6(BO_{ij}, \Delta_j)$$

$$E_{val} = f_7(BO_{ij}) * f_7(BO_{jk}) * f_8(\Delta_j) * \{p_{val1} - p_{val} * \exp[(\Theta_0 - \Theta_{ijk})^2]\}$$

$$E_{pen} = p_{pen1} * f_9(\Delta_j) * \exp[-p_{pen2} * (BO_{ij} - 2)^2] * \exp[-p_{pen2} * (BO_{ij} - 2)^2]$$

$$E_{coa} = p_{coa1} * \frac{1}{1 + \exp(p_{coa2} * \Delta_i^{val})} * \exp[-p_{coa3} * (-BO_{ij} - \sum_{n=1}^{neighbours(i)} BO_{in})^2] * \exp[-p_{coa3} * (-BO_{jk} + \sum_{n=1}^{neighbours(i)} BO_{kn})^2] * \exp[-p_{coa4} * (BO_{ij} - 1.5)^2] * \exp[-p_{coa4} * (BO_{jk} - 1.5)^2]$$

$$E_{c2} = \begin{cases} k_{c2} * (BO_{ij} - \Delta_i - 0.04 * \Delta_i^4 - 3)^2 & \text{if } BO_{ij} - \Delta_i - 0.04 * \Delta_i^4 > 0 \\ 0 & \text{otherwise} \end{cases}$$

$$E_{trip} = p_{trip1} * \exp[-p_{trip2} * (BO_{ij} - 2.5)^2] * \frac{\exp[-p_{trip4} * (\sum_{k=1}^{neighbours(i)} BO_{ik} - BO_{ij})] + \exp[-p_{trip4} * (\sum_{k=1}^{neighbours(i)} BO_{jk} - BO_{ij})]}{1 + 25 * \exp[p_{trip3} * (\Delta_i + \Delta_j)]}$$

$$E_{tors} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) * \sin \Theta_{ijk} * \sin \Theta_{jkl} * \left[\frac{1}{2} V_1 * (1 + \cos \omega_{ijkl}) + \frac{1}{2} V_2 * \exp\{p_{tor1}(BO_{jk}^\pi - 1) + f_{11}(\Delta_j, \Delta_k)^2\} * (1 - \cos 2\omega_{ijkl}) + \frac{1}{2} V_3 * (1 + \cos \omega_{ijkl}) \right]$$

$$E_{conj} = f_{12}(BO_{ij}, BO_{jk}, BO_{kl}) * p_{cot1} * [1 + (\cos \omega_{ijkl} - 1) * \sin \Theta_{ijk} * \sin \Theta_{jkl}]$$

$$E_{H-bond} = p_{hb1} * [1 - \exp(p_{hb2} * BO_{XH})] * \exp \left[p_{hb3} * \left(\frac{r_{hb}^0}{r_{HZ}} + \frac{r_{HZ}}{r_{hb}^0} - 2 \right) \right] * \sin^8 \left(\frac{\Theta_{XHZ}}{2} \right)$$

$$E_{vdW} = Tap * D_{ij} * \left\{ \exp \left[\alpha_{ij} * \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 * \exp \left[\frac{1}{2} * \alpha_{ij} * \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\}$$

$$E_{coulomb} = Tap * C * \frac{q_i * q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$$

- **Parameterization** is a way of expressing a model as a function of some number of independent parameters
- Currently only looking at parameters related to atoms and bonds
- 60+ parameters per element, not including the cross interactions
- It's complicated!
- The parameters incorporate physics

Optimization Scheme



Training data set
Considered to be the "truth"
 Originating from DFT

Originating from experiment

Optimization Engine

- Sample parameter space
- Identify best representation of training data

Python scripting

- File management
- Creation of force field based upon parameters provided by OE
- Extract QoI from MD result
- Perform comparison to training data

