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Practical Methods in Time-Dependent Density Functional Theory (TDDFT) at Elevated Temperatures

R.J. Magyar,
L. Shulenburger, A. Baczewski

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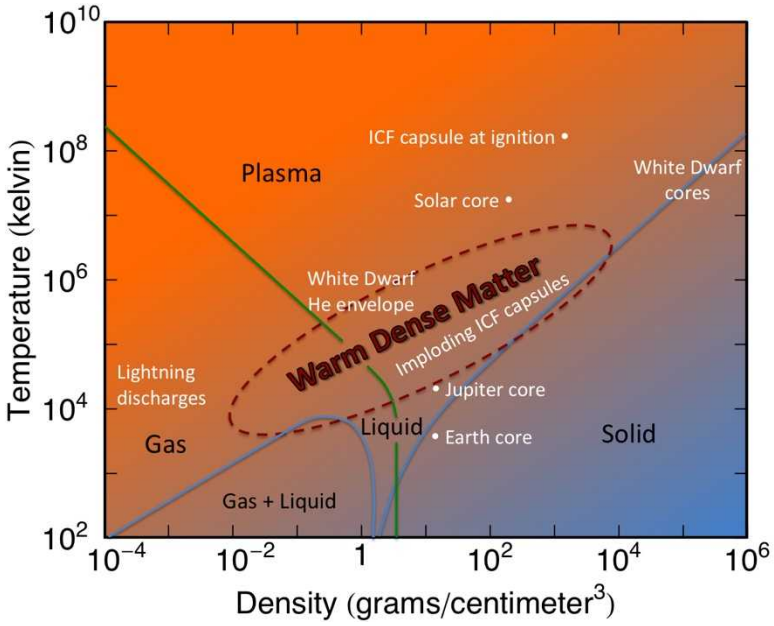
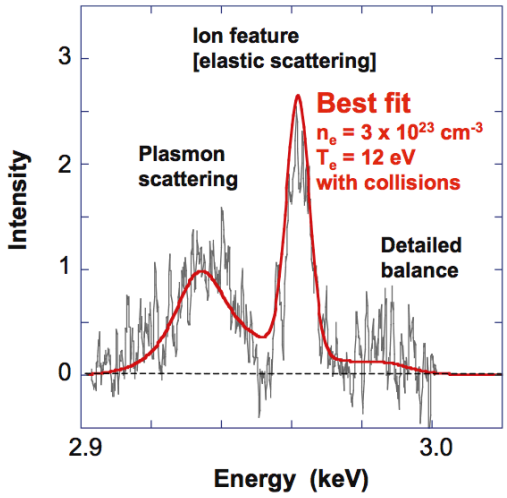
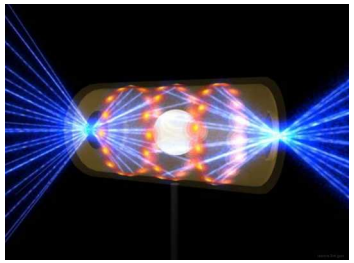
X-ray Response of Warm Dense Matter





- Highly compressed matter with electron densities 2-4 fold solid density
- Temperature on the order of several eVs, 10s of kK
- Regimes that are hard to explore experimentally
- Errors from materials models vs. numerical problems of higher level codes.

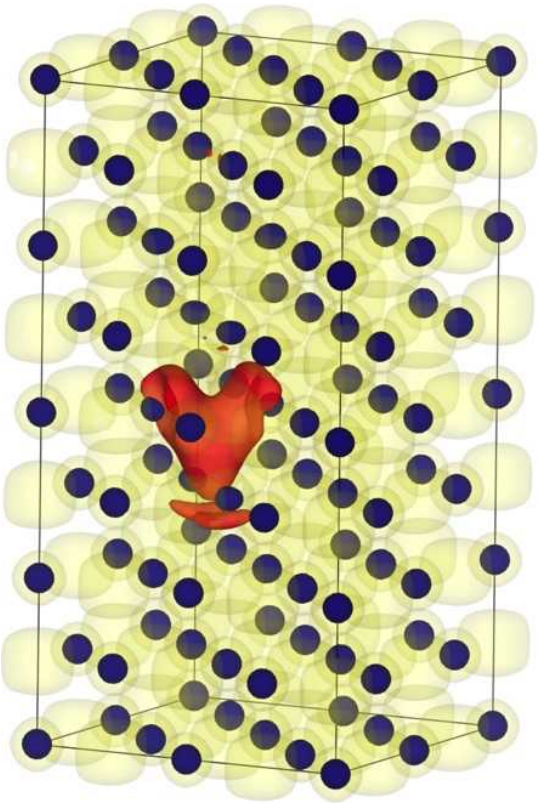
Giant impact event



Laser-driven implosion in ICF

Developments Required for Time-Dependent Density Functional Description of WDM

1. Extended system for dense disordered materials ✔
2. Real-time evolution of the electrons ✔
3. Finite temperature theory of the electrons ✔
4. Coupled electron-ion motion - Velocity per ion at 10 K, approx 0.01 Å/fs. Significant ion motion on the order of 10 fs. Motion greater than 10% of H bond *?*
5. Correlated electron-ion energy transfer ✗

