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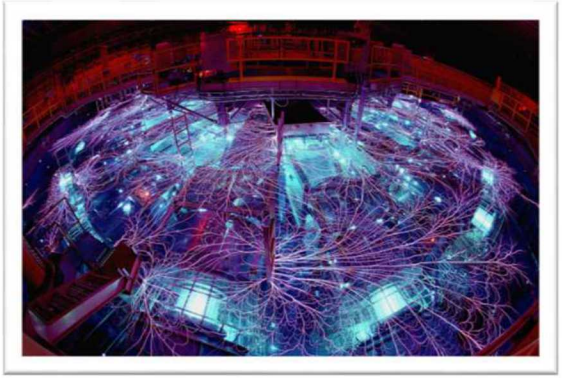
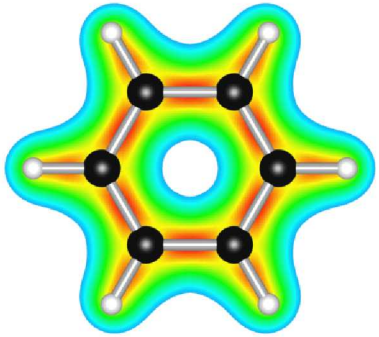
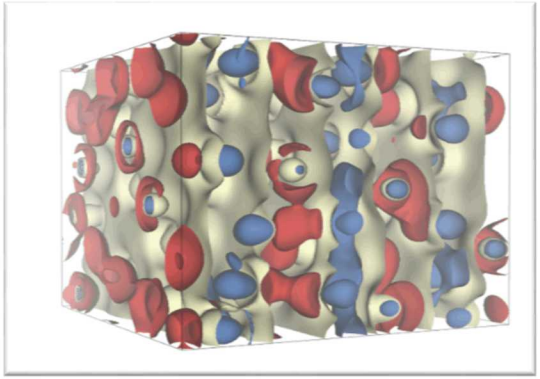






Time-Dependent DFT and Real-Time Electron-Ion Dynamics

Andrew Baczewski

Sandia National Laboratories

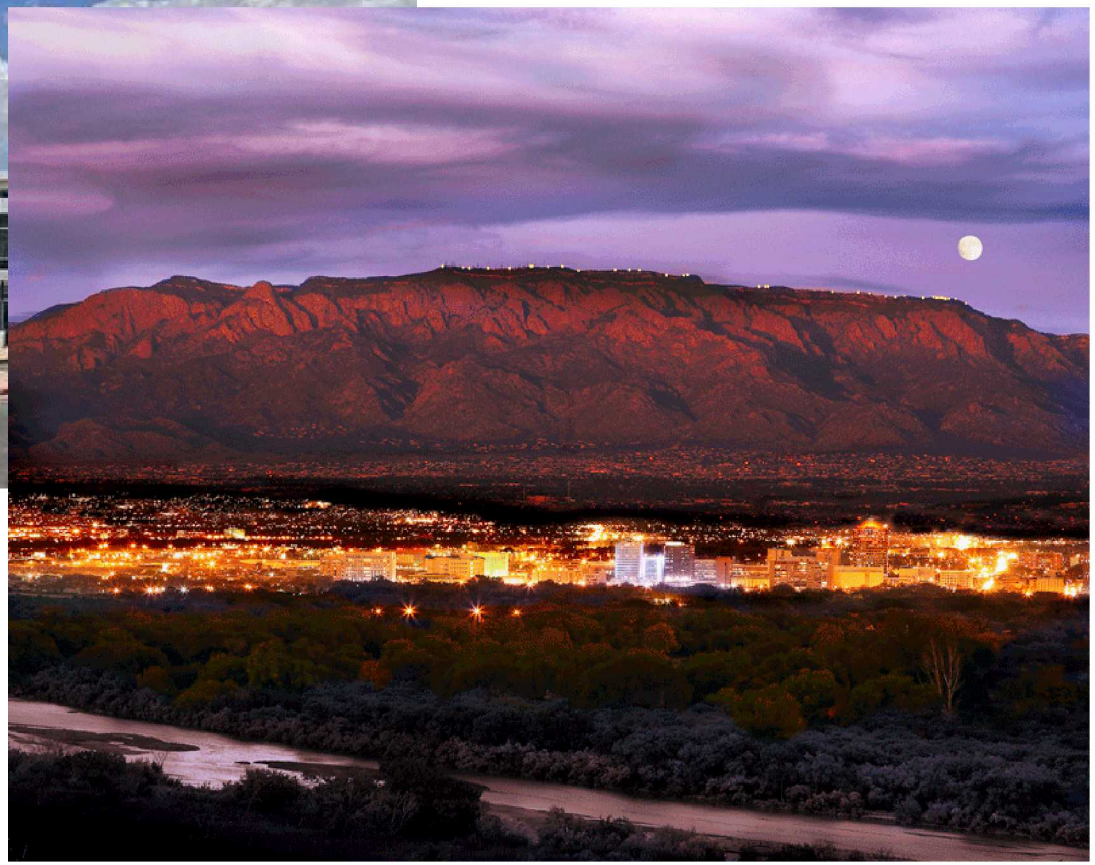
SATE/CORE-CM

09/04/2015

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

- **Center for Computing Research** at Sandia National Laboratories
  - Almost 200 Ph.Ds - from **Computer Science to Cognitive Science**
  - **High performance computing**
  - **Applied math**
  - **Post-CMOS computing**

- Not on an Air Force Base for easy academic access
- At the corner of Research and Innovation (literally)



- Located in sunny Albuquerque, New Mexico in the shadow of the Sandias

- …but there is still snow…

What Do I Do?

Sandia National Laboratories

- **PhD:** fast algorithms for classical physics on classical computers

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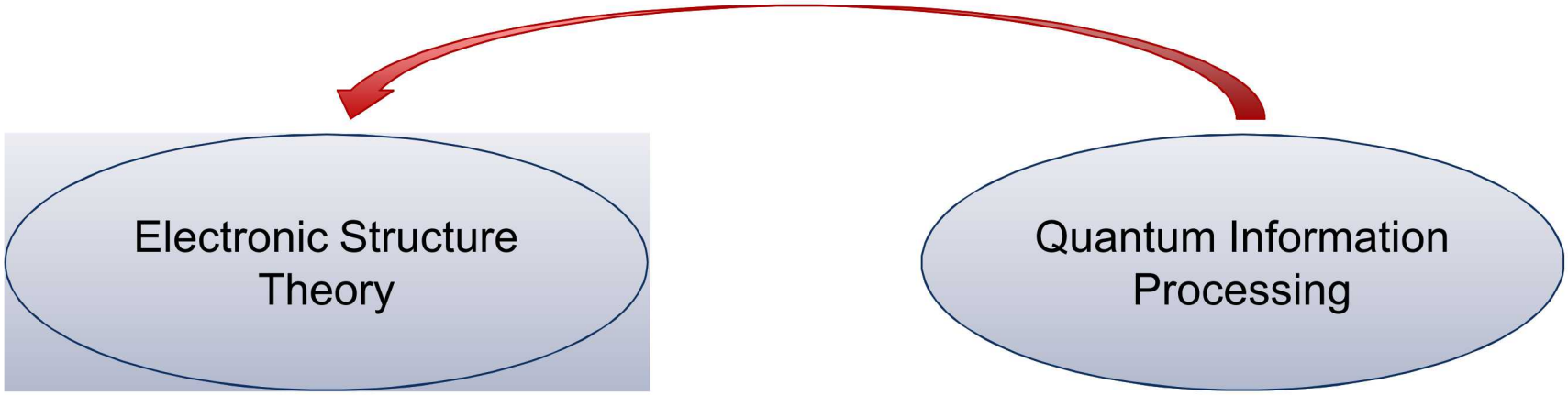
"Many-body quantum states **cannot** be simulated efficiently by classical computers – Richard Feynman said so 30 years ago!"



What Do I Do?

- **PhD:** fast algorithms for classical physics on classical computers
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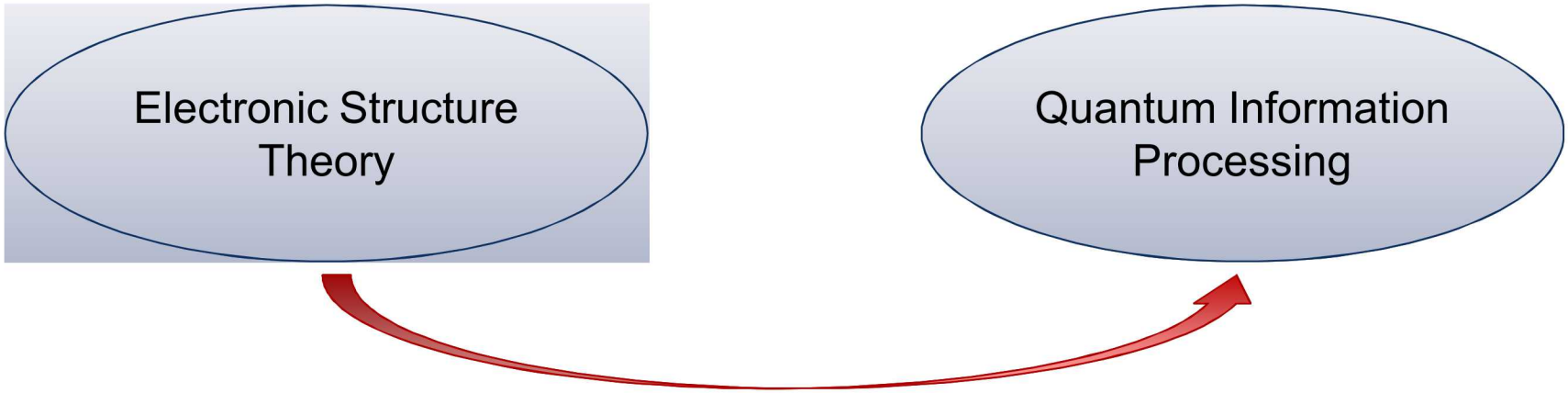
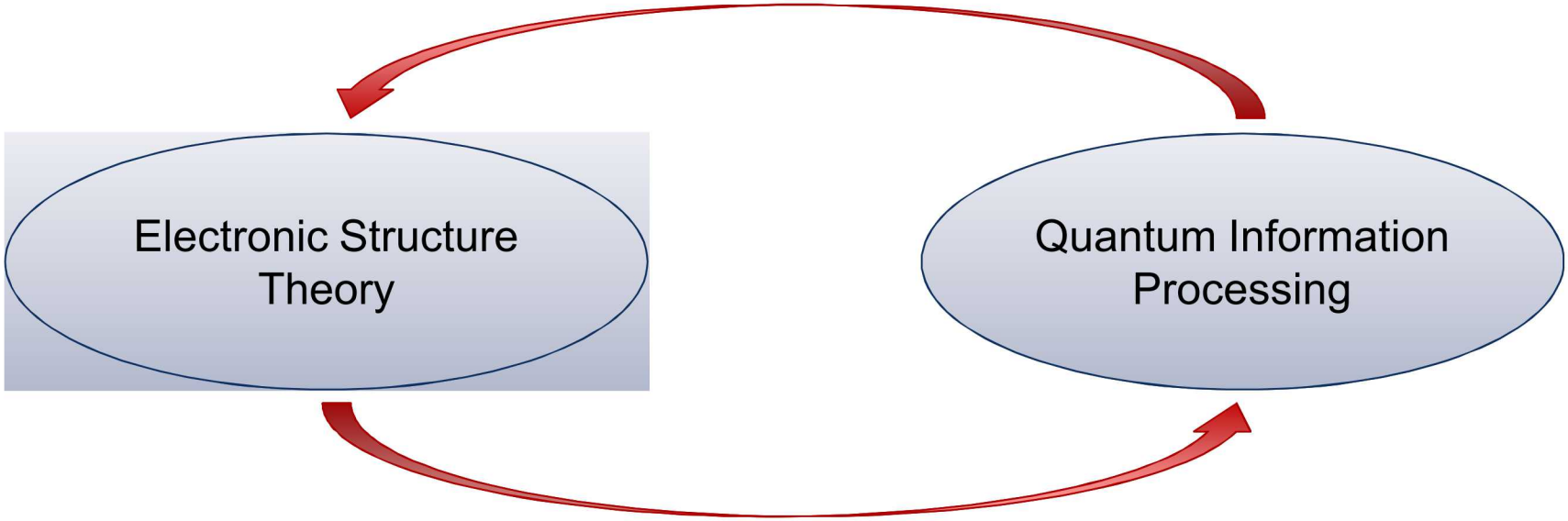


