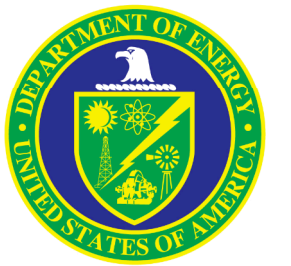
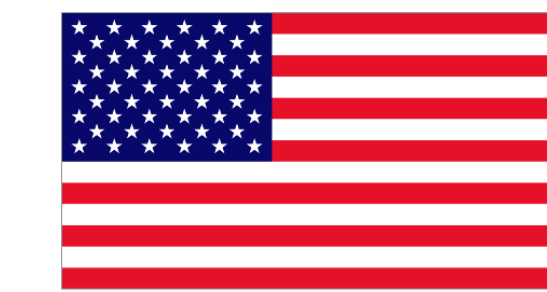


# Time-Dependent Density Functional Theory of Extreme Environments

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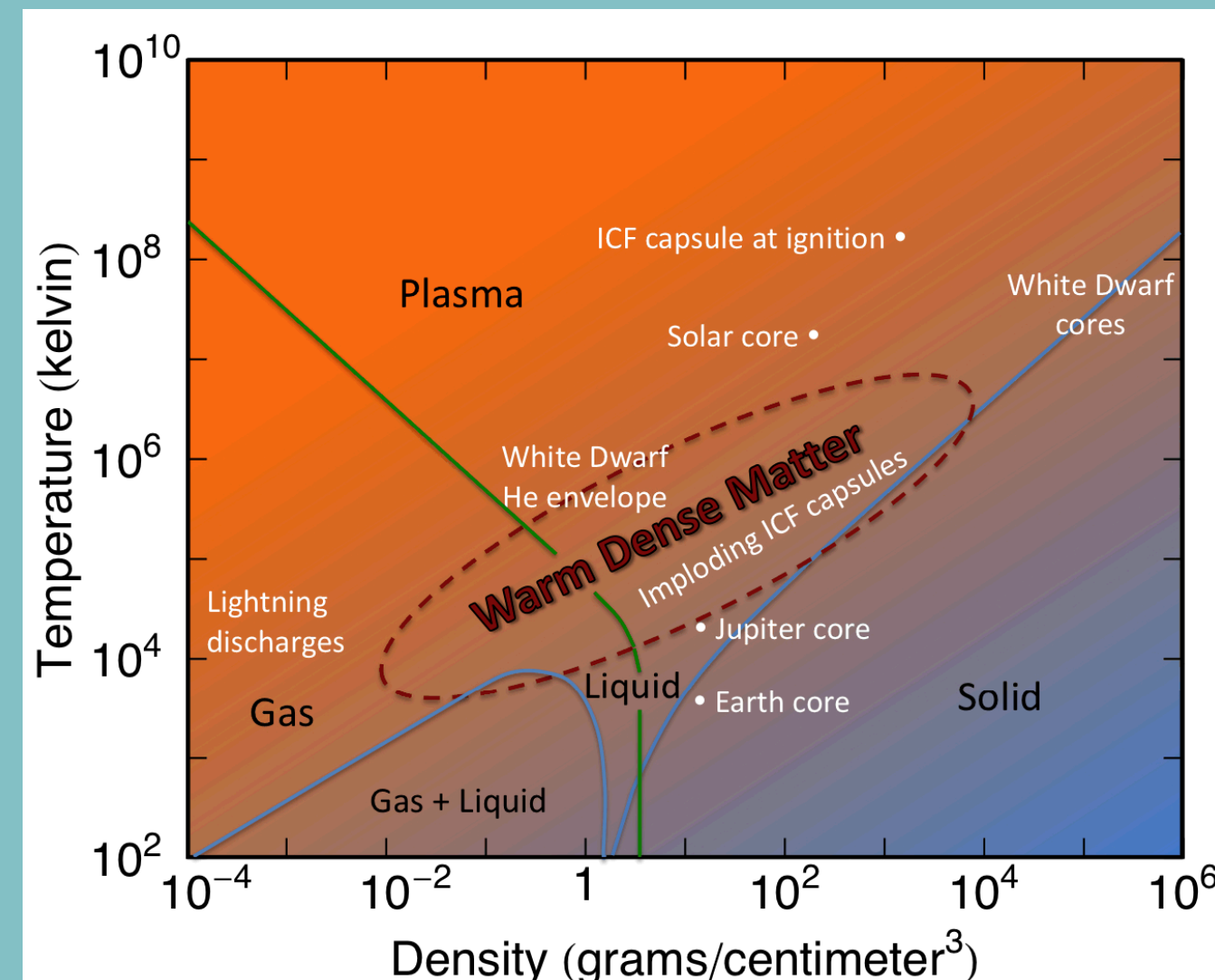
We describe the challenges involved when using time-dependent density functional theory (TDDFT) to describe warm dense matter (WDM) within a plane-wave, real-time formulation. WDM occurs under conditions of temperature and pressure (over 1000 K and 1 Mbar) where plasma physics meets condensed matter physics. TDDFT is especially important in this regime as it can describe ions and electrons strongly out of equilibrium. Several theoretical challenges must be overcome including assignment of initial state orbitals, choice of time-propagation scheme, treatment of PAW potentials, and inclusion of non-adiabatic effects in the potential energy surfaces. The results of these simulations are critical in several applications. For example, we will explain how the TDDFT calculation can resolve modeling inconsistencies in X-ray Thompson cross-sections, thereby improving an important temperature diagnostic in experiments. 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.

