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Real-Time TDDFT of Warm Dense Matter: Linear Response and Beyond

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9th International Workshop on Warm Dense Matter
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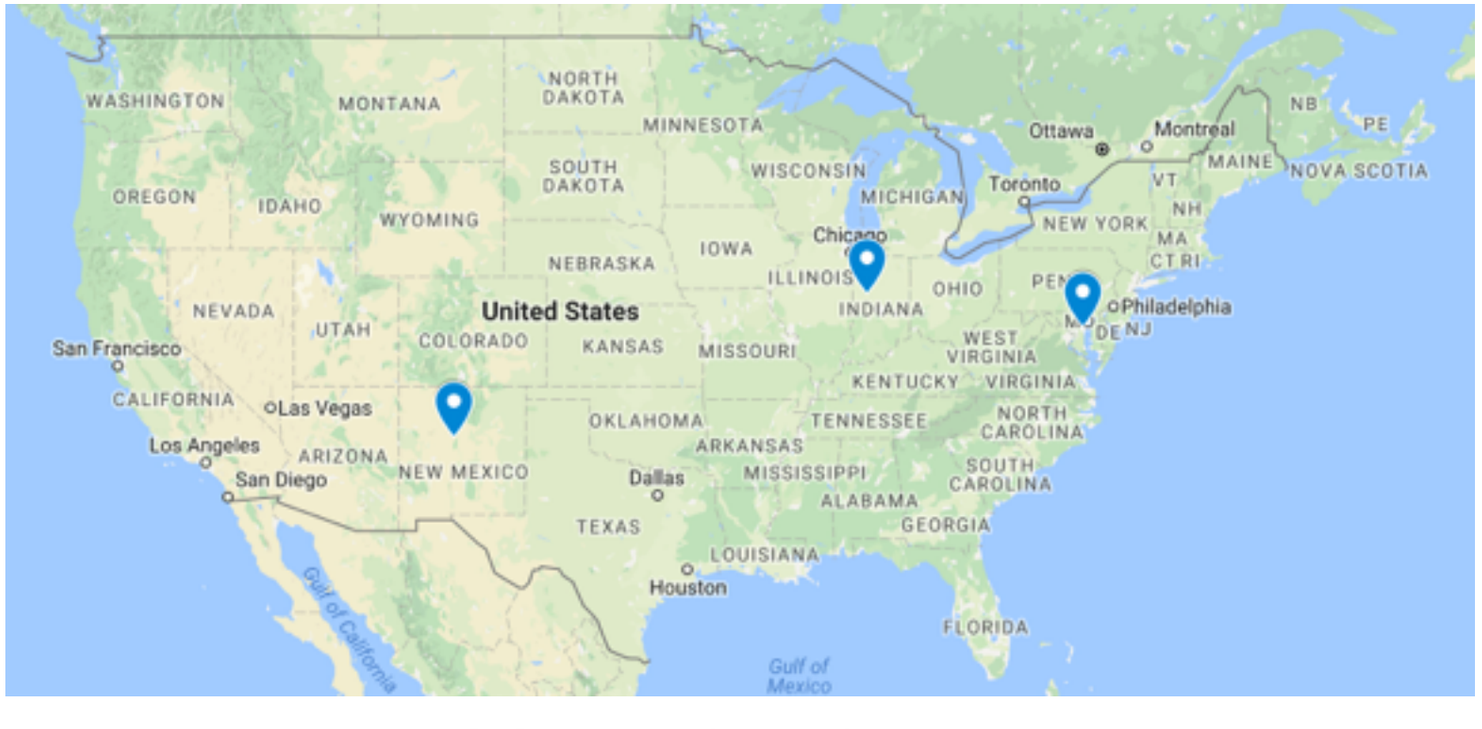
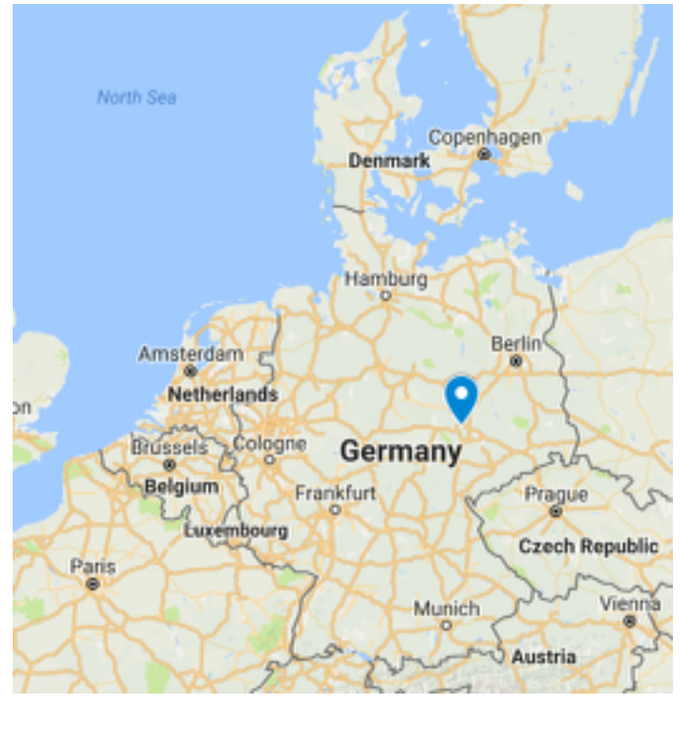
Collaborators





Many thanks to my **collaborators**

New staff from MPI Halle → **Attila Cangi**

Daniel Jensen ← New postdoc from Purdue Uni

Michael P. Desjarlais

Stephanie B. Hansen

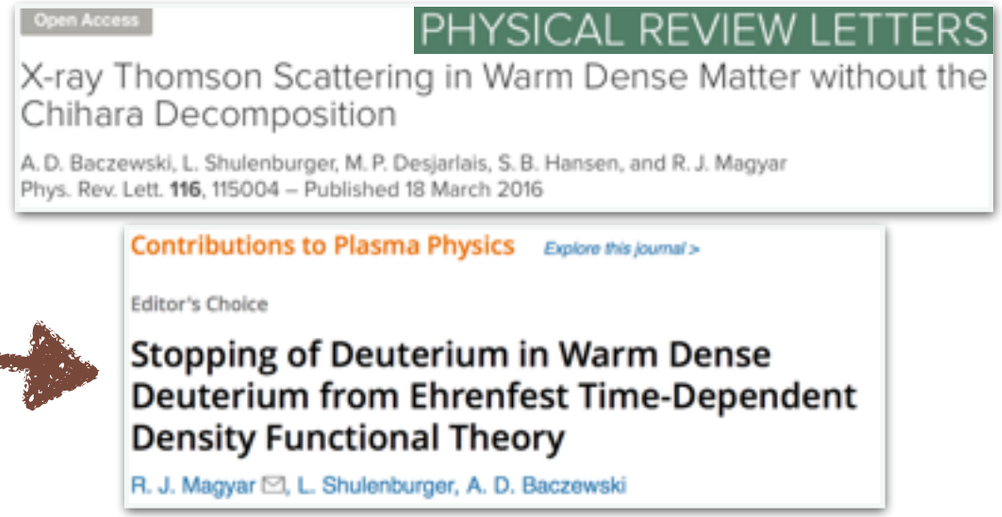
Luke Shulenburger

Now at Northrop-Grumman → **Rudolph J. Magyar**

Overview

- At Sandia, we have a **first principles** capability for studying excitations in **warm dense matter**.

- We can study:
  - Dynamic structure factor
  - Stopping power
  - Optical conductivity



- Our method is **computationally expensive**, but all electrons are treated **consistently** and we have **few free parameters.**

- Using our XRTS work as motivation, we will describe:
  - What happens when we (naively) go **beyond linear response**
  - Point to deficiencies in our TDDFT (as implemented)
  - Sketch out a path forward

