SAND2017-11784C

Stopping Power of Warm Dense Matter from TDDFT-Ehrenfest Molecular Dynamics

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59th Annual Meeting of the APS Division of Plasma Physics
October 23 - 27, 2017, Milwaukee, Wisconsin

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Concise summary of stopping power

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- Average force on projectile traveling through target material

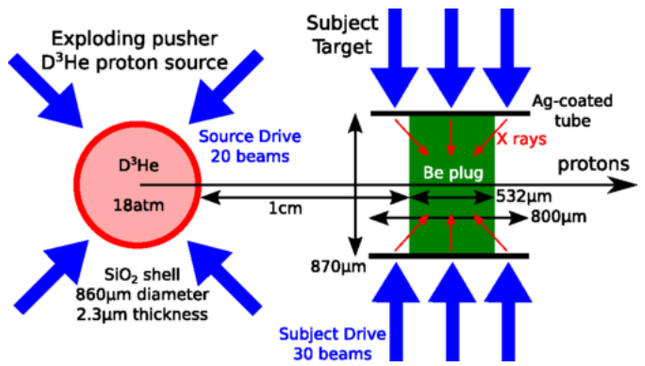
$$S(x) = \frac{dE}{dx}$$

- Relevant for radiation damage, fission, and fusion applications

- Stopping mechanisms
  - Nuclear stopping (lattice vibrations)
  - Electronic stopping (electronic excitations, quantum effects)

- Large body of literature
  - Empirical approximations
    - Rutherford[1], Thomson[2], Darwin[3], Bohr[4], Bethe[5]
  - Parameter-free atomistic simulations
    - Electronic structure coupled to molecular dynamics
    - Cold stopping power
      - Echenique[6], Correa[7], Artacho[8], Schleife[9]

- *Our objective:*
  Electronic stopping in warm dense target materials



Zylstra et al. [10]

Thermal density functional theory

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Electronic Hamiltonian	$\hat{H}_{el} = -\sum_i \frac{1}{2}\nabla_i^2 + \sum_{i<j} \frac{1}{\lvert\mathbf{r}_i - \mathbf{r}_j\rvert} - \sum_{I,i} \frac{Z_I}{\lvert\mathbf{R}_J - \mathbf{r}_i\rvert}$
Runge-Gross theorem[11]	$v(\mathbf{r},t) \overset{\Psi_0}{\longleftrightarrow} n(\mathbf{r},t)$
Equations of motion	
TD KS equations	$\mathrm{i}\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left\{-\frac{\nabla^2}{2} + v_{\mathrm{S}}(\mathbf{r},t)\right\}\phi_i(\mathbf{r},t)$ $v_{\mathrm{S}}(\mathbf{r},t) = v(\mathbf{r},t) + \frac{\delta U[n]}{\delta n(\mathbf{r},t)} + \frac{\delta E_{\mathrm{XC}}[n]}{\delta n(\mathbf{r},t)}$ $v_{\mathrm{XC}}[n](\mathbf{r},t) = v_{\mathrm{XC}}[n_0](\mathbf{r})\vert_{n_0(\mathbf{r})\to n(\mathbf{r},t)}$ $n(\mathbf{r},t) = \sum_i f_i\, \phi_i^*(\mathbf{r},t)\, \phi_i(\mathbf{r},t)$
Ehrenfest MD[12]	$M_I\ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E[\mathbf{R}_I, n(\mathbf{r},t)]$
Plane wave expansion[13]	$\phi_i(\mathbf{r},t) = \psi_{j\mathbf{k}}(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} c(\mathbf{G},t)\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$

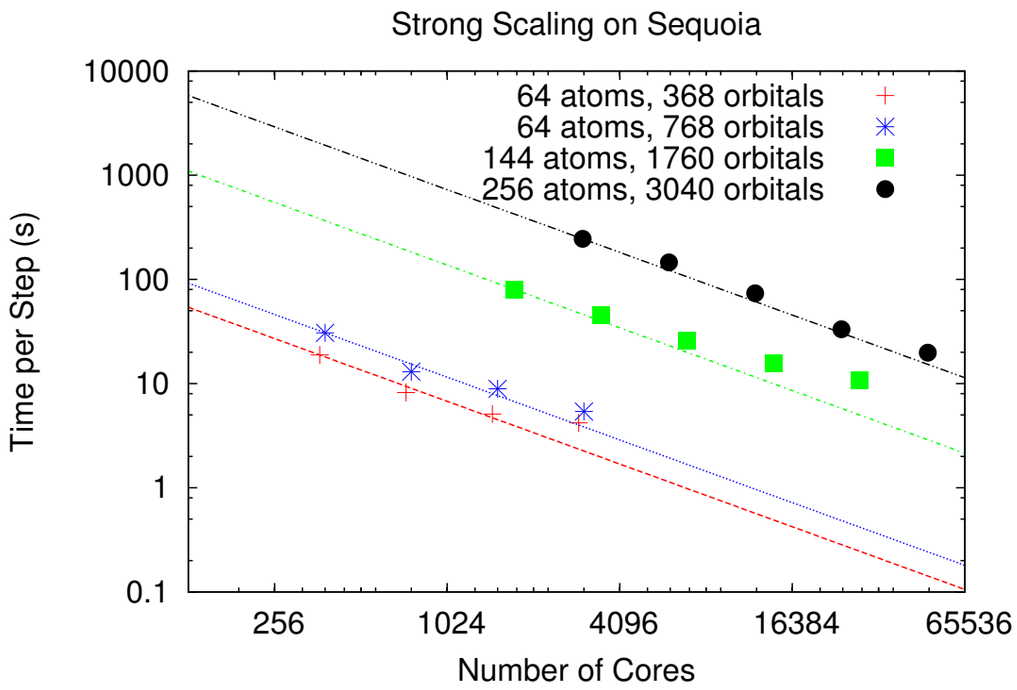
Implementation details

- Sandia implementation of TDDFT-Ehrenfest MD in VASP (*Andrew Baczewski*)

- About 10k extra lines of Fortran
  - Plane wave basis
  - Projector-augmented wave (PAW) formalism
  - Crank-Nicholson time integration (unitary)
  - Generalized minimal residual method

- Scales well on DOE's machines

- Orders of magnitude more expensive
  - Typically **100s of cores, a few hours**
  - No "free" parameters (takes mass density, # of electrons, and exchange-correlation functional)



Why TDDFT-Ehrenfest MD?