"We **efficiently (but approximately)** simulate chemical/material systems every day – but some systems are obviously harder than others."

What Do I Do?

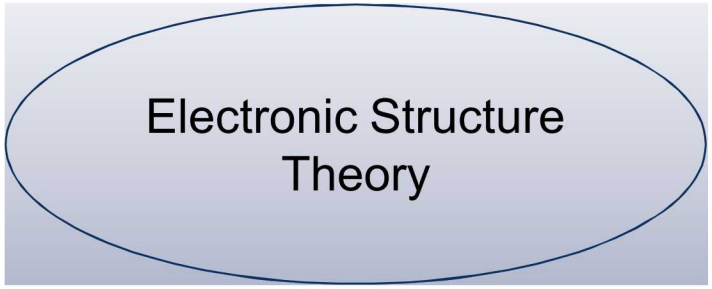
Sandia National Laboratories

"If you answer basic materials questions that will help us build a QIP device, we will tell you about which systems are intrinsically hard and why."



"Deal…so long as I can still study non-QIP materials."

What Do I Do?



But today we will strictly be talking about electronic structure…

Goal of "Ab Initio" Electronic Structure

Sandia National Laboratories

- Given a set of nuclear positions/charges, and the number of electrons…

$$\left[\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}\right] |\Psi\rangle = E|\Psi\rangle$$

- Compute…
  - Total energy: stability of phases
  - Forces on nuclei: equilibrium structure, molecular dynamics
  - Spectrum of excitations: energies and oscillator strengths
  - Exotica: correlation functions, electron-ion equilibration rates, order parameters, etc.
- We would like to do this with as little empirical input as possible

- Broadly speaking – there are density functional methods and wave function methods

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- I practice both – today we will be talking about density functional theory

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Sandia National Laboratories

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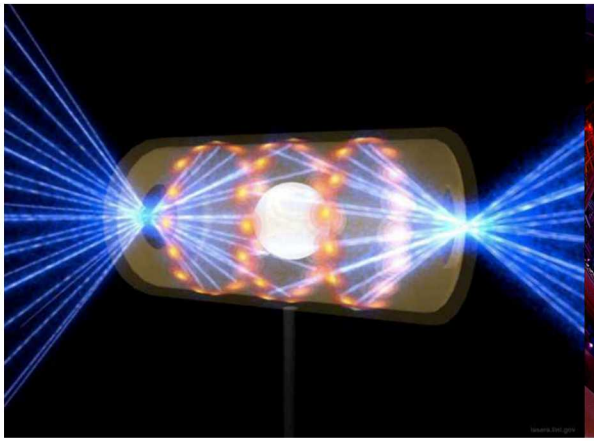
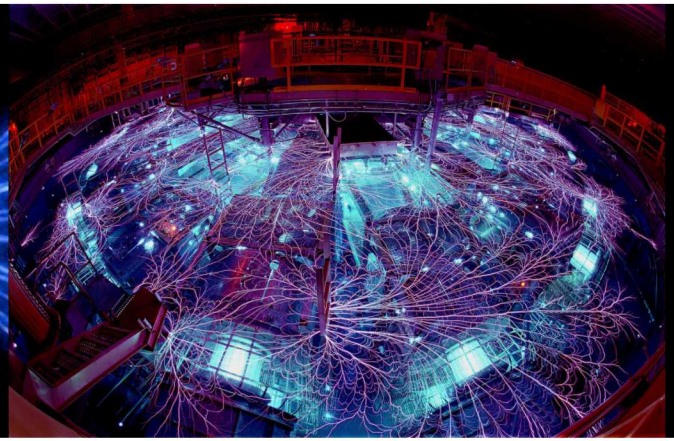
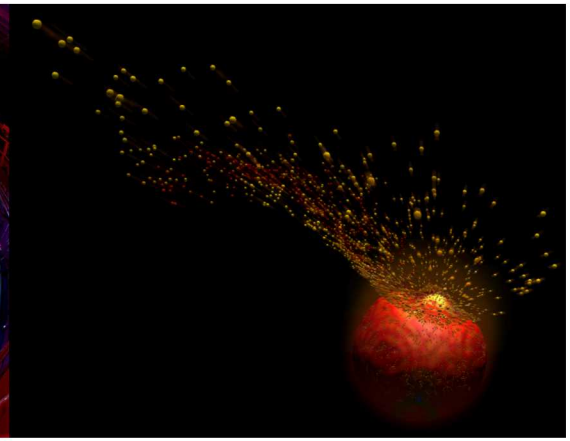
- Broadly speaking – there are density functional methods and wave function methods

- I practice both – today we will be talking about density functional theory
- **We will focus on applications to warm dense matter**

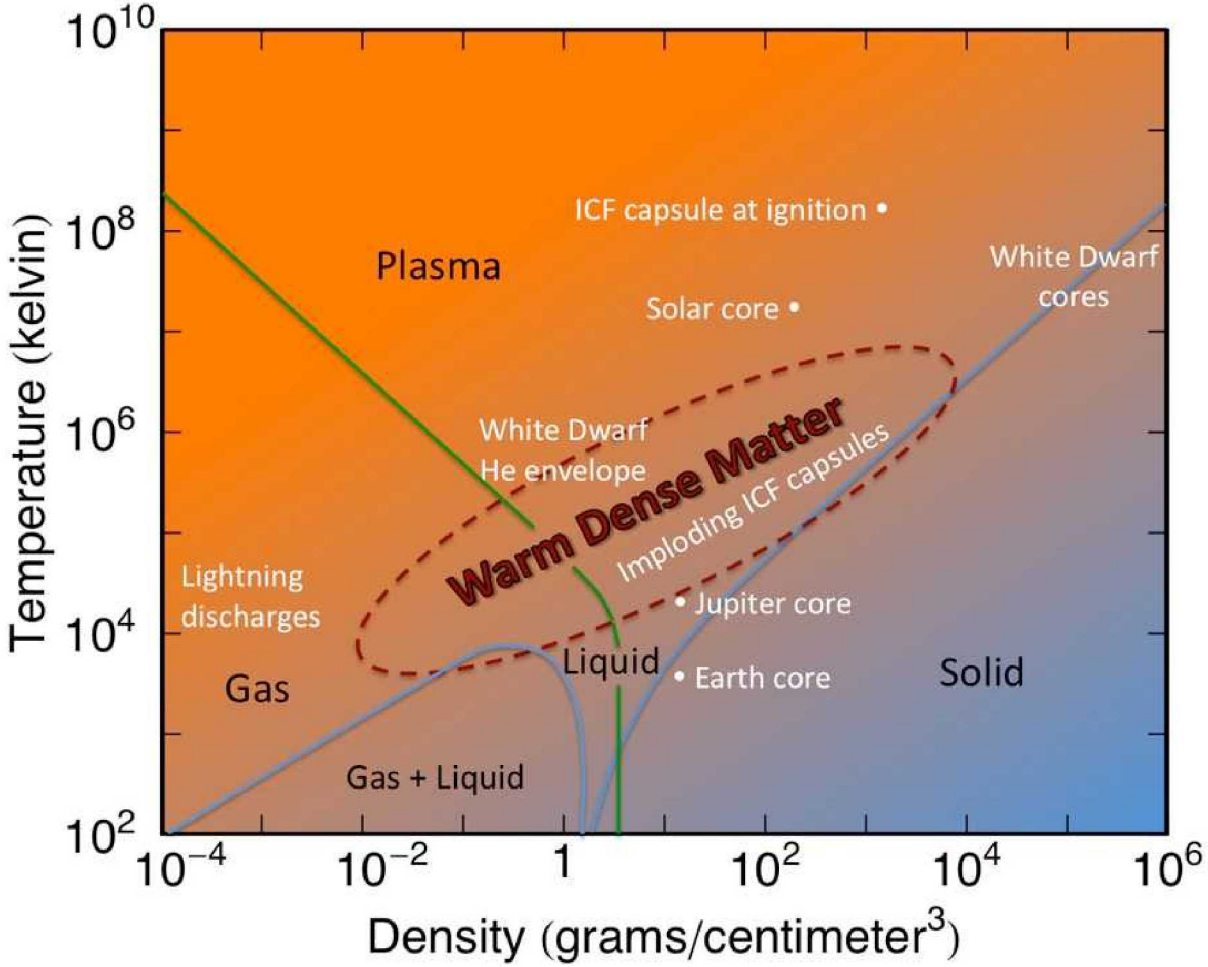
What is Warm Dense Matter?