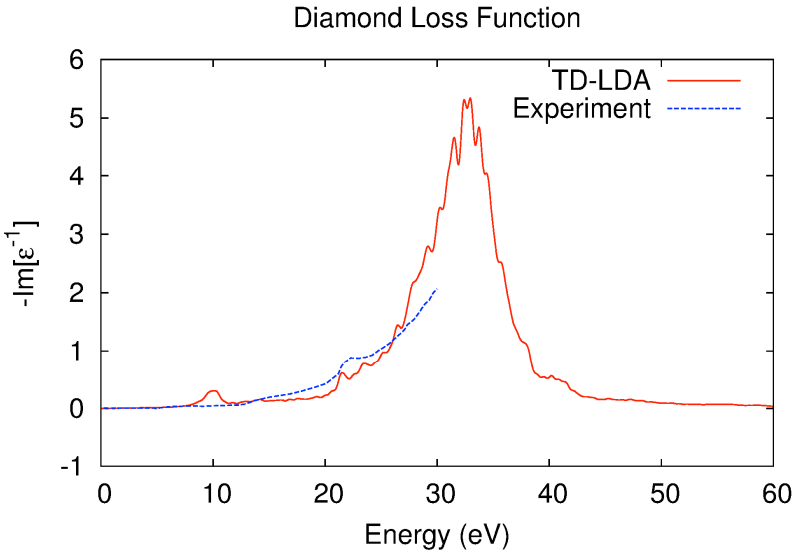


A proton stopping in Al

Extended System Response to X-Rays

Real-time TDDFT Optical Absorption on Solids

- TDDFT for Bloch KS orbitals
- Additional dynamical equation for A, the vector potential
- X-rays wavelengths are typically commensurate with the size of the super-cells
- Response properties are inferred from the induced contribution to the vector potential



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G. F. Bertsch, J.-I. Iwata, Angel Rubio, and K. Yabana, Phys Rev. B 62, 7998 (2000).
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FPSEID – Y. Miyamoto and H. Takahara

Born-Oppenheimer, Ehrenfest Dynamics, and Beyond

$$H\left[\left\{R_i\right\}\right]\phi = \varepsilon\phi \quad \text{vs.} \quad H\left[\left\{R_i\right\}\right]\phi = i\frac{d}{dt}\phi$$

$$F_i = -\left\langle \nabla V \right\rangle$$

- **Separate model for coupled electron ion dynamics**
- Limited electron dynamics Born-Oppenheimer
- No electron-ion correlation in Ehrenfest
- No branching of trajectories. (photochemistry, electron relaxation, charge transfer, surface chemistry)
- Probabilistic hop from one electronic state to another imparting momentum to the ions (ala Tully, T. Martinez, O. Prezhdo)
- Trouble: no mechanism within TDDFT to hop surfaces, TD-KS PE surfaces are not real surfaces. Coupling terms within TDDFT are hard to define as they are wave-function properties.

Thermal (Mermin) DFT

$$\hat{\rho}^{Exact} = \sum_i W_{i,\beta} \left|\Psi_i\right\rangle\left\langle\Psi_i\right|$$

$$\hat{\rho}^{Mermin} = \sum_i w_{i,\beta} \left|\phi_i(w_{i,\beta})\right\rangle\left\langle\phi_i(w_{i,\beta})\right|$$

In exact theory, the energy Eigen basis for the density matrix does not depend on the weights.
In Mermin-DFT, it does through the effective density-potential map.
Approximate functionals see ensemble density -> ensemble contamination error.

