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Real-time TDDFT beyond the linear response regime

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Overview

TDDFT is a promising capability for *ab initio* linear response calculations in WDM

- Dynamic structure factor [1]
- Optical conductivity
- Stopping power* [2]

* Technically beyond linear response, but existing adiabatic functionals work well

Using XRTS calculations as a motivator, we will:

- See what happens beyond linear response (naively)
- Point to deficiencies in TDDFT, as implemented
- Sketch out a framework for *ab initio* x-ray heating

To describe non-LTE properties, we need to go beyond adiabatic TDDFT

Linear response in real-time

Time-evolve orbitals from Mermin Kohn-Sham DFT

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

Weak perturbation looks like **probe x-ray envelope**

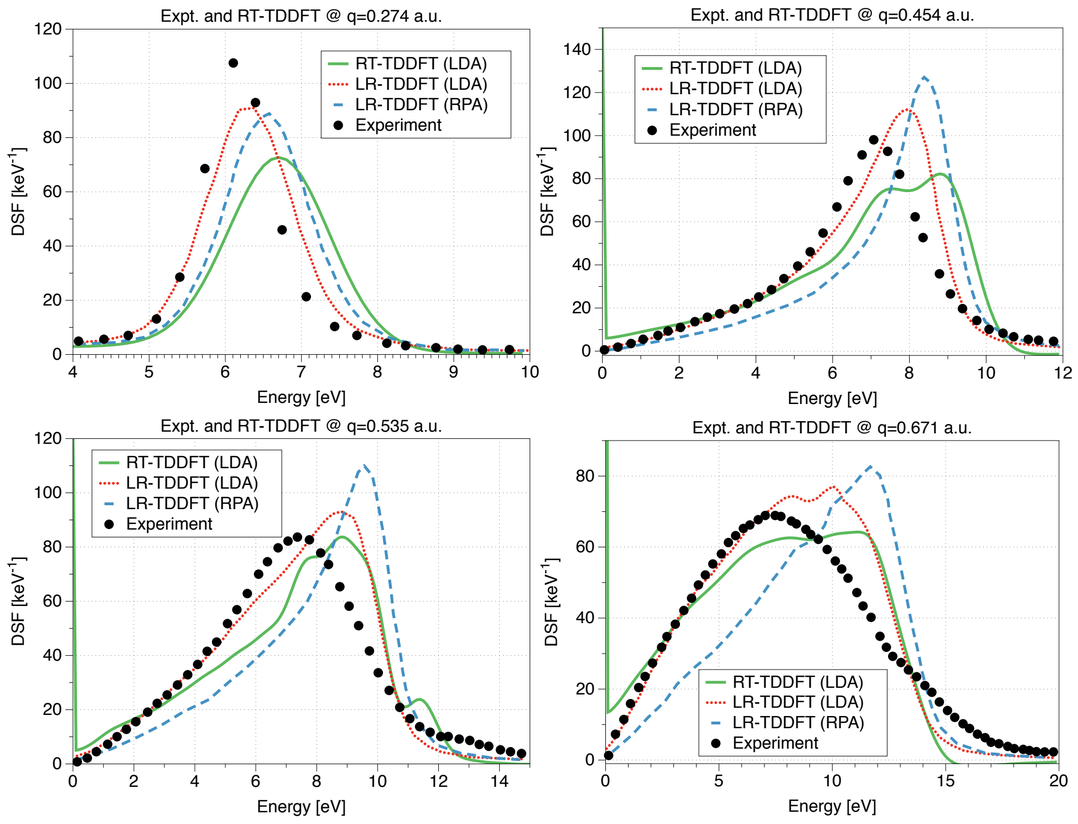
$$v_S\left[\rho\right](\mathbf{r},t) = v_{ext}(\mathbf{r},t) + v_H\left[\rho\right](\mathbf{r},t) + v_{xc}\left[\rho\right](\mathbf{r},t)$$