Simulation

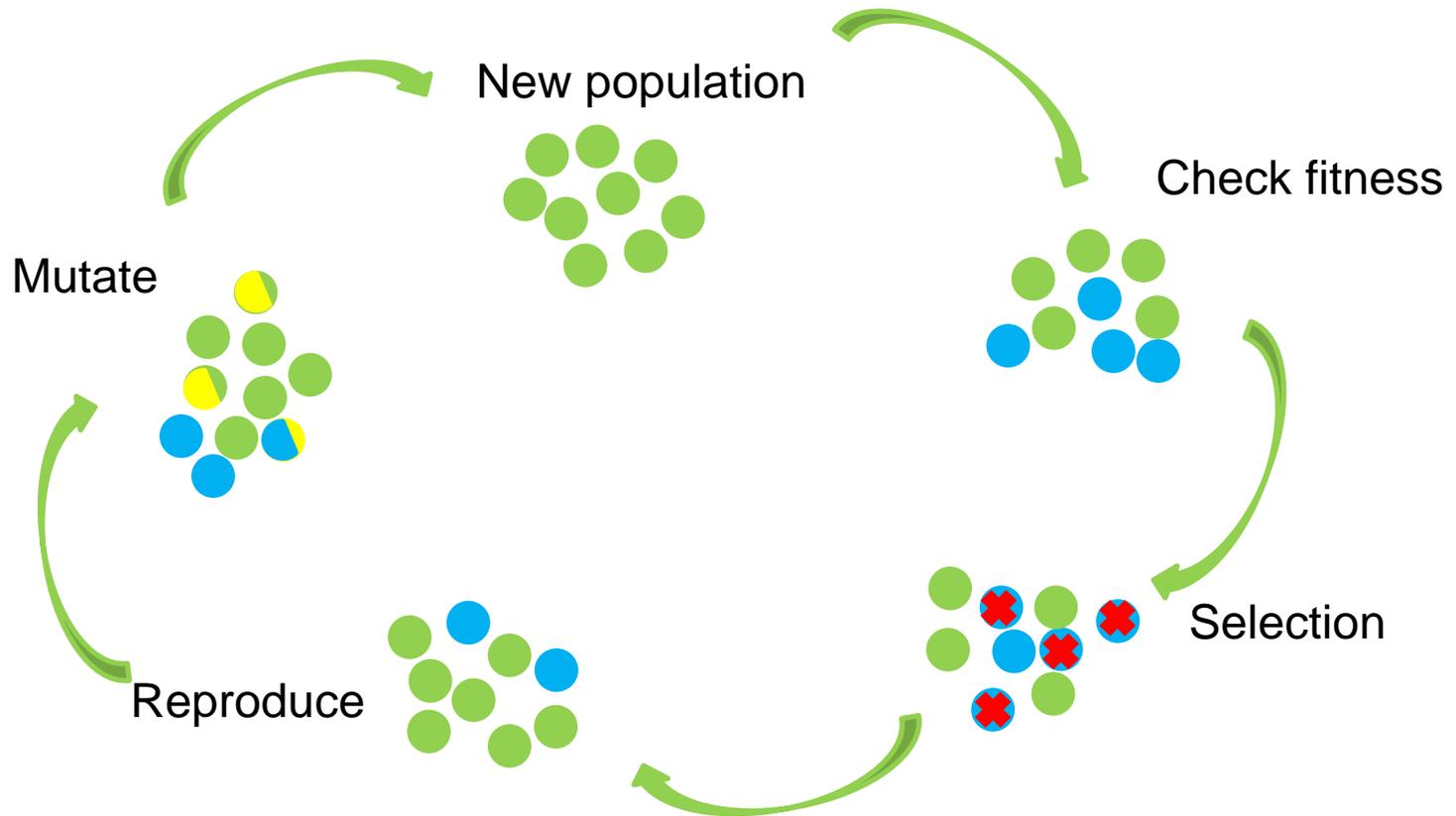
- Performs LAMMPS
- unique force field parameterization
- Variety of modules: NEB, elastic properties, etc.
- Designed to obtain comparison to training data

- Utilize Dakota and a genetic algorithm as an optimization engine to run multiple, small MD simulations to extract QoI
- Strong connection between training data, simulation module, and scripting

What is a Genetic Algorithm?



