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Trajectories and pseudization in first-principles calculations of electronic stopping in warm dense matter

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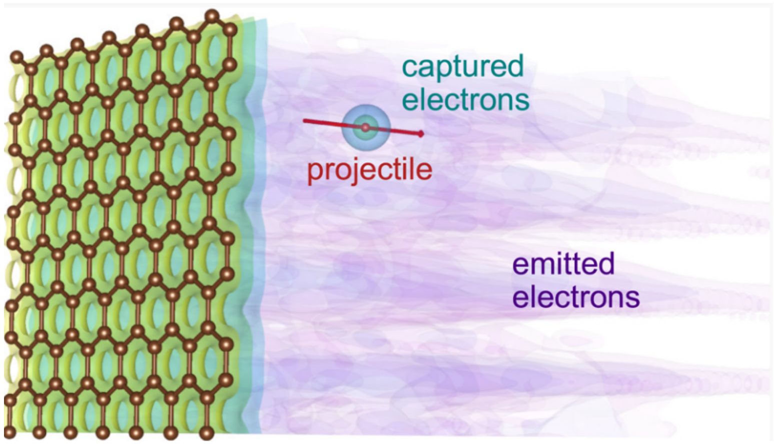
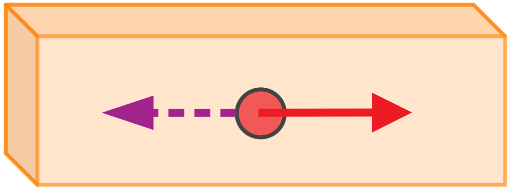
Motivations for ion-irradiated materials

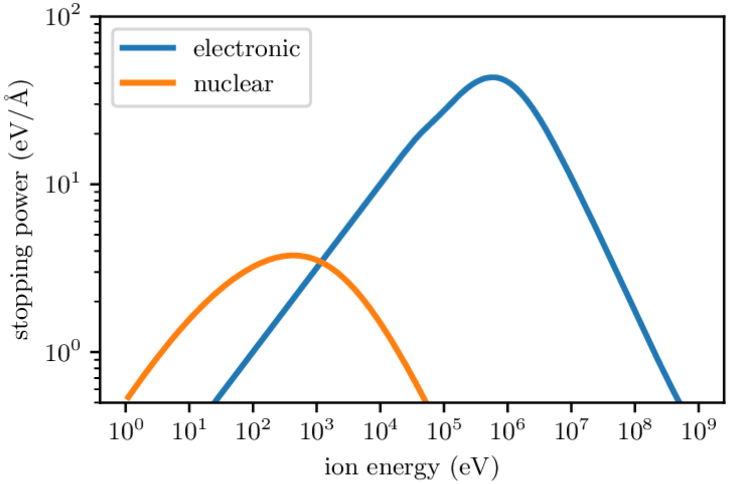
- Targeting tumors in radiation therapy
- Radiation hardness in space and nuclear environments
- Controlling damage, defects in materials imaging and processing
- Achieving ignition for fusion energy

stopping power:
friction force experienced by an ion traversing matter



Kononov and Schleife, Nano Lett. 21 (2021)
Kononov et al., 2D Mater. 9 (2022)

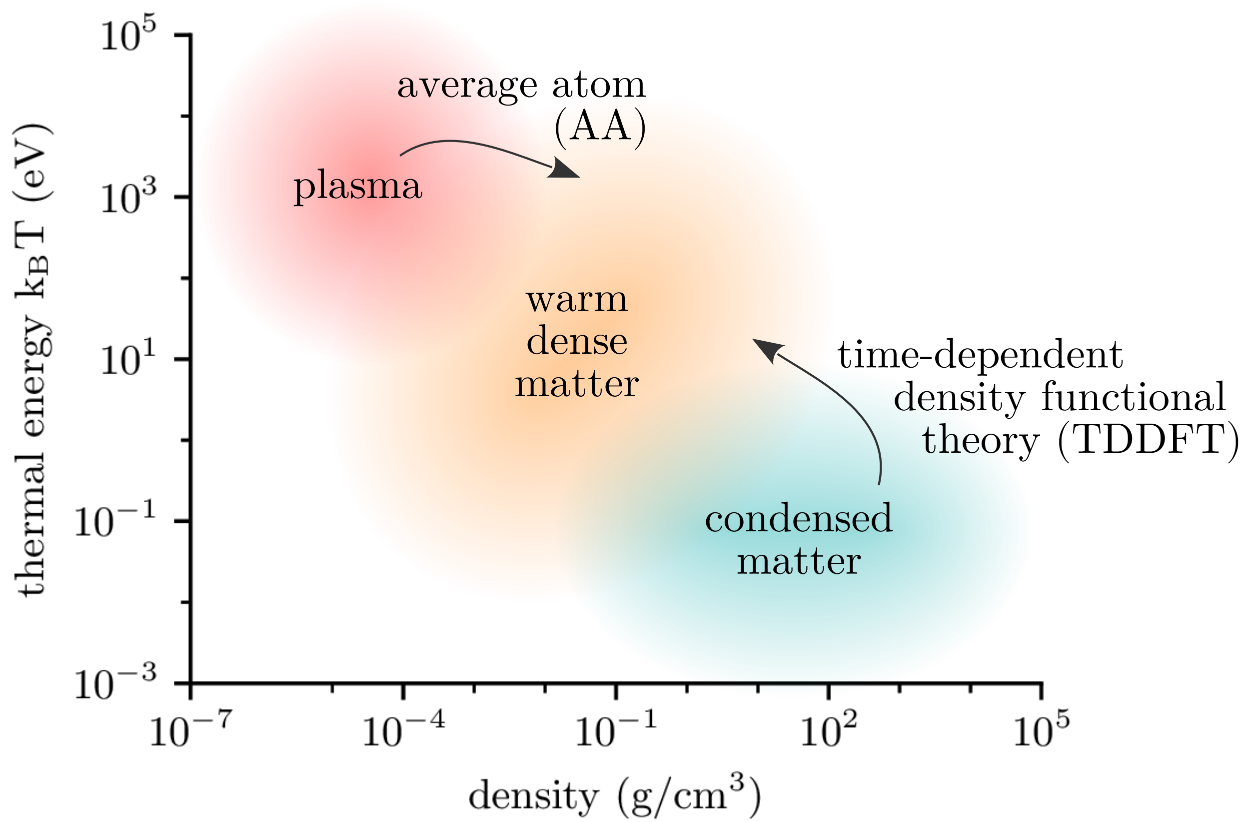




Bridging the Gap between Plasma and Condensed Matter

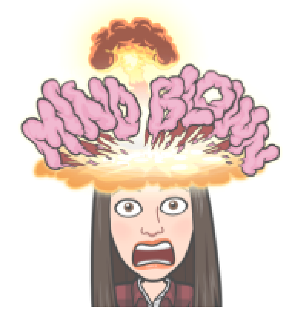
Goals:

- develop first-principles understanding of T-effects (pseudization)
- reduce cost of TDDFT stopping calculations (trajectories)
- benchmark cheaper AA against more accurate but expensive TDDFT



$$n(\mathbf{r}, t) = \sum_j f_j(T)|\phi_j(\mathbf{r}, t)|^2$$

- Many thermally occupied KS states
- ~10 million CPU-hours per data point!