## The Study of Warm Dense Matter is Critical in the Design of Equations of State Needed to Model Complex Phenomena

### Warm Dense Matter (WDM) is

- Compressed matter with electron densities of  $10^{21}$ - $10^{26}$  electrons /  $\text{cm}^3$
- Temperature on the order of several eVs, 10s of kK
- Significant electron degeneracy
- Typically disordered
- Often liquid metal

- Planetary Collision Science
- Geoscience
- Exoplanets
- Materials Science
- Stopping Power
- Laser induced shocks
- Inertial Confinement Fusion
- Space vehicles



## Proposed Approach to Model the Response to X-Ray Pulses in Extended Systems

1. Use elevated temperature DFT to get initial state of electrons and ions with electrons and nuclei at same temperature  $\geq 1000$  K.

$$n(r, t=0, T) = \sum_i w_i |\phi_i(r, t)|^2$$

1. Note that in equilibrium for thermalized electrons (and nuclei) the density matrix is constant in time.  $\dot{\rho} = 0$
2. Use the wave-function with fractional occupancies and its self-consistent potential give the correct isolated and unperturbed dynamics of the thermal state.

$$i \frac{\partial}{\partial t} \phi_i(r, t) = \left[ -\frac{1}{2} \nabla^2 + v_{KS}^M[\Psi_0 @ T, \Phi_0 @ T, n](r, t) \right] \phi_i(r, t)$$

1. Get optical response through a time dependent real-space run with coupled co-evolution of a vector potential.

$$H_{KS}^i = -\nabla^2 + v_{ext}(r) + v_{HXC}(r) + iA(t)\nabla + \frac{1}{2}A^2(t)\hat{s}$$

$$\frac{\Omega}{4\pi} \frac{d^2}{dt^2} A_z(t) + i \sum_{occ} \langle \phi_i | \nabla_z | \phi_i \rangle + A_z N_e = 0$$

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G. F. Bertsch, J.-I. Iwata, Angel Rubio, and K. Yabana, Phys. Rev. B 62, 7998 (2000).  
S. Sugiino and Y. Miyamoto, Phys. Rev. B59, 2579 (1999); ibid, Phys. Rev.

2. We will calculate both the dynamic structure factor and dielectric function. Both provide information about the the X-ray response.

$$\frac{1}{\epsilon(q \rightarrow 0, \omega)} = \frac{\int_0^{\infty} dt e^{i\omega t - \eta t} \frac{d}{dt} \mathbf{A}_{tot}(t)}{\int_0^{\infty} dt e^{i\omega t - \eta t} \frac{d}{dt} \mathbf{A}_{ext}(t)} = 1 + \frac{\int_0^{\infty} dt e^{i\omega t - \eta t} \frac{d}{dt} \mathbf{A}_{ind}(t)}{\int_0^{\infty} dt e^{i\omega t - \eta t} \frac{d}{dt} \mathbf{A}_{ext}(t)}$$

$$S_{ee}^{tot}(k, \omega) = \frac{1}{N_{ion}} \left\langle \left| \rho_e^{tot}(\mathbf{k}, \omega) \right|^2 \right\rangle = \frac{\epsilon_0 \hbar k^2}{\pi e^2 n_e} \left( \frac{1}{1 - e^{-\hbar\omega/k_B T_e}} \right) \text{Im} \epsilon^{-1}(k, \omega)$$

