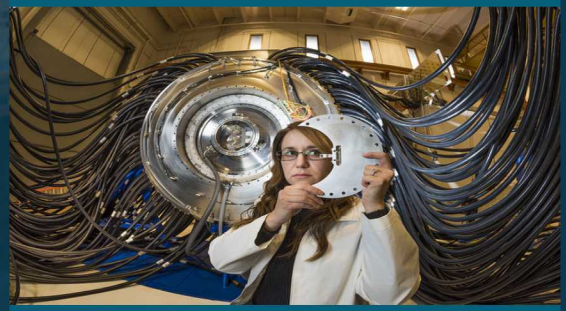
SAND2019-5444PE

Next Generation EOS and Transport Modeling



PRESENTED BY

Luke Shulenburger, 1641

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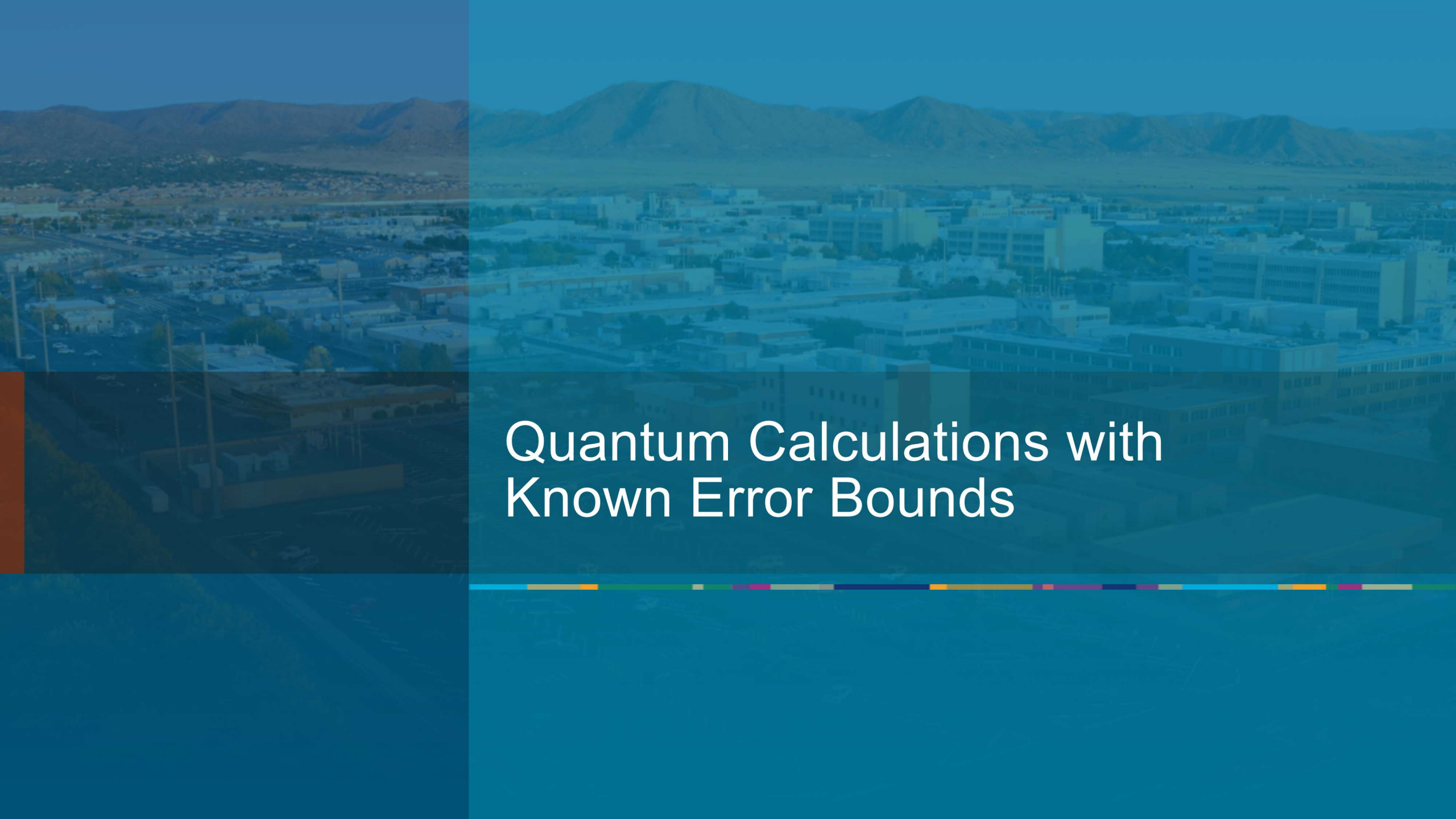


Quantum Calculations with Known Error Bounds

Goal: EOS Modeling

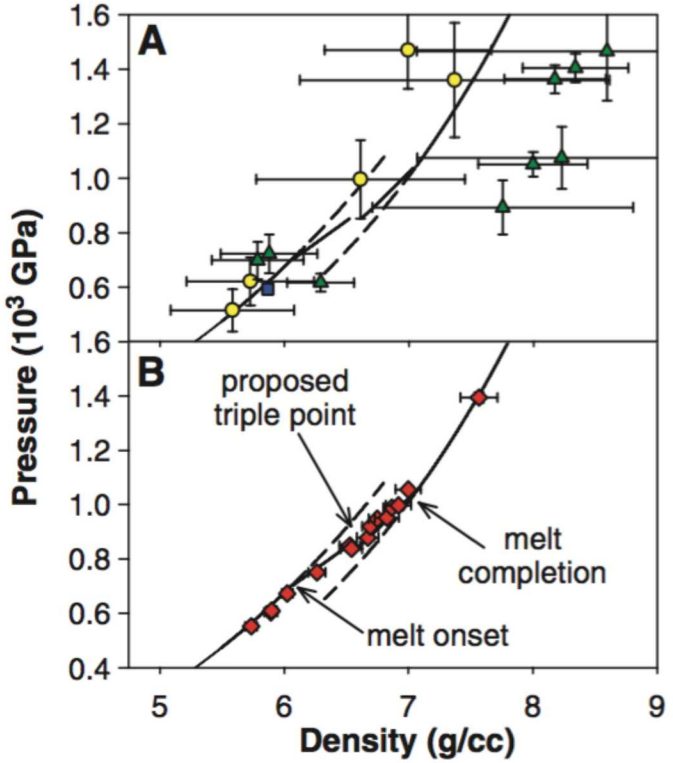
Develop a capability to predict the thermodynamic properties of any material under any conditions with known accuracy in a manner suitable to inform UQ capable EOS models

Team:
Luke Shulenburger
Andrew Baczewski
Chandler Bennett
John Carpenter
Raymond Clay
Kyle Cochrane
Mike Desjarlais
Thomas Mattsson
Cody Melton
Joshua Townsend

Density Functional Theory is a very successful technique

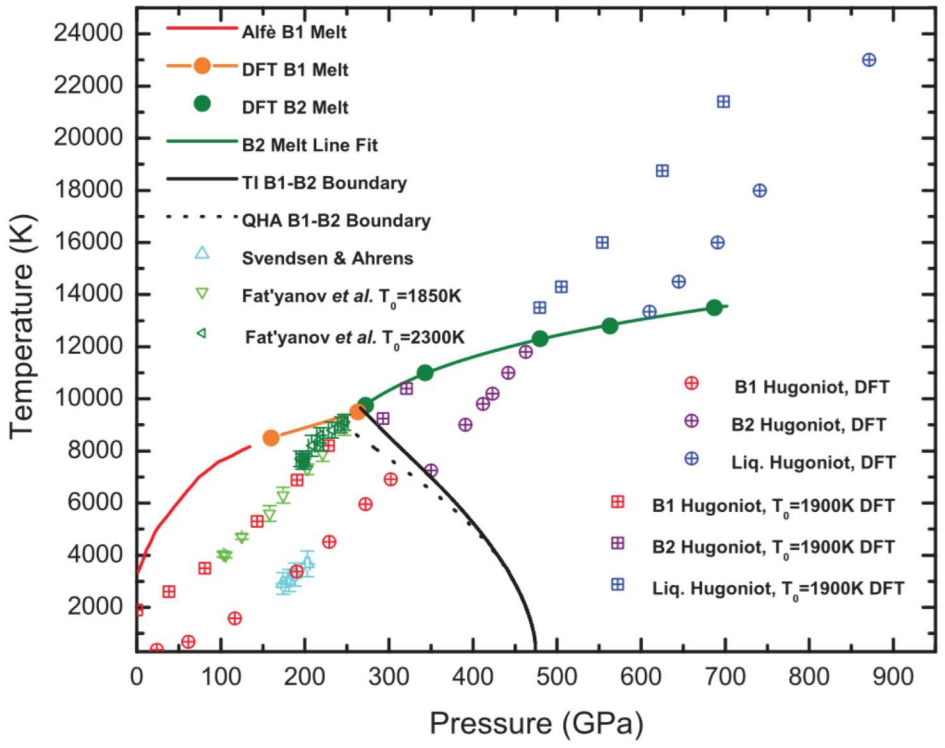
Careful DFT / QMD calculations can complement experiment by providing additional information