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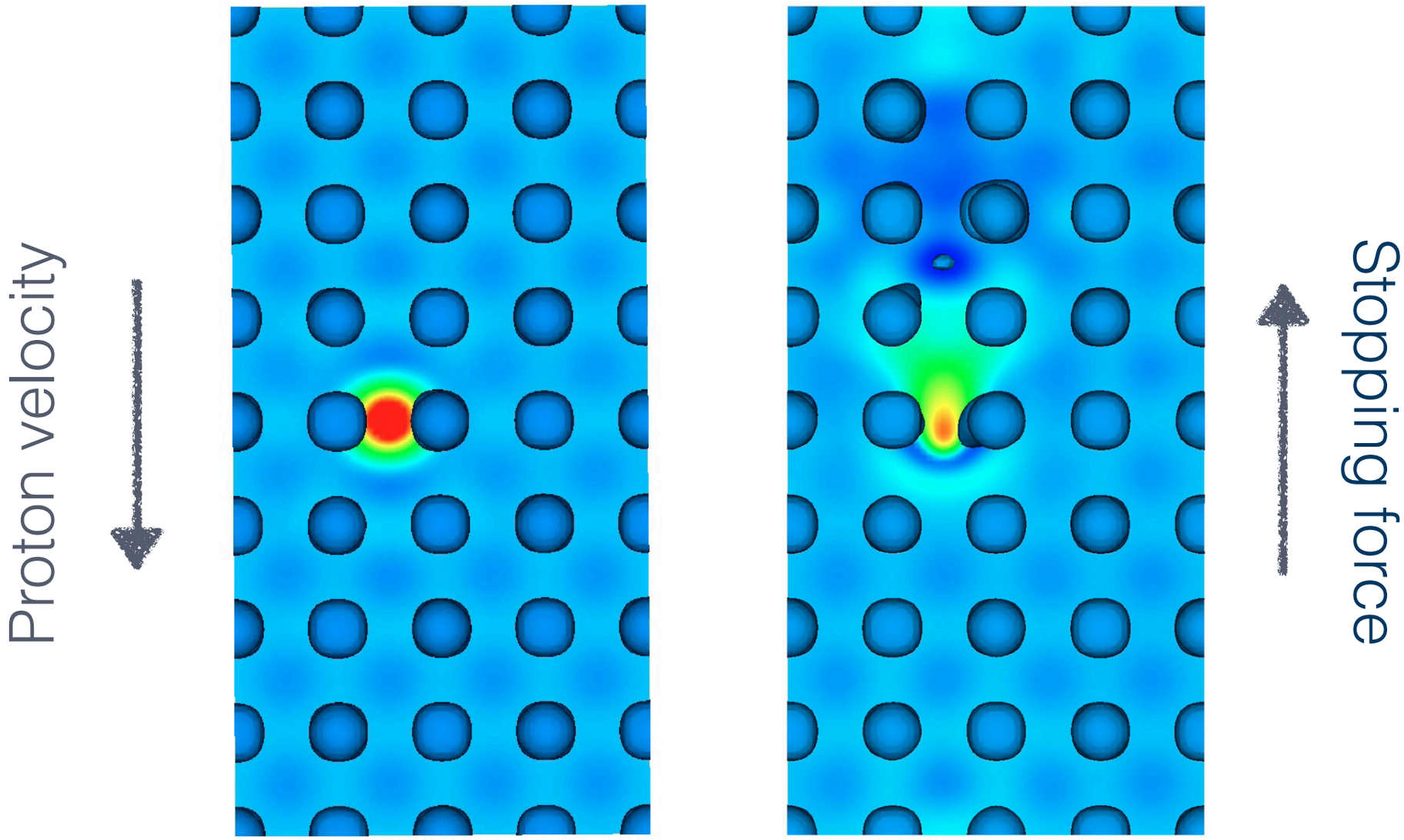
Consider a channeling proton moving in solid Al at the Fermi velocity…

Born-Oppenheimer **Ehrenfest**



0 stopping power (unphysical)