## Rung-Gross Revisited

Is a wave-function with non-integer occupations allowed?  
Can we restart using arbitrary wave-functions that yield density?  
Should we use the energies of TD-KS orbitals to constrain dynamics?

$$\frac{\partial}{\partial t} \langle \Psi(t) | \hat{Q}(t) | \Psi(t) \rangle = \langle \Psi(t) | \left( \frac{\partial}{\partial t} \hat{Q}(t) - i [\hat{Q}(t), \hat{H}(t)] \right) | \Psi(t) \rangle$$

$$\hat{Q}(t) \leftarrow j_p(r) = \frac{1}{2i} \sum_{j=1}^N w_j \left( \nabla_{r_j} \delta(r - r_j) + \delta(r - r_j) \nabla_{r_j} \right)$$

## Electron Dynamics

$$\left[ S(t) + \frac{1}{2} H_{smooth}(t + \frac{\Delta}{2}) \right] \Psi_{n,smooth}(t + \Delta) = \left[ S(t) - \frac{1}{2} H_{smooth}(t + \frac{\Delta}{2}) \right] \Psi_{n,smooth}(t)$$

$$iS(t) \frac{\partial}{\partial t} \Psi_{n,smooth}(t) = (H_{smooth}(t) + P(t)) \Psi_{n,smooth}(t)$$

- Crank-Nicholson propagation is unitary and time reversible
- Inverse is replaced with inverse linear solver routine

## Coupled Electron-Ion Motion: Born-Oppenheimer vs. Ehrenfest Dynamics

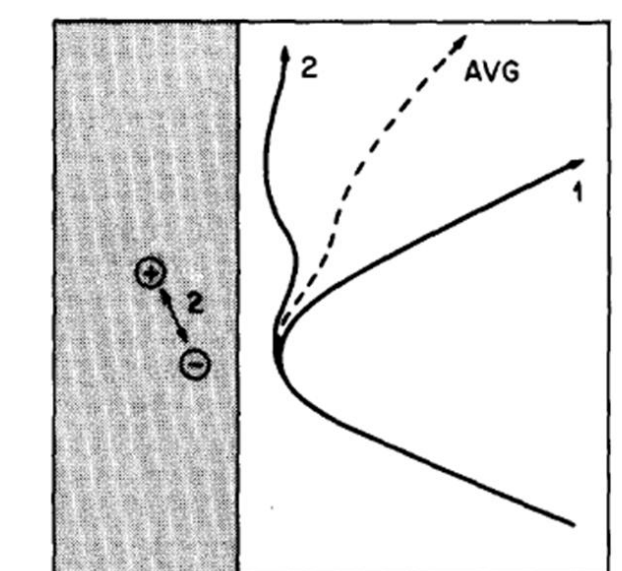
$$H[\{R_i\}] \phi = i \frac{d}{dt} \phi \quad \text{vs.} \quad H[\{R_i\}] \phi = \epsilon \phi \quad F_i = -\langle \nabla V \rangle$$

## Surface Hopping

- Born-Oppenheimer and Ehrenfest potential energy surfaces with classical nuclei fail near certain crossings
- In what sense does this matter?
- Landau Zener