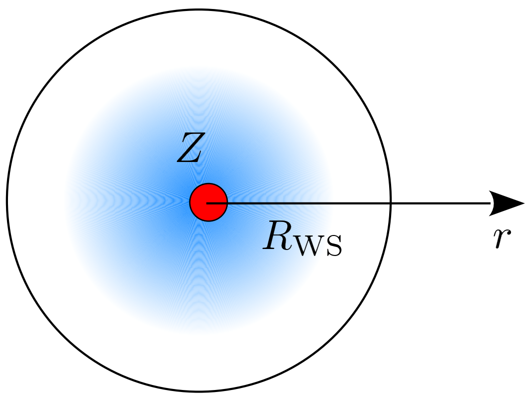
Average Atom Models

- Mean-field model of electronic ground state of a single atom
- Assume spherical symmetry
- Self-consistently solve for $n(r)$ within Wigner-Seitz sphere

$$\hat{H}[n(r)]\phi_j(r) = \varepsilon_j \phi_j(r)$$

$$n(r) = \frac{1}{4\pi r^2} \sum_j f(\varepsilon_j) 2(2\ell_j + 1) |\phi_j(r)|^2$$

$$\hat{H}[n(r)] = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + V_{\mathrm{Har}}[n(r)] + V_{\mathrm{xc}}[n(r)] + \frac{\ell_j(\ell_j+1)}{r^2}$$



$$\frac{4}{3}\pi R_{\mathrm{WS}}^3 = \frac{1}{n_{\mathrm{ion}}}$$

- Apply various models to compute observables from atomic orbitals and energy levels
  - often separate treatment of “bound” and “free” electrons

✔ Efficient and “accurate” across wide range of plasma conditions

✗ Breaks down at high densities in warm dense matter regime

✔ Extensions relax symmetry assumptions

✗ Band structure, dynamics, effects beyond GS orbitals challenging

Stopping powers from RT-TDDFT

Initial condition: equilibrium state from Mermin-DFT

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \hat{H}[n(\mathbf{r},t)]\phi_j(\mathbf{r},t)$$

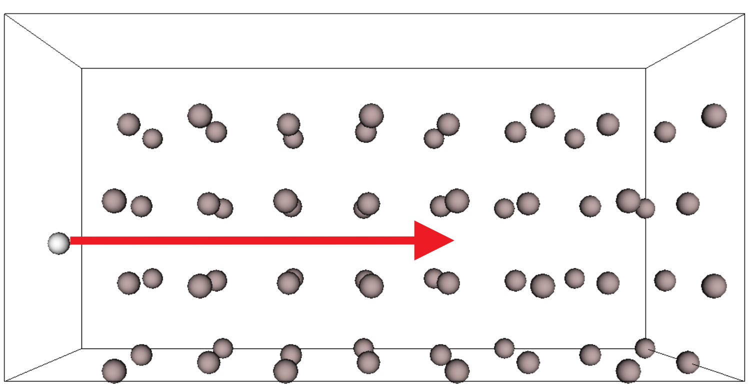
Evolve electron density $n(\mathbf{r},t)$ in real time

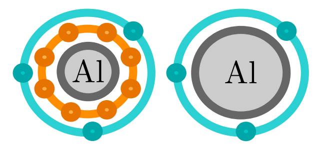
$$n(\mathbf{r},t) = \sum_j f_j(T)|\phi_j(\mathbf{r},t)|^2$$

$$\hat{H}[n(\mathbf{r},t)](t) = -\frac{\nabla^2}{2} + V_{\text{ext}}(t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'^3 + V_{\text{xc}}[n(\mathbf{r},t)]$$

explicit time-dependence from moving ion

- often nonlinear
- requires real-time treatment
- in some sense, approximate!





pseudopotential approximation

- neglects core excitations
- allows detailed insights into mechanisms

adiabatic local density approximation

- seems sufficient
- alternatives too expensive
- memory effects unknown
- thermal effects unknown

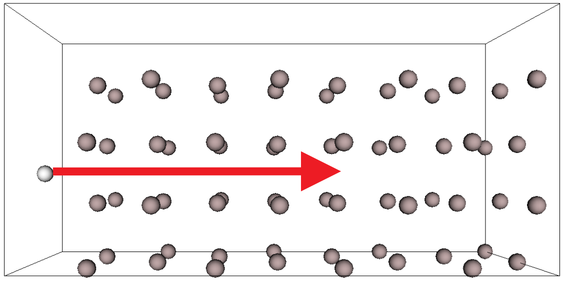
$$\mathrm{S} \sim \mathbf{F}_\alpha[n](t) = -\left\langle \frac{\partial \hat{H}[n]}{\partial \mathbf{R}_\alpha} \right\rangle + \text{PAW terms}$$

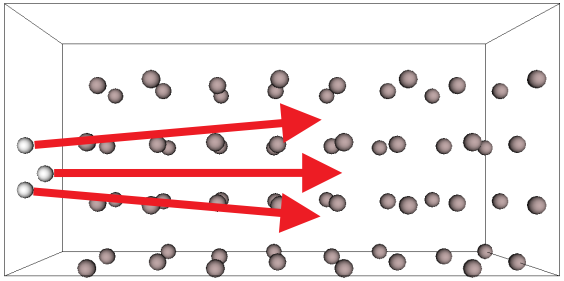
Projectile trajectory: theory vs. experiment

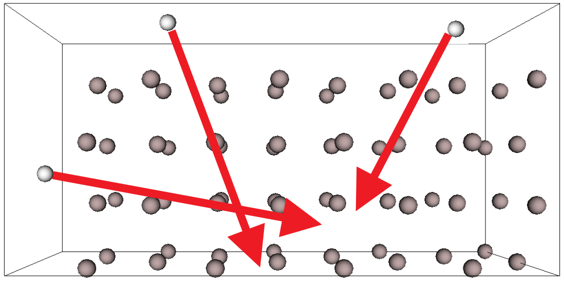
A TDDFT calculation models a particular path through the material...