- **"I know it when I see it."**
  - Occurs in planetary science and inertial confinement fusion

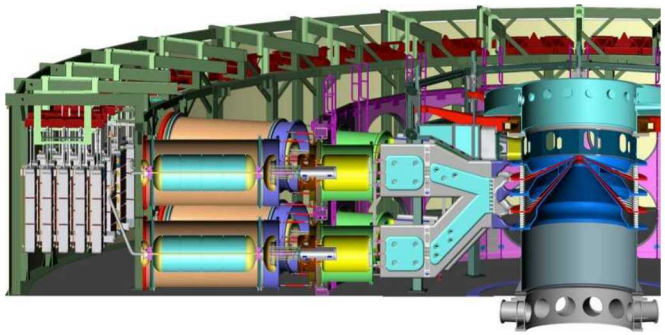
- **What is it?**
  - **Warm:** temperatures on the order of eVs (10kK+)
  - **Dense:** electron densities 1-4x solid
  - **Exotic:** neither condensed phase nor ideal plasma
  - **Challenging:** for experiment and theory

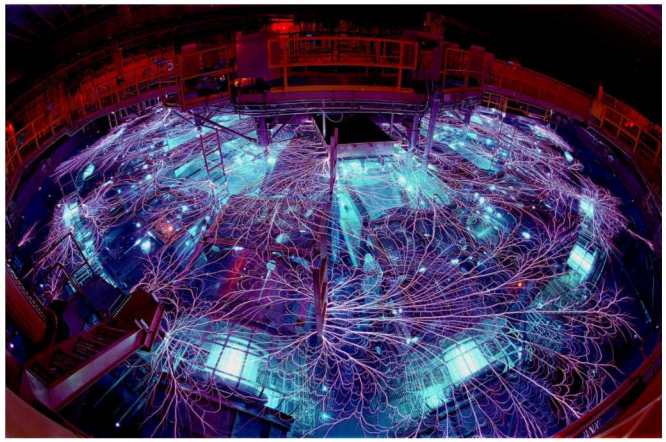
What is Warm Dense Matter?



"Warm" for a plasma physicist…

Warm Dense Matter at SNL





- **Z-Machine:** world's most powerful pulsed power machine
- Accelerates Al flyer plates to 40 km/sec.
- Delivers 27 MegaAmps in 95 nanoseconds.
- Achieves Pressures > 10 Mbar (1 TPa).
- Reached 840 Gpa / 149kK in Xe. **Root, et. al., PRL, 2010**
- Recently, abrupt metallization of hydrogen around 300 GPa. **Knudson, et. al., Science, 2015**

Indirectly but accurate measures pressures and densities

Shock Physics vs. Ultrafast Spectroscopies

Sandia National Laboratories

- Shock experiments on WDM are a type of pump-probe experiment.
  - Pump a system with a flyer plate (Z), or a laser (OMEGA and LCLS)
  - Probe with x-rays (or a laser, e.g., VISAR)
- Pump is typically ~ 1 ns, important part is establishing high pressure and temperature, and probing warm dense state
- Relaxation isn't irrelevant, but experiments are hard enough

- Ultrafast spectroscopies:
  - Temperatures and pressures aren't as extreme
  - Sub-picosecond dynamics can be observed
  - Real probe of non-equilibrium electron-ion dynamics

Shock Physics vs. Ultrafast Spectroscopies

Sandia National Laboratories

- My interest:
  - Developing methods for realistic electron-ion dynamics out of equilibrium
  - Accessible time scales: sub-as time step, a few ps is feasible
  - Today you will see results for inelastic x-ray spectroscopy and stopping germane to warm dense matter…
  - …but I can simulate real-time excitation, and the beginning of relaxation

- Challenges:
  - Ground state of complex materials is still difficult to determine (ab initio)
  - Same with ground state electron-phonon coupling
  - What makes us think that we can get reliable first principles results out of equilibrium?
  - Some of my work on TDDFT in warm dense matter may shed light on what is needed to get to this point

Take Home Message

Sandia National Laboratories

- Key idea of experimental physics
  - If I'm interested in knowing something about a system…

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Sandia National Laboratories

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  - If I'm interested in knowing something about a system…
  - …then I can throw something at it…

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  - If I'm interested in knowing something about a system…
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  - …and watch what happens.

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- Key idea of experimental physics
  - If I'm interested in knowing something about a system…
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- If I have a really large computer…

Sequoia at LLNL

Take Home Message

Sandia National Laboratories

- Key idea of experimental physics
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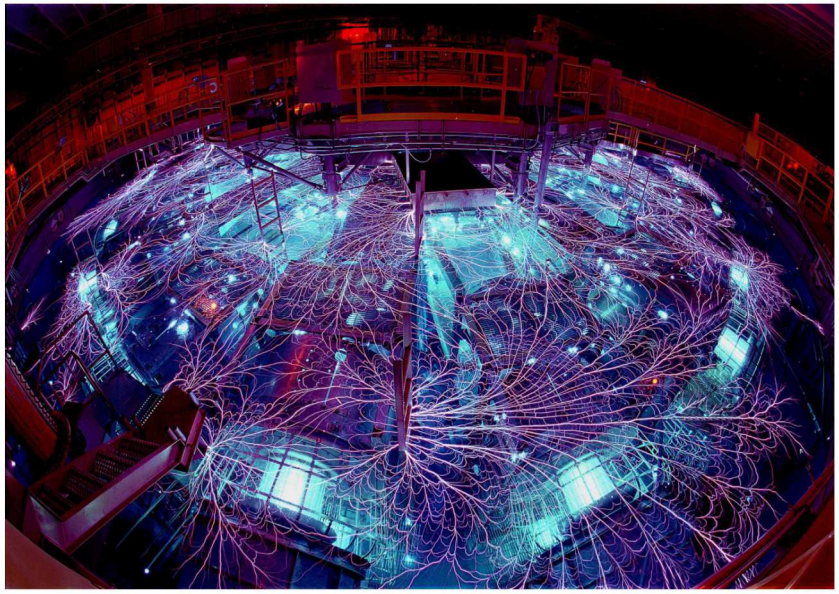
- If I have a really large computer…
- …and I want to know something about an experiment…



Z-Machine at SNL

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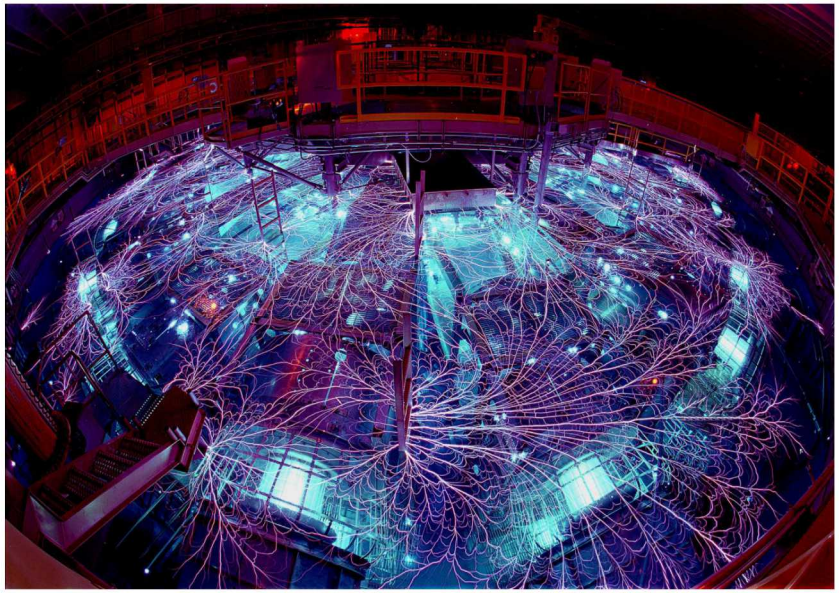

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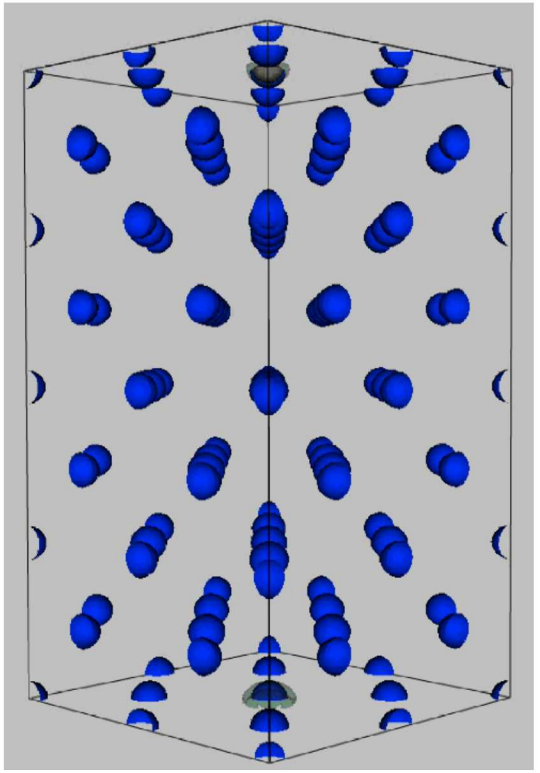

Density response of a proton in Al

Take Home Message

Sandia National Laboratories

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  - If I'm interested in knowing something about a system…
  - …then I can throw something at it…
  - …and watch what happens.

- If I have a really large computer…
- …and I want to know something about an experiment…
- …then I can simulate throwing something at a system…
- …and watch what happens.

- TDDFT efficiently (but approximately) dictates the many-body dynamics of our virtual experiment

Overview

Sandia National Laboratories

- What is DFT/TDDFT?
- Our TDDFT implementation
- Spectroscopy of WDM
- Non-equilibrium Properties of WDM
- Developing better methods

Overview

Sandia National Laboratories

- **What is DFT/TDDFT?**
- Our TDDFT implementation
- Spectroscopy of WDM
- Non-equilibrium Properties of WDM
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What is DFT?