Build density from **TD orbitals + fixed Mermin weights**

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

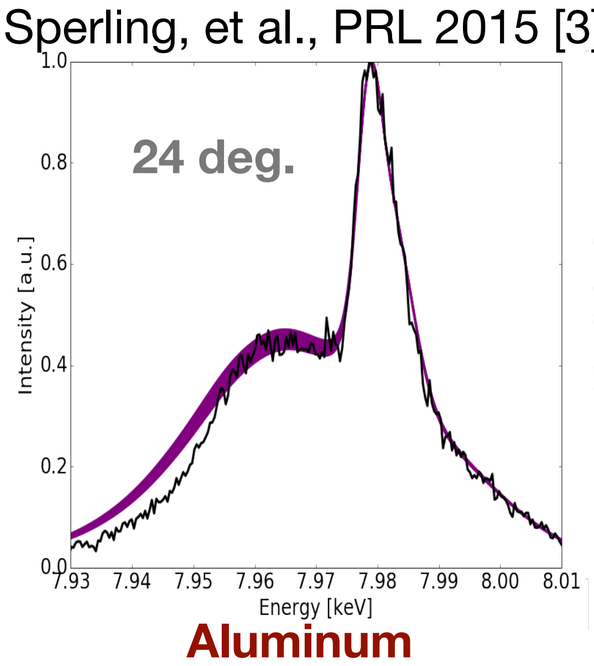
$$\chi_{\rho,\rho}(\mathbf{q},-\mathbf{q},\omega) = \frac{\delta\rho(\mathbf{q},\omega)}{\delta v_{ext}(\mathbf{q},\omega)} \quad\Rightarrow\quad S(\mathbf{q},\omega) = -\frac{1}{\pi}\frac{\Im\left[\chi_{\rho,\rho}(\mathbf{q},-\mathbf{q},\omega)\right]}{1-e^{-\omega/k_BT_e}}$$

Methods consistent with each other & experiment [x]



Ambient crystalline sodium

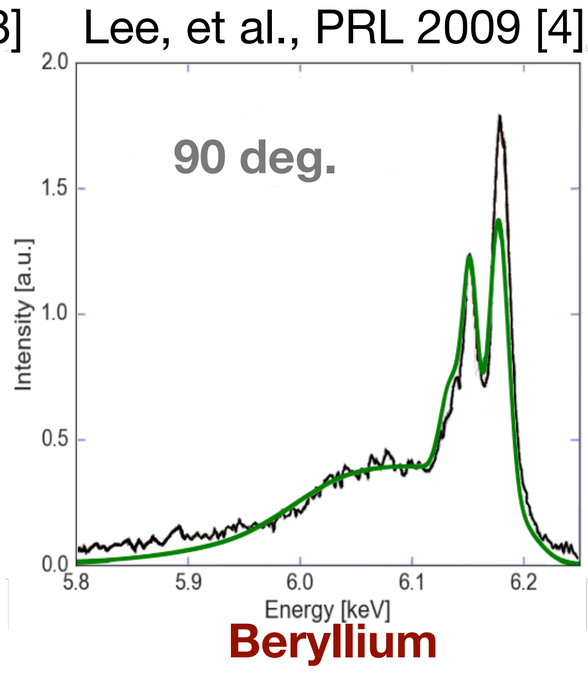
Sperling, et al., PRL 2015 [3]



Aluminum

Isochoric, Te = 6 eV

Lee, et al., PRL 2009 [4]

