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Time-Dependent Density Functional Theory of Extreme Environments

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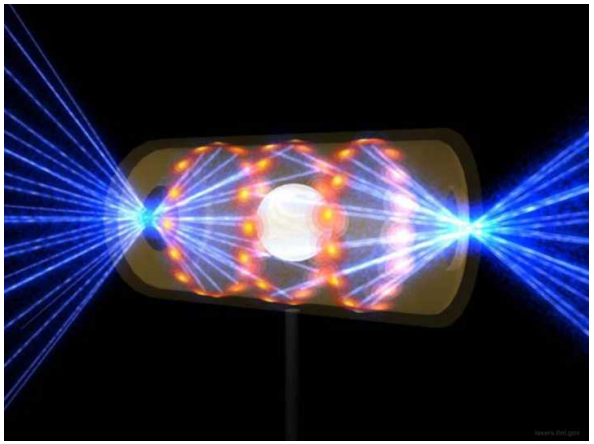
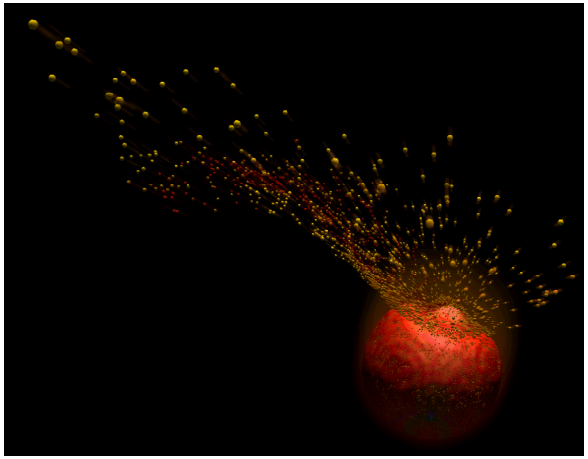
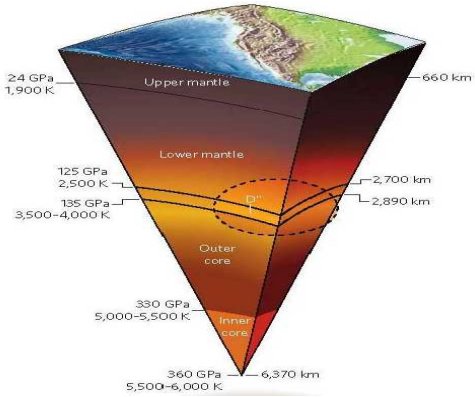
Equations of State are Needed to Model Complex Phenomena

- Models at plasma conditions
- Planetary collision science
- Geoscience
- Materials science
- Inertial confinement fusion

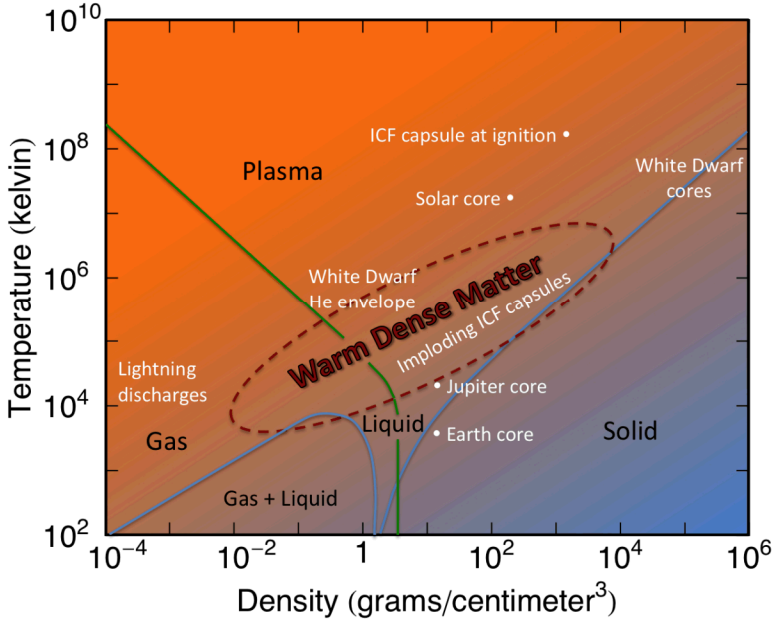


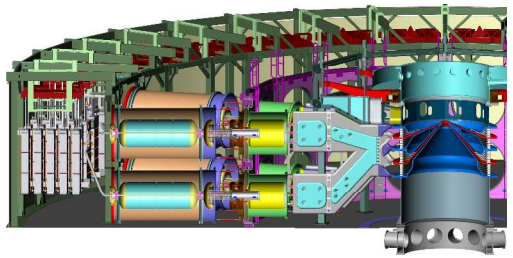




Warm Dense Matter

- Highly compressed matter with electron densities of 10^{21}-10^{26} electrons / cm^3
- Temperature on the order of sever eVs, 10s of kK
- Electron degeneracy significant
- Bound-free electron correlations significant
- Accessible to experiment and theory - Warm dense matter near-solid density, 10^{21}-10^{22} / cm^3
- The plasmon energy, ω_p ~1-4 eV