Sandia National Laboratories

- **Goal:** compute the total energy of a molecule or bulk material

$$\left[\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}\right] |\Psi\rangle = E|\Psi\rangle$$

- Many-body wave function of bulk system is too complicated to be useful

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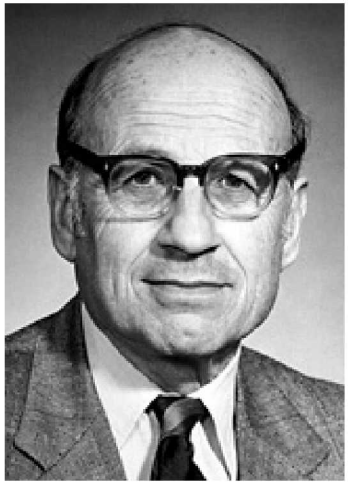


Walter Kohn

Hohenberg-Kohn theorems (1965)

- There is a 1-1 mapping $\hat{V}_{ext} \leftrightarrow \rho_0(\mathbf{r})$ so $\rho_0(\mathbf{r}) \rightarrow \Psi\left[\rho_0\right]$
- There is a universal energy functional $E_{v_{ext}}\left[\rho\right]$ minimized by the ground state density
- Neither theorem is constructive
- Neither theorem says anything about complexity*

*Barring an unexpected hierarchy collapse – DFT is formally hard, even for a quantum computer see Rassolov + Garashchuk, Chem. Phys. Lett. (2008) or Schuch + Verstraete, Nature Phys. (2009)

Kohn-Sham DFT

- **DFT:** find $\rho(\mathbf{r})$ that minimizes $E_{v_{ext}}[\rho]$

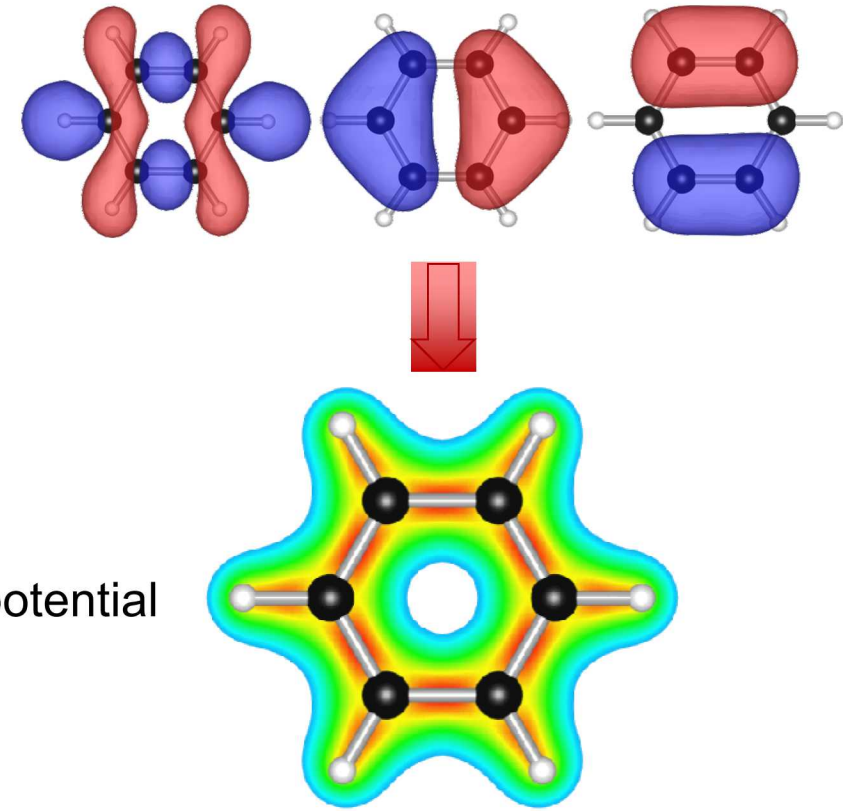
$$E_{v_{ext}}[\rho] = T_s[\rho] + \int d\mathbf{r}\; v_{ext}(\mathbf{r}) + E_H[\rho] + E_{xc}[\rho]$$

Spirit of Thomas-Fermi theory (1927)

- **Kohn-Sham (1965):** build density from eigenfunctions of auxiliary Hamiltonian

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

$$\hat{\mathcal{H}}_{KS}[\rho]\,|\psi_{n,\mathbf{k}}\rangle = \varepsilon_{n,\mathbf{k}}|\psi_{n,\mathbf{k}}\rangle$$



- Fermi degeneracy built into kinetic energy

- Density-dependent exchange-correlation potential is the key ingredient

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}$$

What isn't DFT?

Sandia National Laboratories

- **So, DFT pretty much just gives you total energies…**
  - …but you can take derivatives -> forces in electronic ground state
  - Eigenvalues of Kohn-Sham Hamiltonian aren't so far off…
  - …but they don't formally mean anything (except in special cases)

- We would like a method that produces:
  - Real information about excitations
  - Forces in the presence of electronic excitation
  - Transport coefficients
  - Correlation functions

- TDDFT is one such method that is computationally efficient enough to be applied to complex systems…

What is TDDFT?

Sandia National Laboratories

- **Goal:** compute the time evolution of a many-body system + TD perturbation

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

- Many-body wave function of bulk system is still too complicated to be useful

Hardy Gross

Runge-Gross theorem (1984)

- There is a 1-1 mapping $\rho(\mathbf{r},t) \leftrightarrow v_{ext}(\mathbf{r},t)$ so $\rho(\mathbf{r},t) \rightarrow \Psi_{ext}\left[\rho(\mathbf{r},t), \Psi_0\right](t)$

van Leeuwen theorem (1999)

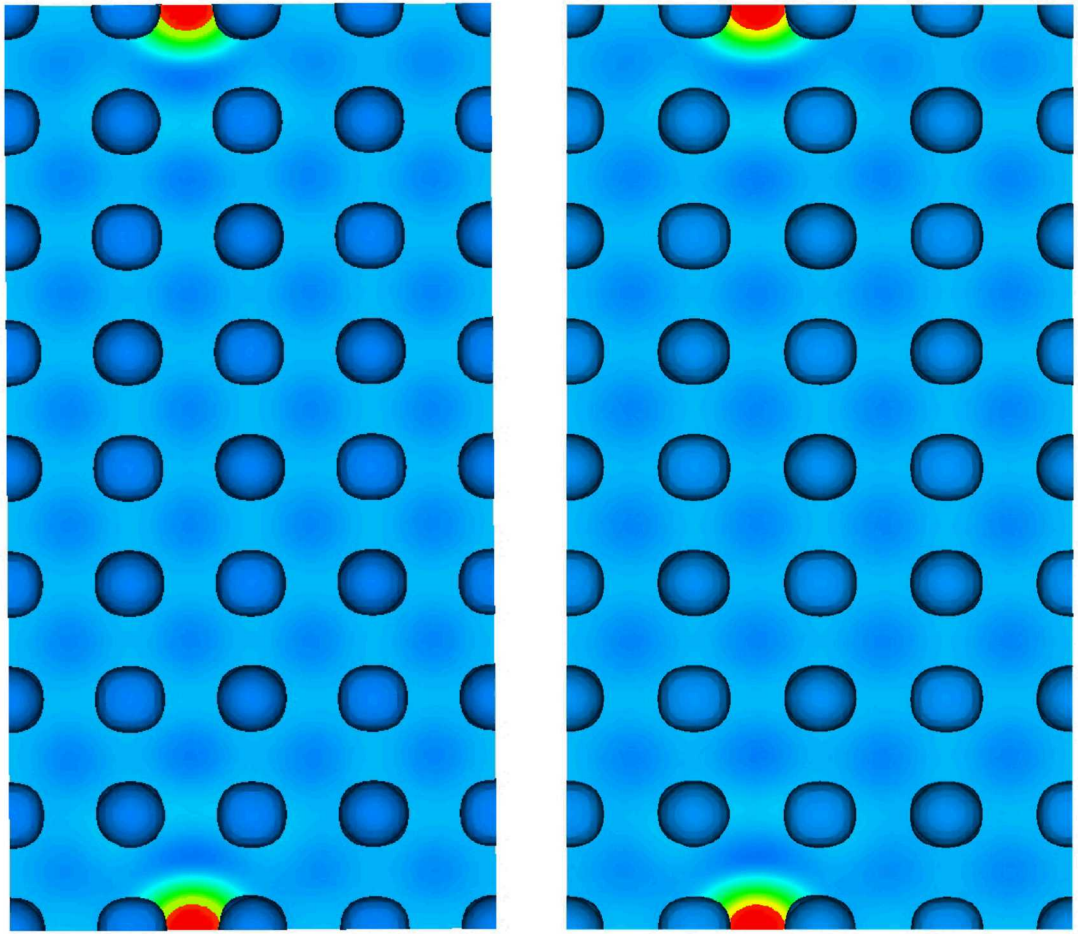
- You can almost always construct an auxiliary non-interacting system that reproduces an interacting many-body density
- Neither theorem is constructive
- Neither theorem says anything about complexity*

*Surprisingly, TDDFT is something that a quantum computer can do efficiently, see Whitfield, et. al., New J. Phys., (2015)… a classical computer, too (in a restricted sense)

Born-Oppenheimer vs. Ehrenfest

- **Born-Oppenheimer (DFT-MD) -> electrons stuck in equilibrium state**
- **Ehrenfest (TDDFT-MD) -> electrons are free to move around**

- **Important example:** throw a proton into an Al crystal at v=1-5 a.u.
- Proton's primary energy loss mechanism = excitation of plasmons
- No plasmons in DFT-MD
- No stopping in DFT-MD



Overview

- What is DFT/TDDFT?
- **Our TDDFT implementation**
- Spectroscopy of WDM
- Non-equilibrium Properties of WDM
- Developing better methods

Implementation Details

- **Key contribution:** implementing Ehrenfest-TDDFT in VASP
  - Plane wave basis
  - Projector Augmented-Wave + frozen core
  - PAWs work best for pressures we care about