- **To describe non-LTE properties, we need to expand vanilla TDDFT**

TDDFT for XRTS

Open Access

PHYSICAL REVIEW LETTERS

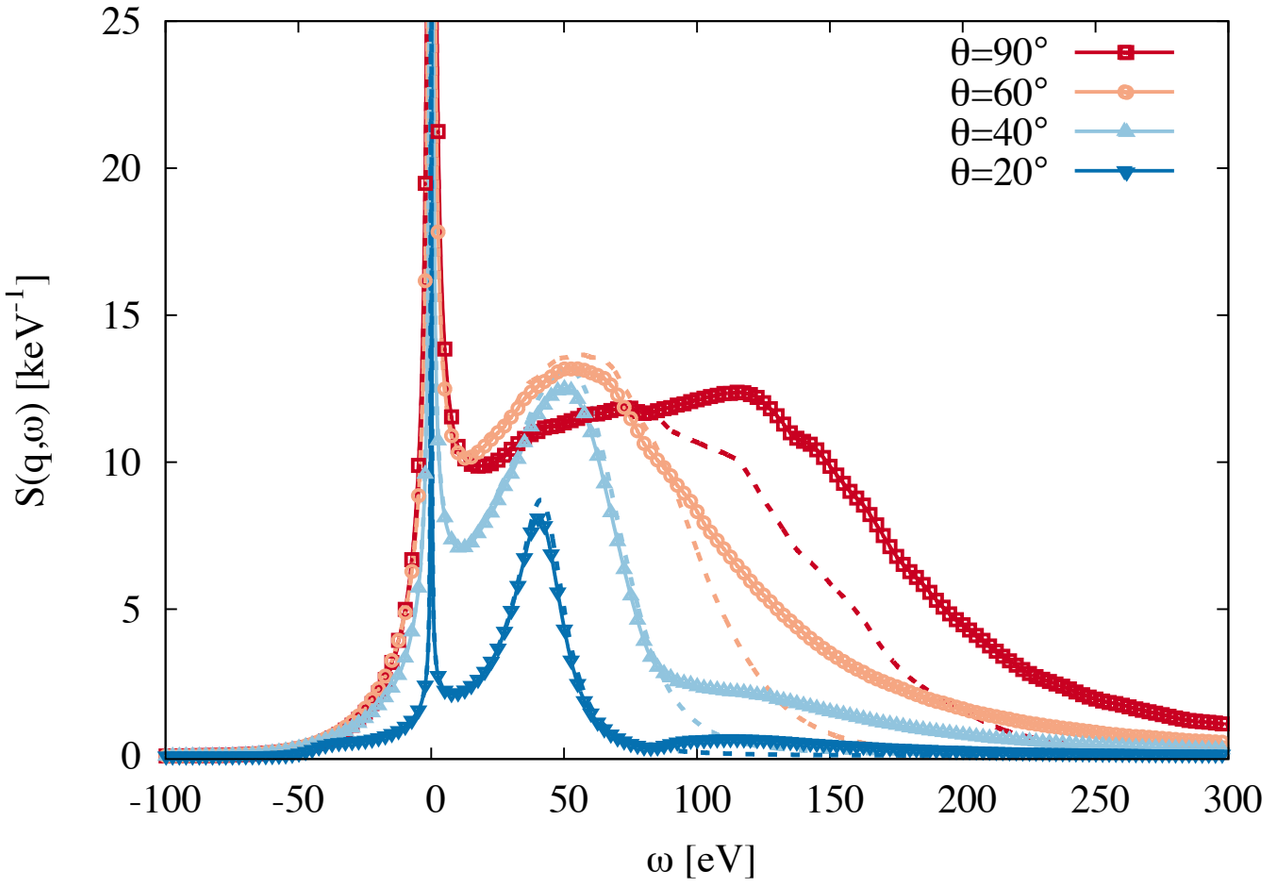
X-ray Thomson Scattering in Warm Dense Matter without the Chihara Decomposition

A. D. Baczewski, L. Shulenburger, M. P. Desjarlais, S. B. Hansen, and R. J. Magyar

Phys. Rev. Lett. **116**, 115004 – Published 18 March 2016

DSF of 3x-compressed Be

Lee, et al., PRL **102** (2009)



Consistent treatment of all electrons

Dashed lines = **frozen** K-shell

Decorated lines = **thawed** K-shell

TDDFT for XRTS

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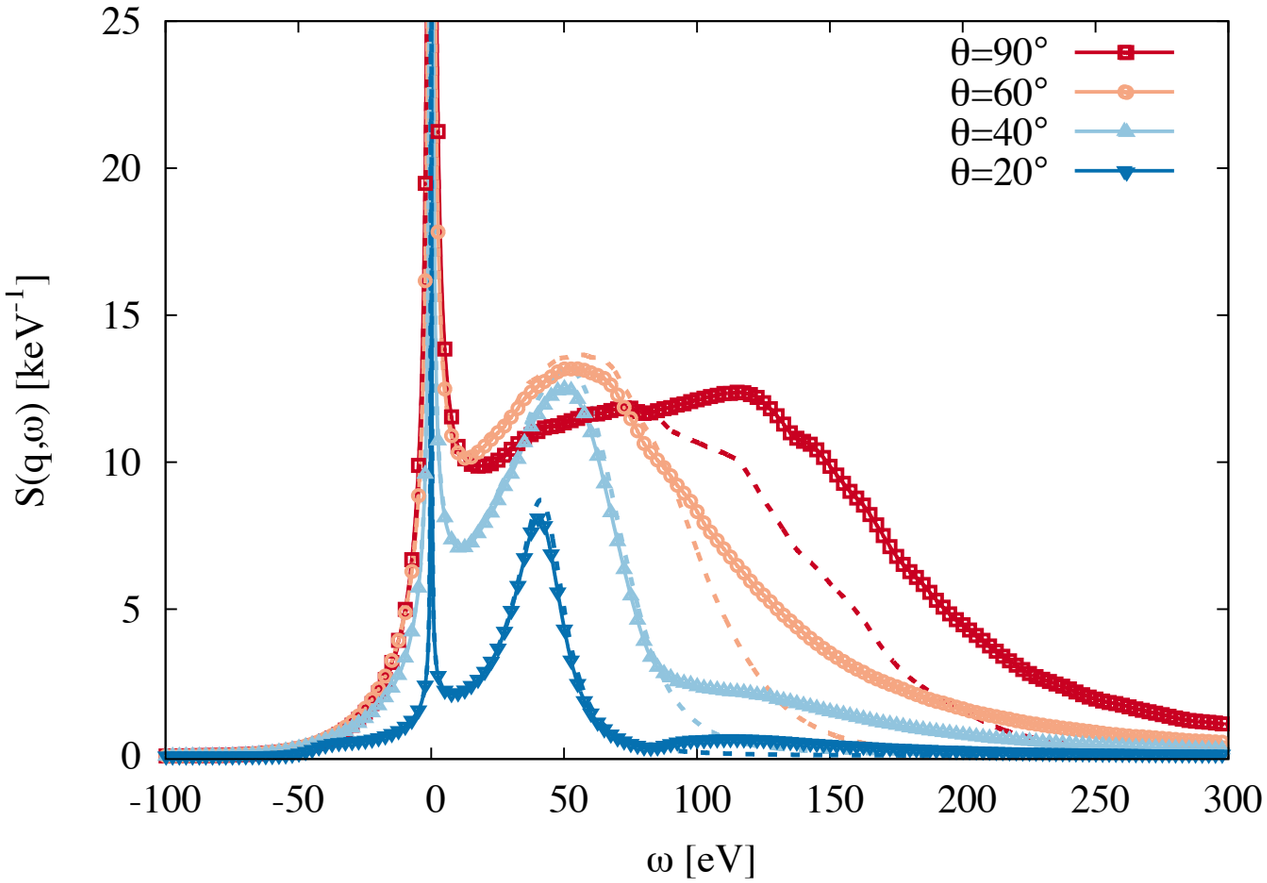

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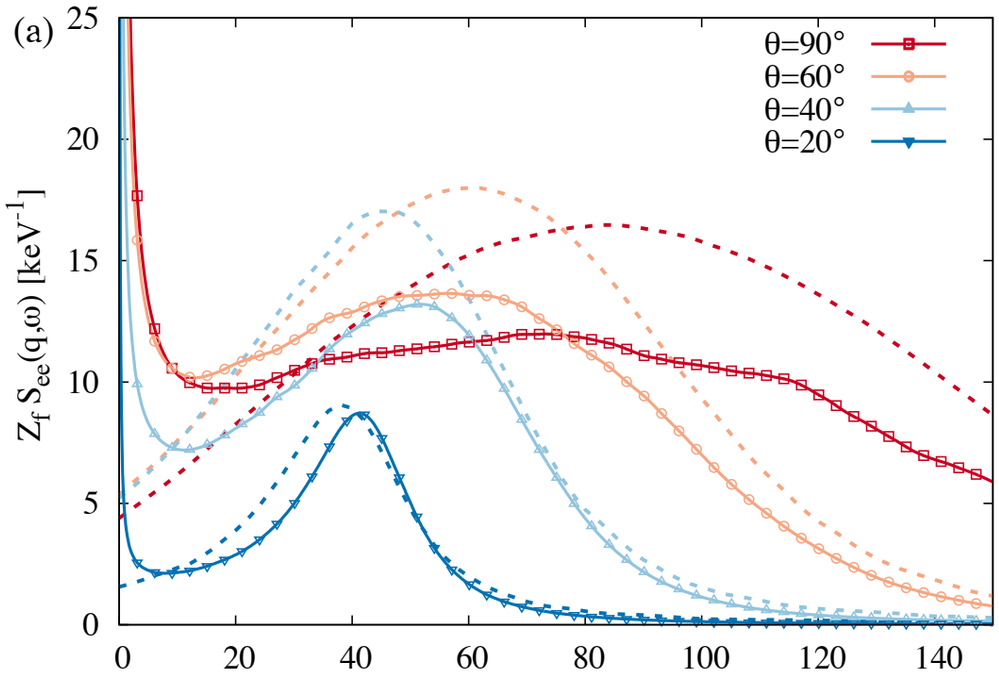

Dashed = Mermin dielectric + ab-initio conductivity

Plagemann, et. al., NJP **14** (2012)

