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Dielectric Response in Extreme Conditions Using Time-Dependent Density Functional Theory

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Strongly Coupled Coulomb Systems
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Outline

- Dielectric Response of Warm Dense Matter
- Our Implementation of Ehrenfest-TDDFT
- Stopping Power
- X-Ray Thomson Scattering
- Conclusion

- **Nomenclature:**
  - BO → Born-Oppenheimer
  - BZ → Brillouin Zone
  - DFT → Density Functional Theory
  - DSF → Dynamic Structure Factor
  - KS → Kohn-Sham
  - MD → Molecular Dynamics
  - PAW → Projector Augmented-Wave
  - TD → Time-Dependent
  - WDM → Warm Dense Matter
  - XRTS → X-ray Thomson Scattering

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Warm Dense Matter

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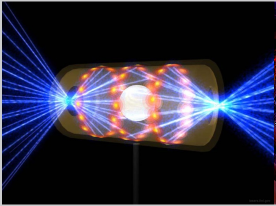
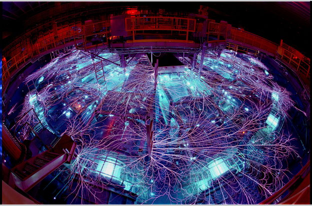
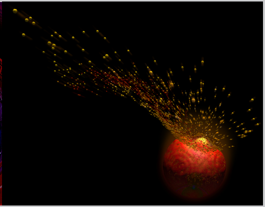
- Motivation: ICF, shock diagnostics, planetary science

- **What is it?**
  - Warm: temperatures on the order of eVs (10kK+)
  - Dense: electron densities 2-4$\times$ solid
  - ‘Exotic’: neither standard condensed phase nor ideal plasma
  - Challenging: both experimentally and theoretically

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Dielectric Response of WDM

- **How do we study it?**
  - Time-honored tradition among physicists...
  - Throw something at it, watch what happens.

$$\begin{bmatrix} \delta\rho(\mathbf{r},t) \\ \delta\mathbf{j}(\mathbf{r},t) \end{bmatrix} = \int dt' d\mathbf{r}' \begin{bmatrix} \chi_{d,d}(\mathbf{r},\mathbf{r}',t-t') & \chi_{d,c}(\mathbf{r},\mathbf{r}',t-t') \\ \chi_{c,d}(\mathbf{r},\mathbf{r}',t-t') & \chi_{c,c}(\mathbf{r},\mathbf{r}',t-t') \end{bmatrix} \cdot \begin{bmatrix} V_{ext}(\mathbf{r}',t') \\ \mathbf{A}_{ext}(\mathbf{r}',t') \end{bmatrix}$$

- **What can we compute?**
  - Stopping power
  - Optical response
  - XRTS spectrum
- We seek to model experimental process, i.e., throw and watch
- **Real-time electron dynamics → dielectric response**

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Our Approach

- **Ehrenfest-TDDFT:** MD simulation with concurrent electron-ion motion
  - Ehrenfest: ionic forces on average potential energy surface
  - TDDFT: theory in which real-time electron dynamics evolve
- **Method:**
  - Start in Mermin state: $n_0(\mathbf{r}) = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2$
  - Integrate TD-KS equations in the presence of perturbing potential:

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

  - Compute ionic forces along the way, update (x,p) if needed
  - Record response in terms of observables (density functionals):

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

- **Goal of Talk:** describe capabilities developed over the past 16 months

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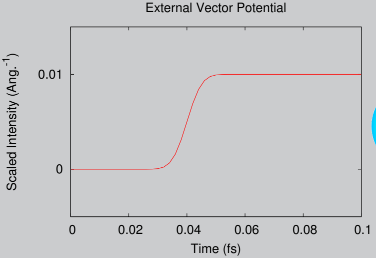
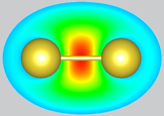
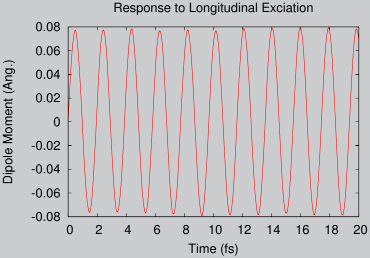
- Ignoring ionic motion for a moment...
- Consider subjecting a Na dimer to a homogeneous vector potential