- Basic methodology:
  - Get **Mermin state** from standard calculation

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

  - Defines initial conditions for **TD Kohn-Sham** equations

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

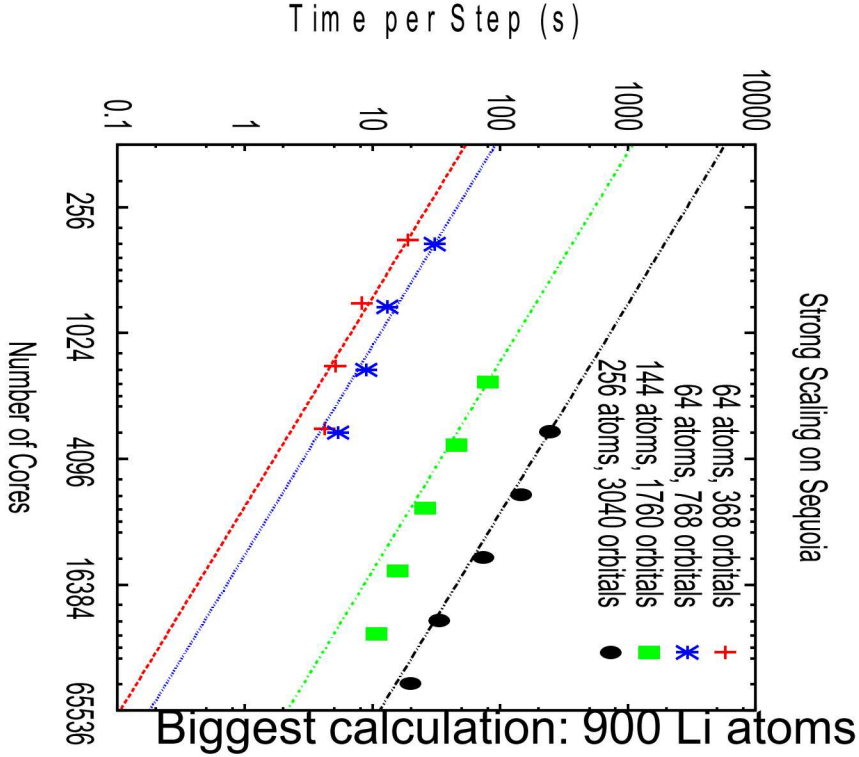
  - Compute **ionic forces** as needed (from TD density)

  - Record response in terms of **observables (density functionals)**

$$\langle \hat{O}(t) \rangle = O\left[\rho(\mathbf{r},t)\right] \qquad \rho(\mathbf{r},t) = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(\mathbf{r},t)|^2$$

Bells and Whistles

- **Ehrenfest-TDDFT in VASP:**
  - PAW method (**direct access to all-electron quantities, soft cutoffs**)
  - Exactly charge conserving time integration
  - Scalable on BG/Q
  - Rare capability for extended systems (Octopus, GPAW, Quantum Espresso)
- **Advantages:**
  - Easier to scale than BOMD
  - Lower cost complexity
  - "Real" information about excitations
  - PAWs good for WDM
- **Disdvantages:**
  - Small time step (attoseconds!)
  - Reliance upon adiabatic functionals
  - Making PAWs for TDDFT…?



Biggest calculation: 900 Li atoms

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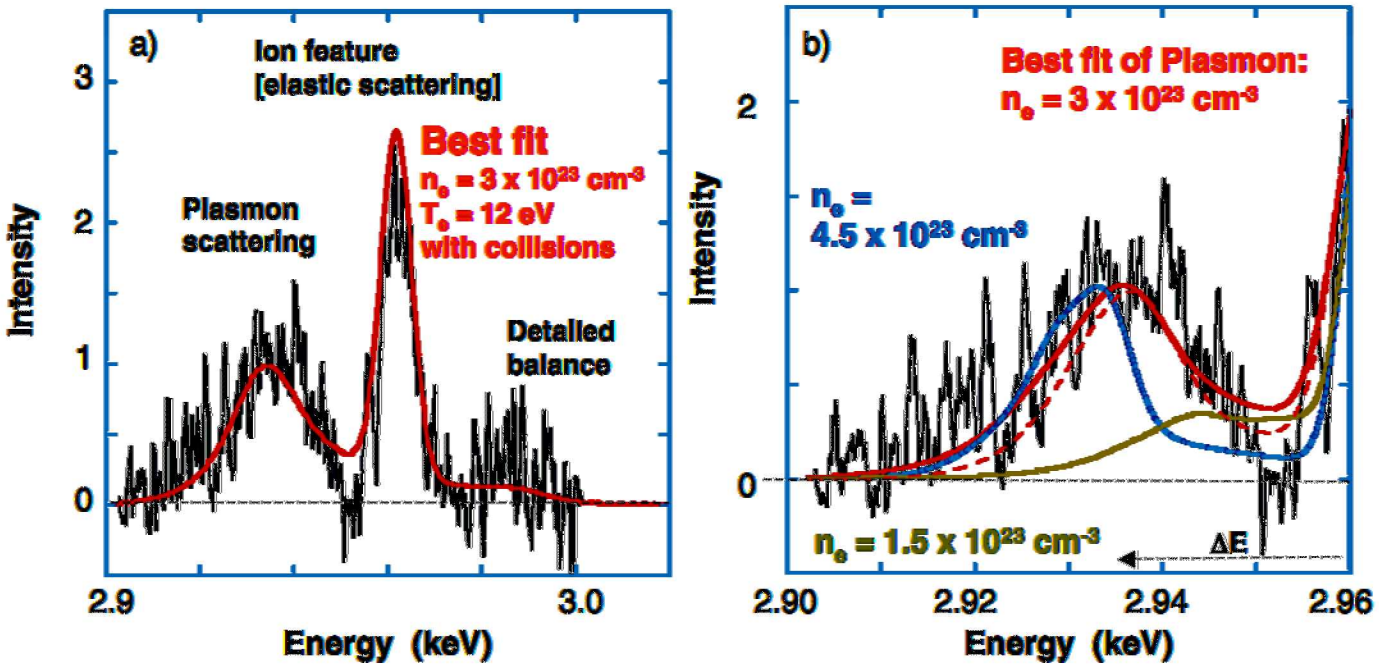
X-Ray Thomson Scattering

- **What is it?**
  - Inelastic x-ray scattering -> temperature, density, and ionization state in WDM
  - Angular dependence -> ion-ion correlations, dispersion of plasmons

$$\frac{d^2\sigma}{d\Omega d\omega} \sim S(\mathbf{q},\omega)$$

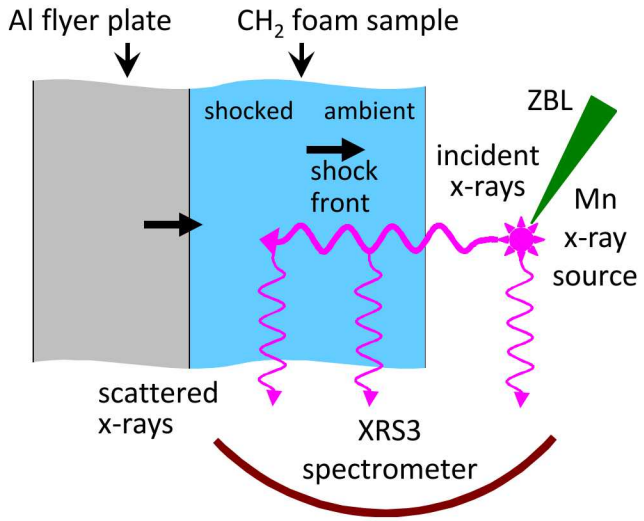


Glenzer, et. al., PRL (2007)

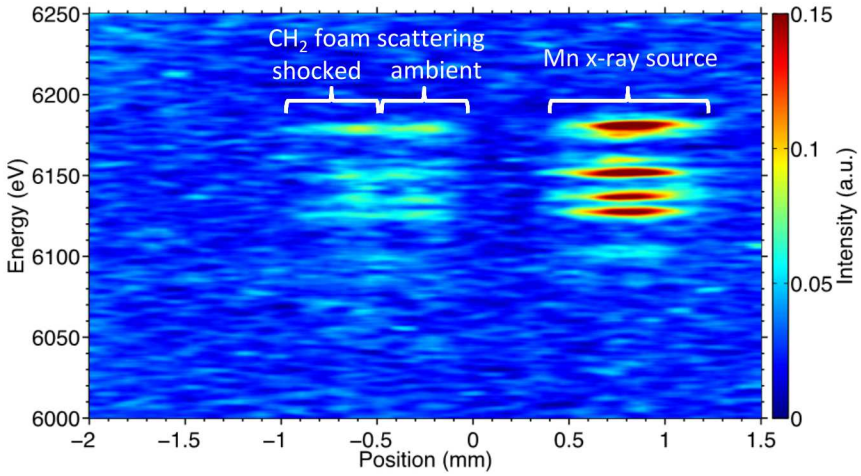
X-Ray Thomson Scattering at SNL

Sandia National Laboratories

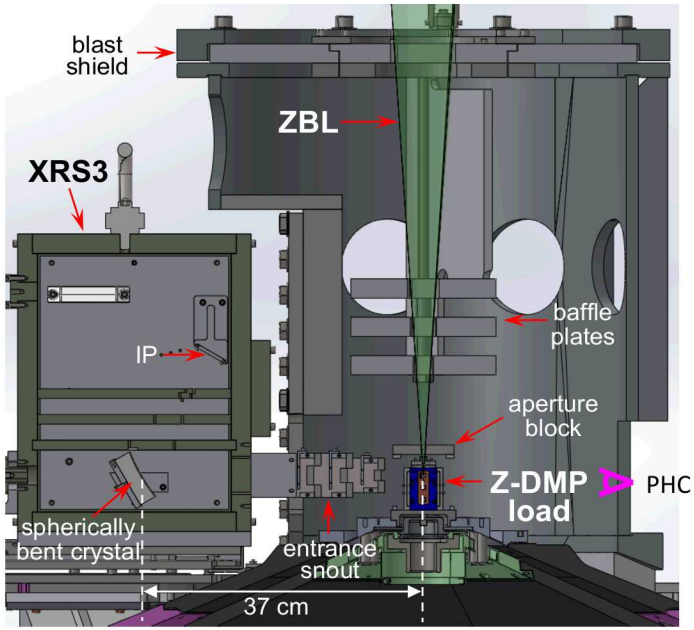
Z-XRTS load (top-view)



- XRTS expands diagnostic capabilities on Z beyond pressure and density measurements
- Importance of XRTS measurements with spatial resolution demonstrated on Z



XRS3 data



Target chamber (cross–section view)