Dotted = **TDDFT "free-free"**

TDDFT for XRTS

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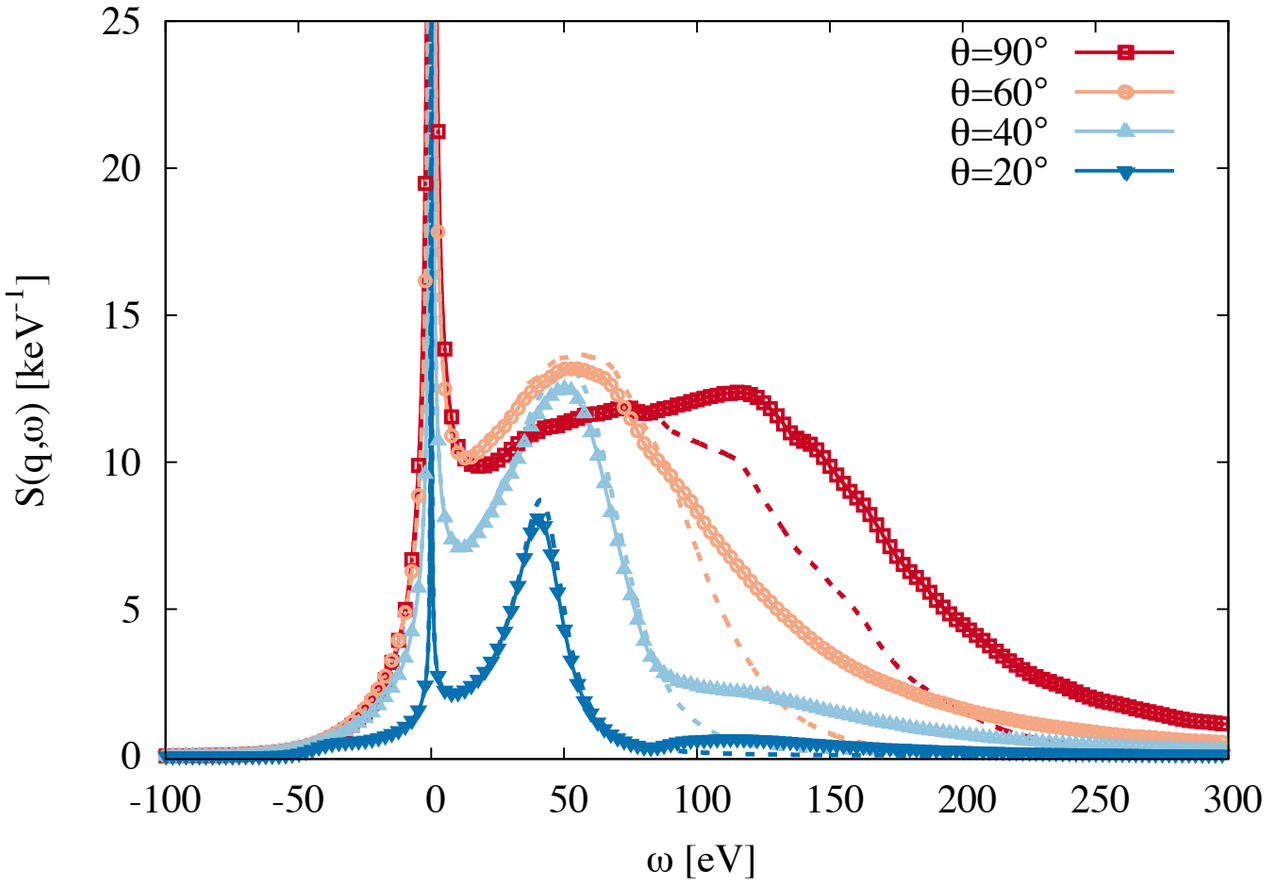

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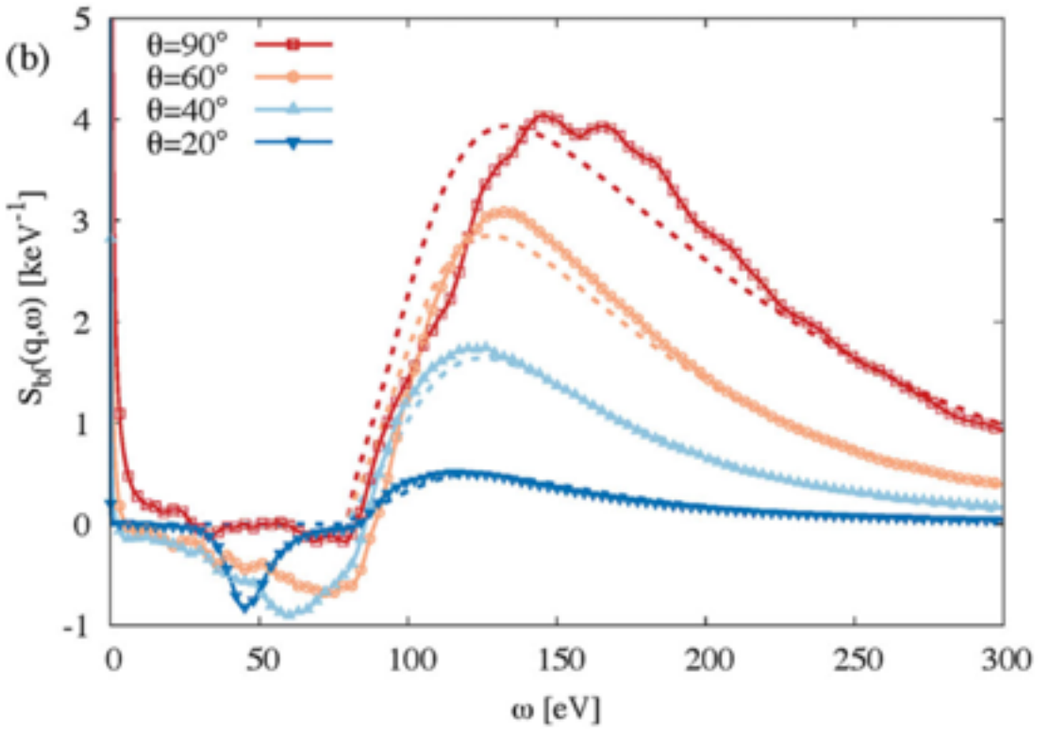

Dashed = Average atom with Slater exchange

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

Dotted = **TDDFT "bound-free"**

Real-time thermal TDDFT

- Density built from **TD** orbitals with **fixed** Mermin weights

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

- Orbitals verify the **TD Kohn-Sham equation**

$$i\frac{\partial}{\partial t}\phi_{n,\mathbf{k}}(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_S\left[\rho\right](\mathbf{r},t)\right)\phi_{n,\mathbf{k}}(\mathbf{r},t)$$

- Potential = **x-ray probe envelope** + **adiabatic** Hxc approximation

$$v_S\left[\rho\right](\mathbf{r},t) = v_{ext}(\mathbf{r},t) + v_H\left[\rho\right](\mathbf{r},t) + v_{xc}\left[\rho\right](\mathbf{r},t)$$

- **Fluctuation-dissipation** gives us an **exact** DSF functional

$$\chi_{\rho,\rho}(\mathbf{q},-\mathbf{q},\omega) = \frac{\delta\rho(\mathbf{q},\omega)}{\delta v_{ext}(\mathbf{q},\omega)} \rightarrow S(\mathbf{q},\omega) = -\frac{1}{\pi}\frac{\Im\left[\chi_{\rho,\rho}(\mathbf{q},-\mathbf{q},\omega)\right]}{1-e^{-\omega/k_BT_e}}$$

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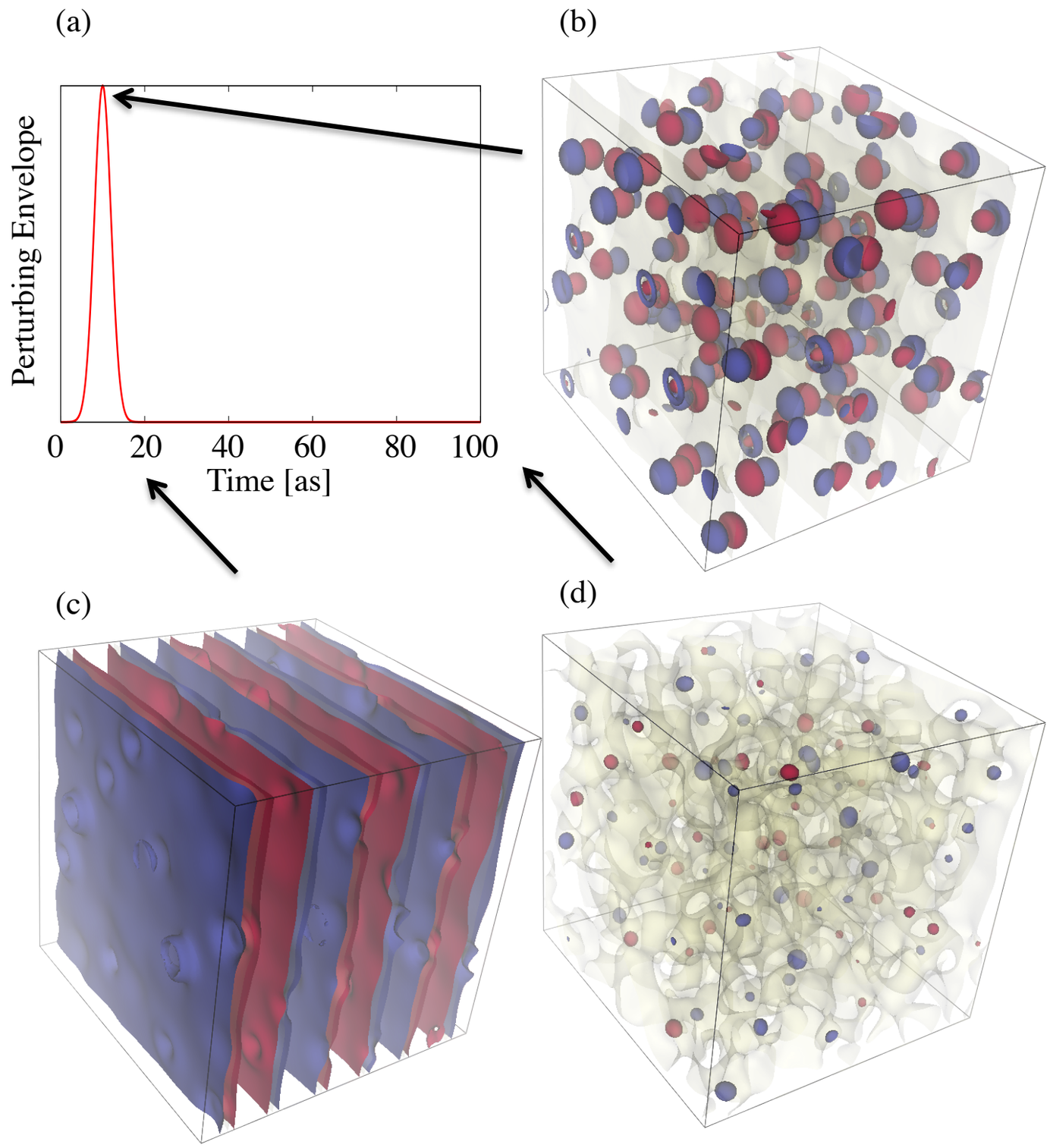
Cartoons > mathematics

A. Time-dependence of perturbing pulse

B. Density response at pulse peak

C. Density response at response peak

D. Plasmons ring around system at late times



Why real-time thermal TDDFT?