Shock melting of diamond



Knudson, Desjarlais and Dolan,
Science **322**, 1823 (2008)

Phase diagram of MgO

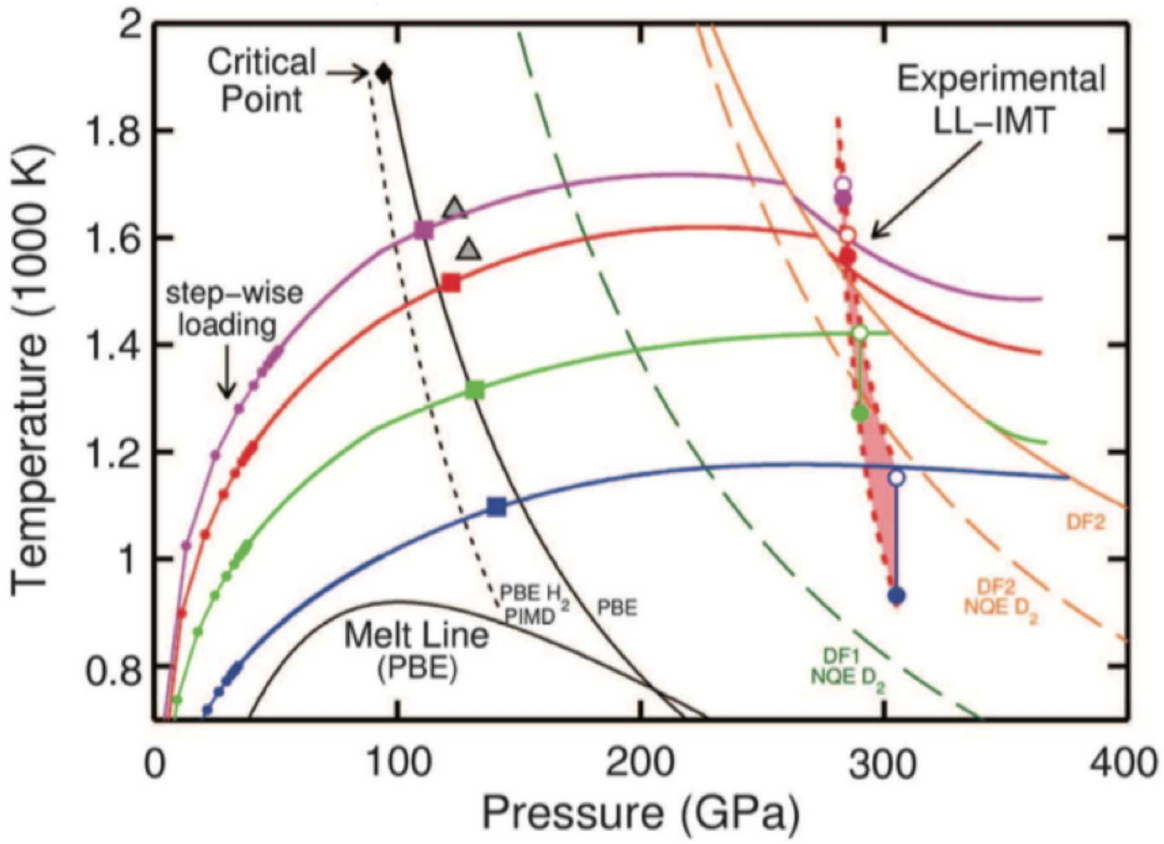


Root, LNS, Lemke, Dolan, Mattsson and Desjarlais,
PRL **115**, 198501 (2015)

DFT approximations are not always small

- DFT predictions of pressure vary widely between approximations
  - Impossible to determine a priori which one is correct
- Approximations are notoriously difficult to improve
- Particularly troubling given complexity of experimental analysis
- Can we do better?

H_2 / D_2 liquid-liquid phase transition



Knudson, Desjarlais, Becker, Lemke, Cochrane, Savage, Bliss, Mattsson and Redmer, Science **348**, 1455 (2015)

Quantum Monte Carlo Calculations offer another possibility

- Calculate properties from the exact Hamiltonian using a stochastic process
- Use guiding (trial) wavefunction, Ψ, for importance sampling and for fixed node approximation
- Variational principle lets you know when your approximation is improving
- Ψ is not the exact many-body wavefunction
  - Energy only depends on Ψ=0 manifold

A bird's eye view

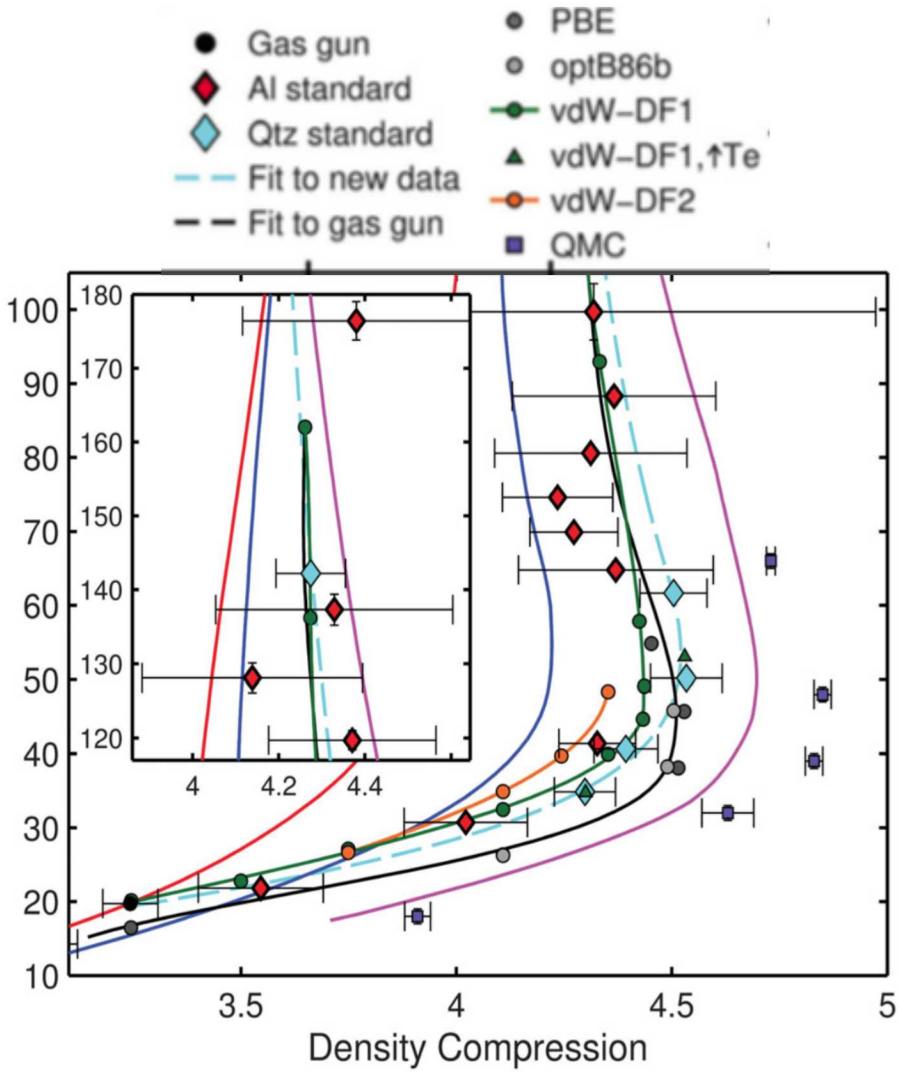
$|\Psi_T\rangle$ $\xrightarrow{\exp(-\beta\hat{H})}$ $|\Psi_{FN}\rangle$

$\xrightarrow{\exp(-\beta\hat{H})}$

$\xrightarrow{\exp(-\beta\hat{H})}$

Quantum Monte Carlo Calculations in Practice – D_2 Hugoniot

- Coupled electron-ion calculation of Hugoniot
- Significantly more compressible than experiment
- This includes non-controversial gas gun experiments
- With DFT either there is good agreement or we switch functional to try to better match experiment
- With QMC we can try to improve the approximation directly