But experiments involve finite-width beams...

And applications involve randomly oriented radiation!



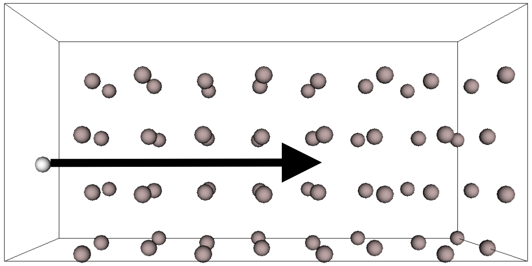




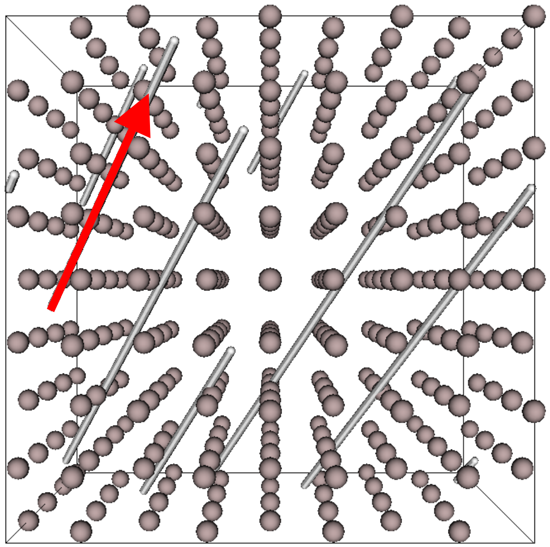
Trajectories Determine Core Excitation Sampling

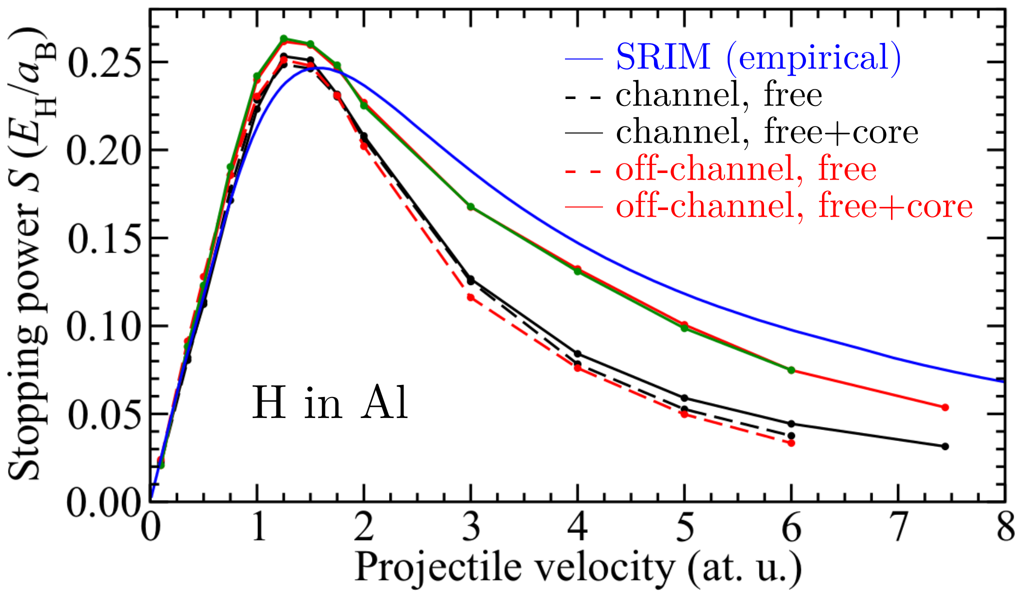
- Channeling trajectory does not excite core
- Free-electron stopping ~independent of trajectory
- Core-electron stopping very sensitive!
- Close collisions needed to excite core and capture experiment

channeling



off-channeling





Schleife et al., PRB 91 (2015)

Projectile trajectory: theory vs. experiment

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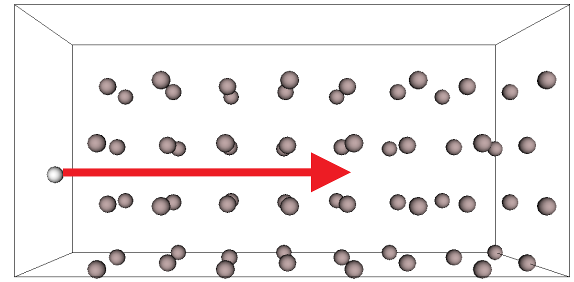
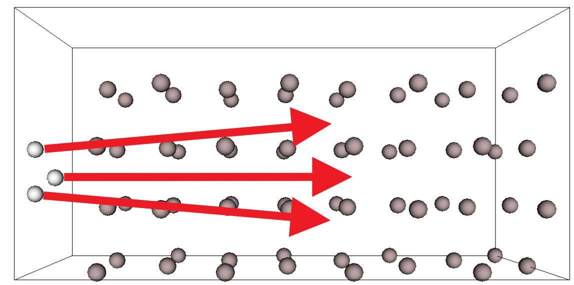
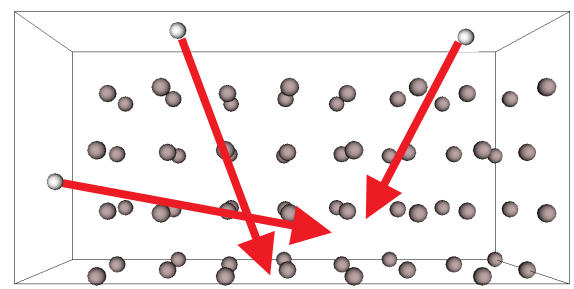


But experiments involve finite-width beams...



And applications involve randomly oriented radiation!