Energy domain

$$\chi_{\rho,\rho} = \chi^0_{\rho,\rho} + \chi_{\rho,\rho}\left(v_C + f_{xc}\right)\chi^0_{\rho,\rho}$$

- Diagonalize dense matrix (cubic)
- Requires many unoccupied virtual states
- Limited scalability (100s of CPUs)
- Restricted to linear response

Time domain

$$i\frac{\partial}{\partial t}\phi_{n,\mathbf{k}}(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_S\left[\rho\right](\mathbf{r},t)\right)\phi_{n,\mathbf{k}}(\mathbf{r},t)$$

- Propagate KS orbitals (linear)
- Requires only thermally occupied states
- Massively parallel implementation (100ks of CPUs)
- Linear response is simply one limit of the theory

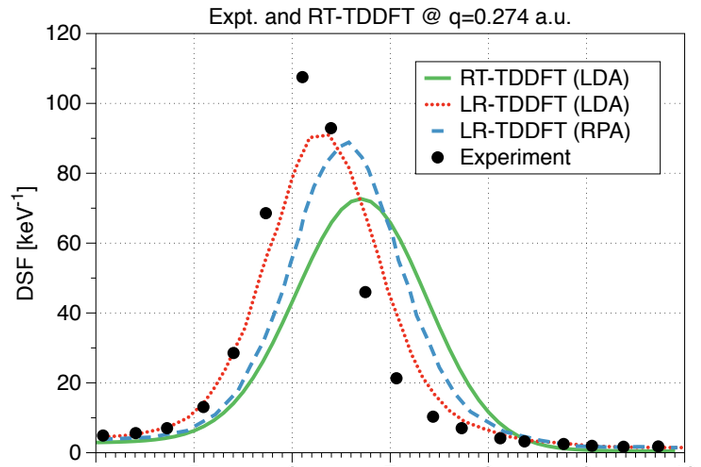
- Just because we CAN go beyond linear response, doesn't mean it is easy…

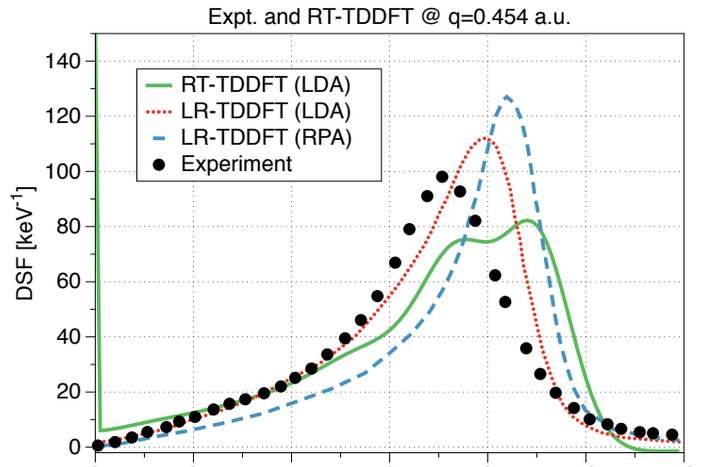
How does this compare to experiment?

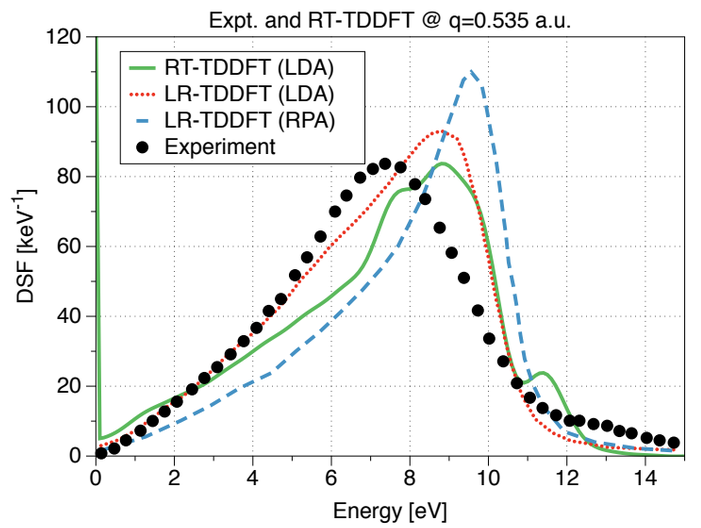
High resolution data from condensed matter **calibrates expectations**

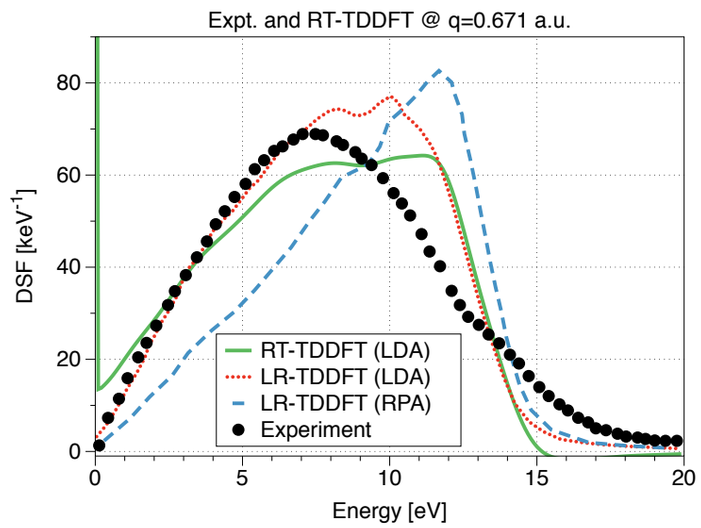
Compare to energy domain TDDFT and experiment from **Cazzaniga, et al., PRB (2011)**

RPA = time-dependent Hartree approximation, but **not** applied to jellium









3x-compressed Be, non-collective

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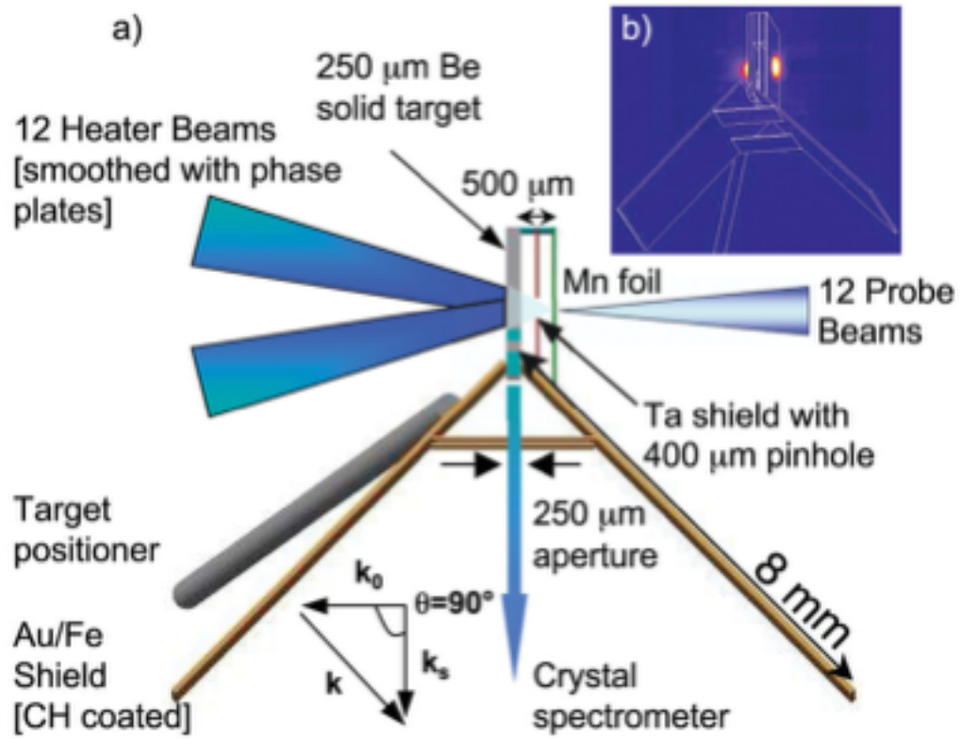
X-Ray Thomson-Scattering Measurements of Density and Temperature in Shock-Compressed Beryllium

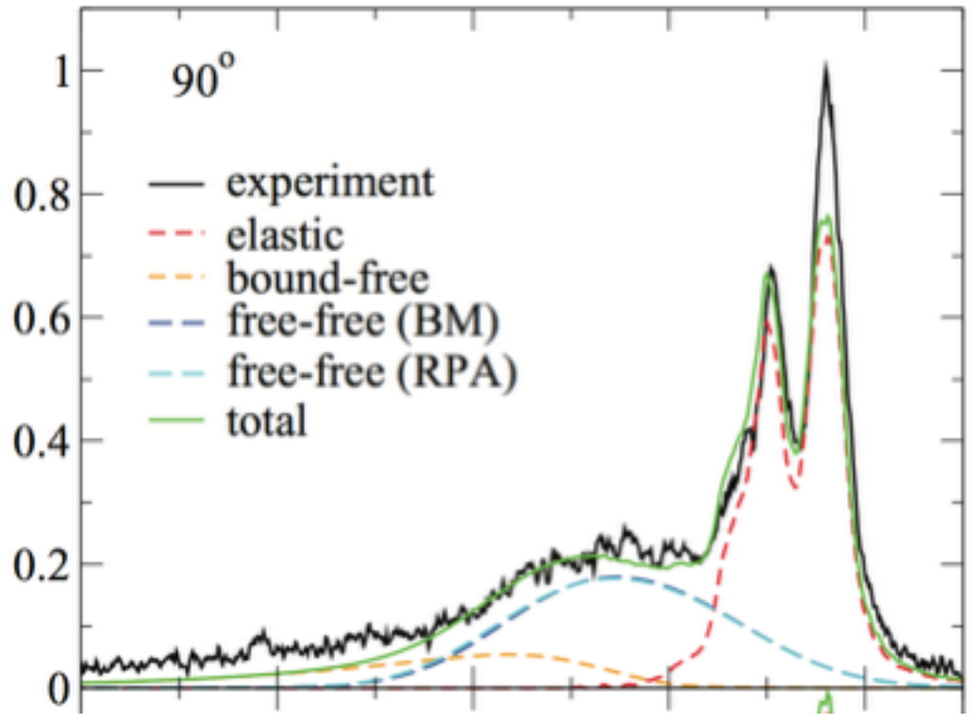
H. J. Lee, P. Neumayer, J. Castor, T. Döppner, R. W. Falcone, C. Fortmann, B. A. Hammel, A. L. Kritcher, O. L. Landen, R. W. Lee, D. D. Meyerhofer, D. H. Munro, R. Redmer, S. P. Regan, S. Weber, and S. H. Glenzer