- **Time evolved dipole moment → polarizability/optical absorption**

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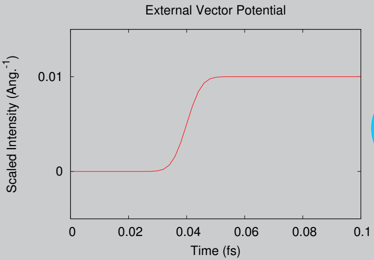
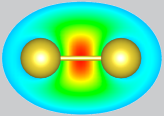
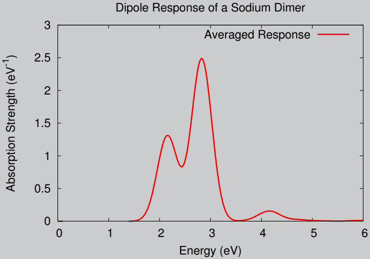
A Simple Example

- Ignoring ionic motion for a moment. . .
- Consider subjecting a Na dimer to a homogeneous vector potential



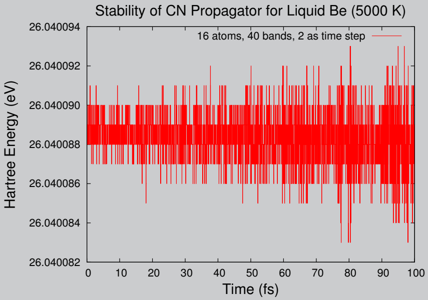


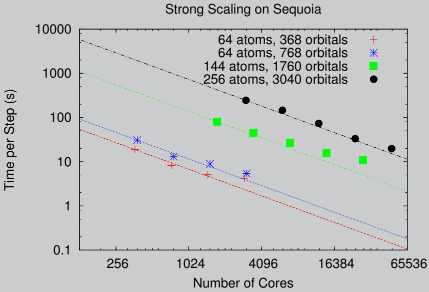


- **Time evolved dipole moment → polarizability/optical absorption**

Implementation Details

- **Ehrenfest-TDDFT in VASP:**
  - Uses PAW method
  - Crank-Nicolson time integration w/gauge correction
  - Demonstrated scalability on BGQ
  - 1 of 3 implementations for extended systems
- **Advantages:**
  - Easier to scale than BOMD
  - Lower cost complexity
  - “Real” information about excitations
- **Disadvantages:**
  - Small time step





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- **Electronic contribution:** dielectric response to charged particle

$$\delta\rho(\mathbf{r},t) = \int dt' \int d\mathbf{r}' \chi_{d,d}(\mathbf{r},\mathbf{r}',t-t') V_{ion}(\mathbf{r}' - \mathbf{v}t')$$

- Average force of medium on ion as a function of velocity and Z
- **BOMD:** stopping power zero
- **Ehrenfest-TDDFT:** agrees well with experiment
- **Note:** Movies are 2D projection of 3D simulation

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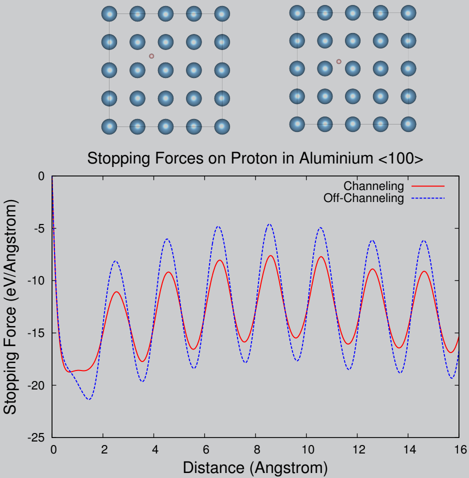
Stopping Validation



- Validation against Correa, et. al., PRL **108**, 213201 (2012)
- **Proton stopping in fcc Al**
  - 193 electrons
  - 20 k-points in BZ
  - Fixed resolution of path
  - $\Delta t \leq 2$ as
- Experimental error $\sim$ 10%
- Disagreement beyond peak
  - Core excitations?
  - Trajectory sampling?