- **A genetic algorithm or GA** is an optimization technique that is inspired by the process of natural selection



Why so Complicated?

11



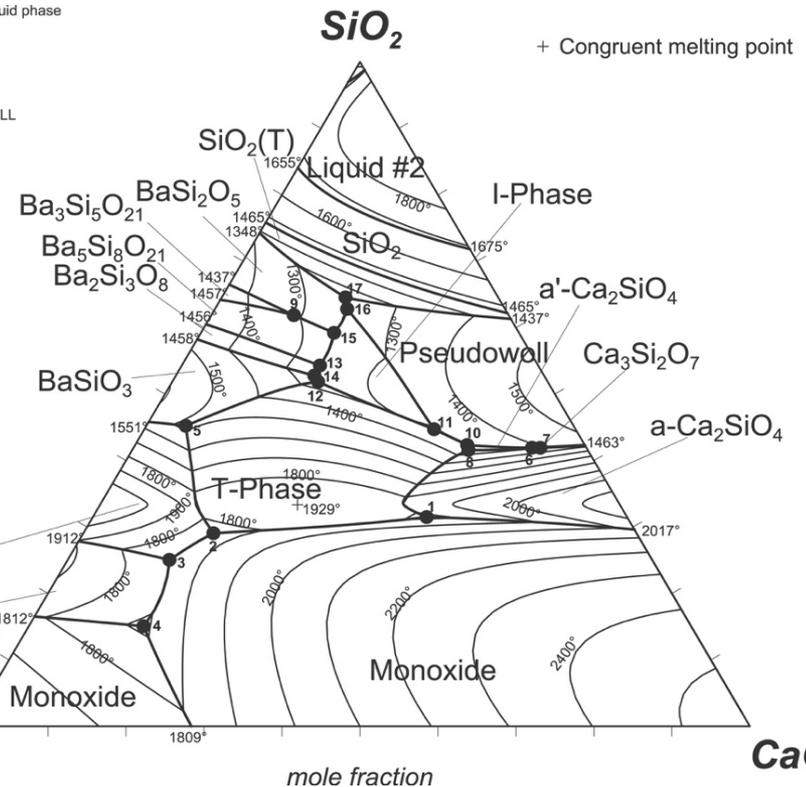
- You might say, “This sounds complicated. There are easier ways. Why would you want to do it this way?”
- Provides the opportunity to fit for a range of training data, not just DFT. **ANY** quantity of interest that we can extract from an MD simulation, we can train our parameterization for it

- Pitfall: method is agnostic to analytical forms of potential energy interactions. We must be cognizant of the physical meaning of each parameter

Four-Phase Intersection Points with liquid phase

- 1: Monoxide / a-Ca₂SiO₄ / T
- 2: Monoxide / a'-Ca₂SiO₄ / T
- 3: Ba₃Si₅O₂₁ / Monoxide / a'-Ca₂SiO₄
- 4: Ba₃Si₅O₂₁ / Monoxide#1 / Monoxide#2
- 5: a'-Ca₂SiO₄ / BaSiO₃ / T
- 6: a'-Ca₂SiO₄ / a-Ca₂SiO₄ / Ca₃Si₂O₇
- 7: a'-Ca₂SiO₄ / Ca₃Si₂O₇ / PSEUDOWALL
- 8: a'-Ca₂SiO₄ / a-Ca₂SiO₄ / T
- 9: Ba₃Si₅O₂₁ / Ba₂Si₃O₈ / BaSiO₃
- 10: a'-Ca₂SiO₄ / PSEUDOWALL / T
- 11: I-phase / PSEUDOWALL / T
- 12: BaSiO₃ / I-phase / T
- 13: Ba₃Si₅O₂₁ / Ba₂Si₃O₈ / I-phase
- 14: Ba₃Si₅O₂₁ / BaSiO₃ / I-phase
- 15: Ba₃Si₅O₂₁ / BaSiO₃ / I-phase
- 16: BaSiO₃ / I-phase / PSEUDOWALL
- 17: BaSiO₃ / PSEUDOWALL / SiO₂