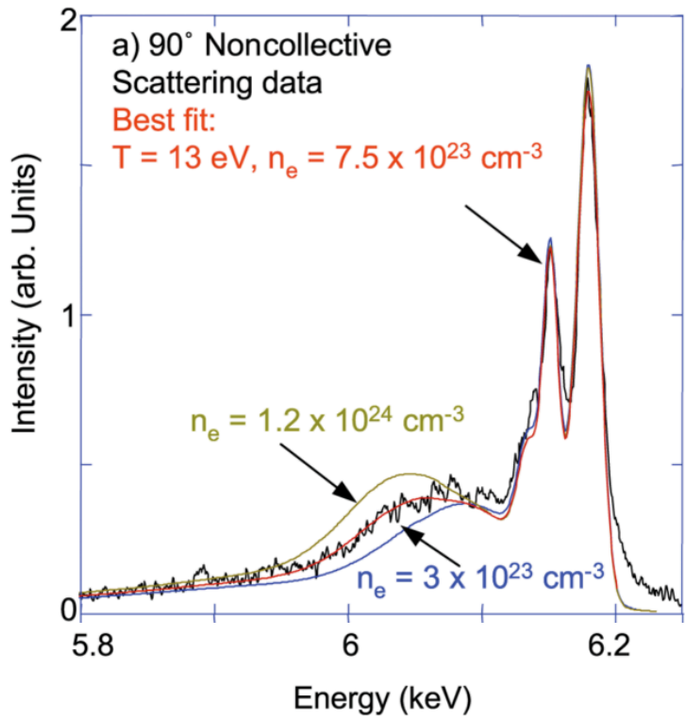
Phys. Rev. Lett. **102**, 115001 – Published 16 March 2009

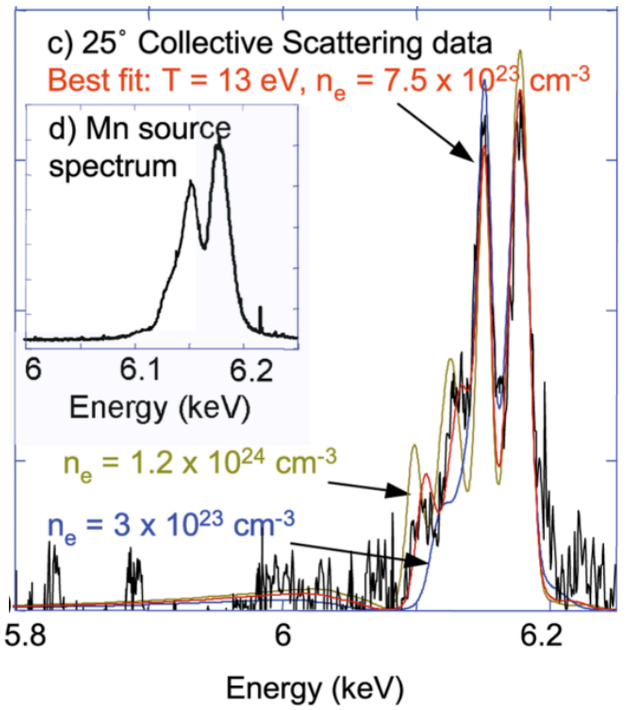
3x-compressed (+/-7%) Be
Ti=Te=13 eV (+/- 3 eV)



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







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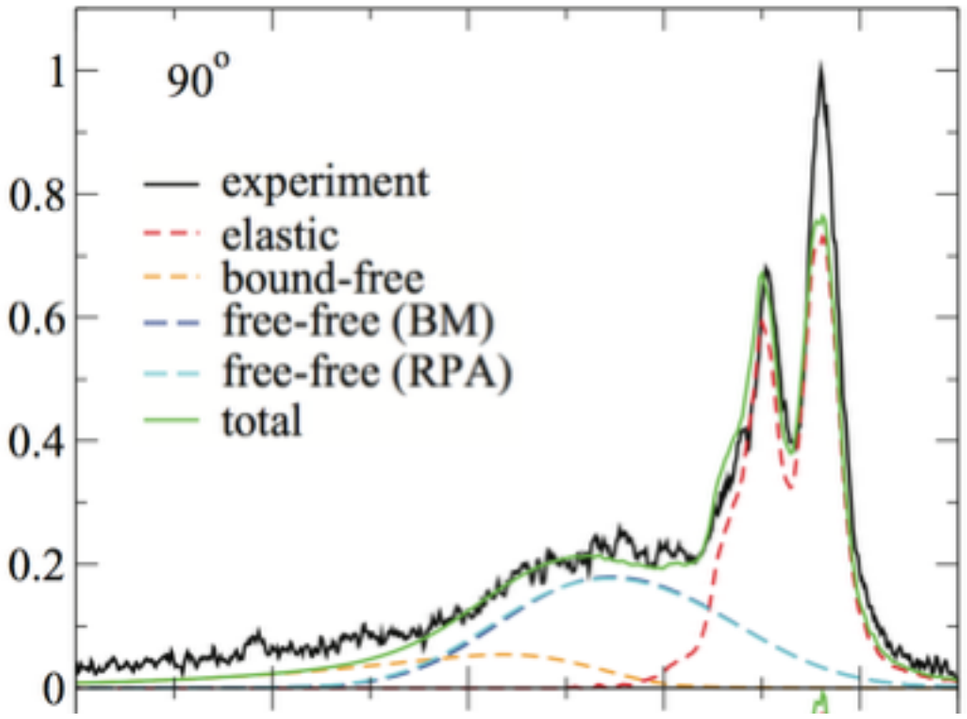
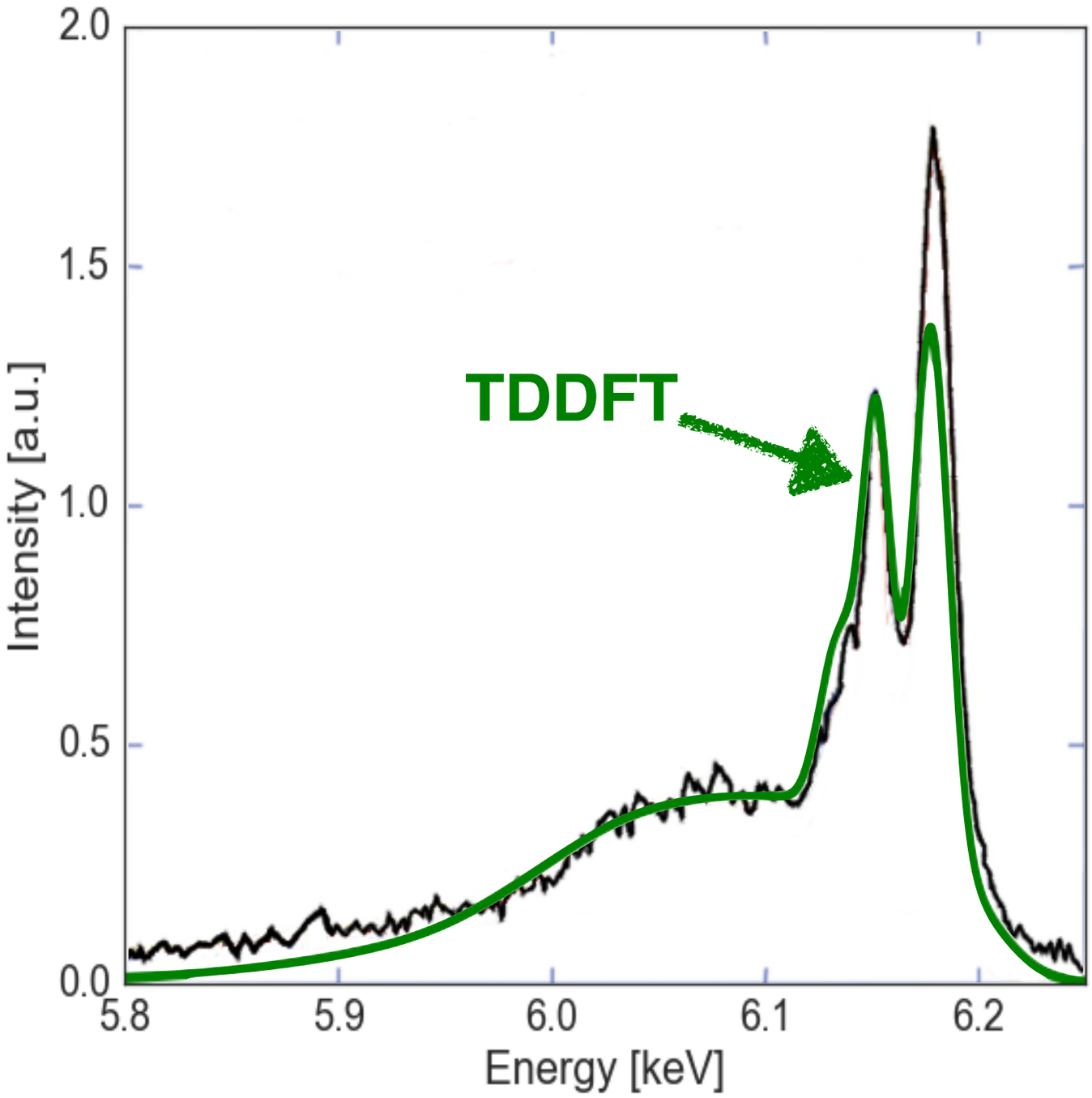
3x-compressed Be, non-collective