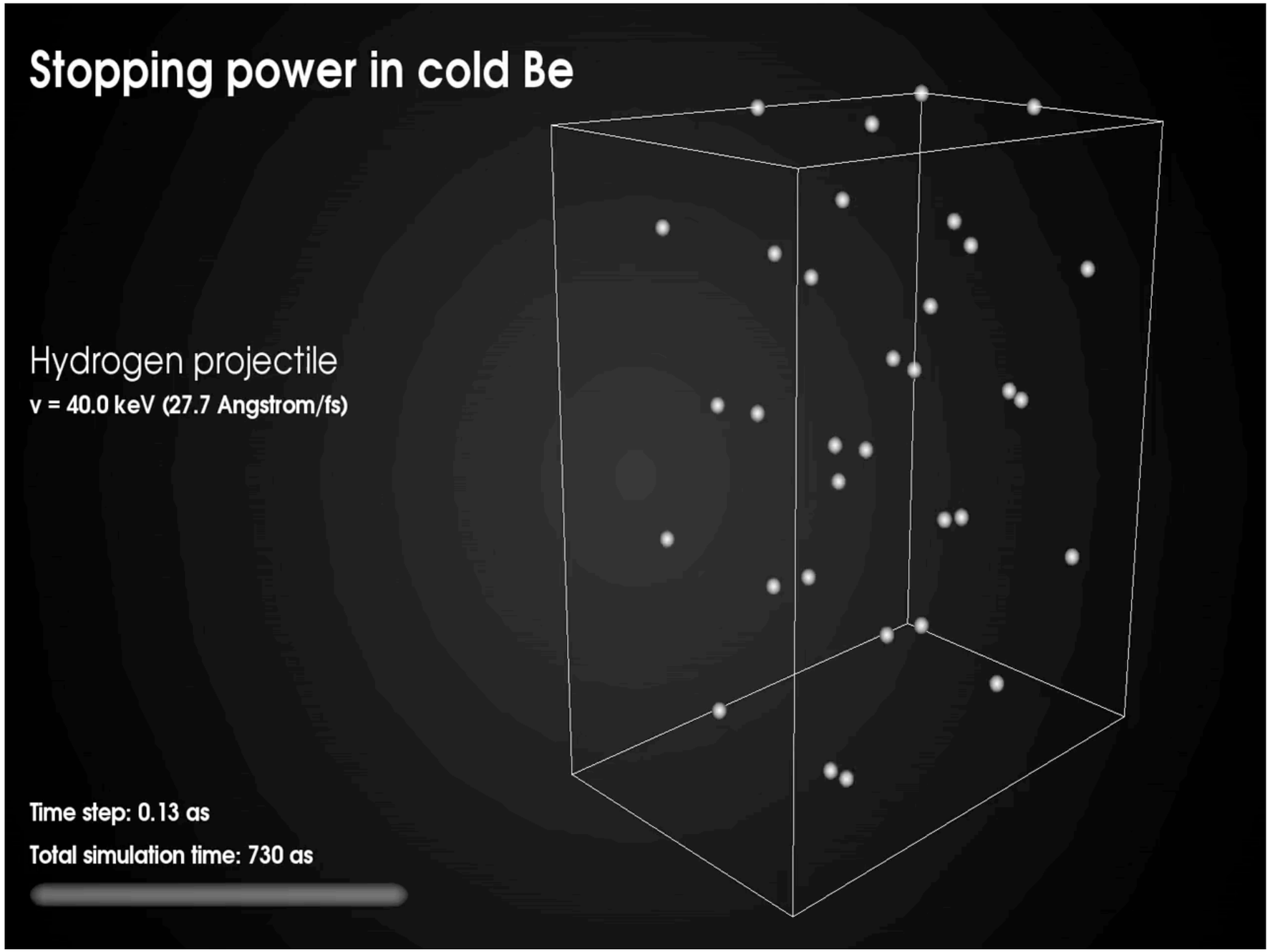
Matches experimental stopping power

H/Be simulation

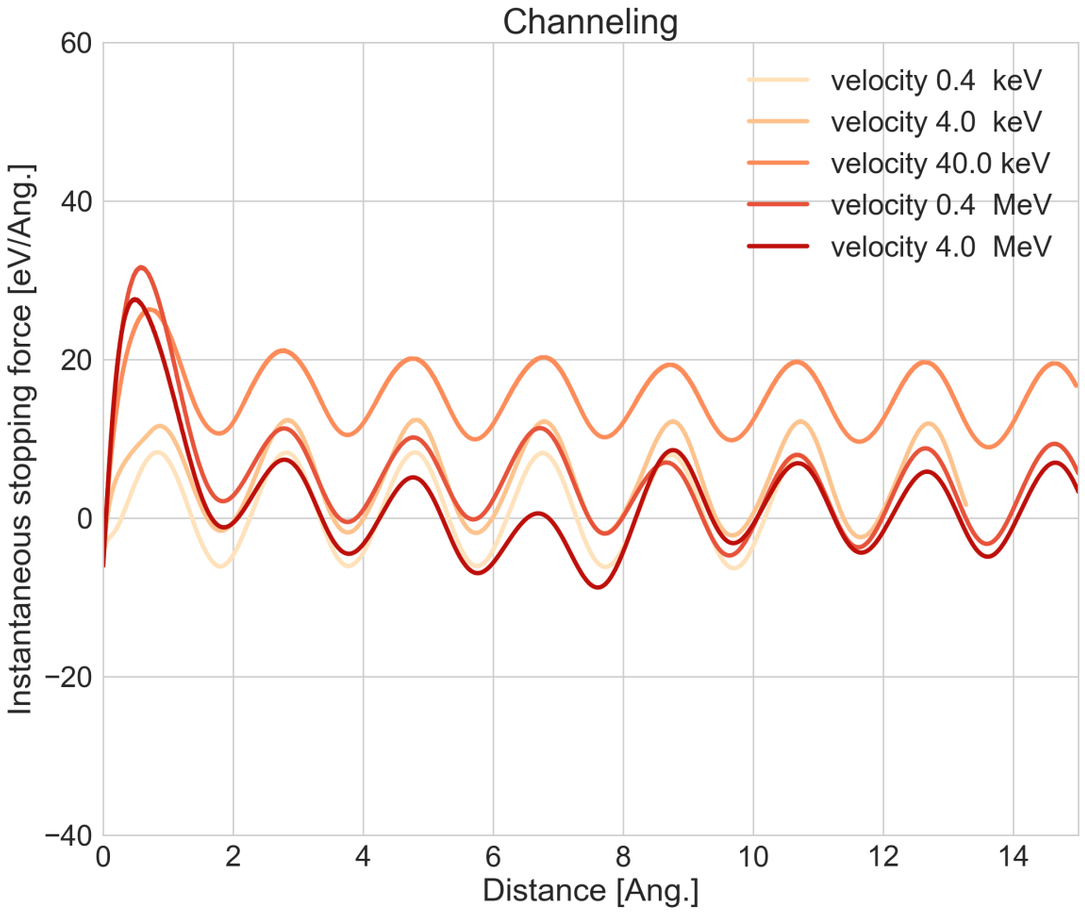
1. Converge *(1) cold static DFT*, *(2) warm static*, and *(3) thermalized DFT-MD* calculations for a given atomic configuration of the target material.

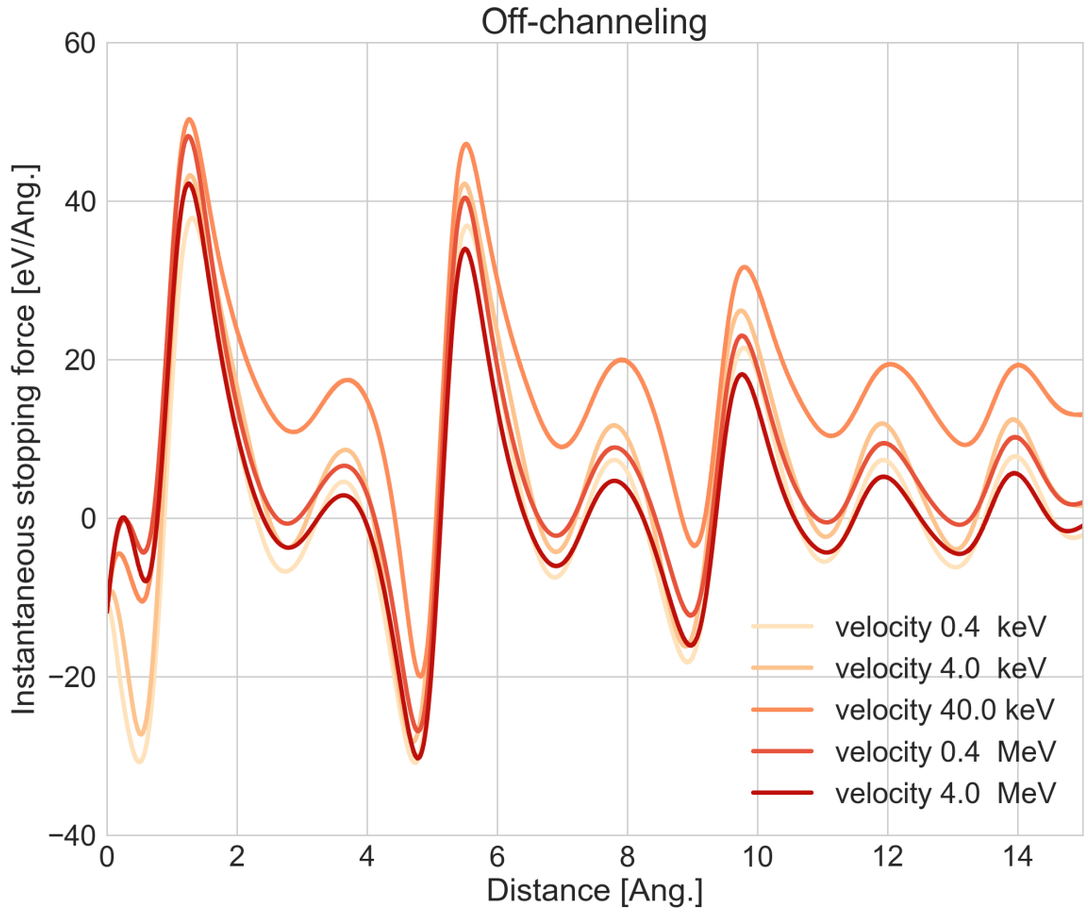
2. Prepare initial state and add projectile (hydrogen atom).

3. Run TDDFT-Ehrenfest simulation and evaluate forces on the projectile for an ensemble of trajectories (channeling and off-channeling).