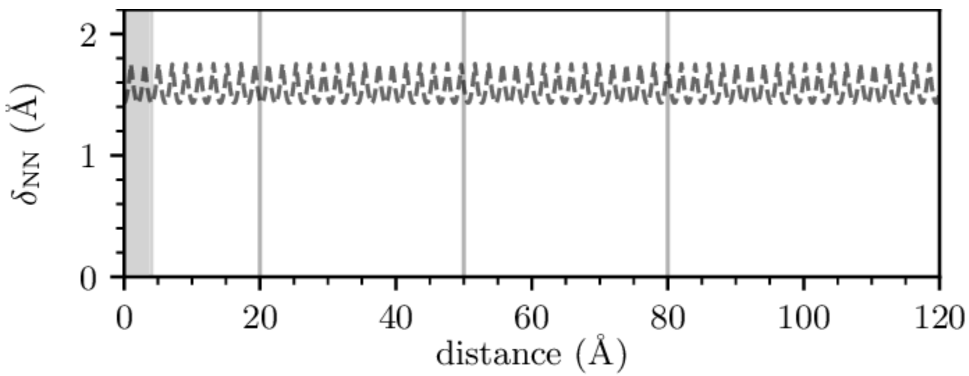


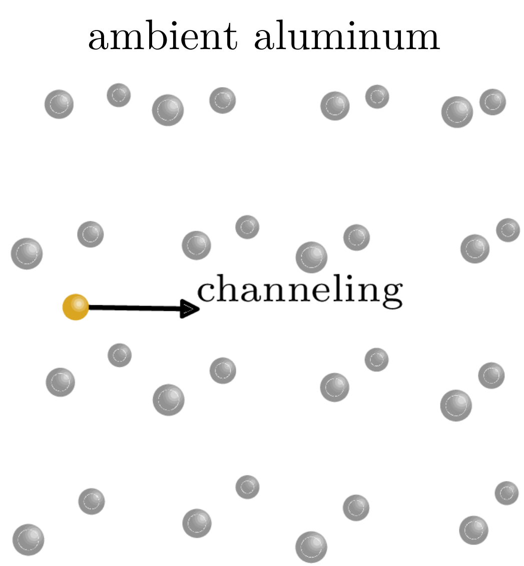
Solutions:

- Use a single, random trajectory – could get unlucky
- Average TDDFT results over many trajectories – expensive
- Use a single, carefully chosen, representative trajectory

Quantitative Metric to Evaluate Trajectories

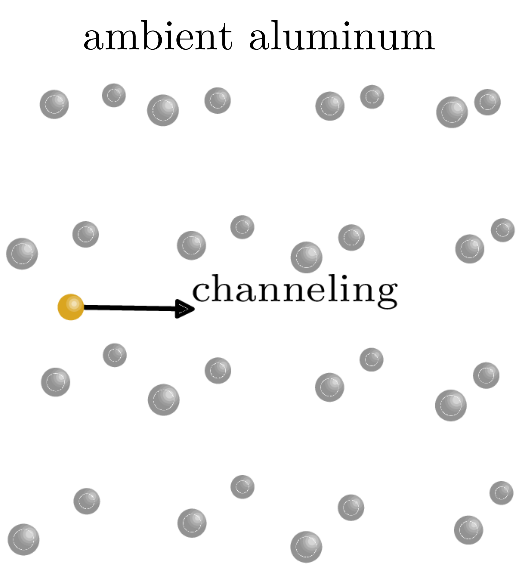
- Projectile should experience representative NN distances

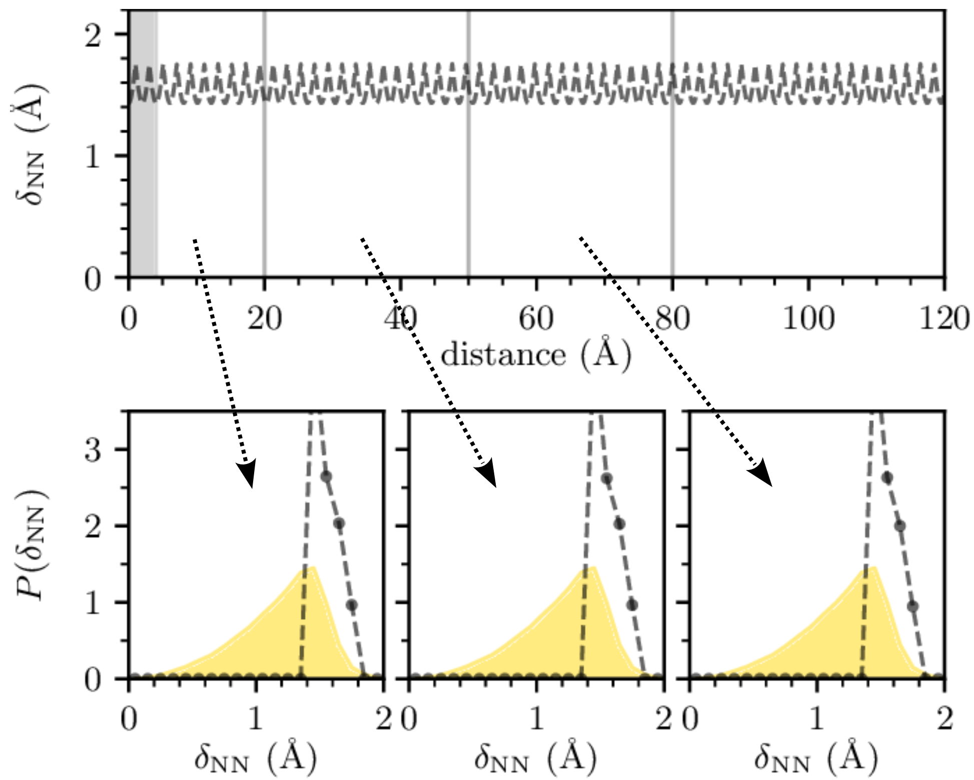




Quantitative Metric to Evaluate Trajectories

- Projectile should experience representative NN distances
- Ideal NN distribution: sample random points in cell