- Convolving with Mn source yields **agreement with experiment** comparable to other levels of theory

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





Isochoric Al, collective

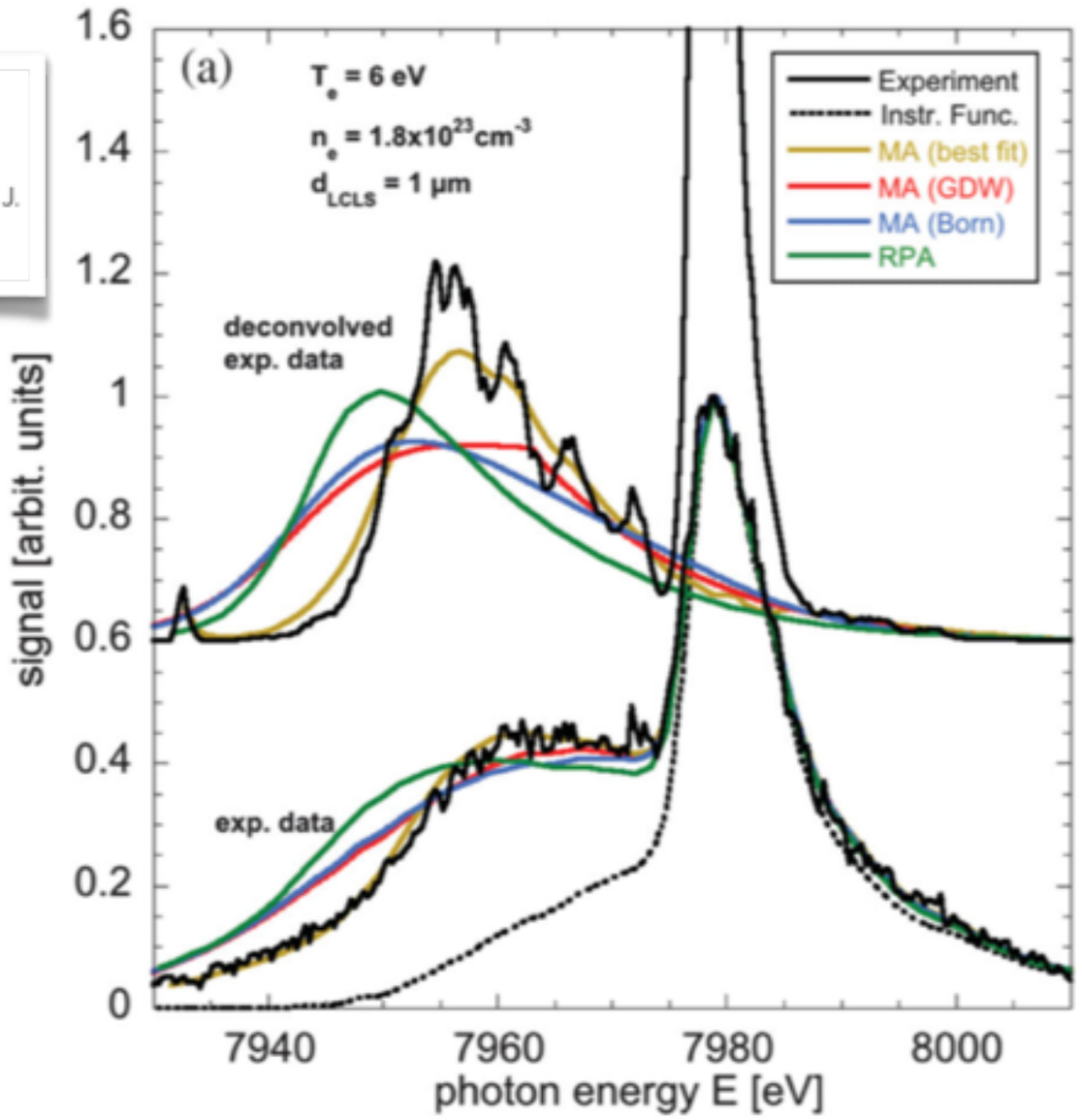
Free-Electron X-Ray Laser Measurements of Collisional-Damped Plasmons in Isochorically Heated Warm Dense Matter

P. Sperling, E. J. Gamboa, H. J. Lee, H. K. Chung, E. Galtier, Y. Omarbakiyeva, H. Reinholz, G. Röpke, U. Zastrau, J. Hastings, L. B. Fletcher, and S. H. Glenzer

Phys. Rev. Lett. **115**, 115001 – Published 9 September 2015

- LCLS beam used to isochorically heat and probe **Al to Te = 6 eV**

- Collision models **beyond Born approximation** needed for fit



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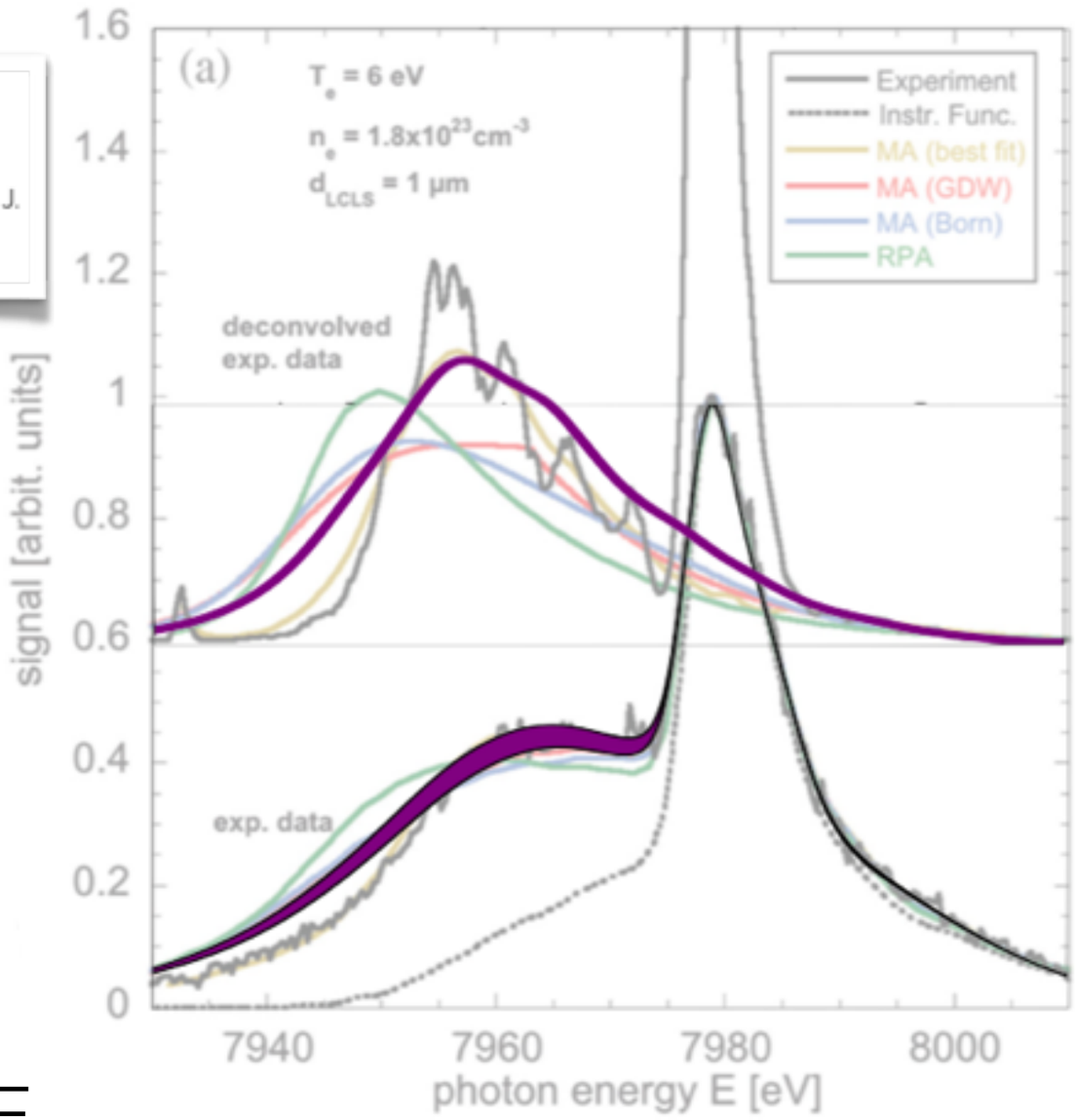

- Collision models **beyond Born approximation** needed for fit

- TDDFT uses 11-electron PAW + PBE
- Spread indicates plausible range of ion features

Can we simulate both the pump and the probe?

Can TDDFT capture isochoric heating?