Current Theoretical Standard

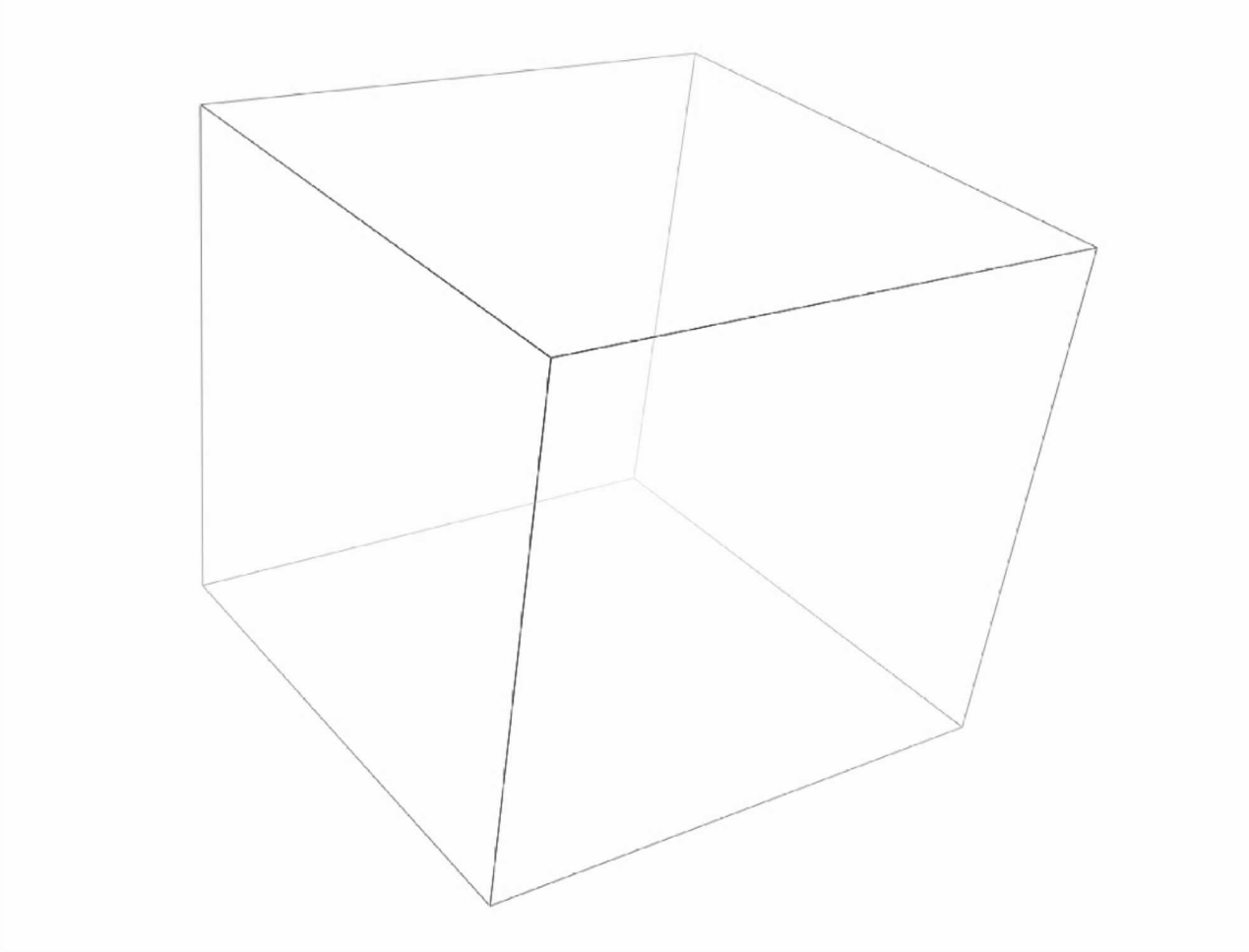
- **Chihara model:** widely used empirical form of the DSF

$$S(\mathbf{q},\omega) = |f_I(|\mathbf{q}|) + q(|\mathbf{q}|)|^2 S_{ii}(\mathbf{q},\omega) + Z_f S_{ee}(\mathbf{q},\omega) + S_{bf}(\mathbf{q},\omega)$$

  - Phenomenological decomposition into 3 terms
  - Relies on partition of electrons into bound and free
  - Different approximations for different terms
    - **Term 1:** static structure factor from MD + atomic form factor from table
    - **Term 2:** electron density + temperature + RPA (+LFCs or lifetimes)
    - **Term 3:** overlap of average atom states with continuum states
  - What about **sum rules?**
- **We are doing the first calculations independent of this model**

XRTS without Chihara

- **We explicitly model the real-time dynamics of the x-ray hitting the system**
  - The first 100 as of a strong x-ray pulse hitting 3x compressed Be (150 kK)

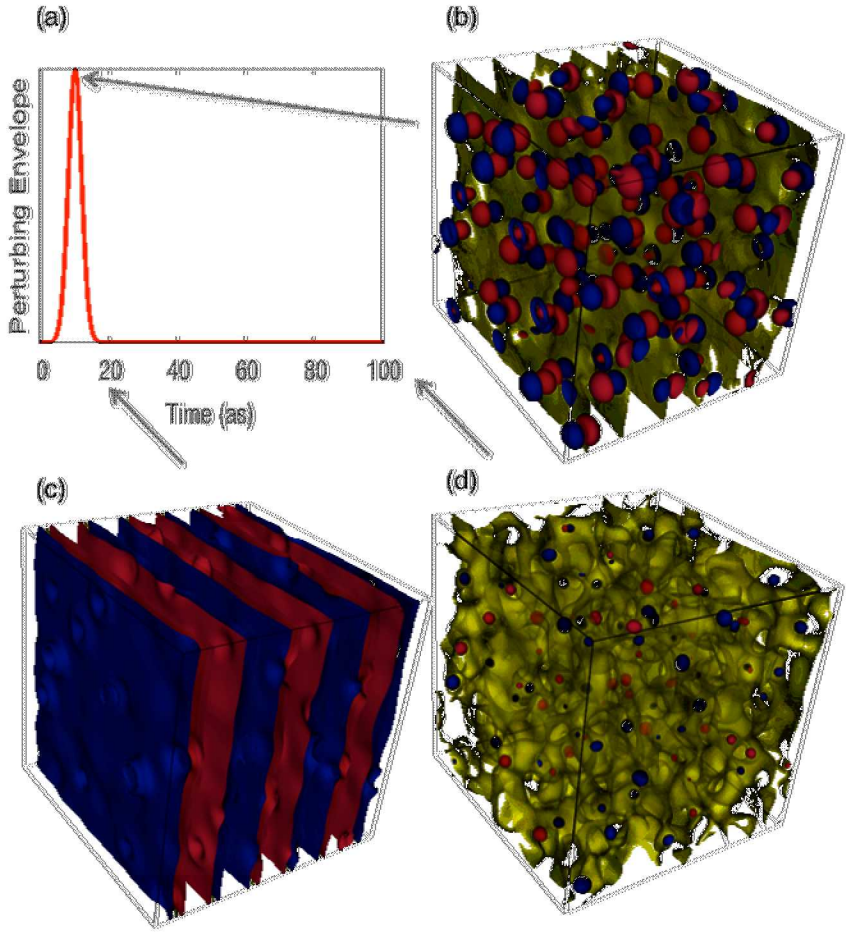


XRTS without Chihara

- **We explicitly model the real-time dynamics of the x-ray hitting the system**
  - The first 100 as of a strong x-ray pulse hitting 3x compressed Be (150 kK)

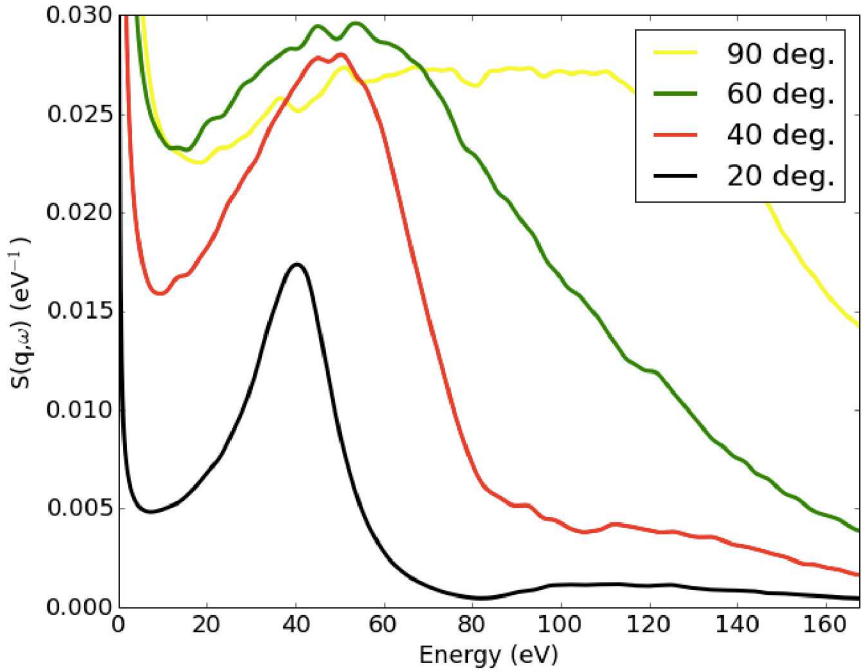
(a) envelope of the x-ray
(b) response at x-ray peak
(c) peak response
(d) plasmons, etc.

- TD charge density
- Density-density response
- Dynamic structure factor
- **Pure density functional**



Results for 3x Compressed Be (150 kK)

- **Compute dynamic structure factor at 4 different scattering angles**
  - Adiabatic LDA should work well -> all q values less than $2k_f$
  - Effectively all electron calculations



- Experimental plasmon ~40 eV close to 20°
- Peak disperses as expected
- Sum rules satisfied
- Core contributions critical

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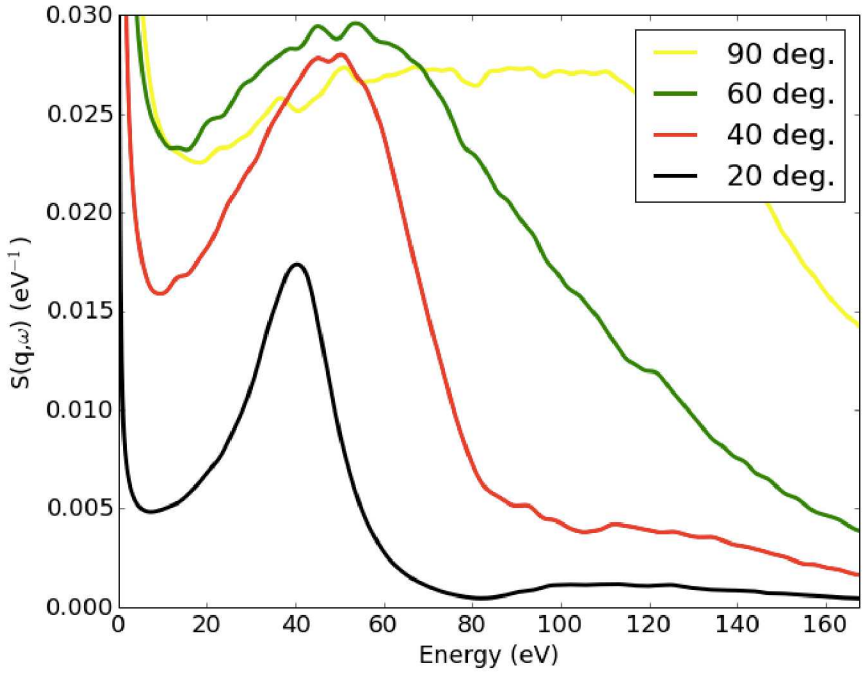