Electronic stopping force





Statistics of electronic stopping force

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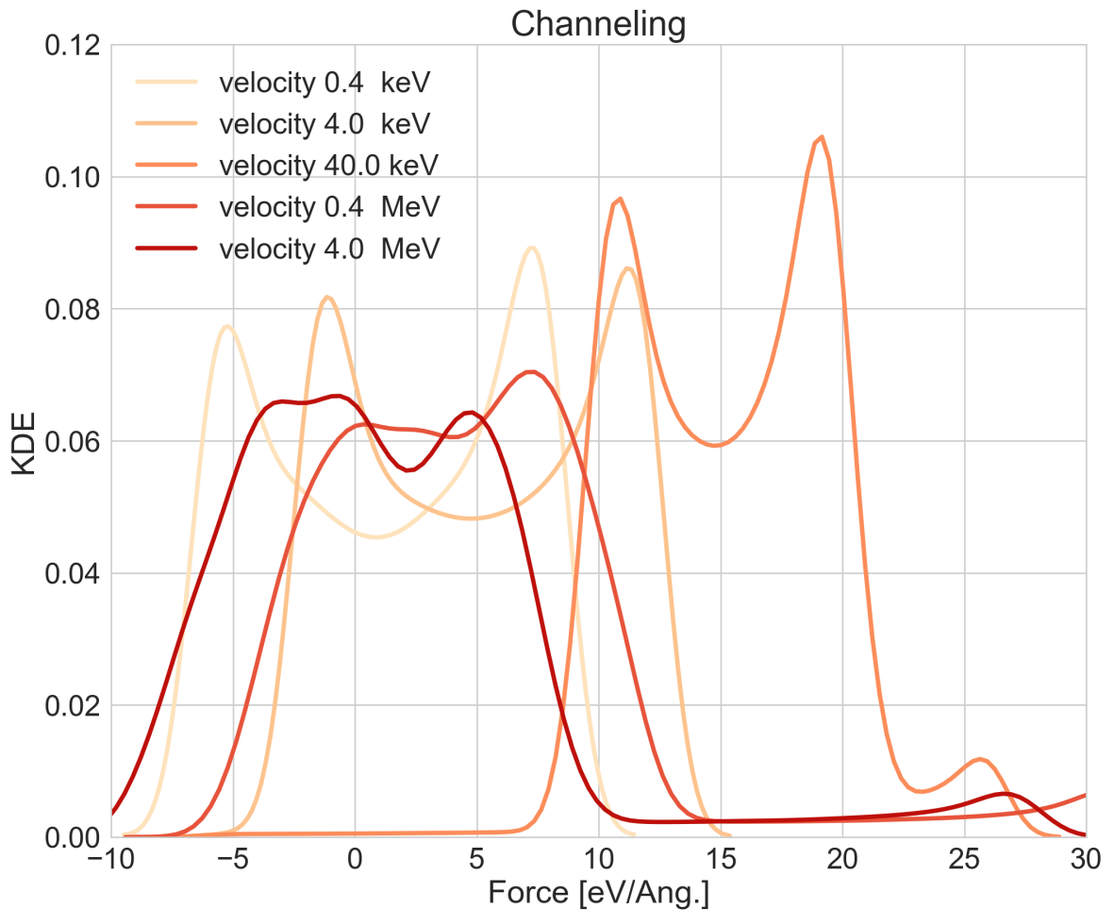
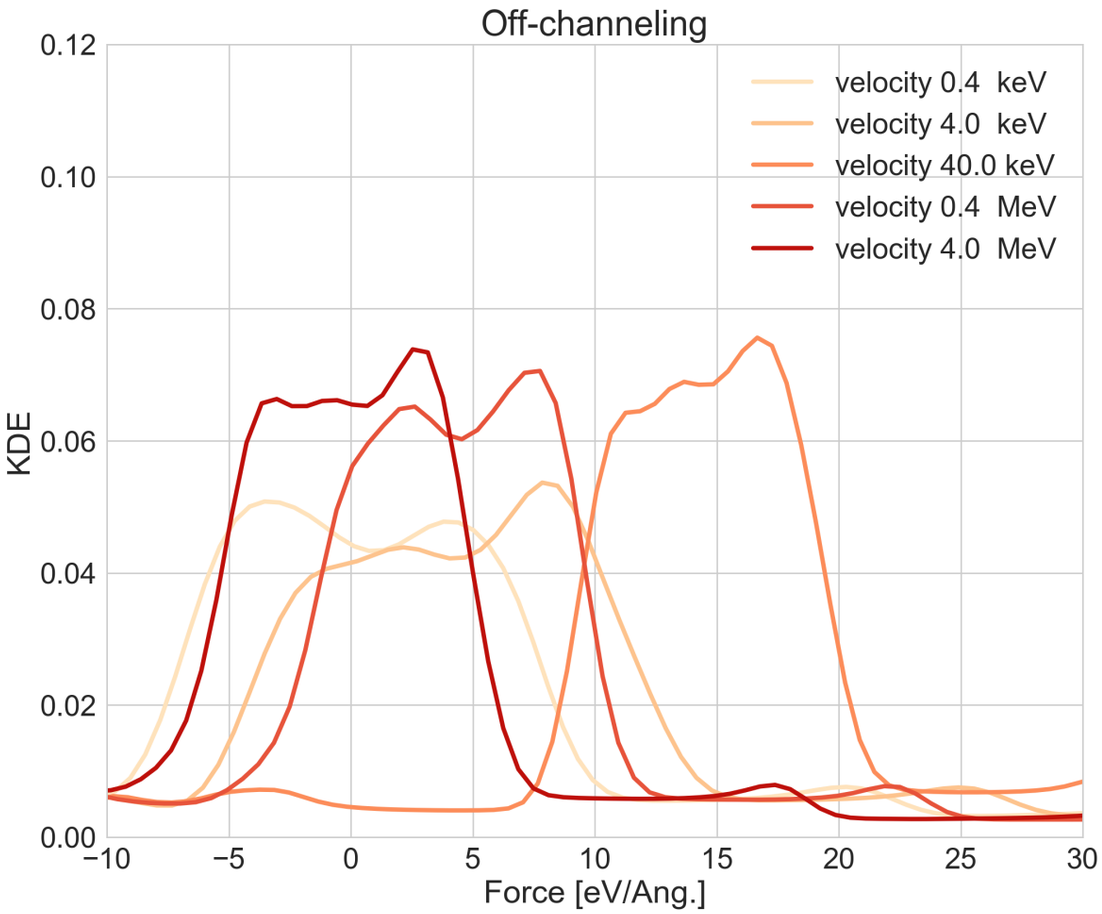
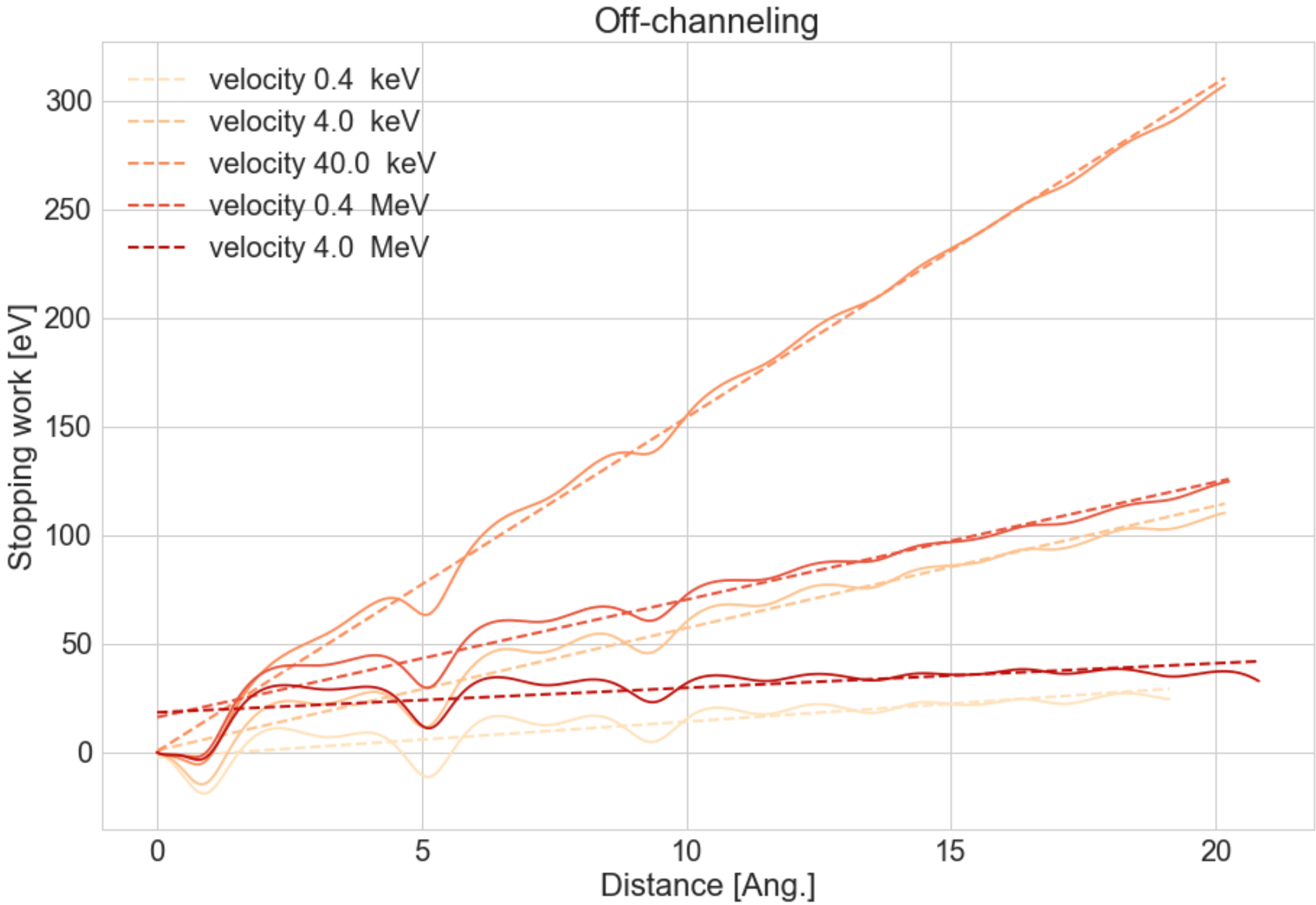
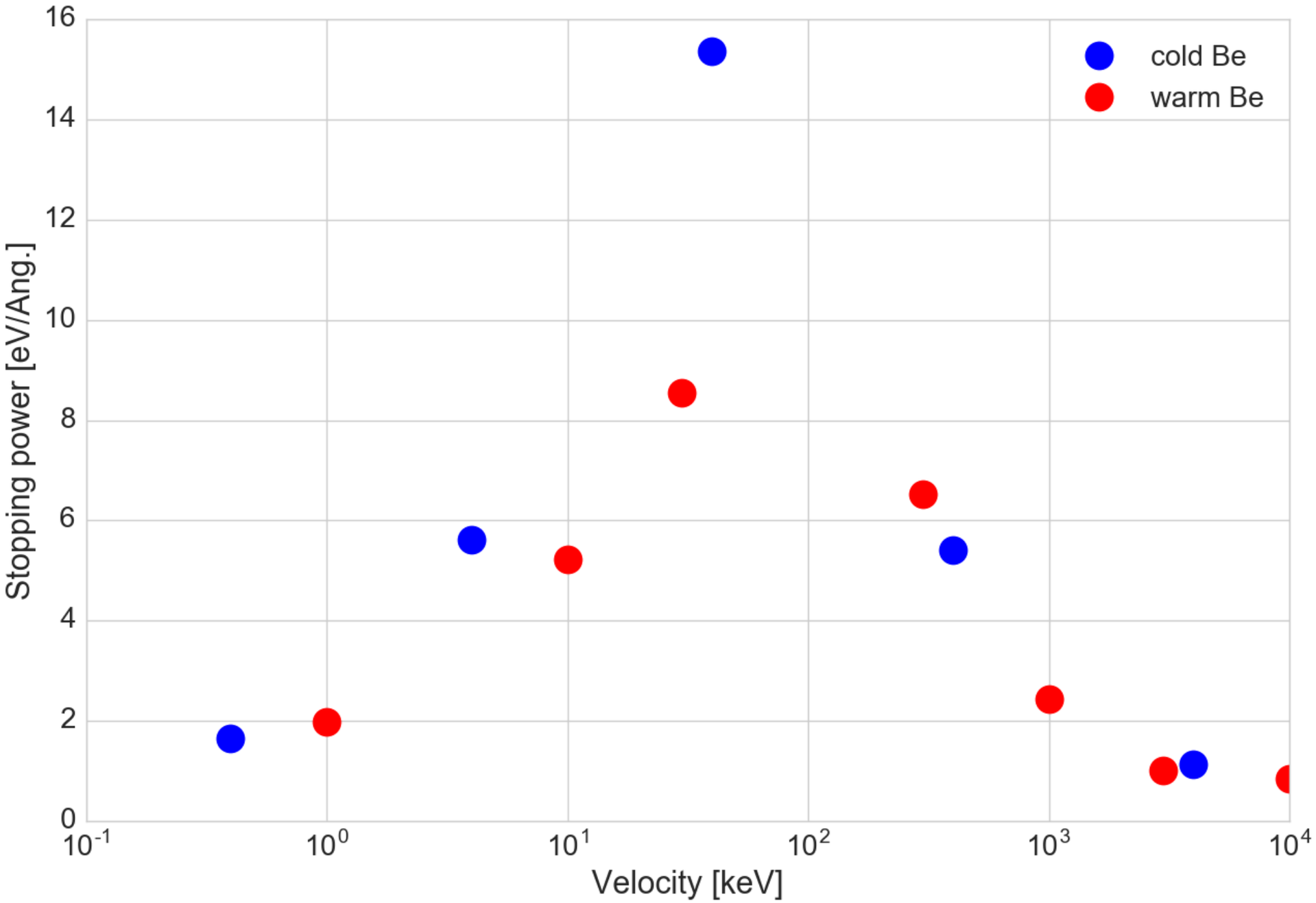