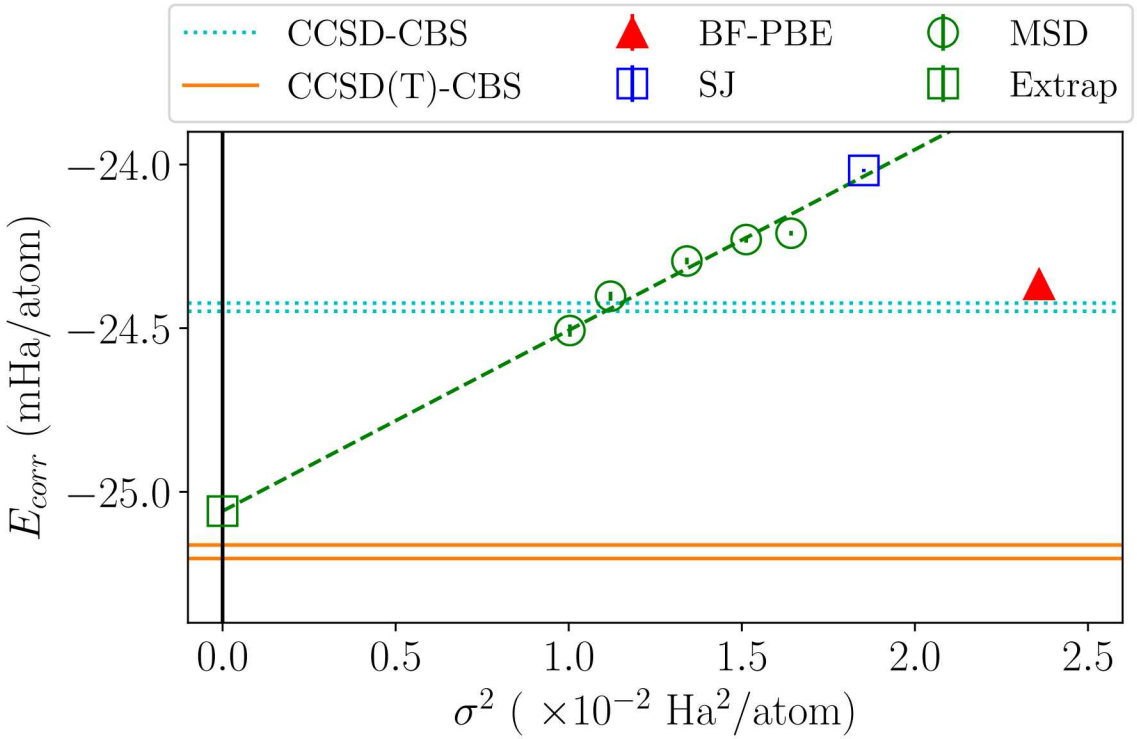


Knudson and Desjarlais, PRL **118**, 035501

Take the next step for the Hugoniot calculation

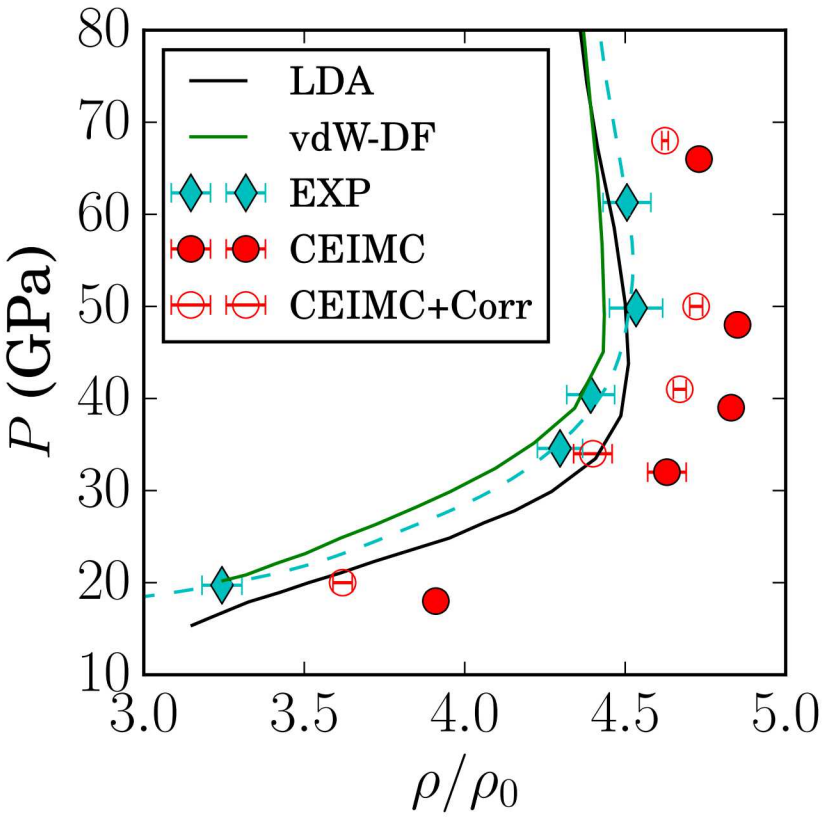
- Apply QMC with various trial wavefunctions to a representative snapshot of the compressed gas
- Carefully constructed classes of trial wavefunctions allow for extrapolation
- QMC gives a hint about how accurate the calculation is: Follow the noise!
  - As sampling variance goes down, answer improves
  - Can extrapolate to exact answer
- Currently only possible for small systems

Extrapolating zero error for warm dense deuterium



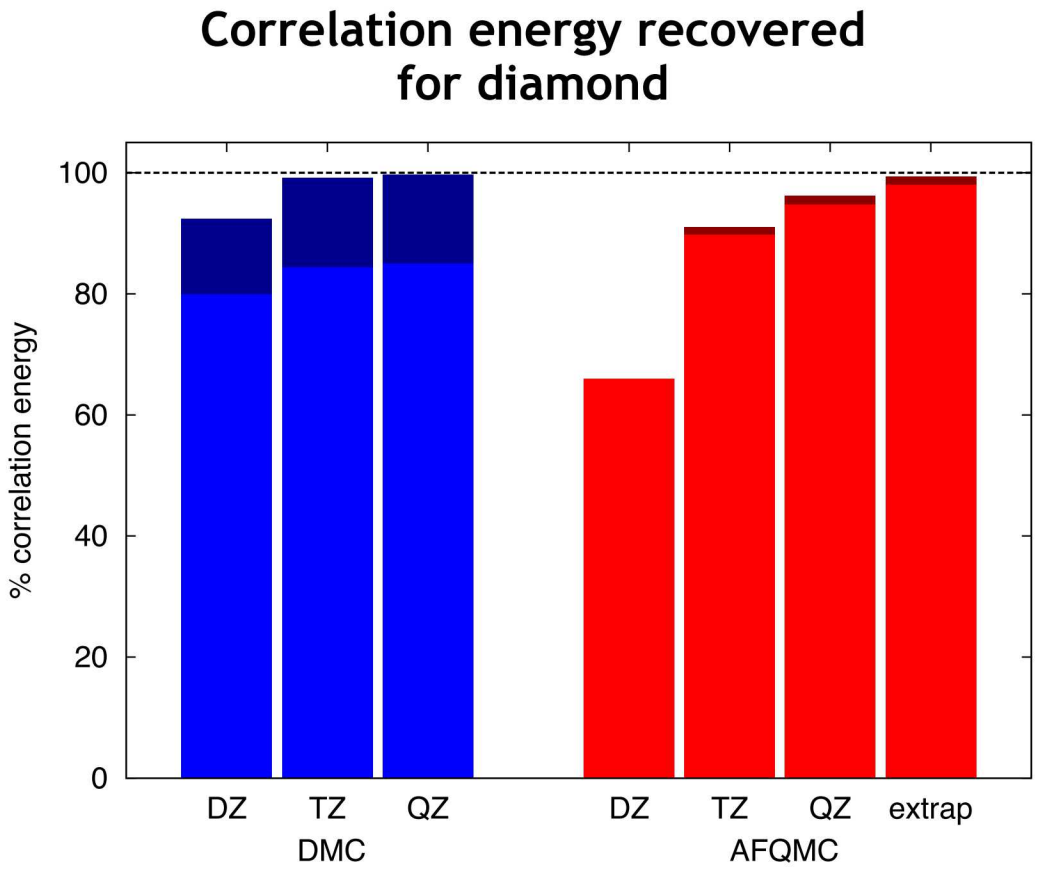
Leverage this to understand effects of errors on the calculated Hugoniot

- Derived a perturbative formula to see how errors in pressure and density affect the Hugoniot
- QMC had small but unbalanced errors
  - Initial dilute gas was almost exact
  - Shocked state had errors
- DFT errors were much larger, but largely cancelled
- Systematic improvement was much more important (and feasible) than eliminating errors entirely



Clay et al. in preparation

We are gaining experience on how to do this for more complicated materials



Light bars – Single Determinant Trial
Dark Bars – Multideterminant Improvement

Applying two different QMC methods with different classes of approximation

- Should agree if approximations are made arbitrarily small

Learn from comparison about strengths and weaknesses of the methods and how to improve them going forward

QMC can offer a new way of performing calculations

- Standard quantum calculation techniques are quite useful, but their accuracy is unknown
  - It is not always clear (even to experts) when calculations will show errors
- QMC has the advantage of performing calculations using the ab initio Hamiltonian
  - This does not always guarantee higher accuracy than DFT
- There are ways to control errors with QMC
  - For example, comparing variance to total energy
  - May allow one to say how accurate their calculations actually are!