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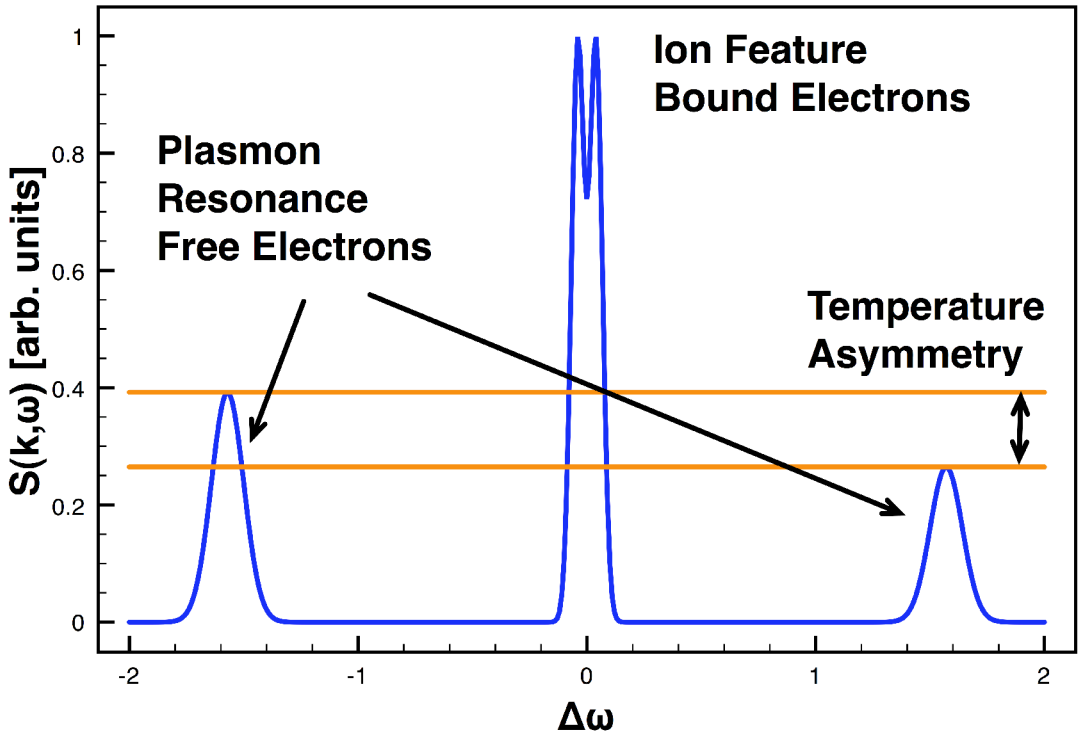
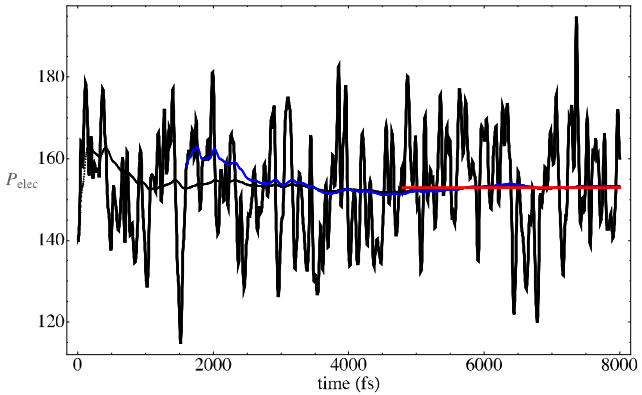
Temperature Diagnostic
X-Ray Thompson Scattering



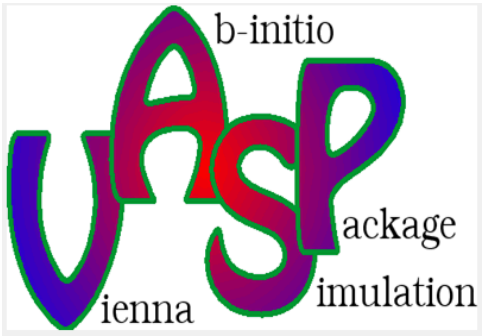
- Temperature diagnostic for warm dense matter
- Structural information about a material
- *Works* at low k based on models (Chihara) that use unphysical ion structure factors from classical plasma simulations with *effective quantum potentials*

Density Functional Theory (DFT) is a Value Tool in Warm Dense Matter Physics.