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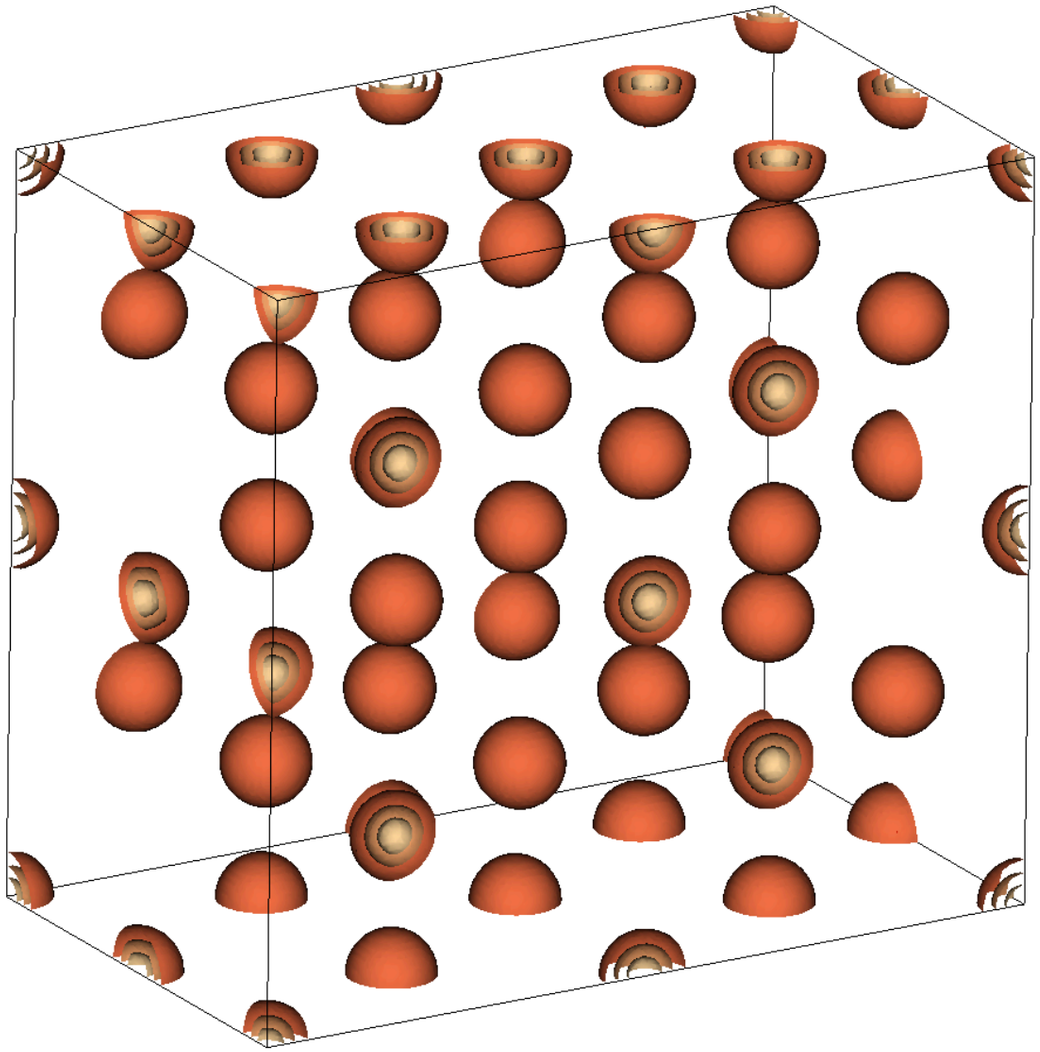
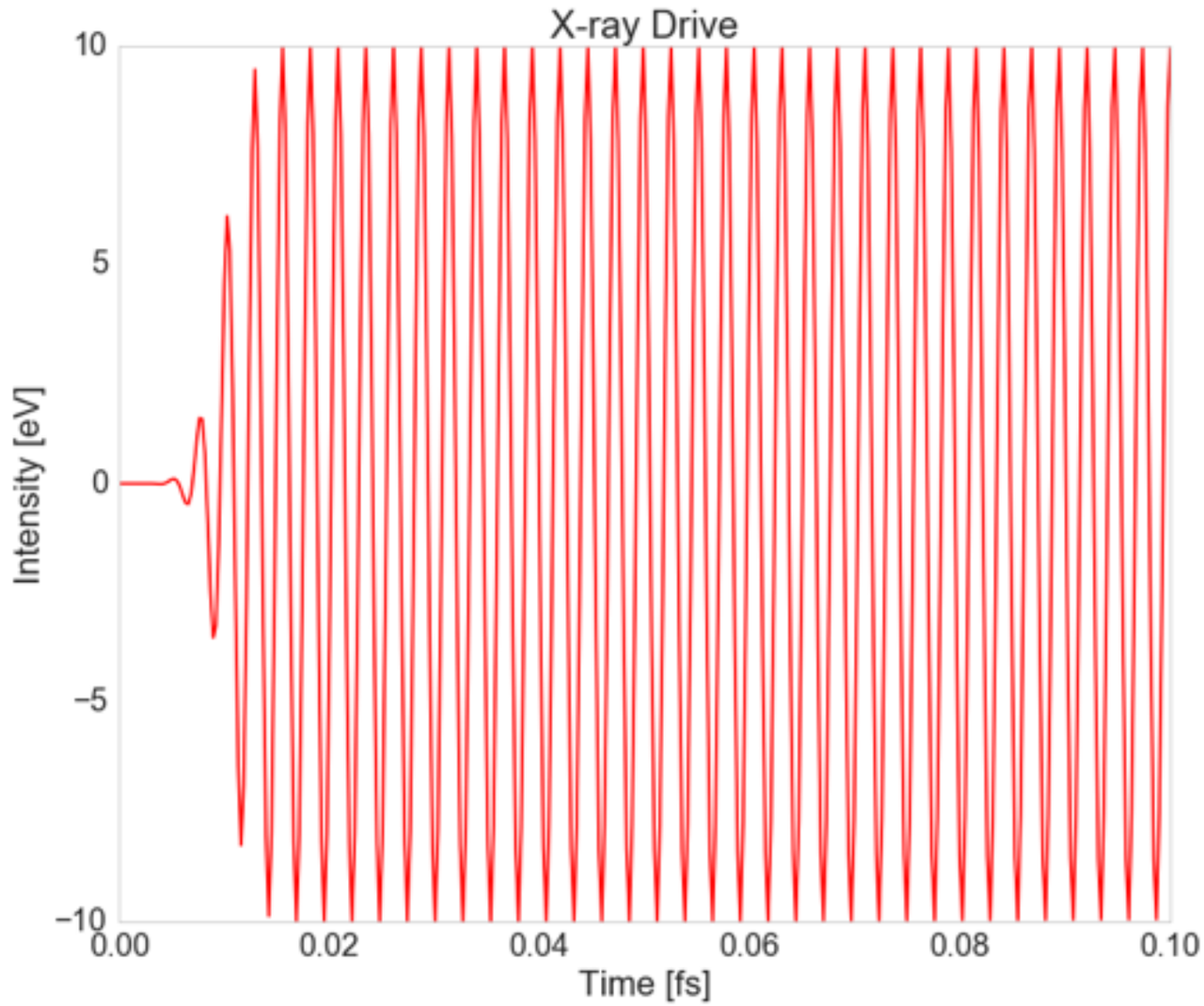
Ambient Be...