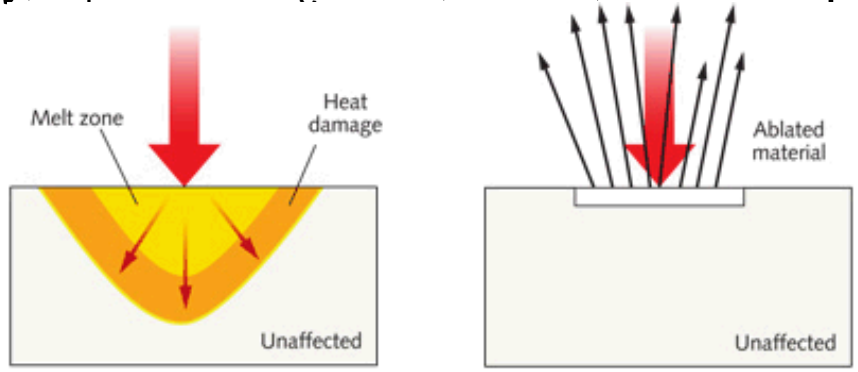
Ψ is a many-body wave-function in 3N dimensions. (Orthonormal, normalized, complete)
Φ is a KS wave-function in 3 dimensions.
β is an inverse measure of electron temperature. In Mermin-based molecular dynamics is is often fixed or tied to the classical ion temperature or kinetic energy.

Electron-Ion Equilibration

High energy laser excited electrons induce changes in a solid. For example, laser ablation.

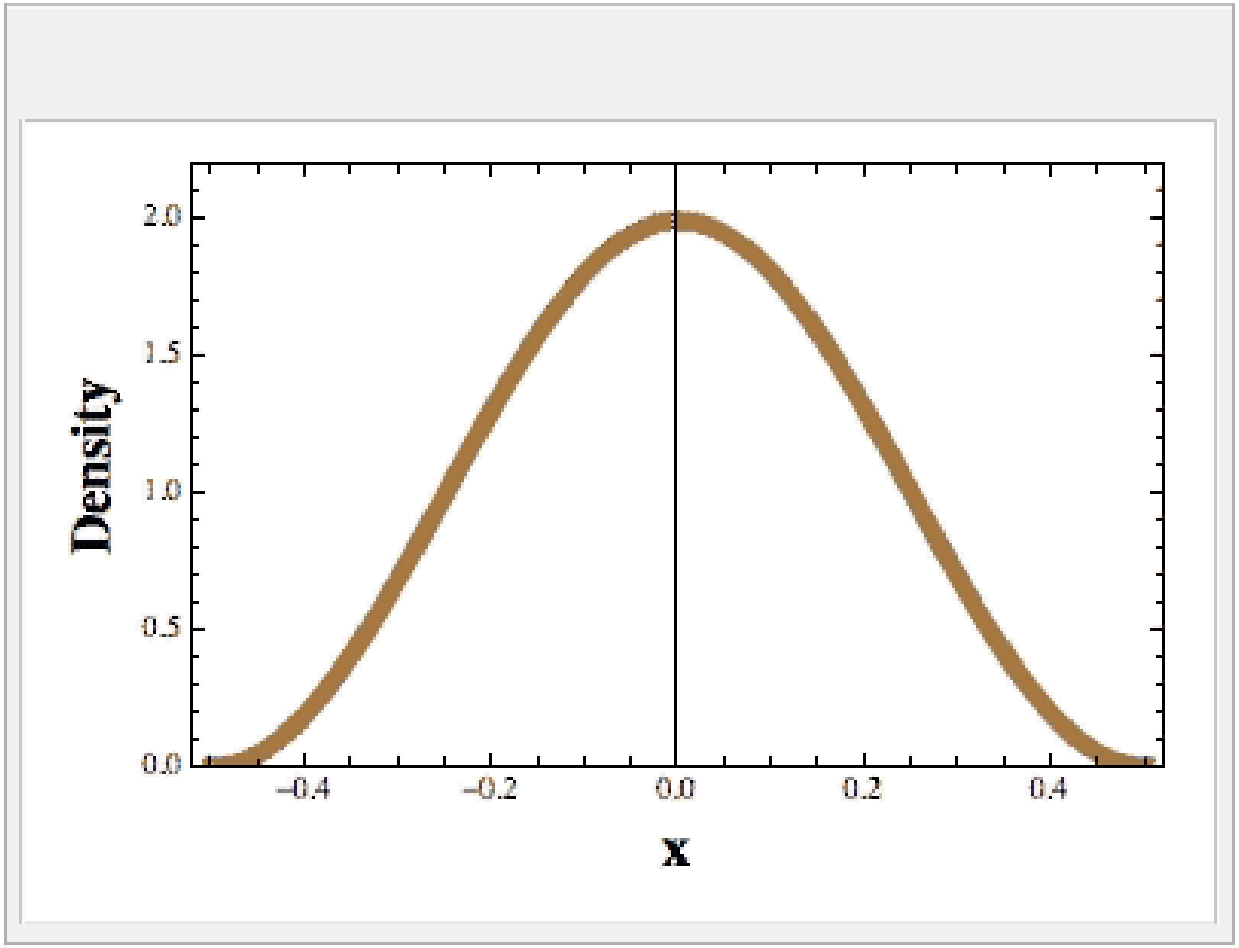
Often modeled in terms of a 2 temperature model