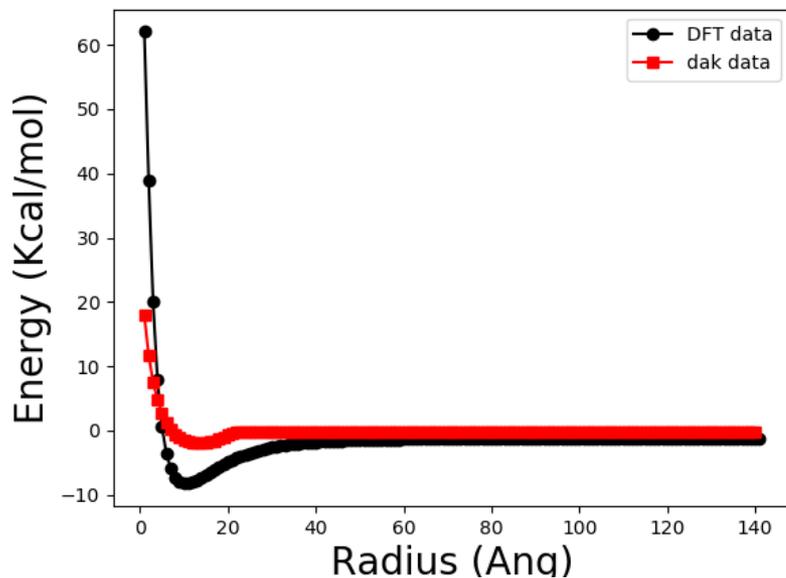
	X(A)	X(B)	X(C)	°C
1:	0.31479	0.25697	0.42824	1767.86
2:	0.29056	0.54255	0.16689	1734.48
3:	0.25040	0.61901	0.13059	1701.78
4:	0.15060	0.70207	0.14733	1678.50
5:	0.45216	0.49732	0.05052	1473.47
6:	0.41909	0.05903	0.52188	1396.55
7:	0.41929	0.06970	0.51101	1383.01
8:	0.41570	0.15298	0.43132	1326.44
9:	0.61864	0.27542	0.10594	1311.86
10:	0.42333	0.15071	0.42596	1294.61
11:	0.44703	0.18138	0.37159	1294.51
12:	0.51852	0.29434	0.18714	1257.31
13:	0.54259	0.27981	0.17729	1254.97
14:	0.52786	0.29447	0.17767	1252.76
15:	0.59220	0.23705	0.17075	1240.22
16:	0.62804	0.20240	0.16956	1222.01
17:	0.64535	0.19578	0.15886	1215.63