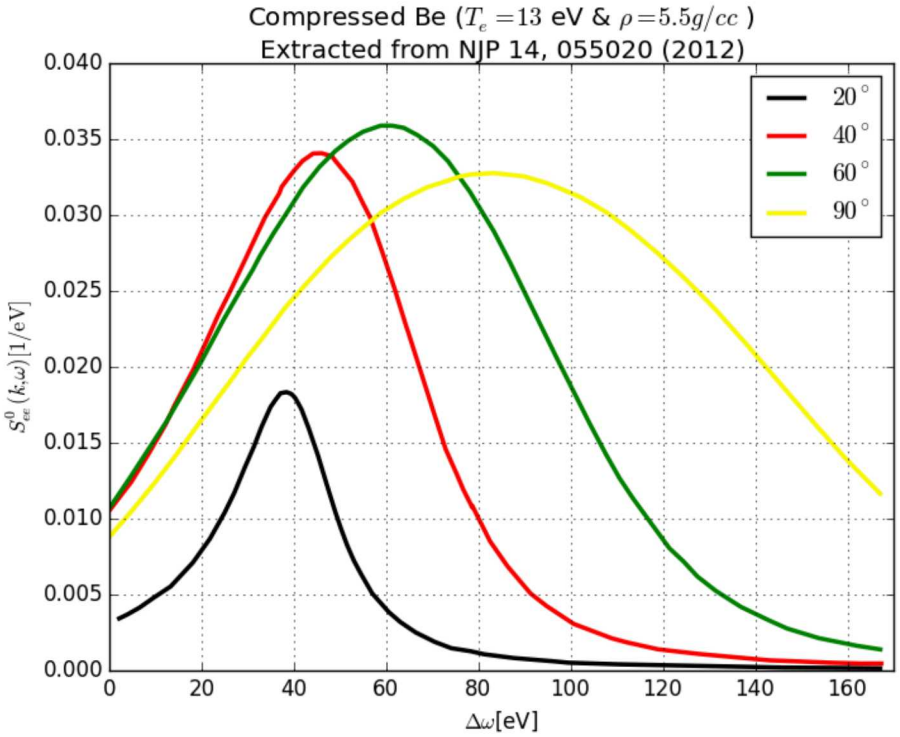

Compared with free-free Chihara model bootstrapped from DFT

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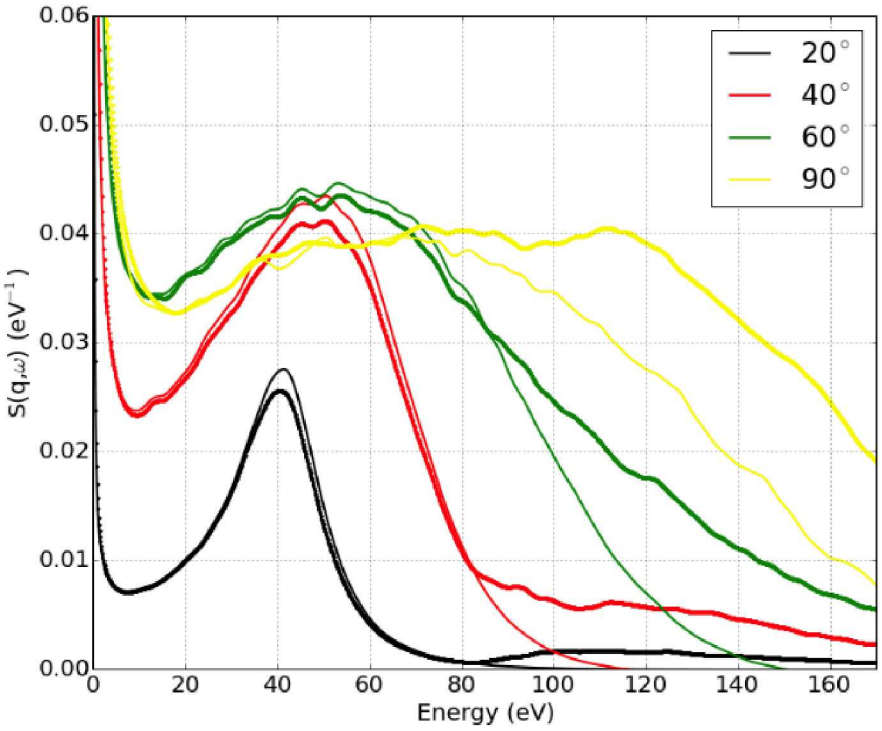

- **Thick lines:** all-electrons free
- Thin lines: $1s^2$ frozen

- Deficiencies:
  - New functionals needed to go to forward scattering limit
  - Electrons and ions are equilibrated

Overview

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- What is DFT/TDDFT?
- Our TDDFT implementation
- Spectroscopy of WDM
- **Non-equilibrium Properties of WDM**
- Developing better methods

Stopping and Electron-Ion Equilibration

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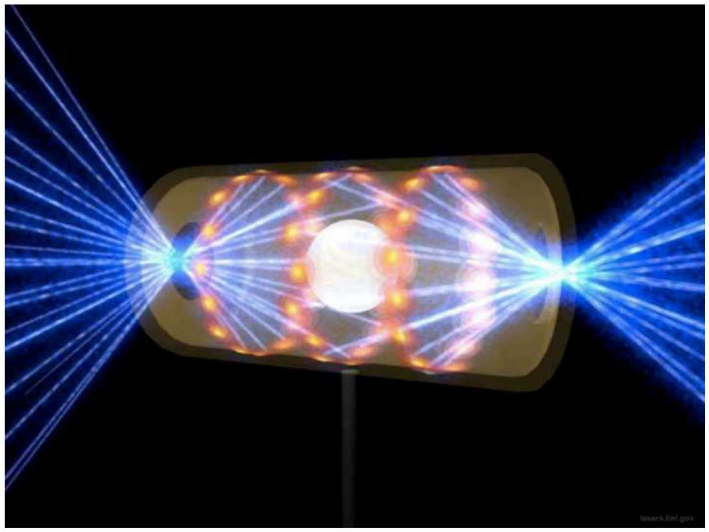
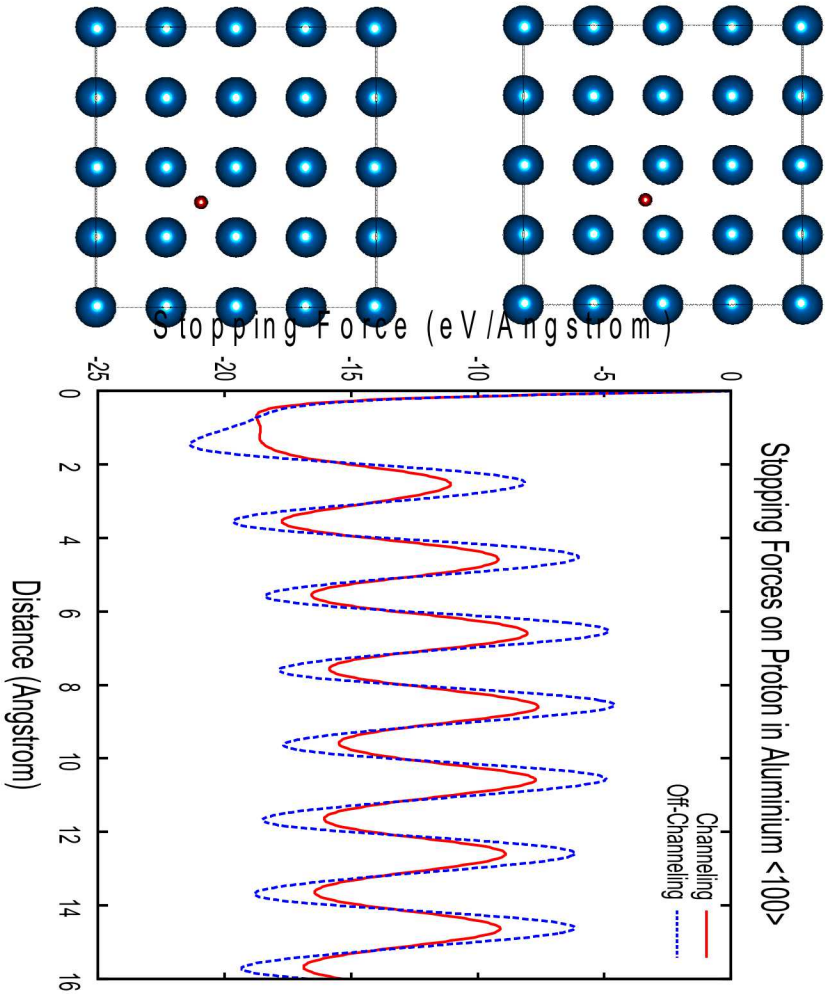
- Stopping power critical to ICF science:
  - Average force on ion with charge Z vs. velocity
- Ions often in energy range dominated by electronic stopping
  - velocity < v_f : adiabatic, stopping increases
  - velocity > v_f : non-adiabatic, stopping decreases
- Z-oscillations: competition b/w increased charge and screening by closed shells



- Related problem: electron-ion equilibration
  - Femtosecond lasers heat electrons, which deposit energy into ions
  - Mechanical shocks heat ions, which deposit energy into electrons
- Ehrenfest-TDDFT seems like it would be up to this challenge…
- Instead of WDM – an stopping example in cold matter with enticing physics

Stopping Power and Non-Adiabaticity

- **Detailed calculation of stopping power from Ehrenfest-TDDFT**



- Comparison with Correa, et. al., PRL (2012) and SRIM/TRIM
- Proton stopping in fcc Al

- Experimental error ~ 10%
- Disagreement beyond peak
  - Core excitations?
  - Trajectory sampling?
  - Force definition?
  - Nonadiabatic effects