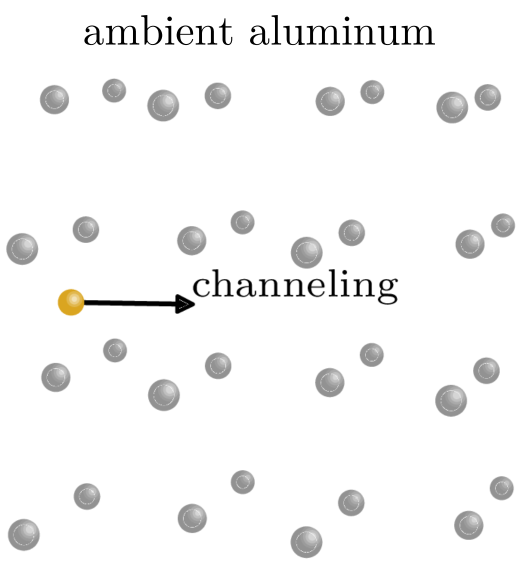


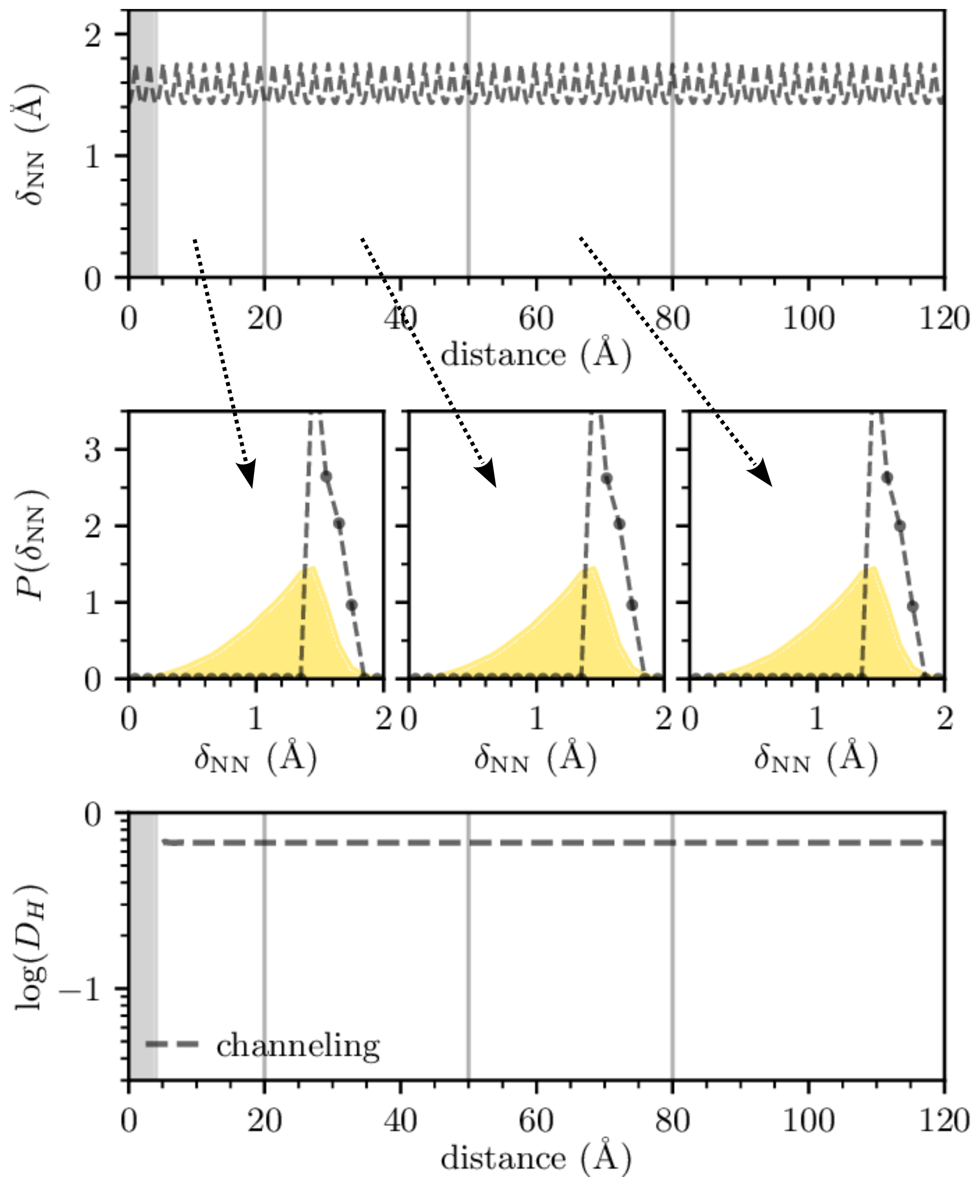


Quantitative Metric to Evaluate Trajectories

- Projectile should experience representative NN distances
- Ideal NN distribution: sample random points in cell
- Good trajectory achieves low Hellinger distance

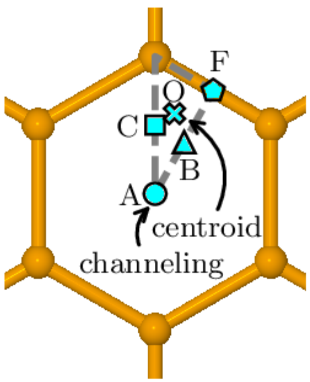
$$D_H^2 = 1 - \int_0^\infty \sqrt{P_{\text{traj}}(\delta_{NN}) P_{\text{ideal}}(\delta_{NN})}\, d\delta_{NN}$$

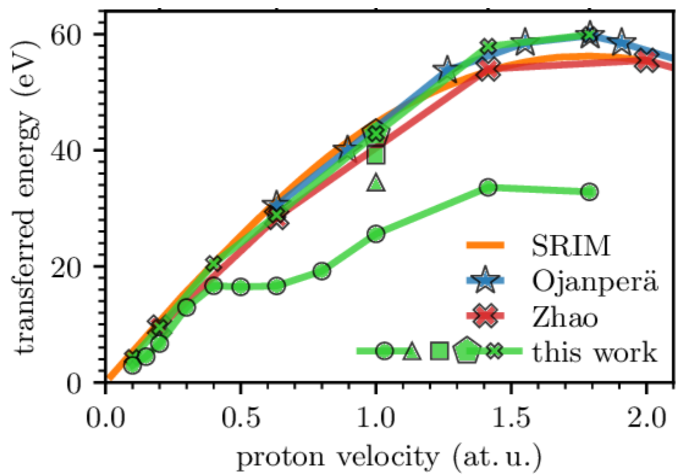




The Centroid Path Approximation

- Helpful for covalently bonded materials, e.g., graphene, near/below peak
- Inadequately captures core contributions at high v, even for low Z materials