Who cares about this work?

The method is general and is applicable to wide swaths of condensed matter physics and chemistry. There are also aspects of interest for high performance computing

Funding has been provides through four venues

- NNSA Science Campaign. (8 years)
- Office of Science: Basic Energy Sciences (5 years)
  - Center for the Predictive Simulation of Functional Materials. (3 years)
- Office of Science: ASCR (3 years)
  - Exascale Computing Project
- ASC / Physics and Engineering Models (6 years)

What does the future hold?

- Closer integration with EOS construction (near-term)
- Extension of methodology to handle relativistic effects (near-term)
- Further improvements in systematically improvable calculation techniques (mid-term)
- Performance portability and application on exascale computers (mid-term)
- Integration of approaches with quantum information processing techniques (long-term)

Modeling for non-LTE

Goals: Beyond Equilibrium

Develop a capability to predict the properties of material when driven out of local thermodynamic equilibrium

Team:
Luke Shulenburger
Andrew Baczewski
Attila Cangi
Mike Desjarlais
Stephanie Hansen

Many phenomena in HED physics can not be captured by equilibrium calculations

We typically employ the Born-Oppenheimer approximation that the electrons are in equilibrium with respect to the ions

A variety of problems in HED physics require this approximation

- Electron-ion equilibration in laser shocks
- Interpreting XRTS spectra
- Calculating energy transfer with fast ions

Beyond the Born-Oppenheimer Approximation – real time TDDFT

The most mature way to perform these calculations is using the time dependent extension of DFT – TDDFT

Consider n electrons that obey:

$$\left(\hat{T}+\hat{V}_{ee}+\hat{V}_{ext}(t)\right)\left|\Psi\right\rangle = i\frac{d}{dt}\left|\Psi\right\rangle$$

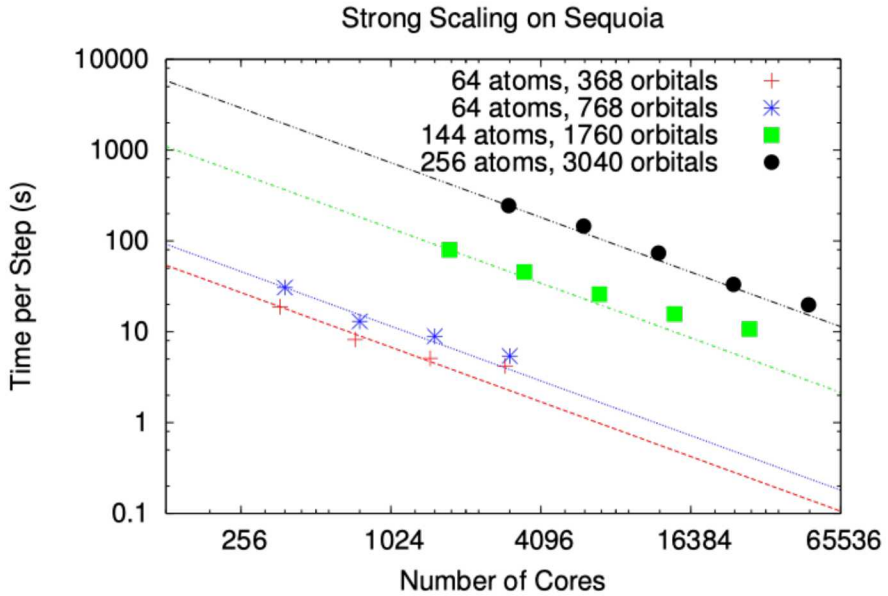
Runge-Gross Theorem and Kohn-Sham ansatz pave way for a time dependent DFT whereby single particle orbitals obey

$$i\frac{d}{dt}\left|\psi_m(t)\right\rangle = H_{KS}(t)[n(t)]\left|\psi_m(t)\right\rangle$$

Our Implementation

TDDFT + Ehrenfest, initial implementation in VASP*
Recently teamed up with Michele Pavanello's QE fork, eQE**

- Self-contained code
- Crank-Nicolson time integrator
  - CGS and GMRES solvers
  - Non-Hermitian corrections for charge conservation
- Correct Ehrenfest forces for PAW



Scaling for Xe (pathological)

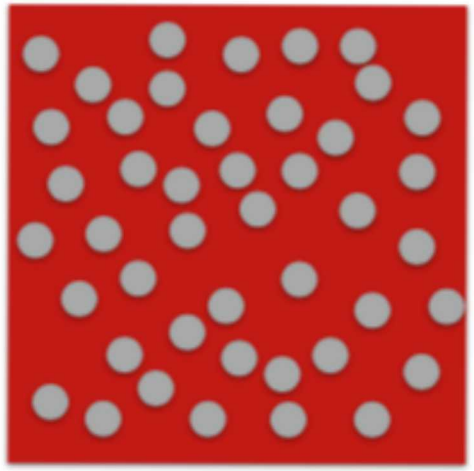
Shock Compression of a Fifth Period Element: Liquid Xenon to 840 GPa

Seth Root, Rudolph J. Magyar, John H. Carpenter, David L. Hanson, and Thomas R. Mattsson
Phys. Rev. Lett. **105**, 085501 – Published 17 August 2010

Mail: adbacze@sandia.gov

Ehrenfest-TDDFT

Start in a Mermin-Kohn-Sham equilibrium state

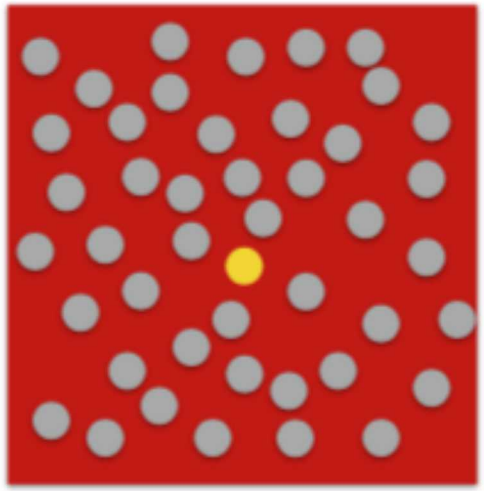


$$\rho_0(\mathbf{r}) = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}}(T_e)|\psi_{n,\mathbf{k}}(\mathbf{r})|^2$$

Ehrenfest-TDDFT

Add a projectile, re-compute MKS state

This is the initial condition for time-dependent Kohn-Sham system

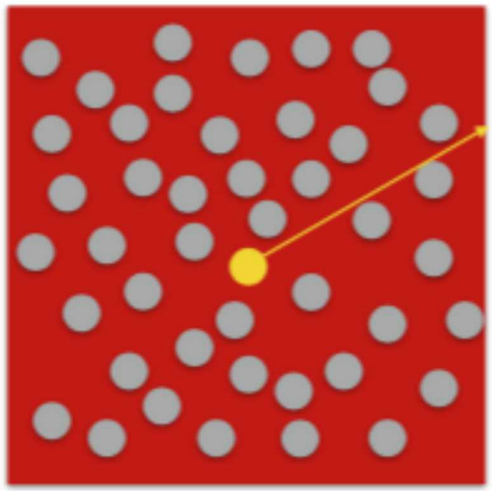


$$i\frac{\partial}{\partial t}\psi_{n,\mathbf{k}}(\mathbf{r},t) = \left[-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r},t) + v_{pert}(\mathbf{r},t)\right]\psi_{n,\mathbf{k}}(\mathbf{r},t)$$