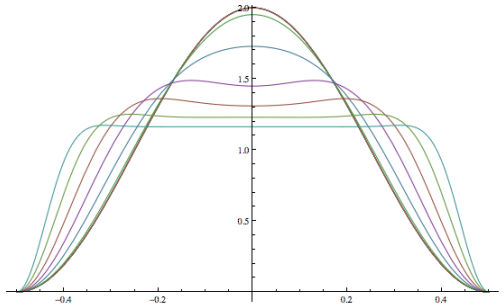
- Take Aluminum for example. Zhigilei et al. web site and standard ref data for cold Al. Very roughly…
- $C_e \approx 10^5$ J/Km^3
- $C_i \approx 10^7$ J/Km^3
- $G_{e\text{-}l} \approx 10^{17}$ W/Km^3
- $T_{equilibration} = 0.33$ -10 ps
- For initially, T_i=0 and T_e=100,000 K, a final equilibrium state is at approx. 1000K.



Laser etching schematic
Laserfocusworld.com
3/1/2012

Non-interacting Electrons in a Box: What Might Exact Heating Look Like





Ensembles in TDDFT - Runge-Gross Leaves the Question of Weights Open

Different representations of TDDFT ensemble densities

NVT thermal density but NVE propagation?!

$$\hat{\rho} = \sum_i \left|\Phi_i\right\rangle\left\langle\Phi_i\right|$$

1. KS singlet occupied representation: easiest to justify under RG, hardest to construct functionals for at finite T, not straightforward to get stationary state (VN)

$$\hat{\rho} = \sum_i w_i \left|\Phi_i\right\rangle\left\langle\Phi_i\right|$$

2. KS DM representation fixed occupations: initial state reproduces realistic density of thermal state, steady state result is reproducible (VN)

$$\frac{d\hat{\rho}_{S,I}}{dt} = -i\left[H_S, \hat{\rho}_{S,I}\right]$$

1. KS DM with varying occupations: additional time dependence built beyond unitary propagation of Hamiltonian, only way to connect 2 different Mermin states (M)

$$\frac{d\hat{\rho}_{S,II}}{dt} = -i\left[H_S, \hat{\rho}_{S,II}\right] + \frac{\partial\hat{\rho}_{S,II}}{\partial t}$$

Trouble with Von Neumann and Thermal States

$$\hat{\rho}_1 = \sum_i w_i^{(1)} \left|\Phi_i\right\rangle\left\langle\Phi_i\right|$$

$$\hat{\rho}_2 = \sum_i w_i^{(2)} \left|\Phi_i\right\rangle\left\langle\Phi_i\right|$$

- Assume for example non-interacting Fermions.
- Try to connect 2 different thermal states through unitary propagation alone.
- Some mechanism to change occupations is required.

$$\hat{\rho}_2 = \sum_i w_i^{(1)} U(T) \left|\Phi_i\right\rangle\left\langle\Phi_i\right| U^{\tau}(T)$$

$$U(t) = \sqrt{w_i^{(2)} / w_i^{(1)}}$$

Projection of an Excited State onto a Thermal State

$$\left|\Phi_i(t)\right\rangle = \sqrt{w_i}\left|\phi_i(t)\right\rangle \quad \left|\Omega_j^M(t)\right\rangle = \sqrt{w_j^M}\left|\omega_j^M(T)\right\rangle$$

$$\Delta(t,T) = \sum_{i,j}\left\langle\Phi_i(t)\middle|\Omega_j^M(T)\right\rangle$$

- Project TD states including the square root of weights unto thermally weighted states at a set of temperatures.
- Define the overlap function.
- For a thermal state at a temperature T, the overlap function will be the number of electrons in the simulation.
- The thermal function between a non-thermal state will return less than this for all T. Peaks can be interpreted as effective temperature of electrons with potentially multiple contributions.

Conclusions

- Extension of TDDFT problems in WDM requires advances in several areas of TDDFT modeling.
- Many of these challenges have been overcome.
- We showed that it is possible to extract useful information about warm systems by propagating the thermal state.

Andrew Baczewski

Thursday, March 6 8:36 AM

S26.00004: Optical Response of Warm Dense Matter Using Real-Time Electron Dynamics

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