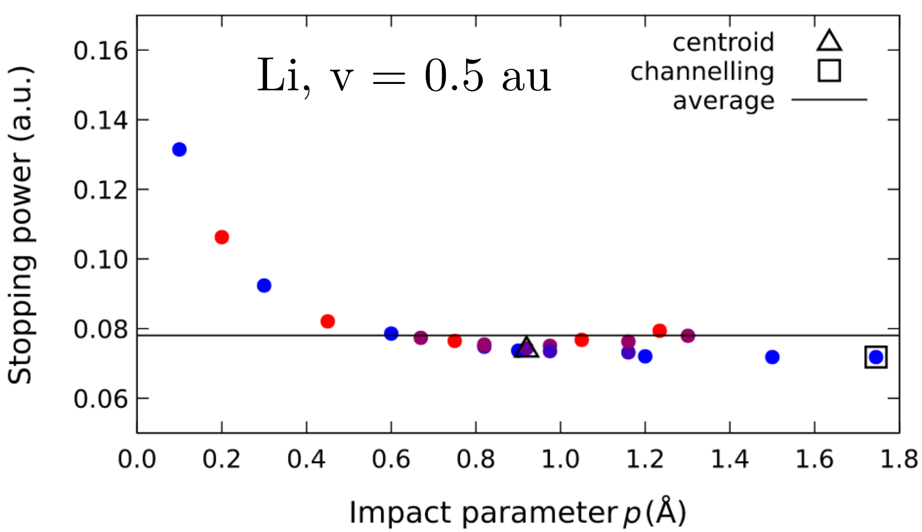


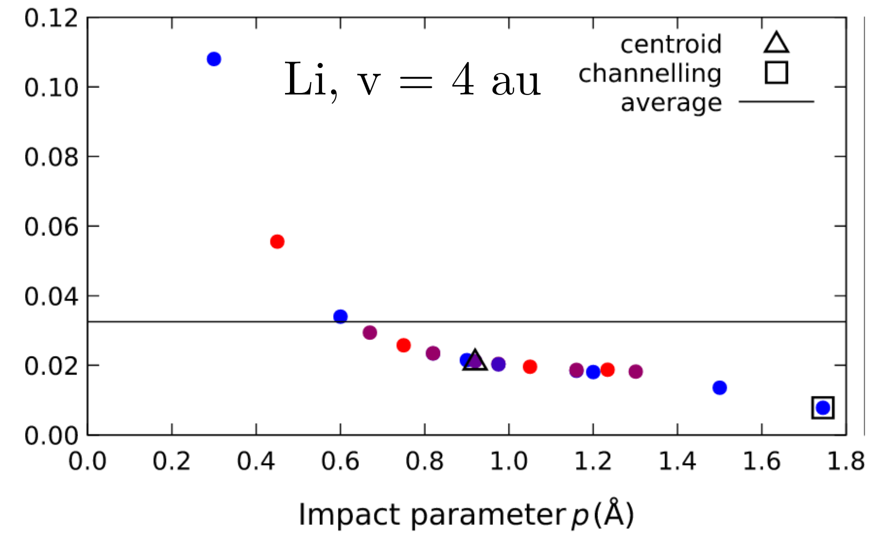
Kononov and Schleife, Nano Lett. 21 (2021)

Ziegler et al., Nucl. Instrum. Meth. B 268 (2010)

Ojanperä et al., Phys. Rev. B 89 (2014)

Zhao et al., J. Phys.-Condens. Mat. 27 (2015)





Maliyov et al., Eur. Phys. J B (2018)

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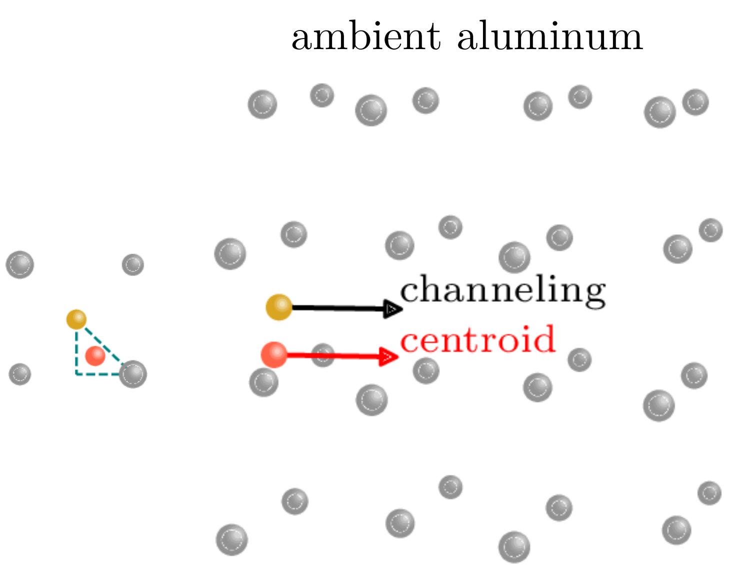