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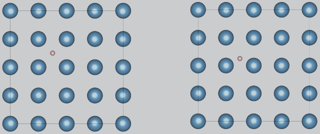

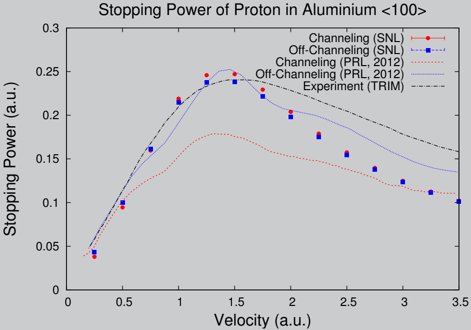

Compared to Correa, et. al., PRL **108**, 213201 (2012)

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Stopping in WDM

- Cold metallic systems are not our primary interest:
  - Warm dense systems
  - Heterogeneous systems (e.g., GDP, Xe+D/T, etc.)

- Stopping in warm dense Be
- Different paths show stronger variation in stopping
- Characteristic of condensed phase rather than plasma
- Gathering data for model
  - Average nearest neighbor distance to projectile
  - Other dependencies?

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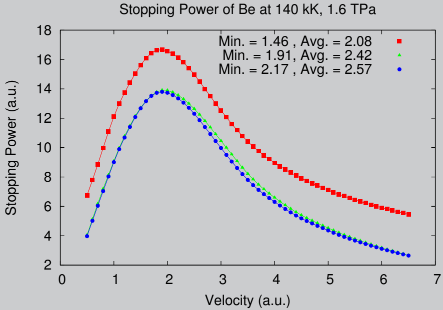

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X-Ray Thomson Scattering

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- Compute response to $V_{ext}(\mathbf{r}, t) = V_0 e^{i\mathbf{k}\cdot\mathbf{r}} f(t)$
- Studying conditions in Lee, et. al., PRL **102**, 213201 (2009)
- 3x compressed Be at T=13 eV, measured in collective regime

- **Method:**
  - Ion configuration from DFT-MD
  - Compute Mermin state
  - Integrate TD-KS equations
  - Ramp up x-ray pulse
  - Record $\Delta\rho(\mathbf{k}, t)$
- $\chi(\mathbf{k}, \omega) = \mathcal{F}\{\Delta\rho(\mathbf{k}, \cdot)\}(\omega)/\mathcal{F}\{V_0 f(\cdot)\}(\omega)$
- $S(\mathbf{k}, \omega) = -\frac{f(\beta_e \omega)}{\pi} \mathrm{Im}\left[\chi(\mathbf{k}, \omega)\right]$

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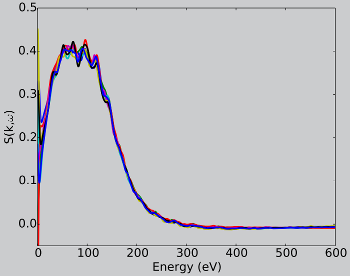

DSF for 10 independent ionic configurations.

- **Our calculation:**
  - Adiabatic AM05 xc-functional
  - Excitation has FWHM of $\approx$ 780 eV
  - Integrated for 2.5 fs at $\Delta t = 1$ as
  - $|\mathbf{k}| = 2.25 a_B^{-1}$
  - 4 electron Be PAW
- **Independent of Chihara model**

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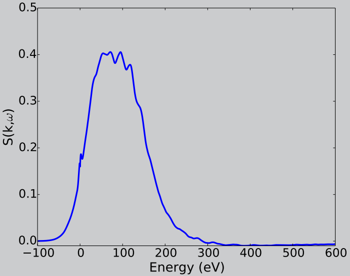

Averaged DSF including negative part of spectrum.

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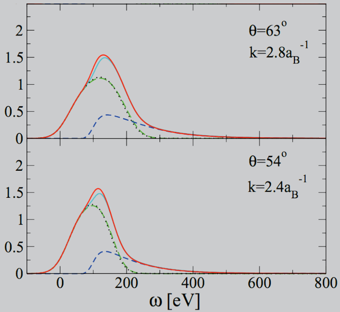

Souza, et. al., PRE **89**, 023108 (2014)

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Summary and Future Work

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- **New tool at SNL:**
  - Ehrenfest-TDDFT for coupled electron-ion dynamics in bulk
  - Stable, accurate, and scalable PAW implementation
  - Real-time electron dynamics $\rightarrow$ dielectric response
- **Ongoing work:** statistics for stopping and XRTS in WDM
- **Future work:** investigation of time-dependent current DFT
- **Long-term challenge:** electron-ion energy transfer in TDDFT?

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