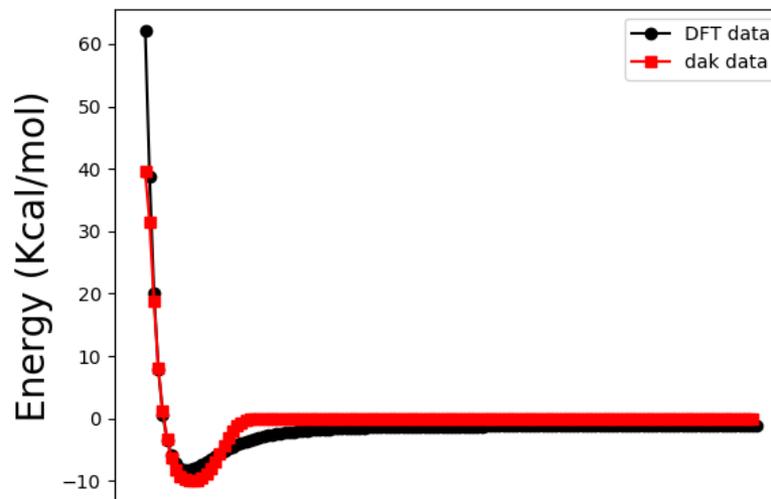
Results



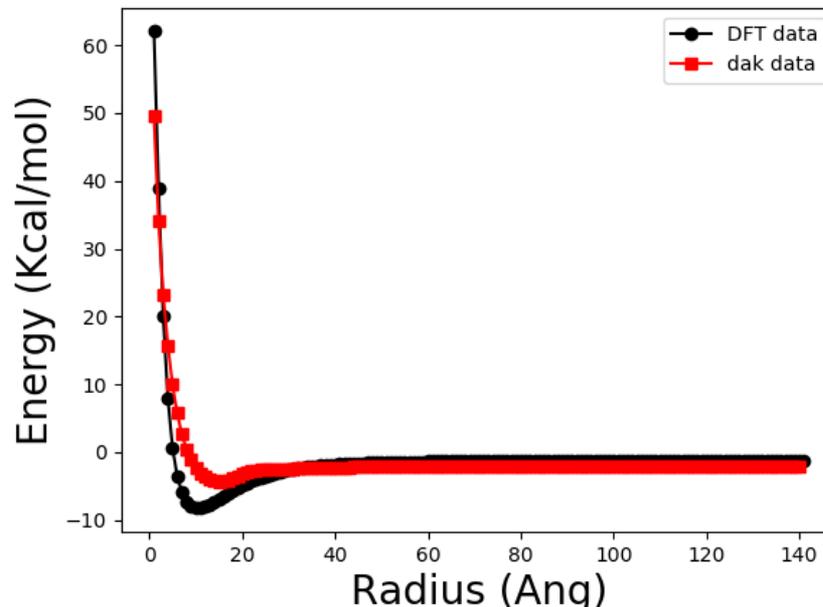
rms = 5.094



rms = 2.486

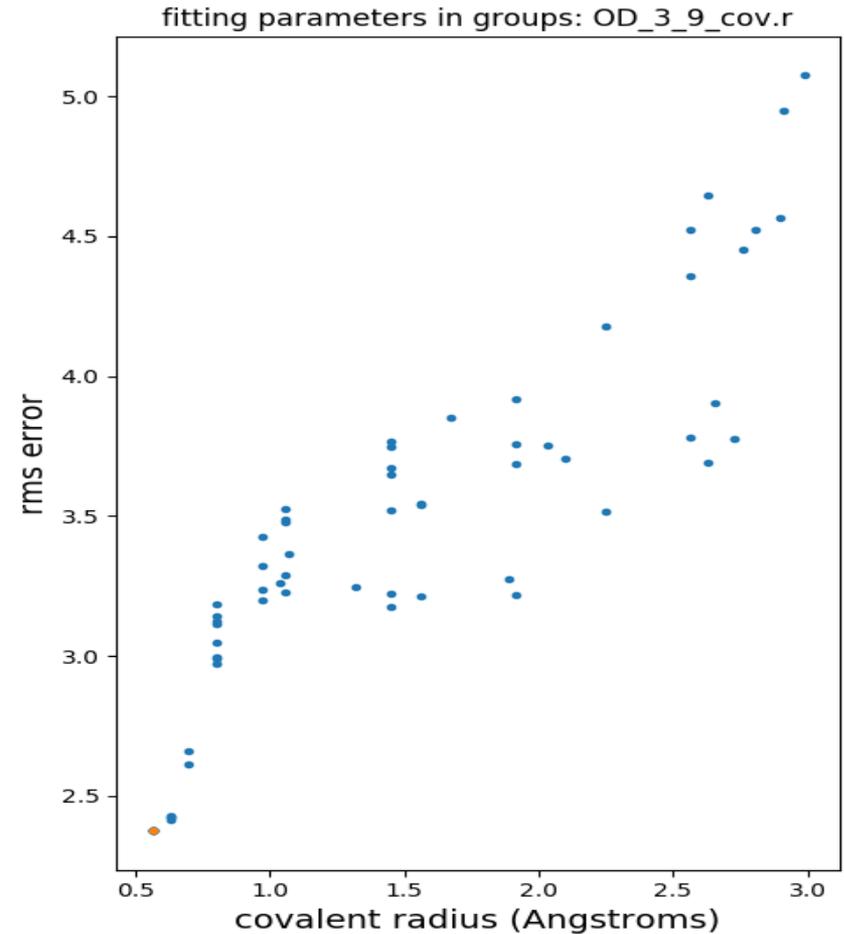