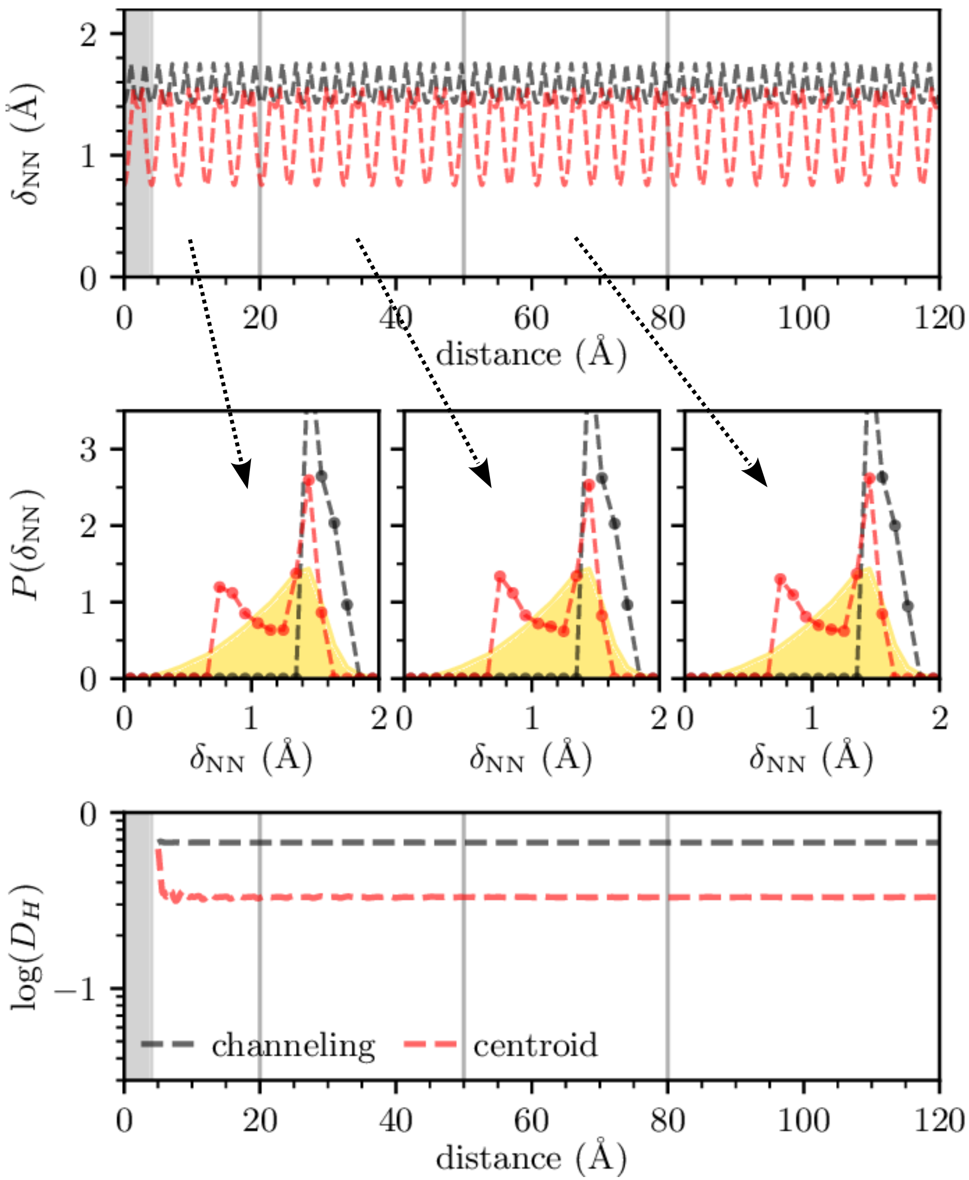

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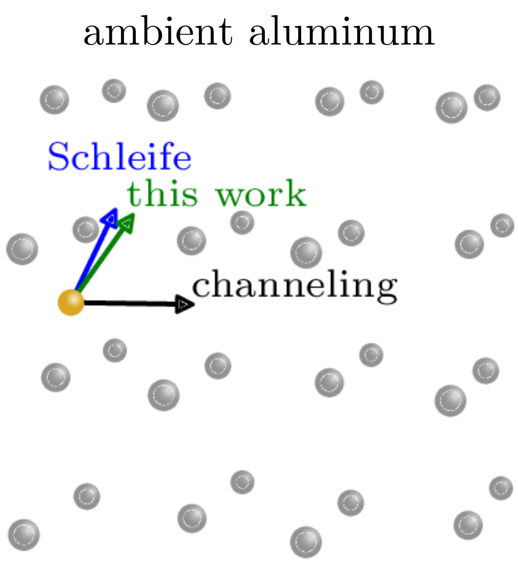

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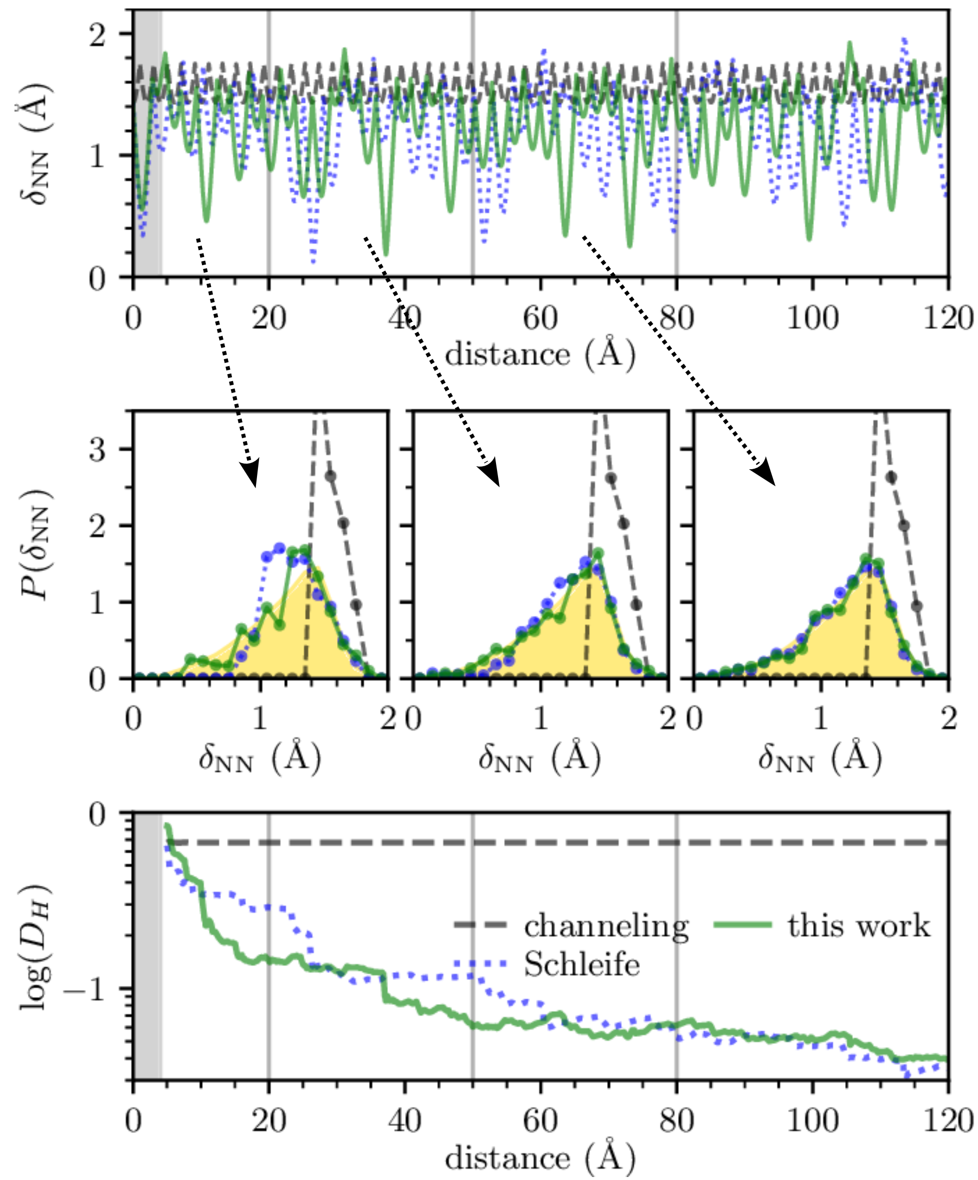