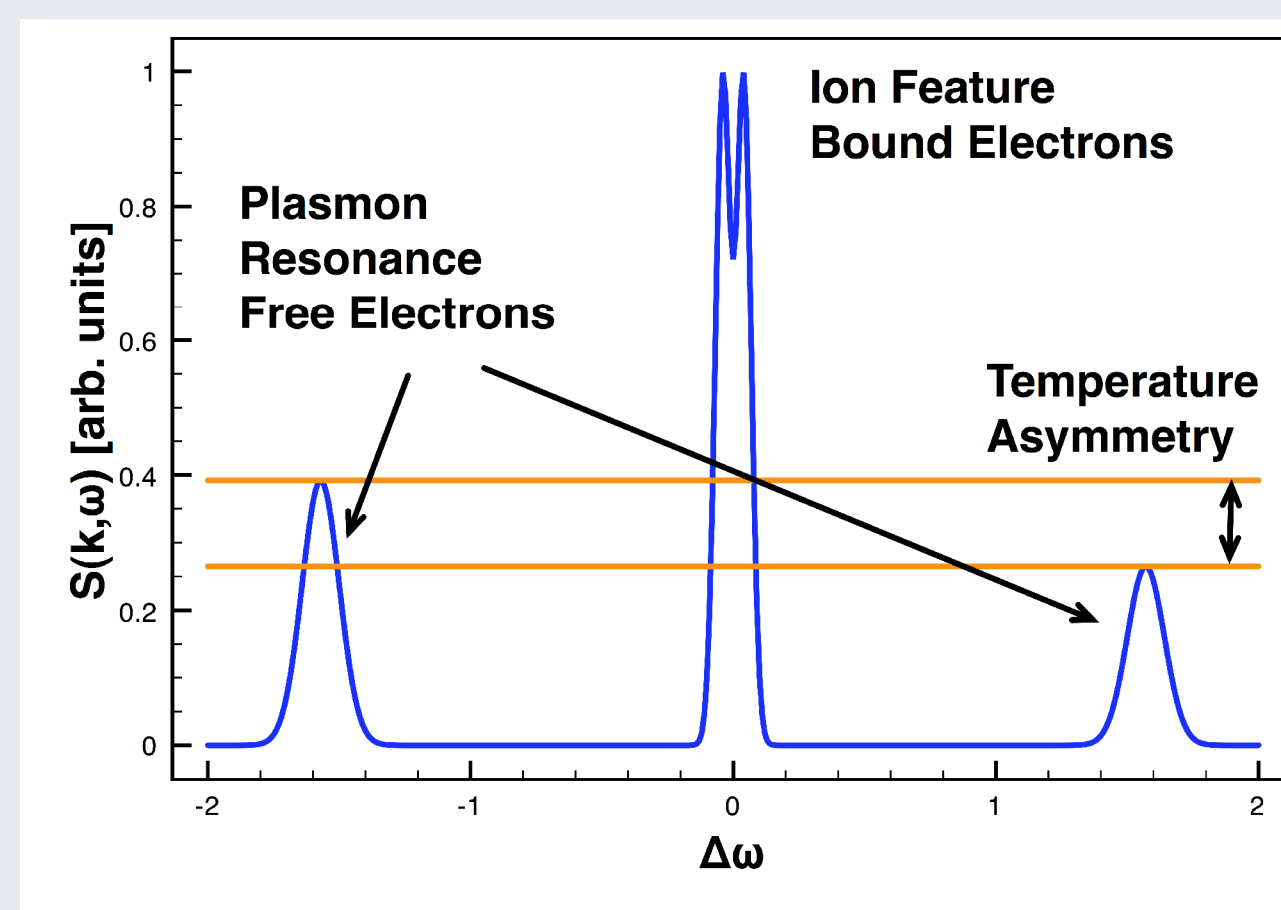
$$P_D = e^{-2\pi\Gamma}$$

$$\Gamma = \frac{a^2/\hbar}{\left| \frac{\partial}{\partial t} (E_2 - E_1) \right|} = \frac{a^2/\hbar}{\left| \frac{\partial q_i}{\partial t} \frac{\partial}{\partial q_i} (E_2 - E_1) \right|}$$



- Tully fewest switches
- When does the mean path fail?
- Detailed balance
- Are surface hops allowed?
- Energy and momentum conservation

## X-Ray Thompson Scattering Diagnostic



$$\frac{d\sigma}{d\omega d\Omega} = \sigma_T S_{ee}^{tot}(k, \omega)$$

- Temperature diagnostic via detailed balance and structural probe
- Theoretical understanding is elusive. At low k, models (Chihara) fail that use unphysical ion structure factors from classical plasma simulations with effective quantum potentials while DFT-MD potentials.

## This is a Time-Dependent Optical Response Problem with Coupled Electron Ion Dynamics

- The plasmon energy,  $\omega_p \sim 1$ -4 eV
- In-coming radiation pulse on order of keV, 10s of nanometers

## Elevated-Temperature Time-Dependent Density Functional Theory

- Canonical versus micro-canonical ensemble at elevated temperature
- 1 optical response to represent an average
- Mermin TDDFT and optical response versus weighted average of responses
- Occupation numbers vary

## Progress and Challenges Ahead

- Time-propagation for stationary state electrons has been implemented in a PAW code and is being tested.
- Nuclear motion must be tested.
- Nonadiabatic transitions need to be considered.
- The tool will provide new insight and lead to revised models of structure factors.
- See Andrew Baczewski's poster.