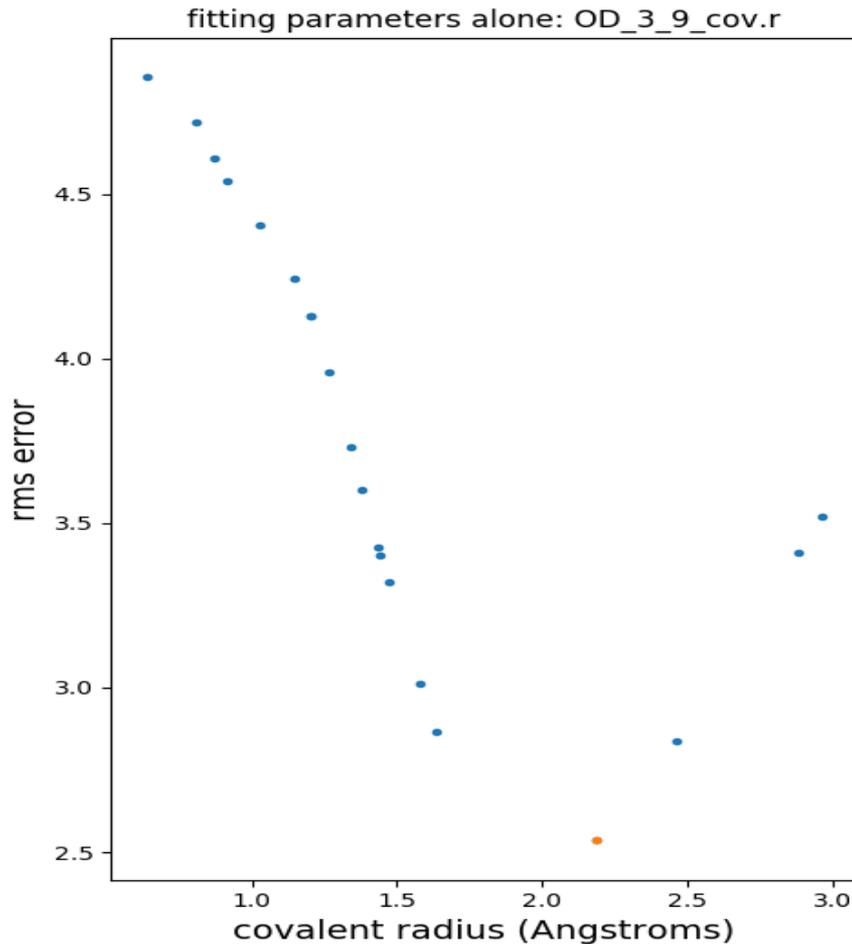


rms = 2.4053



- Not fitting the well
- Fitting parameters one by one
- Looking into how order and parameter fit pairings effect our results