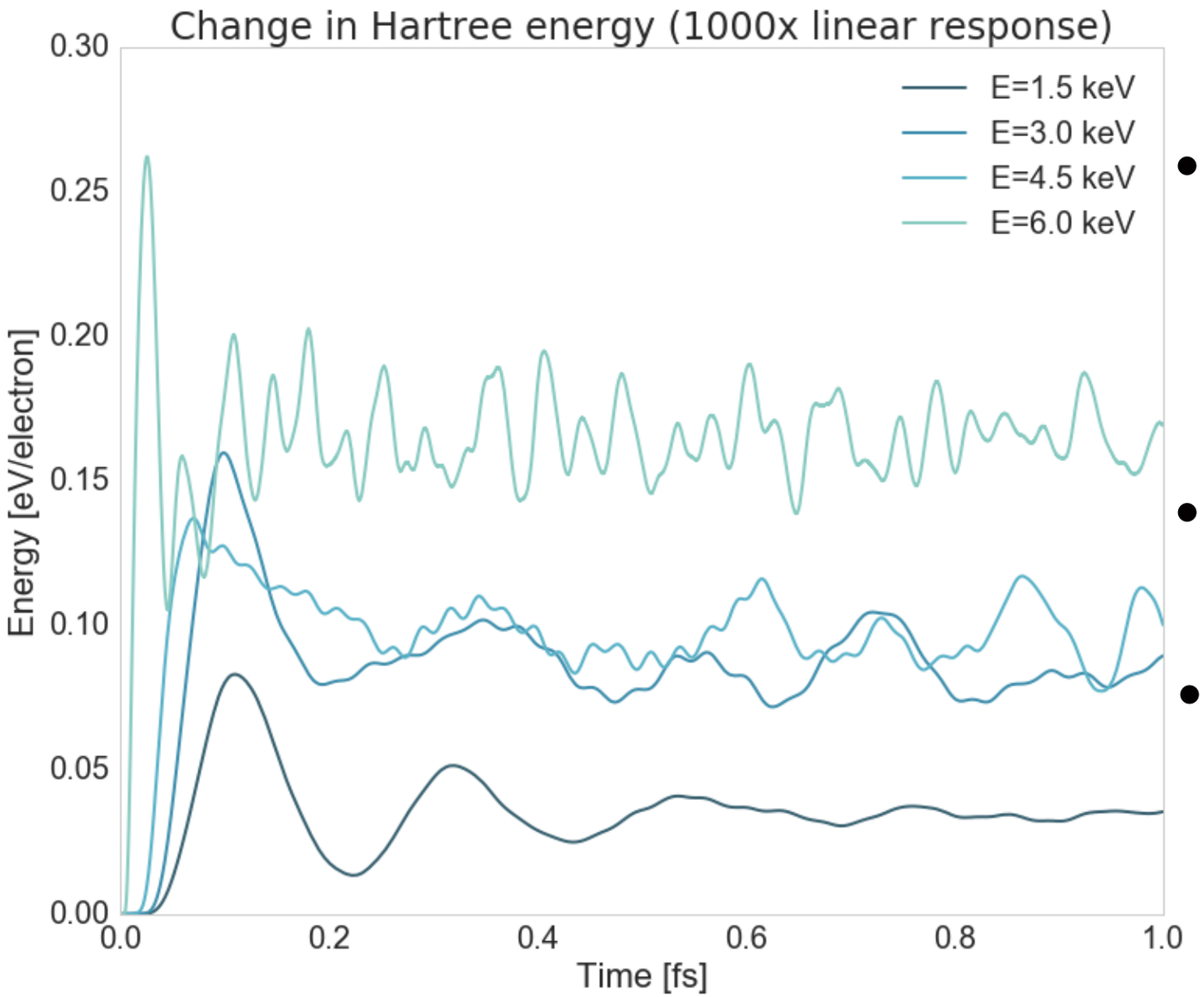
...exposed to 1.5 keV x-ray



Linear response: time step set by **bound-free energy scale**

Beyond linear response: time step set by **x-ray energy scale**

Strongly driven ambient Be

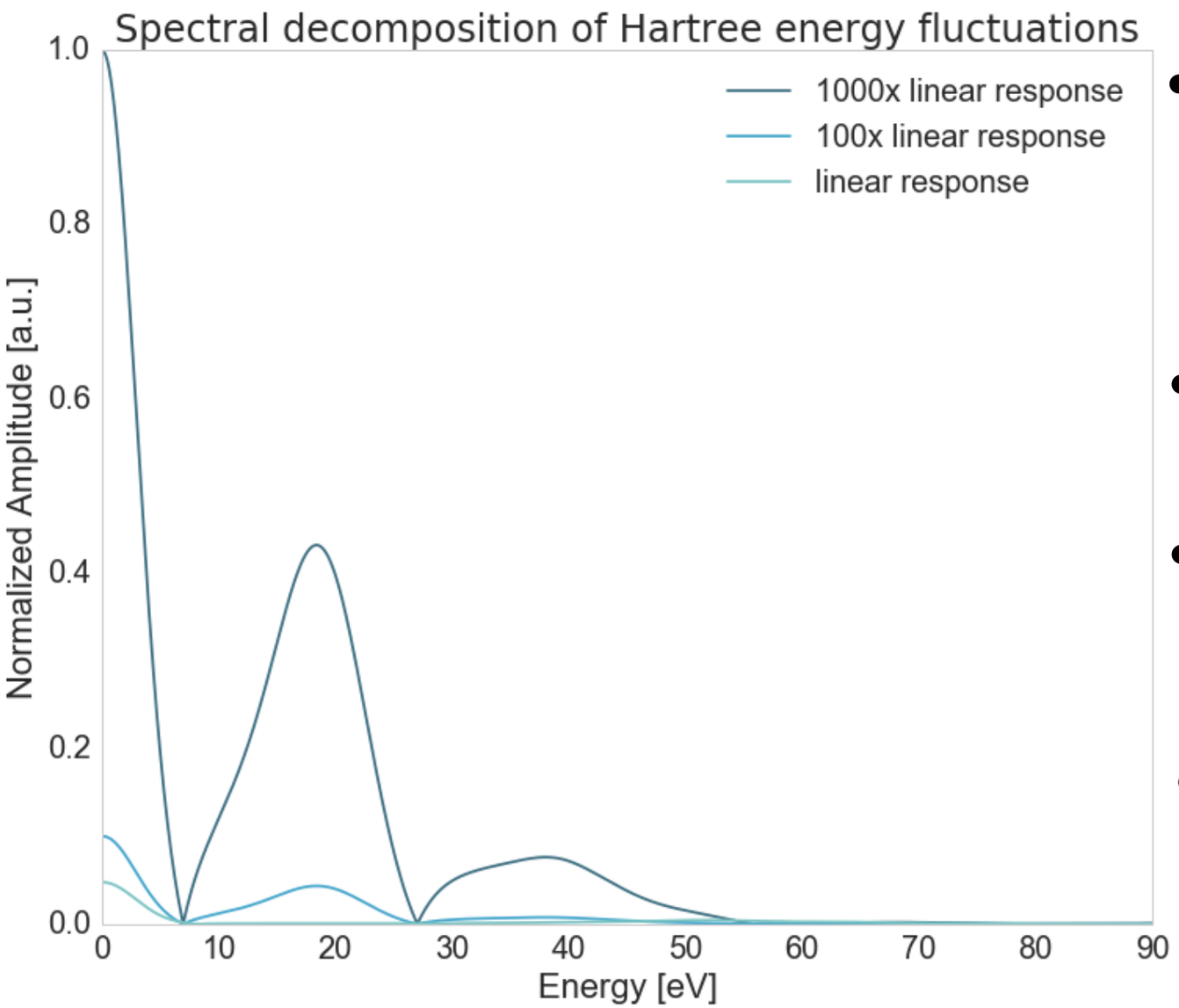


- Drive amplitude is 1000x larger than amplitude that gives **linear response DSF**

- **Hartree energy** is observable

- Increases for < 1 fs and **saturates** for all energies

Strongly driven ambient Be (cont.)



- Spectral decomposition **normalized by drive amplitude**
- **Plasmons** driven off-resonance
- Coupling to K-shell **does not** show up in Hartree energy…
- K-shell band energy **follows x-ray drive…**

What is missing?

1.) Kohn-Sham occupancies **don't know how to change!**

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

2.) Even if they could, **we don't have high (~keV) energy states** into which we can directly drive core electrons…

3.) Nor do we have the possibility of capturing **Auger processes…**

4.) Not only do we need to treat these excitations, but we need a reliable method for capturing their **equilibration…**

Where do we go from here?

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State-of-the-art Kinetics

- Multi-configuration atoms
- Electrons equilibrate instantly or classically
- Heuristic treatment of coupling to environment

Real-time TDDFT

- Single configuration atoms
- Electrons can’t equilibrate on their own
- **Consistent treatment of coupling to environment**

Where do we go from here?

- Partition Hamiltonian into low and high energy sectors:

$$\mathcal{H}_{KS}(\mathrm{Be}^{n+}) + \mathcal{H}_{HE} + \mathcal{H}_{KS,HE}(\mathrm{Be}^{n+})$$

KS-DFT Hamiltonian for each charge config. **Quasi-free electrons** **Coupling at fixed total charge**

- Integrate out high energy sector / create self-energy

$$\mathcal{G}(\mathrm{Be}^{n+}) = \mathcal{G}_{KS}(\mathrm{Be}^{n+}) + \mathcal{G}_{KS}(\mathrm{Be}^{n+})\Sigma(\mathrm{Be}^{n+})\mathcal{G}(\mathrm{Be}^{n+})$$

Art is in creating an efficient approximation
Another self-energy couples charge configs.

- Solve Kadanoff-Baym equations with x-ray drive and ambient initial condition

$$\left[i\frac{d}{dz} - \bigoplus_n \mathcal{H}_{TDKS}(\mathrm{Be}^{n+}, z)\right]\mathcal{G}^o(z,z') = \delta(z,z') + \int_\gamma dz' \tilde{\Sigma}(z,z')\mathcal{G}^o(z,z')$$

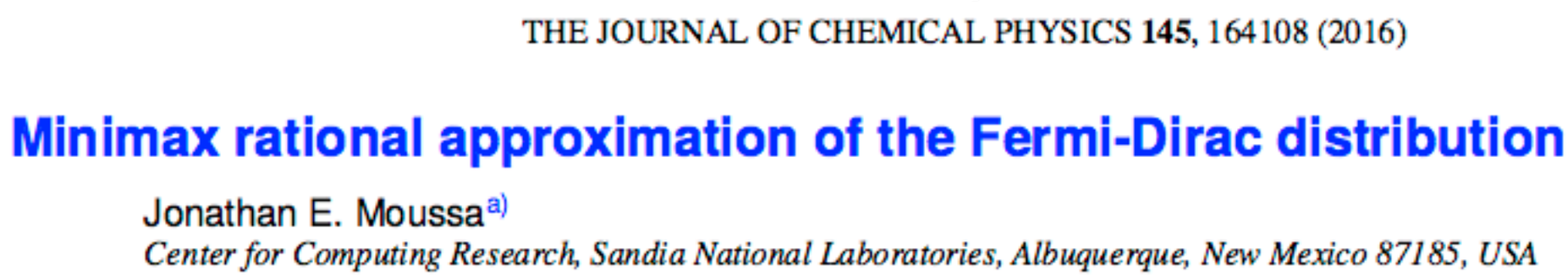
Adiabatic TDDFT Hamiltonian in each charge sector

Self-energy approximation bootstraps in non-adiabatic effects

Conclusion

Real-time TDDFT is a powerful tool for capturing linear response of warm dense matter - but important non-LTE physics can only be captured by extending the theory

- Development of such a formalism is ongoing
- Green's functions in WDM facilitated by recent results from Moussa



THE JOURNAL OF CHEMICAL PHYSICS **145**, 164108 (2016)

Minimax rational approximation of the Fermi-Dirac distribution

Jonathan E. Moussa[a)]
Center for Computing Research, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

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Static structure factor

- DFT may **fail** low q electron-electron static structure factor

Ab initio approach to model x-ray diffraction in warm dense matter

J. Vorberger and D. O. Gericke
Phys. Rev. E **91**, 033112 – Published 24 March 2015

- TDDFT gives **exact functional** for static structure factor …**DFT does not**

$$S_0(\mathbf{q}) = \int_{-\infty}^{\infty} d\omega S(\mathbf{q}, \omega)$$

- TDDFT agrees well with:
  - Quantum Monte Carlo
  - Configuration Interaction