Ehrenfest-TDDFT

Drag the projectile along at the velocity of interest

Compute the force retarding the projectile



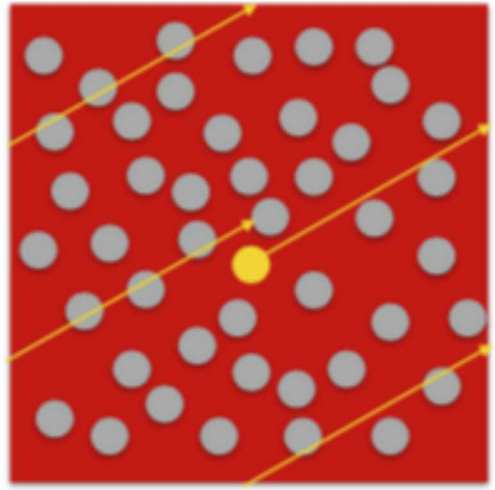
$$\frac{\delta \mathcal{A}}{\delta \mathbf{R}_i} = 0 \rightarrow M_i \frac{d^2\mathbf{R}_i}{dt^2} = \frac{\partial \mathcal{L}_q}{\partial \mathbf{R}_i} - \frac{d}{dt}\frac{\partial \mathcal{L}_q}{\partial \frac{d\mathbf{R}_i}{dt}}$$

$$\mathcal{L}_q = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}}(T_e)\langle\psi_{n,\mathbf{k}}|i\frac{d}{dt} - \frac{\nabla^2}{2}|\psi_{n,\mathbf{k}}\rangle - \mathcal{L}_{a,Hxc}\{\rho(\mathbf{r},t)\}$$

Ehrenfest-TDDFT

Collect as much data as you can

(100 Angstrom trajectories typically feasible)



Others have done this in condensed matter,

Artacho (Cambridge), Correa (LLNL), Kohanoff (Belfast), Schleife (UIUC), and many more

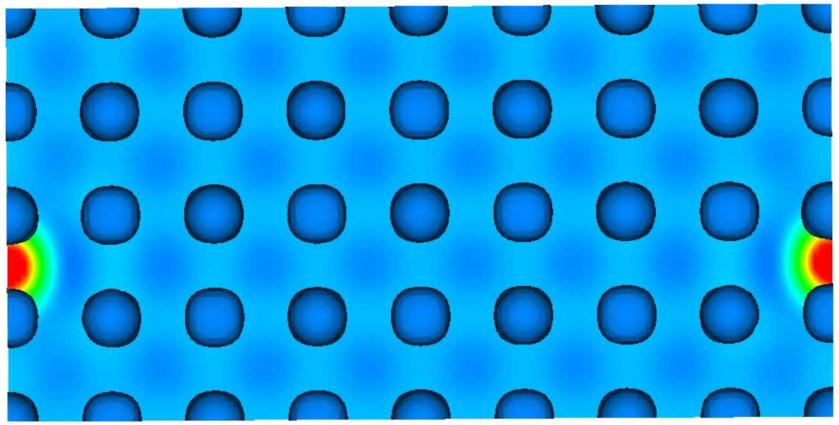
We are looking at higher energies and temperatures

Stopping a fast moving ion

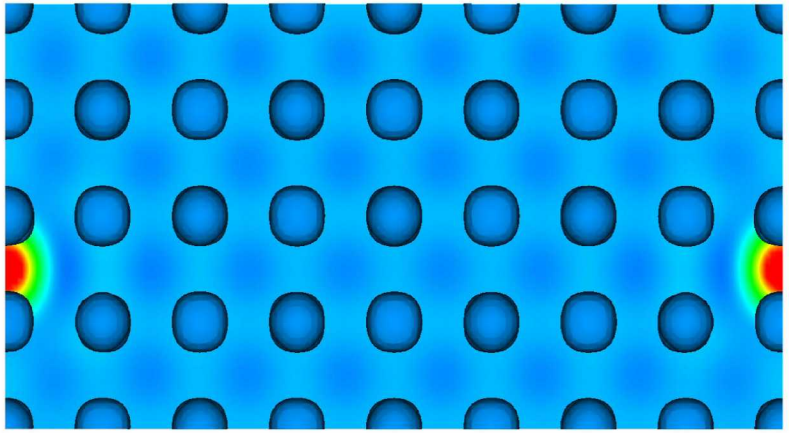
Understanding how fast moving ions are slowed is essential to understanding the energy balance in inertial confinement fusion

- Generation of plasmons necessary to capture the proper behavior

Born-Oppenheimer



TDDFT



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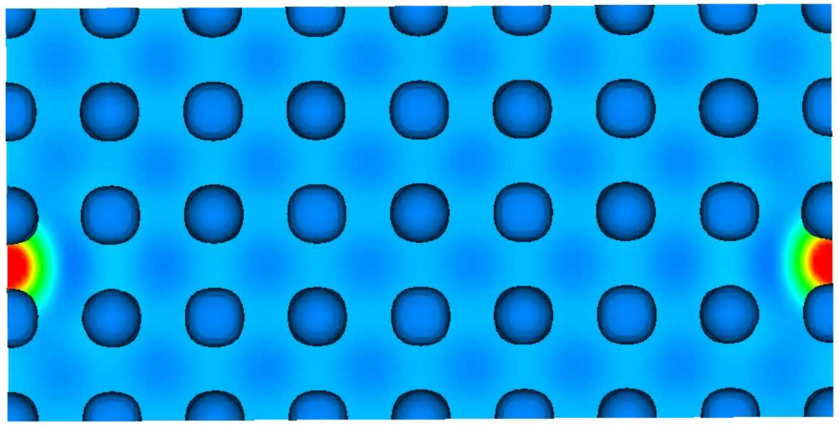

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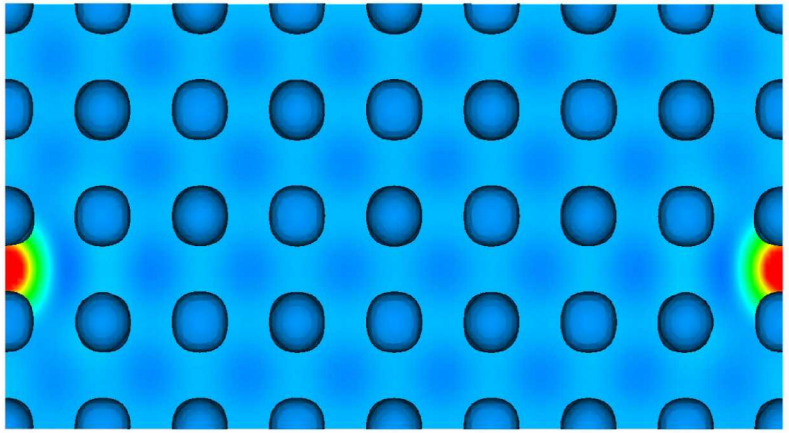

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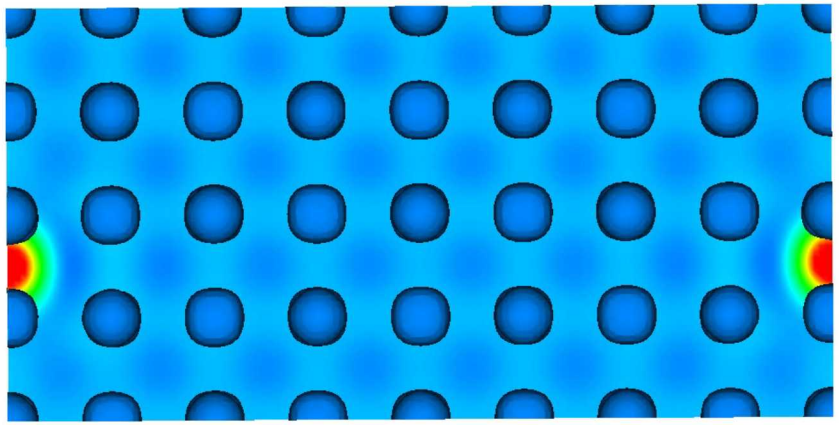