Electronic stopping work



Electronic stopping power



Conclusion

- Stopping power calculations help constrain experiments and lower level methods (averaged-atom models).

- Predictive stopping power calculations over a wide range of materials in the WDM regime
  - mixtures of target materials
  - different types of projectiles

- Extend our current approach
  - more accurate inclusion of non-adiabatic effects
  - corrections from exact factorization approach to coupled electron-ion dynamics

Thanks for your attention :)
Questions?

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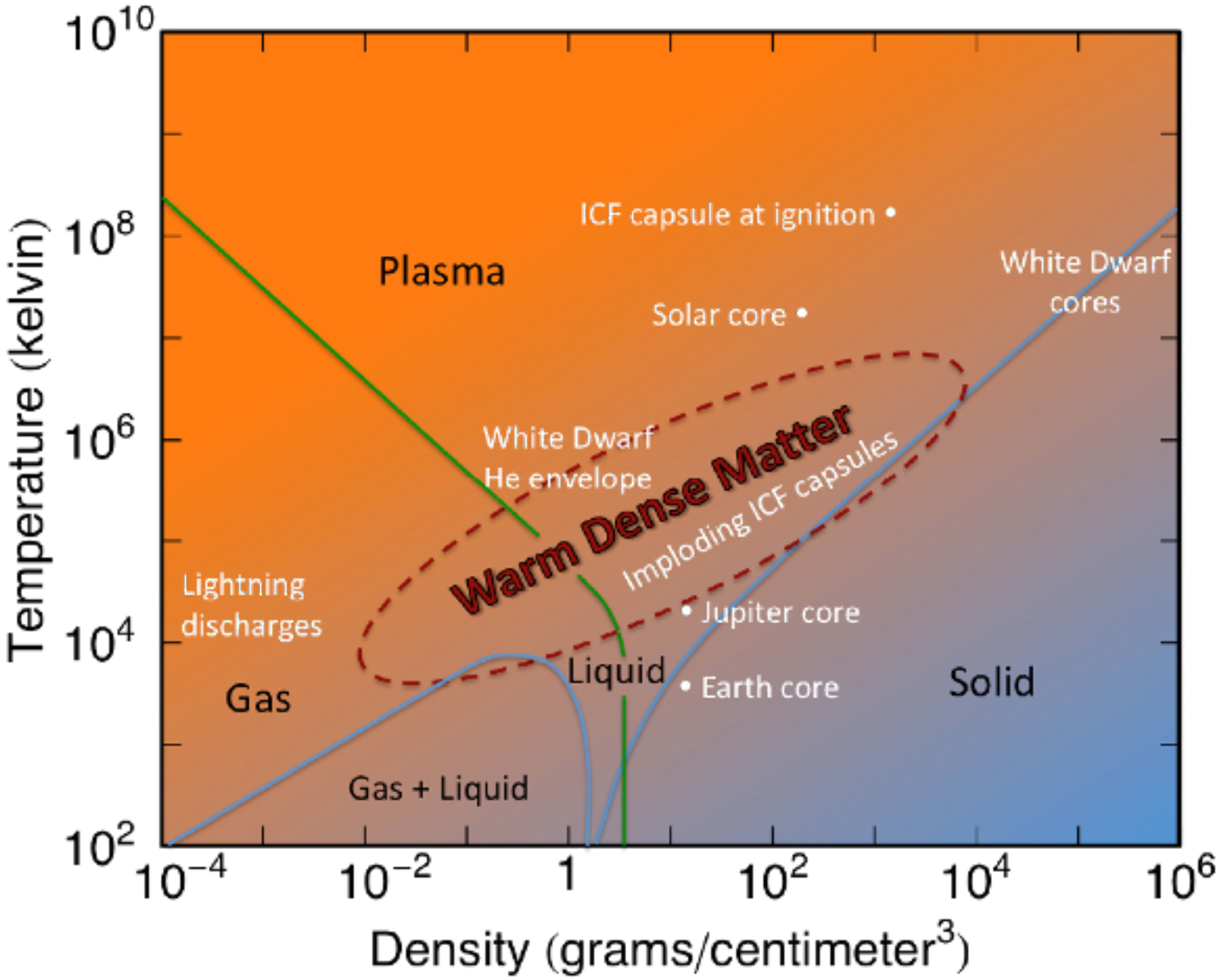
Supplemental material

What is warm dense matter?