Stopping Power and Non-Adiabaticity

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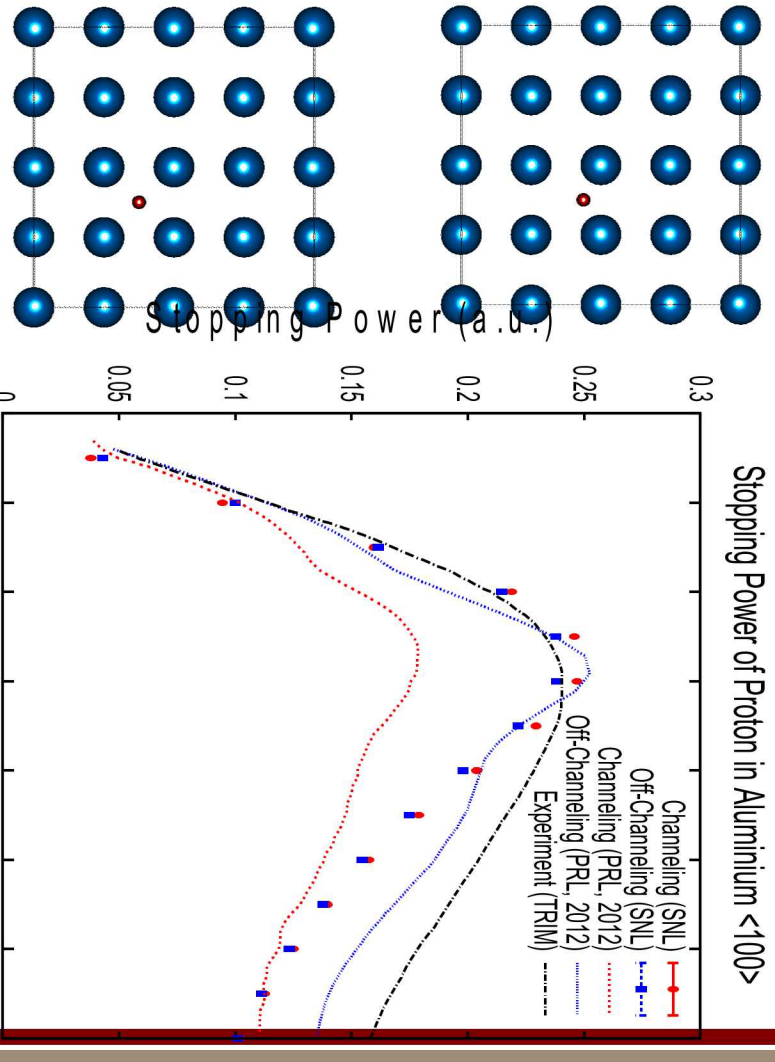

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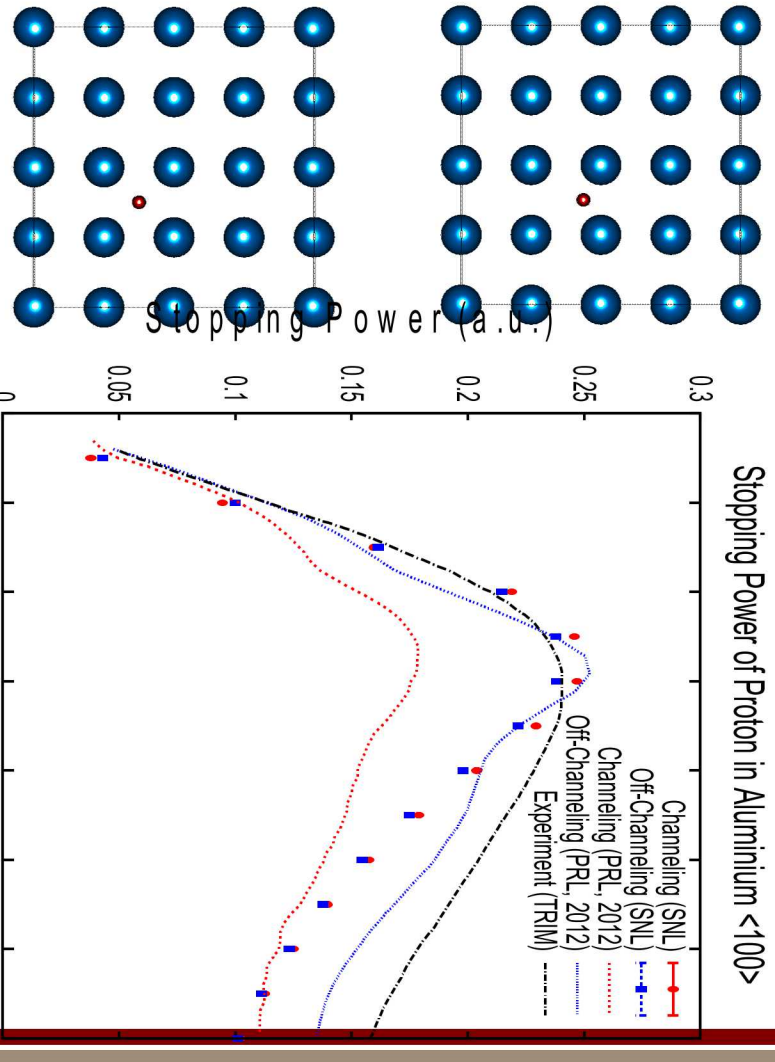

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Overview

- What is DFT/TDDFT?
- Our TDDFT implementation
- Spectroscopy of WDM
- Non-equilibrium Properties of WDM
- **Developing better methods**

The Need for Better Methods

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- Earlier: ground state electronic structure can be hard, why do we think we have a shot at non-equilibrium?

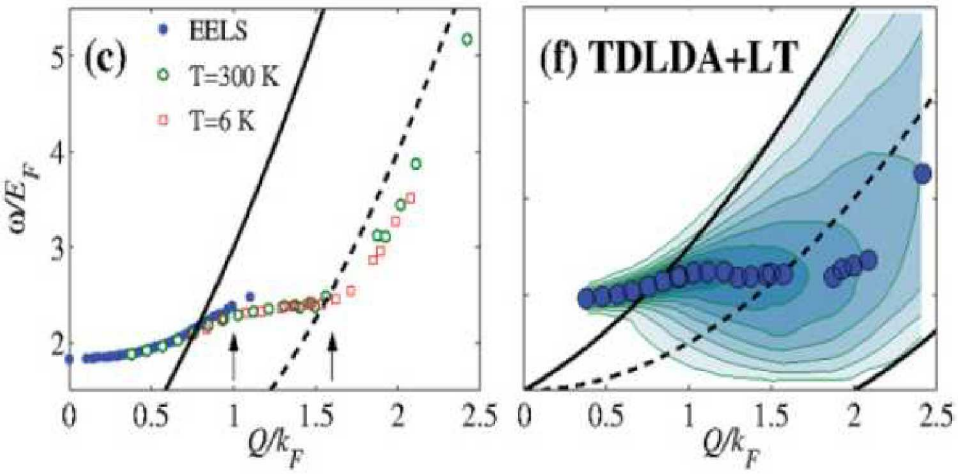
- Ground state DFT: a whole zoo of functionals w/wildly varying costs and accuracies
- TDDFT: only adiabatic local and bootstrapped linear response functionals

- Even so, we can add physics comparable to GW/Bethe-Salpeter at low cost

- TDDFT (let alone Ehrenfest+) of bulk systems is a rare capability/expertise
  - Get qualitative physics first, pursue “chemical accuracy” later
  - Bountiful low hanging fruit

Improving TDDFT I

- Dynamic structure factor is a good probe of missing physics
  - EELS and IXS of ambient Na done at ETSF
  - Linear response TDDFT indicates that quasiparticle lifetime effects needed
  - Hard to translate into real-time functional

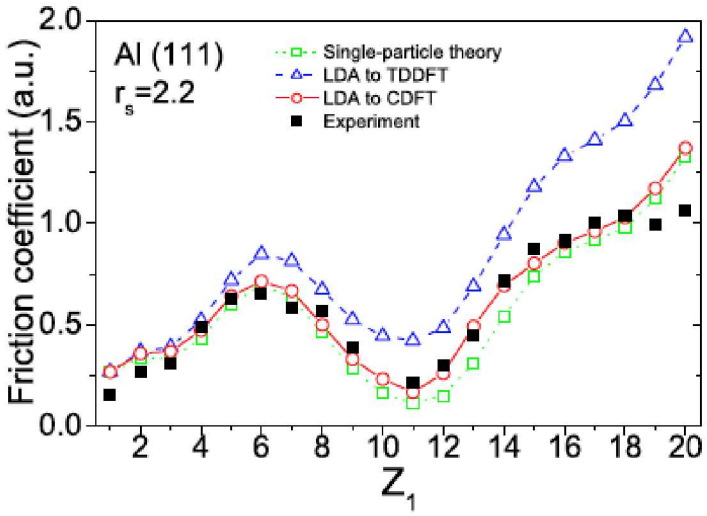


Huotari, et. al., PRB, (2011)

Equivalent exchange-correlation potential is non-local in time and space

Improving TDDFT II

- Z-oscillations in stopping in Al probe non-locality
  - TDLDA underestimates screening
  - Do TDDFT of current density* instead…
  - Local approximations to current XC kernel become non-local when applied to density



Nazarov, et. al., PRB, (2007)

We have 88 years of experience developing approximations in DFT – virtually none in TDCDFT

*Formally, we should be doing TDCDFT in bulk systems – see Maitra, et. al., PRB, (2003)
Nothing holds a DC polarization in pure TDDFT of bulk systems

Bringing TDDFT to the Masses

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- Recently, more exotic physics has been consumed by DFT
  - TDDFT of Coulomb blockade: Kurth, et. al., PRL, (2010)
  - TDDFT of open quantum systems: Yuen-Zhou, et. al., PRL, (2010)
  - DFT of thermoelectricity: Eich, et. al., PRL, (2014)
  - TDDFT of thermal states: Modine and Hatcher, J. Chem. Phys., (2015)
  - DFT of superconductors: Linscheid, et. al., PRB, (2015)
- Investing in developing these methods may lead to first principles calculations of more exotic systems

- Ultrafast spectroscopies play a critical role in providing real data about real-time electron-ion dynamics that theorists should aspire to match

Conclusion

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- Real-time electron-ion dynamics can be computed using Ehrenfest-TDDFT
- We have implemented Ehrenfest-TDDFT for bulk systems in a popular software package (VASP)
- We have used it to study:
  - X-ray Thompson Scattering
  - Stopping Power
  - Optical response
- Plenty of improvements to be made to methodology, but promising advances should encourage us.
- Ultimate goal of “ab initio” modeling of ultrafast experiments can only benefit from ongoing experimental efforts

Acknowledgements

- TDDFT LDRD: Rudy Magyar, Luke Shulenburger, and Mike Desjarlais
- Experimental XRTS slide from Tommy Ao
- SNL and LLNL High Performance Computing

Thank you for your time!