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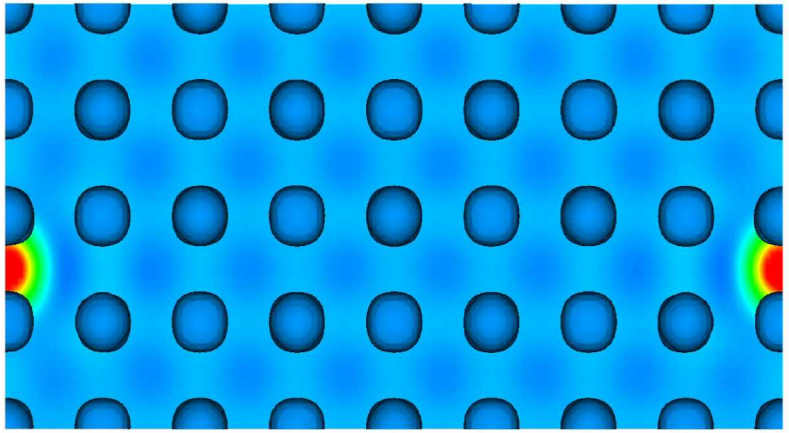
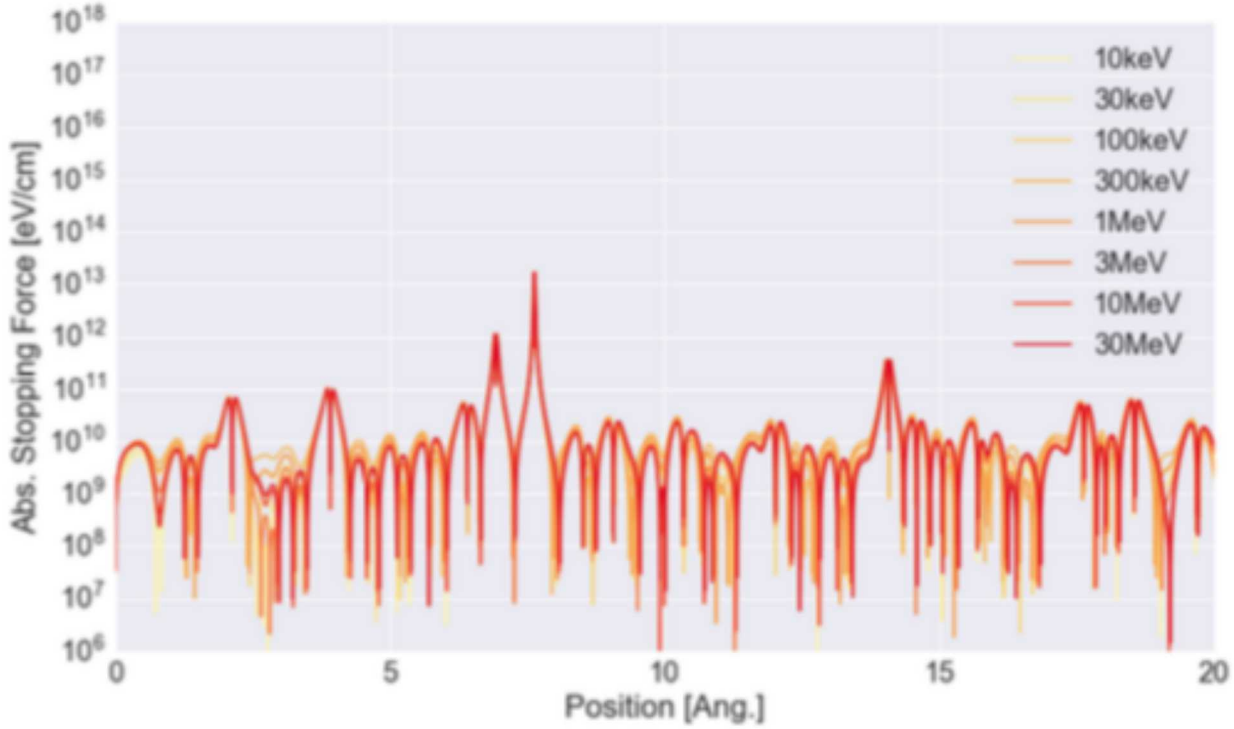
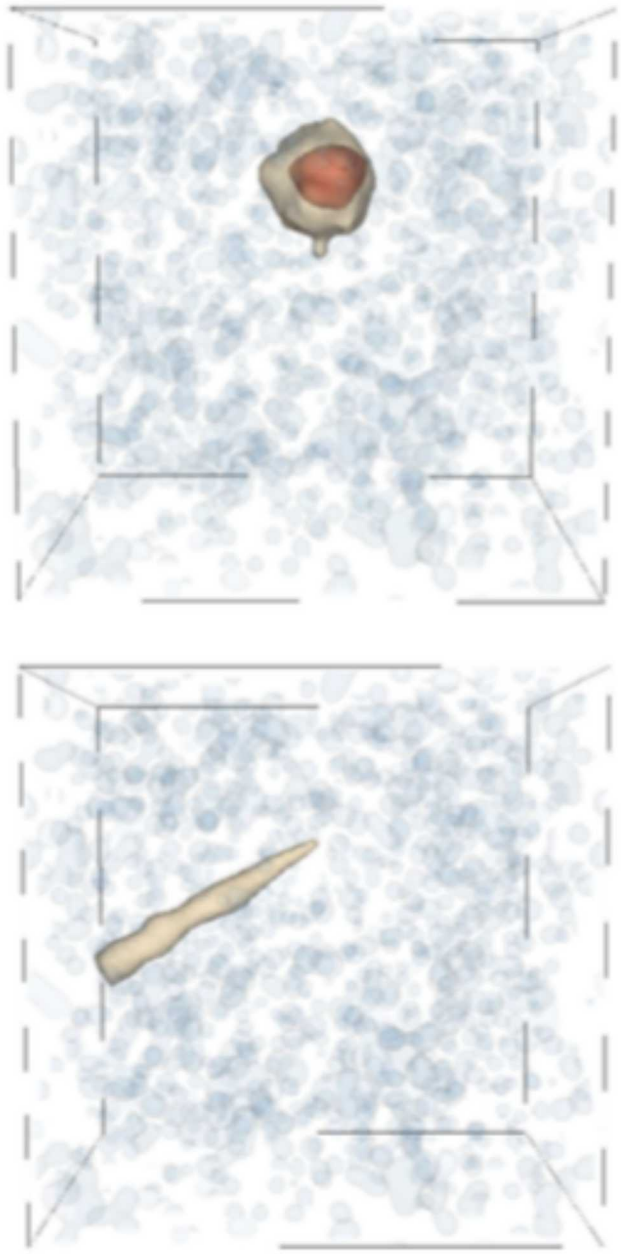


Warm Dense Deuterium

Stopping at 10 g/cc and 2 eV

(dead center of the DOE/Bonitz diagram)





Force on projectile vs. distance traversed

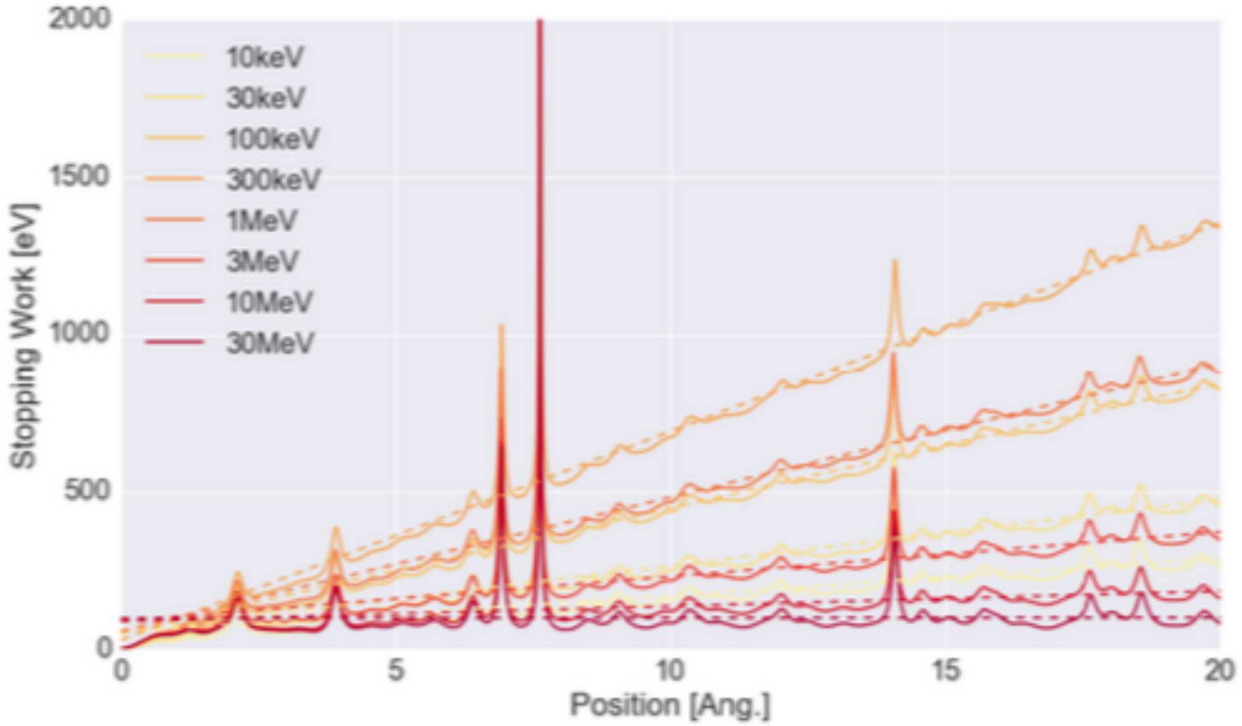
Hard to tell the difference between

300 keV (top) and 30 MeV (bottom)