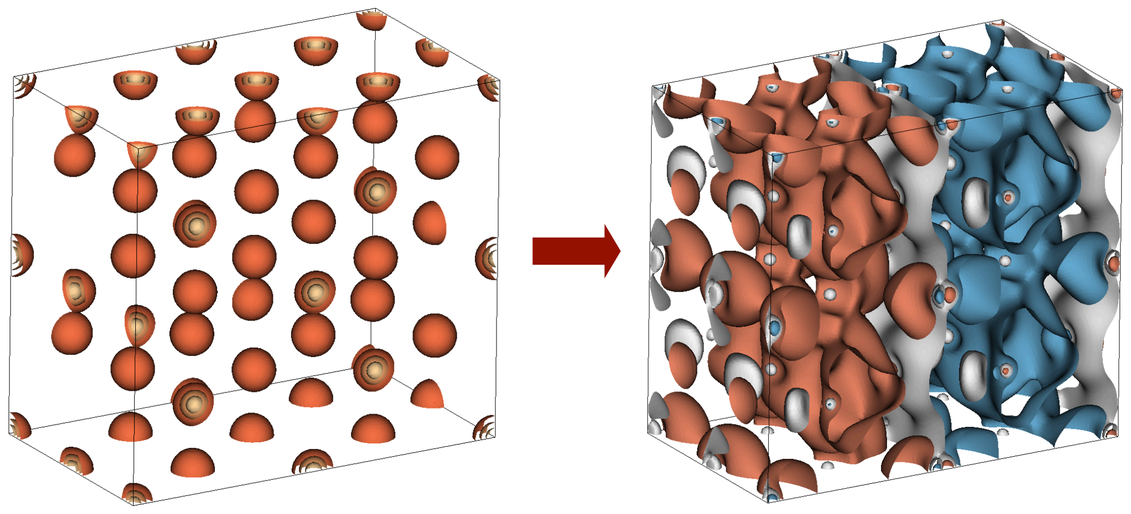


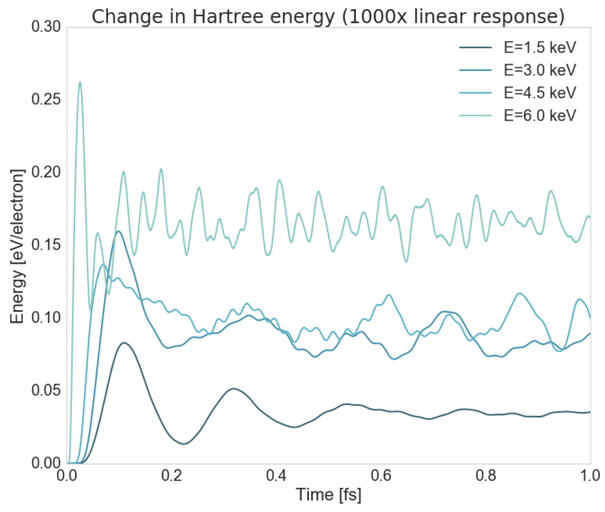
Beryllium

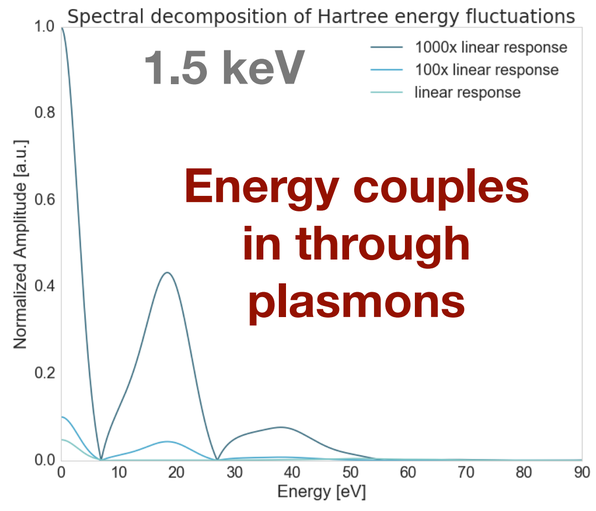
3x-compressed, Te = 13 eV

Beyond linear response

Can we isochorically heat beryllium in TDDFT?







Energy couples in through plasmons

X-ray directly drives plasmons, but TDDFT (as implemented) is missing physics:

- Kohn-Sham occupancies don't know how to change
- No direct core excitations
- No Auger processes
- Ejected high energy electrons cannot drive plasmons

How can we proceed?

State-of-the-art Kinetics	Real-time TDDFT
- Multi-configuration atoms	- Single configuration atoms
- Electrons equilibrate instantaneously	- Electrons can't equilibrate on their own
- Heuristic treatment of coupling to environment	- Consistent treatment of coupling to environment

- 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

$$\left[i\frac{d}{dz} - \bigoplus_{n=0}^{4}\mathcal{H}_{TDKS}(\mathrm{Be}^{n+},z)\right]\mathcal{G}^{<}(z,z') = \delta(z,z') + \int_{\gamma} dz'\tilde{\Sigma}(z,z')\mathcal{G}^{<}(z,z')$$

Adiabatic TDDFT Hamiltonian in each charge sector — **Self-energy approximation bootstraps in non-adiabatic effects**

References

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[3] Cazzaniga, et al., Phys. Rev. B **84**, 075109 (2011)
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