Basic Research Needs for HEDLP, Report of the Workshop on HEDLP Research Needs, DOE (2008).

Coulomb coupling parameter:

$$\Gamma = \frac{V}{T} = \frac{Z\, e^2}{r_S\, k_B\, \tau}$$

Electron degeneracy parameter:

$$\Theta = \frac{k_B\, \tau}{E_F}$$

Warm dense matter regime:

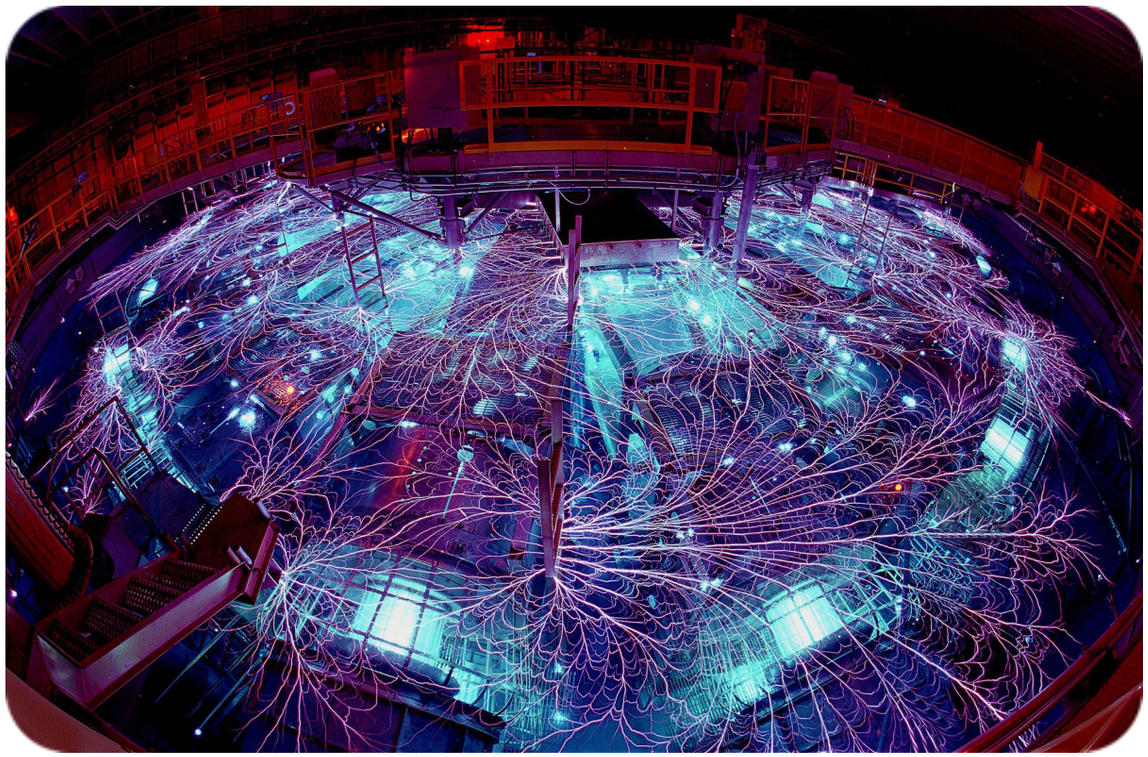
$$\Gamma \approx 1\,, \quad \Theta \approx 1$$

$$n \approx 10^{22} \ldots 10^{24} \mathrm{cm}^{-3}$$

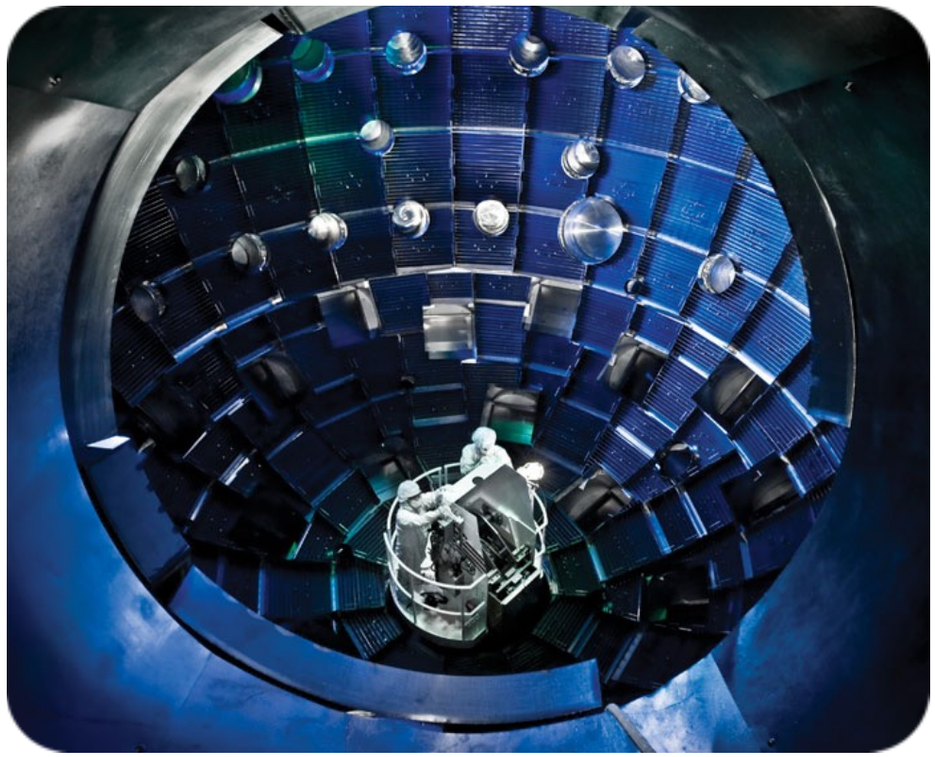
$$\tau \approx 1 \ldots 100 \mathrm{eV}$$

What is warm dense matter?

Creating WDM requires to transfer an enormous amount of energy to a target material in a very short period of time.



Z Machine, Sandia National Laboratories.