Warm Dense Deuterium

Stopping at 10 g/cc and 2 eV

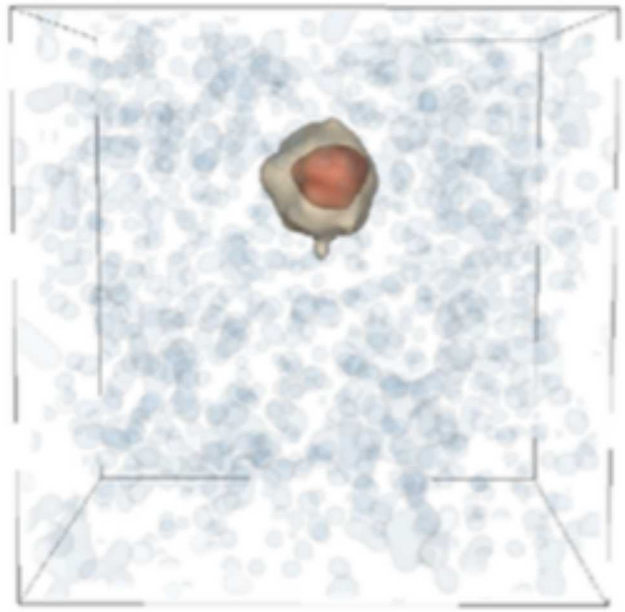
(dead center of the DOE/Bonitz diagram)

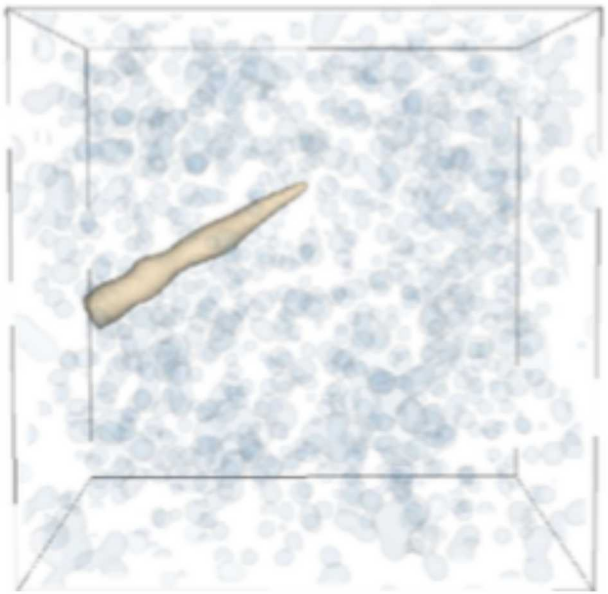


Work on projectile vs. distance traversed

Spikes = close passage to ions

Linear slope = stopping power





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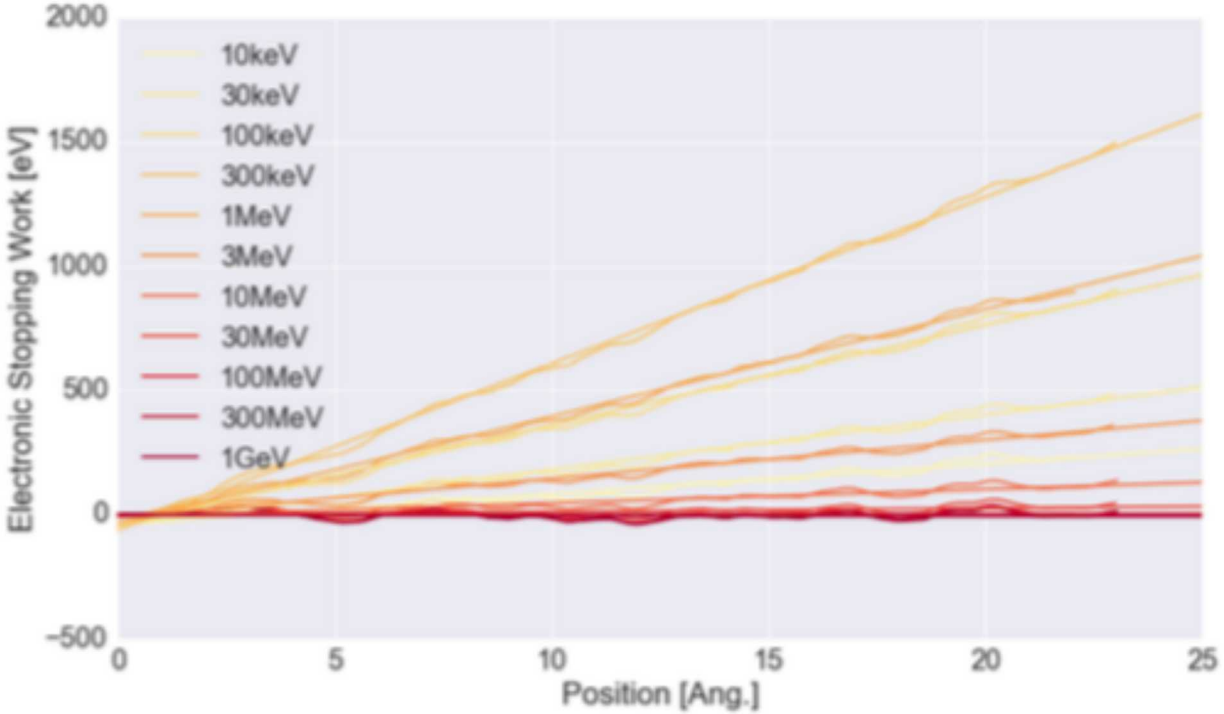
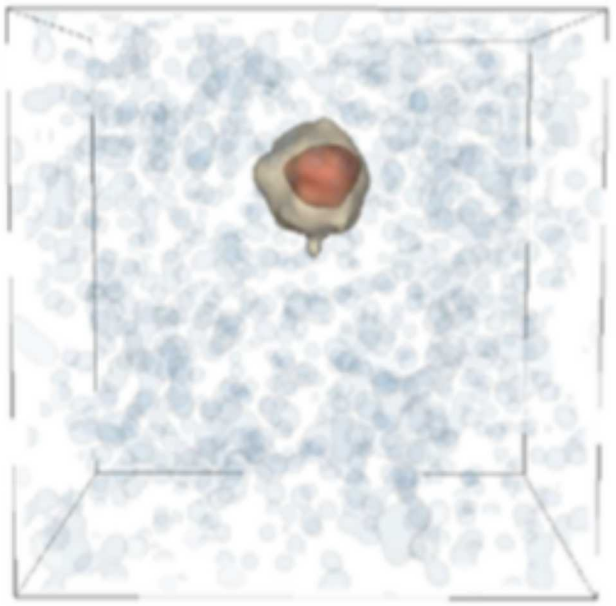
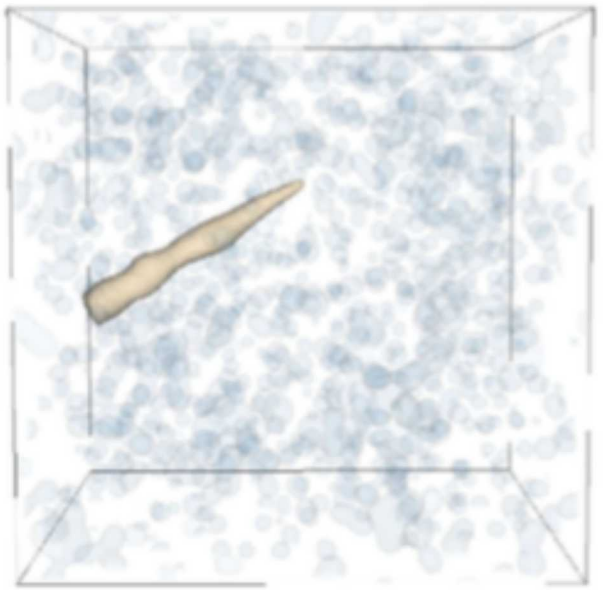