Validation of the Approach



- Wrote a postprocessor that builds histograms of parameters swept by the GA
- GA isn't getting stuck in local minima
- Parameter fitness curves vary wildly depending on order of fitted parameters

Planned Experimental Validation



- Challenge: find a QoI that would varies enough with concentration of Ba
- Possibilities: Constant of thermal expansion (CTE), Density as a function of concentration
- Experiment: Either physically or computationally, steadily increase temperature and measure volume at regular intervals

TABLE 6.46
Thermal Expansion Coefficients of
Rb₂O–BaO–SiO₂ Glasses^a

Composition (mole %)			$\alpha \times 10^7$ ($^{\circ}\text{C}^{-1}$) 0–300 $^{\circ}\text{C}$
Rb ₂ O	BaO	SiO ₂	
13.1	5.3	81.6	139
19.3	5.8	74.9	110
9.4	17.3	73.3	100
21.2	12.9	65.9	135
15.6	19.2	65.2	123
10.3	25.3	64.4	116

^a Data from Simpson (1959, 1961).

Accomplishments this Summer

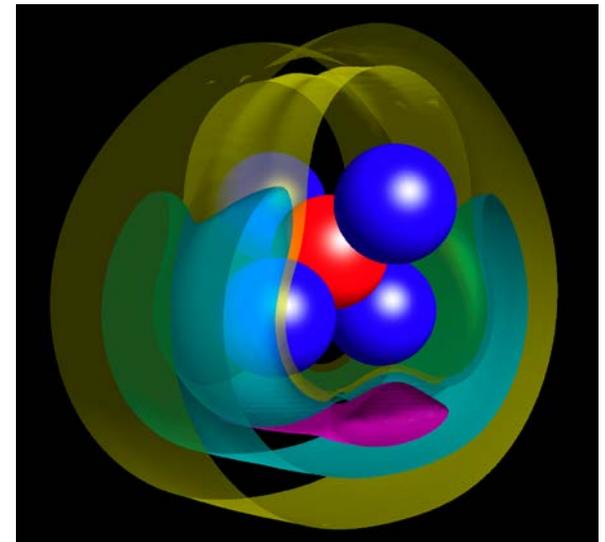
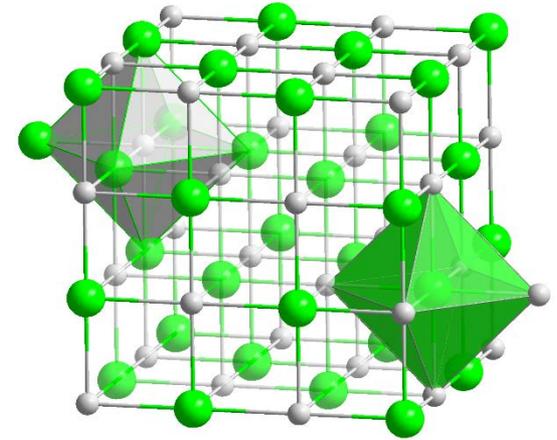


- Familiarized ourselves with Dakota and Lammps documentation
- Researched functional form of ReaxFF reactive Potentials
- Initialized and de-bugged python based Dakota-Lammps interface
- Began fitting Atom, Bond, and Off-diagonal parameter terms
- Wrote a script that will strip DFT/VASP data for fitting simulations
- Wrote post-processing scripts for validation and informing future fits

Future Directions



- Angle / torsions / condensed phase
- How complicated is the next data set? 82,000 DFT simulations!!! No one does that; it was a heroic simulation effort that Normand achieved while on vacation.
- Experimental validation of our parameterization: a BaSiO glass. CTE (coefficient of thermal expansion)
- Quantify the uncertainty in an MD result for a given parameterization
- Goal for time remaining: Fit crystal BaO and compare large radii behavior
- Stretch goal: add Barium to the ReaxFF reactive potential for SiO with confidence



Acknowledgements

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- Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Thank you for listening
Comments? Questions? Concerns?