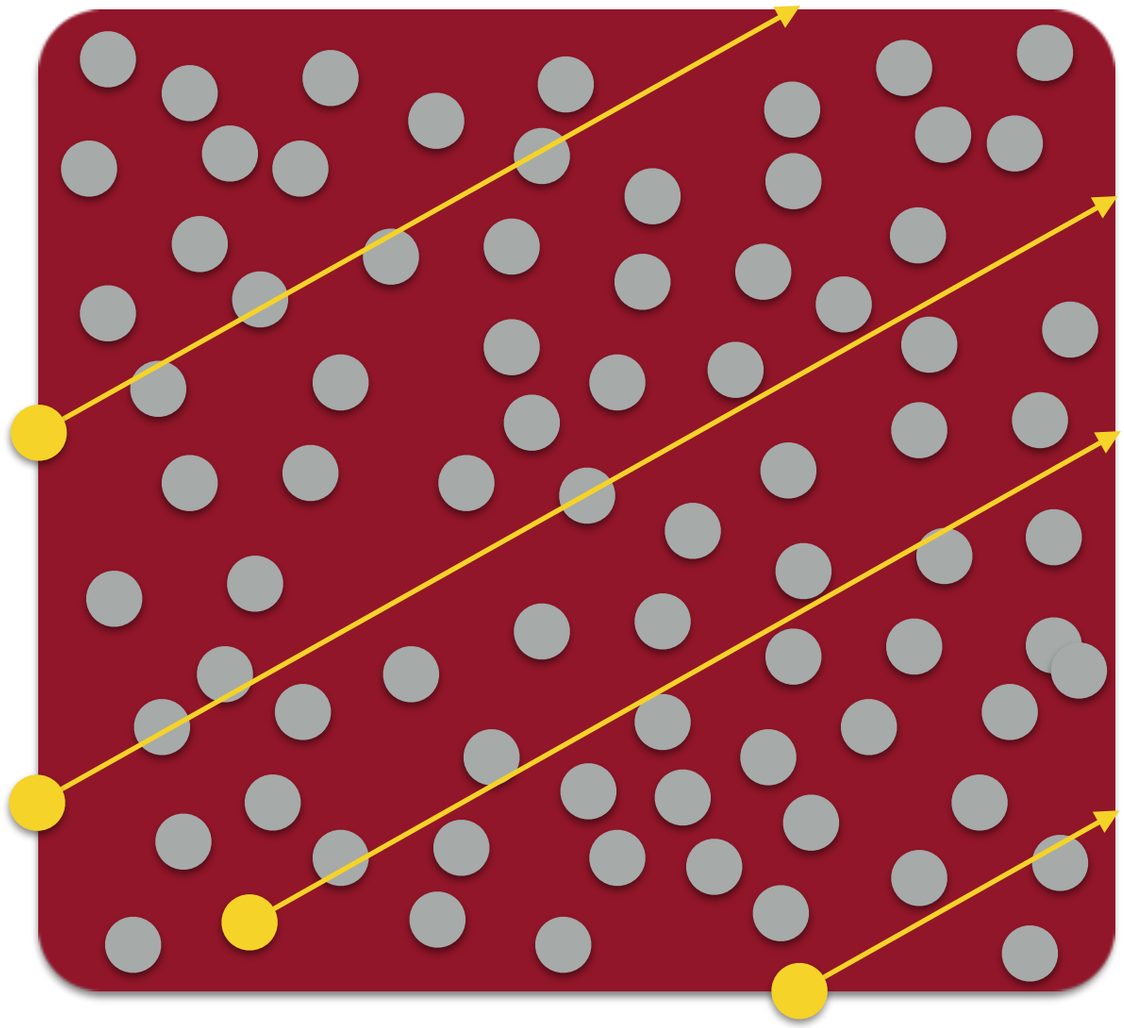
Target chamber, National Ignition Facility, Lawrence Livermore National Laboratories.

General set up

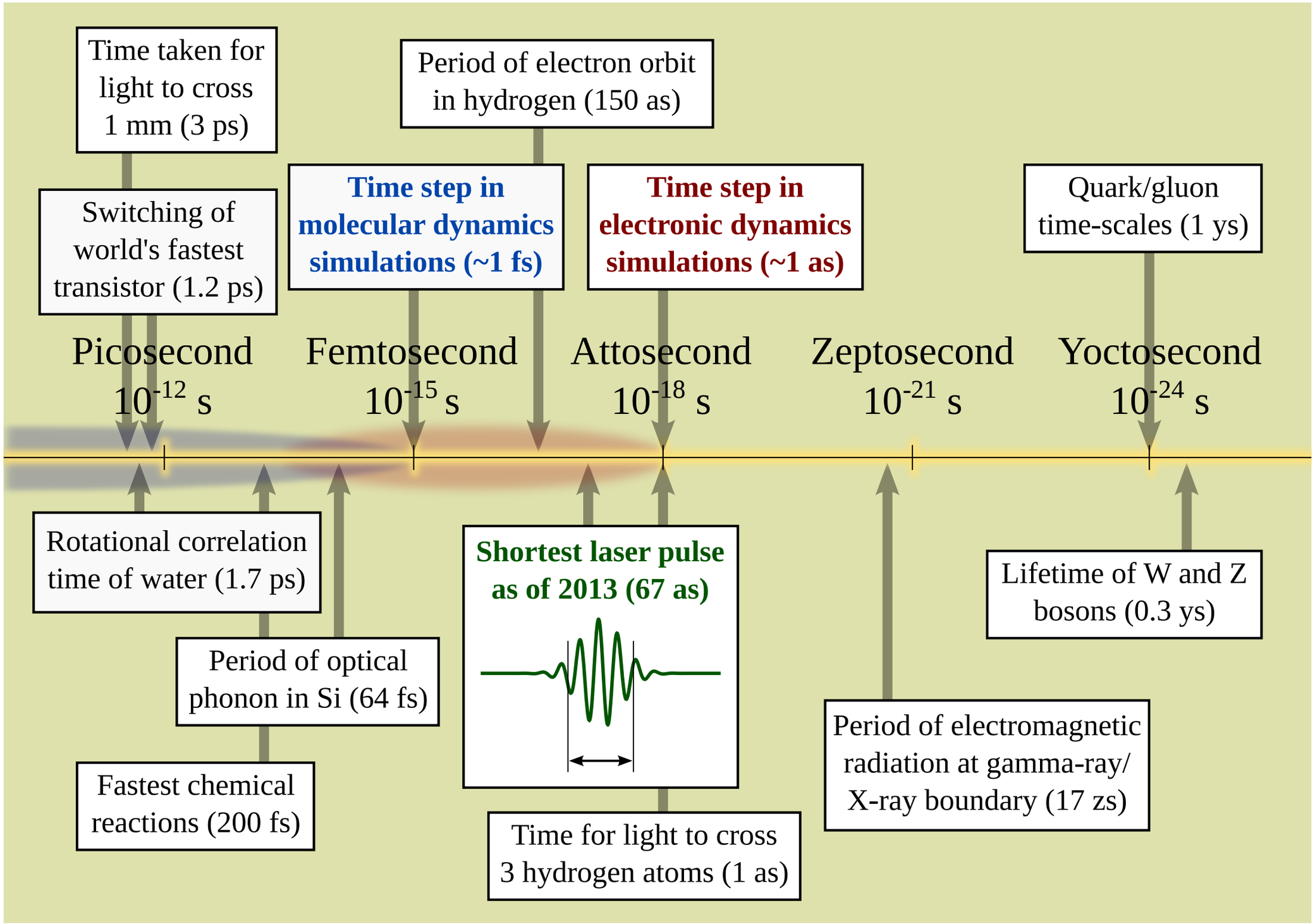
1. Converge thermalized DFT-MD calculations for a given atomic configuration.

2. Prepare initial state and add projectile.

3. Run TDDFT-Ehrenfest simulation and evaluate forces on the projectile.



Time scales



Courtesy of Kay Dewhurst, Max Planck Institute of Microstructure Physics (2015).

Density functional theory

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Electronic Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}$$

Hohenberg-Kohn functional

$$F[n] = \min_{\hat{\Psi}\to n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle$$

$$E_v = \min_n \left\{ F[n] + \int d\mathbf{r}\; n(\mathbf{r})\, v(\mathbf{r}) \right\}$$

Kohn-Sham scheme

$$\left\{ -\frac{\nabla^2}{2} + v_{\text{S}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

$$F[n] = T_{\text{S}}[n] + U[n] + E_{\text{XC}}[n]$$

$$v_{\text{S}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})}$$

Thermal density functional theory

Sandia National Laboratories

Electronic Hamiltonian	$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}$
	$\hat{\Gamma} = \sum_{N,i} w_{N,i} \left\lvert \Psi_{N,i} \right\rangle \left\langle \Psi_{N,i} \right\rvert$
Grand potential	$\hat{\Omega} = \hat{H} + \tau \hat{S} + \mu \hat{N}$
Mermin generalization	$F^\tau[n] = \min_{\hat{\Gamma} \to n} \left\{ T[\hat{\Gamma}] + V_{\text{ee}}[\hat{\Gamma}] - \tau S[\hat{\Gamma}] \right\}$
	$\Omega^\tau_{v-\mu} = \min_n \left\{ F^\tau[n] + \int d\mathbf{r}\ n(\mathbf{r})\ (v(\mathbf{r}) - \mu) \right\}$
Kohn-Sham scheme	$\left\{ -\frac{\nabla^2}{2} + v^\tau_{\text{S}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon^\tau_i \phi_i(\mathbf{r})$
	$n(\mathbf{r}) = \sum_i^N f^\tau_i \phi^*_i(\mathbf{r}) \phi_i(\mathbf{r}) \,, \quad f^\tau_i : \text{FD}$
	$F^\tau[n] = T^\tau_{\text{S}}[n] - \tau S^\tau[n] + U^\tau[n] + E^\tau_{\text{XC}}[n]$
	$v^\tau_{\text{S}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U^\tau[n]}{\delta n(\mathbf{r})} + \frac{\delta E^\tau_{\text{XC}}[n]}{\delta n(\mathbf{r})}$