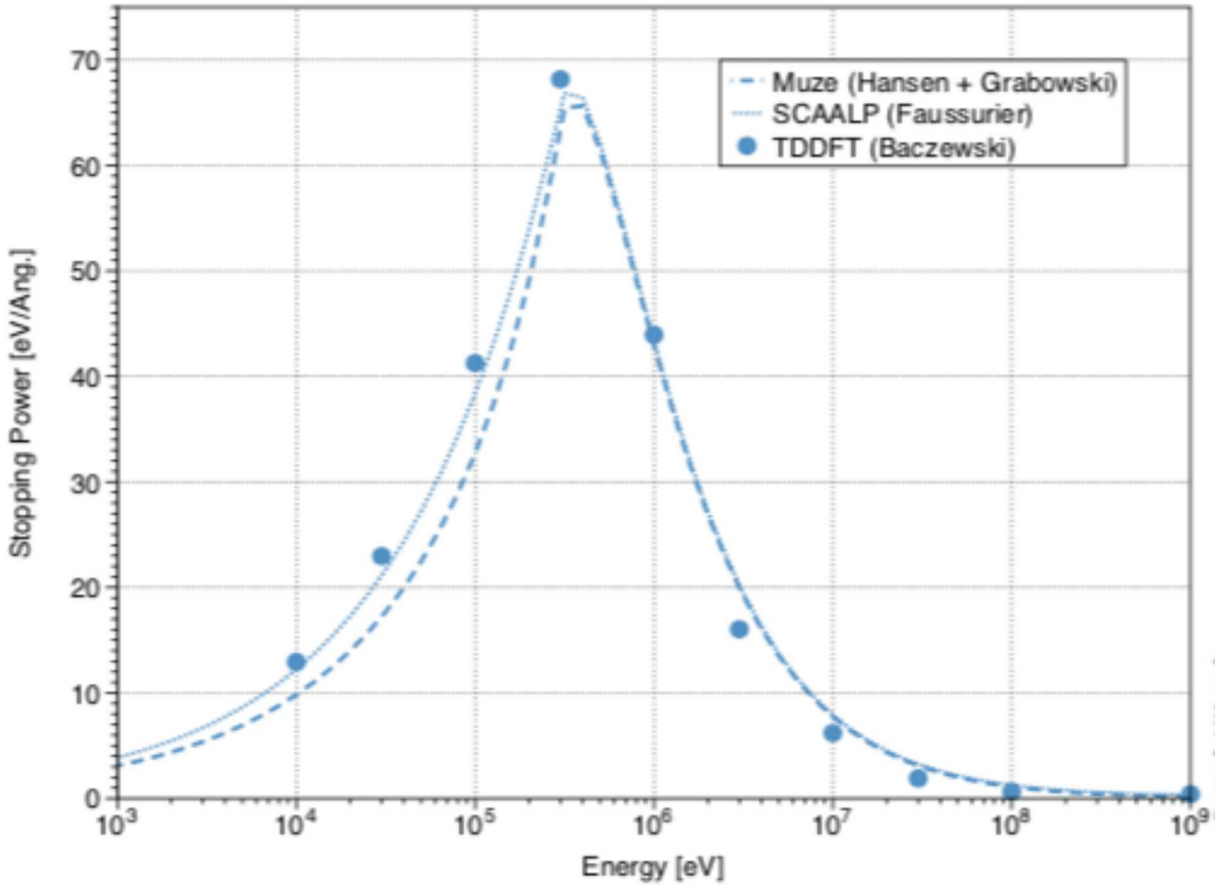
Work on projectile vs. distance traversed

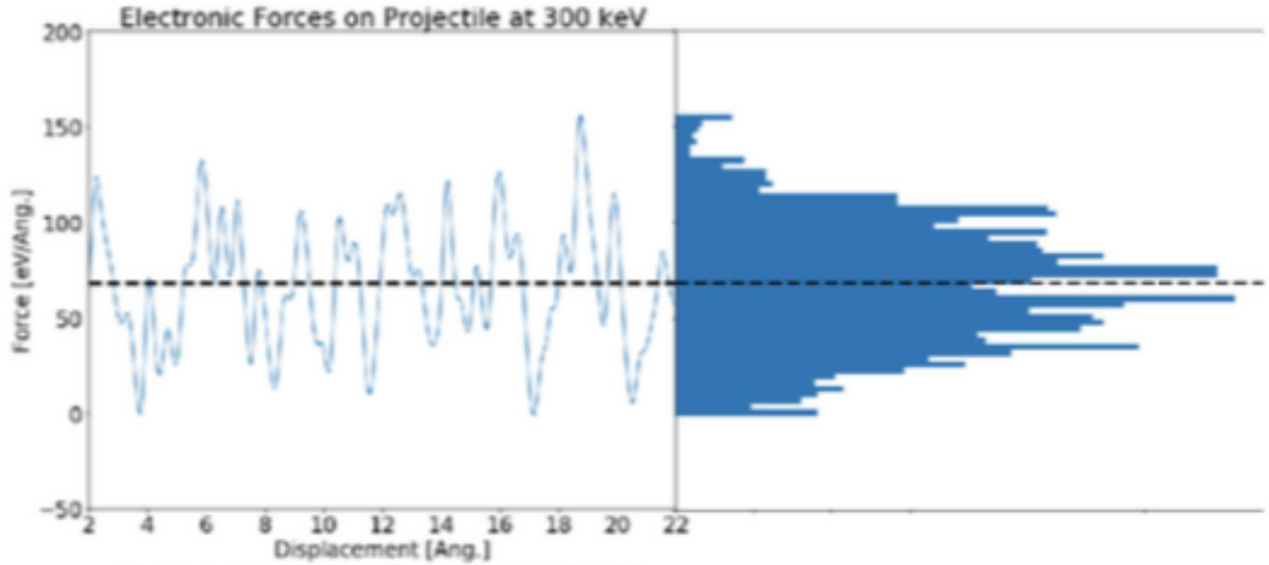
Subtracting out the ion-ion force gives us a purely electronic stopping power

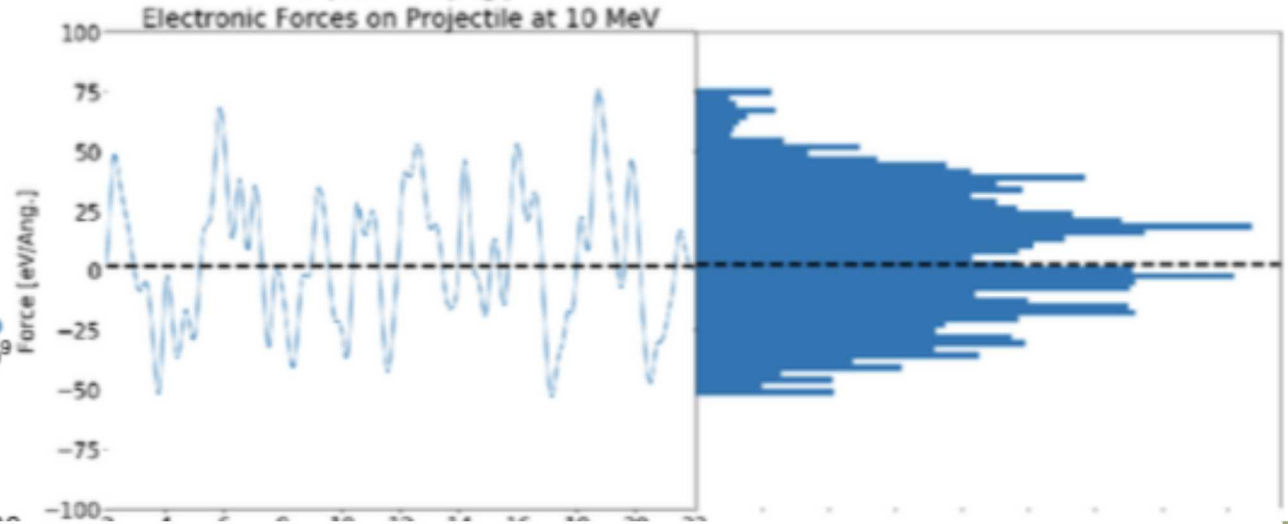
A Closer Look at the Forces

There might is more to extract than a single number

(note: still deuterium at 10 g/cc, 2 eV)







Outlook

- Funding for this work began under an LDRD and transitioned into the Science Campaign
- In future, we will develop this to extract DC conductivity under normal and high field conditions (near-term)
- Also aim to improve non-LTE treatment for extraction of electron-ion energy transfer (medium-term)