- **First-principles simulations using DFT**
  - **VASP – plane-wave code with PAW core-functions**
  - **Great care in convergence**
    - *A. E. Mattsson et. al. Modelling and Simulation in Material Science and Engineering **13**, R1 (2005)*
  - **Importance of exchange-correlation functionals**
    - *A. E. Mattsson et al. JCP **128**, 084714 (2008)*



Molecular dynamics (MD) simulations give thermo-physical properties



Dynamic Structure Factor

- **Real-time TDDFT allows a direct calculation of the structure factor S(k,ω) that**

-Includes quantum degeneracy

-Correlations through semi-local functionals

-Requires a Fourier transform

- **DFT-MD is inadequate because plasmon modes are coupled to ionic motion and must be treated on the same footing.**

$$S_{ee}^{tot}(k,\omega) = \frac{1}{N_{\text{ion}}} \left\langle \left| \rho_e^{\text{tot}}(\mathbf{k},\omega) \right|^2 \right\rangle$$

DFT-Implementation Projector-Augmented Wave-Calculations

- **Efficient and well tested scheme to solve the Kohn-Sham DFT equations**
- **“Generalized pseudo potential”**
- **Frozen core**
- **Carry around PW coefficients and characters**

$$\psi_{n,KS}(r) = \psi_{n,smooth}(r) + \sum_a \sum_i \left(\phi_i^a(r) - \phi_{i,smooth}^a(r) \right) P_{ni}^a$$

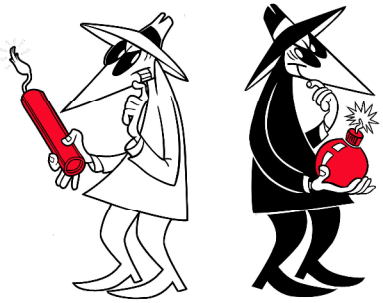
$$H_{smooth} \psi_{n,smooth} = \varepsilon_{n,smooth} S_{smooth} \psi_{n,smooth}$$

Elevated-Temperature Time-Dependent Density Functional Theory (ET-TDDFT)

$$w_{N,i} = \frac{\exp\left[-\beta\left(\varepsilon_{N,i} - \mu N\right)\right]}{\sum_j \exp\left[-\beta\left(\varepsilon_{N,j} - \mu N\right)\right]}$$

- Mermin formulation
- Ground-state exchange-correlation Functionals (local density and gradient approximations)
- Opacities
- Chemical reactions
- Defect formation
- Do occupations change with time?
- Do fractional occupations make sense within the formulation?
- Initial state = thermal state

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



- Thermalized electrons
- Non-equilibrium electron dynamics
- Nonadiabatic transitions (Tully surface hopping)
- Direct calculation of S(k,ω) through a fourier transform of the results of a real time-simulation
- Adiabatic KS potentials used on the first attempts

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

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

Time Integration

- **Crank-Nicholson propagation is unitary and time reversible**

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

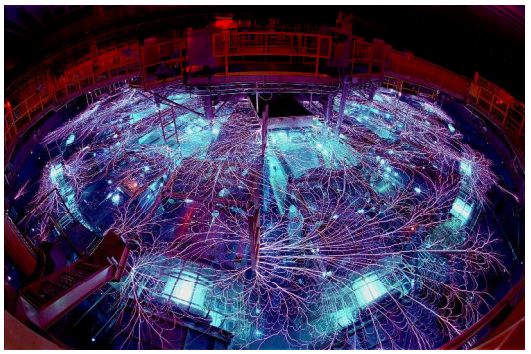
$$\left[S(t)+\frac{i}{2}H_{smooth}\left(t+\frac{\Delta}{2}\right)\right]\psi_{n,smooth}(t+\Delta)$$

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

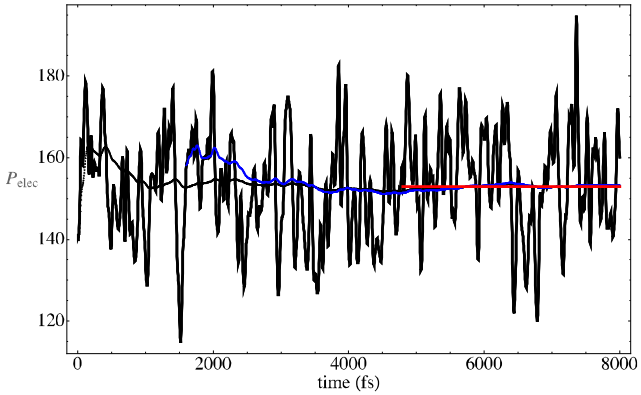
Summary and Conclusions

- **Time-propagation for stationary state electrons has been implemented in a PAW code and is being tested.**
- **The time evolution of the PAW projectors must be coded.**
- **Nonadiabatic transitions need to be considered.**
- **The tool will provide new insight and lead to revised models of structure factors.**

- Acknowledgments
  - The organizers
  - LDRD Funding
  - Sandia High-Performing Computing (HPC) – S. Corwell



Shock experiments on Sandia's Z machine



Density Functional Theory simulations