Time-dependent density functional theory

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Electronic Hamiltonian	$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V}$
Runge-Gross theorem	$v(\mathbf{r},t) \overset{\Psi_0}{\longleftrightarrow} n(\mathbf{r},t)$
TD Kohn-Sham equations	$\mathrm{i}\dfrac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left\{-\dfrac{\nabla^2}{2} + v_{\mathrm{S}}(\mathbf{r},t)\right\}\phi_i(\mathbf{r},t)$ $v_{\mathrm{S}}(\mathbf{r},t) = v(\mathbf{r},t) + \dfrac{\delta U}{\delta n(\mathbf{r},t)} + \dfrac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r},t)}$
Adiabatic approximation	$v_{\mathrm{XC}}[n](\mathbf{r},t) = v_{\mathrm{XC}}[n_0](\mathbf{r})\big\vert_{n_0(\mathbf{r})\to n(\mathbf{r},t)}$

TDDFT with Ehrenfest dynamics

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Full Hamiltonian	$\hat{H} = -\sum_I \frac{1}{2M_I}\nabla_I^2 - \sum_i \frac{1}{2}\nabla_i^2 + \sum_{I<J} \frac{Z_I Z_J}{\lvert\mathbf{R}_I - \mathbf{R}_J\rvert} + \sum_{i<j} \frac{1}{\lvert\mathbf{r}_i - \mathbf{r}_j\rvert} - \sum_{I,i} \frac{Z_I}{\lvert\mathbf{R}_J - \mathbf{r}_i\rvert}$
Lagrangian	$L[\phi, \dot{\phi}, R, \dot{R}] = -\frac{\mathrm{i}}{2}\sum_i \int d\mathbf{r} \left\{\phi_i^*(\mathbf{r},t)\dot{\phi}_i(\mathbf{r},t) - \dot{\phi}_i^*(\mathbf{r},t)\phi_i(\mathbf{r},t)\right\} + \sum_I \frac{M_I}{2}\dot{\mathbf{R}}_I(t)\cdot\dot{\mathbf{R}}_I(t) - E[\phi, R]$
Equations of motion	$\mathrm{i}\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left\{-\frac{\nabla^2}{2} + v_{\mathrm{S}}(\mathbf{r},t)\right\}\phi_i(\mathbf{r},t)$ $M_I\ddot{\mathbf{R}}_I = -\nabla_I E[\phi, R]$
Energy in terms of KS quantities	$E[\phi, R] = T_{\mathrm{S}}[n] - \int d\mathbf{r} \sum_I \left(\frac{Z_I}{\lvert\mathbf{R}_I(t) - \mathbf{r}\rvert}\right) n(\mathbf{r},t) + U[n] + E_{\mathrm{XC}}[n] + \sum_{I<J} \frac{Z_I Z_J}{\lvert\mathbf{R}_I(t) - \mathbf{R}_J(t)\rvert}$

Implementation details

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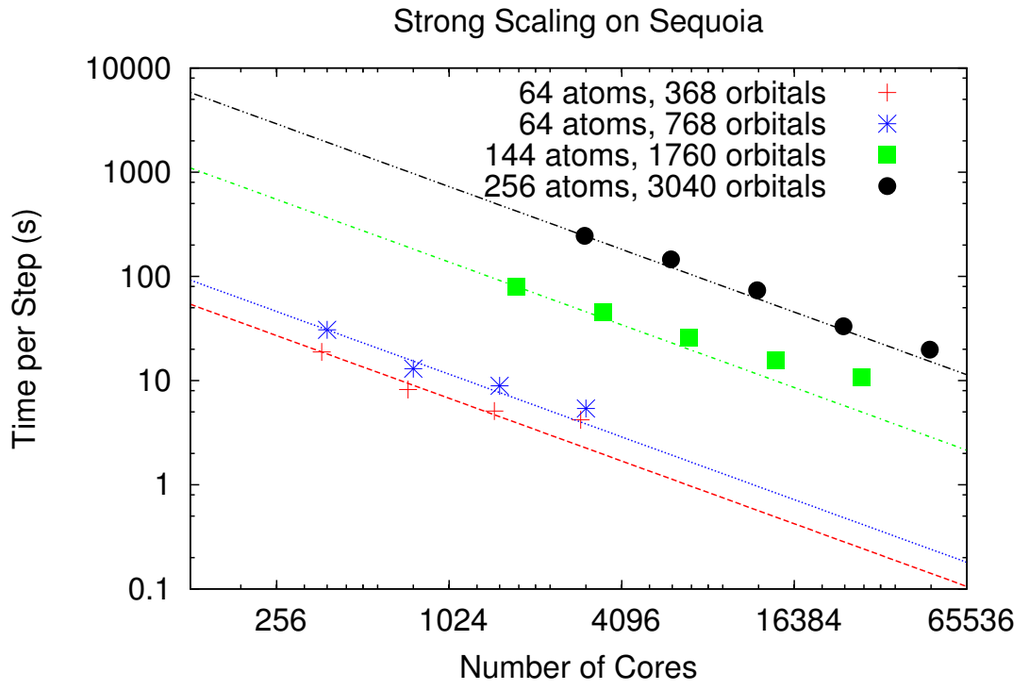
- Sandia implementation of TDDFT + Ehrenfest in VASP (Andrew Baczewski)
  - DFT-MD for **thermodynamics**
  - Kubo-Greenwood for **transport**
  - **Dynamic structure factor**

    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

b-initio VASP ackage ienna imulation

- About 10k extra lines of Fortran
  - Plane wave basis
  - Projector-augmented wave (PAW) formalism
  - Crank-Nicholson time integration (unitary)
  - Generalized minimal residual method
- Scales well on DOE's machines
- Orders of magnitude more expensive
  - Typically **100s of cores, a few hours**
  - No "free" parameters (takes mass density, # of electrons, and exchange-correlation functional)



PAWs

- PAW is among the **most accurate** pseudization frameworks
  - Variational DOFs are **plane wave coefficients**
  - PAW maps plane wave DOFs to **all-electron** quantities through linear transform[1]
  - **Frozen core approximation** still used to reduce problem size

$$|\psi_{n,\mathbf{k}}(\mathbf{r},t)\rangle = \left[1 + \sum_{i,j_1,j_2} \left(|\phi^i_{j_1}\rangle - |\tilde{\phi}^i_{j_1}\rangle\right) \langle \tilde{p}^i_{j_2}|\right] |\tilde{\psi}_{n,\mathbf{k}}(\mathbf{r},t)\rangle$$

- Use of reciprocal space projectors kills O(N) scaling of TDDFT
- Currently testing **real space projectors** for stopping
- Pulay-like terms need to be added to forces, TDKS solve

Time-propagation method

We use **Crank-Nicolson** for integration of the TDKS equations

$$\left[S + \frac{i\Delta t}{2}\{H(t+\Delta t) + P(t+\Delta t)\}\right] |\psi_{n,\mathbf{k}}(t+\Delta t)\rangle = \left[S - \frac{i\Delta t}{2}\{H(t) + P(t)\}\right] |\psi_{n,\mathbf{k}}(t)\rangle$$

Pulay-like term makes effective Hamiltonian **non-Hermitian**

Counterintuitively, this is **necessary to conserve charge!**
(but it also requires very small errors in iterative solve)

Using GMRES and 8 digit tolerance, we lose **9 microelectrons / fs**
(out of 128 at Te=10 eV)