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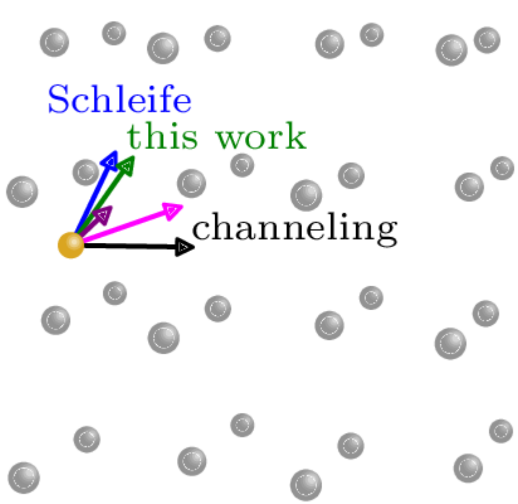
ambient aluminum



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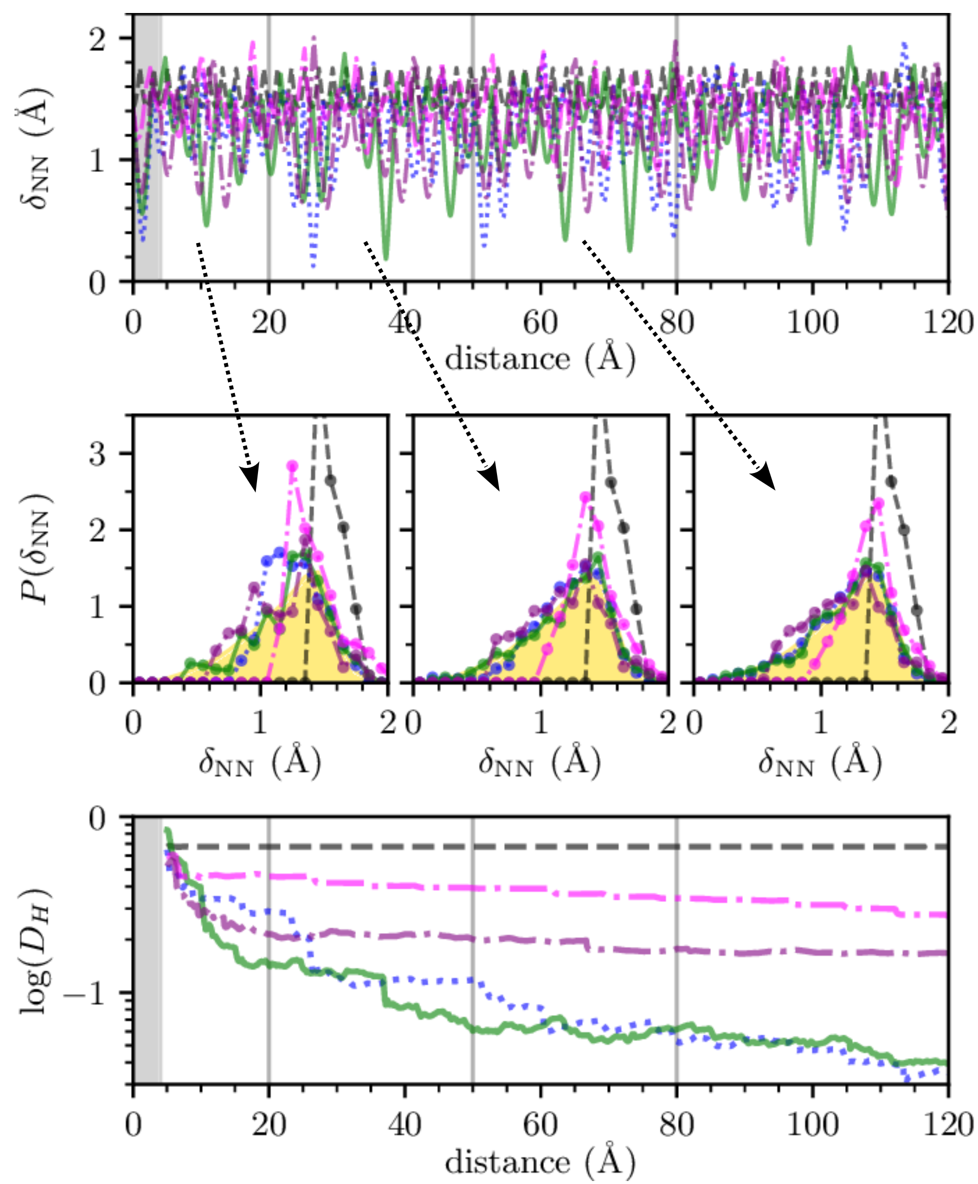

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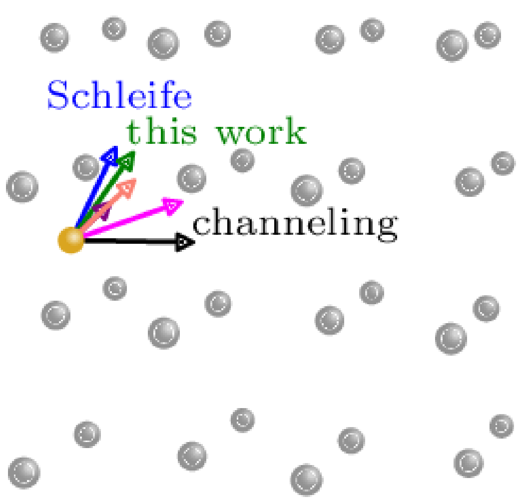

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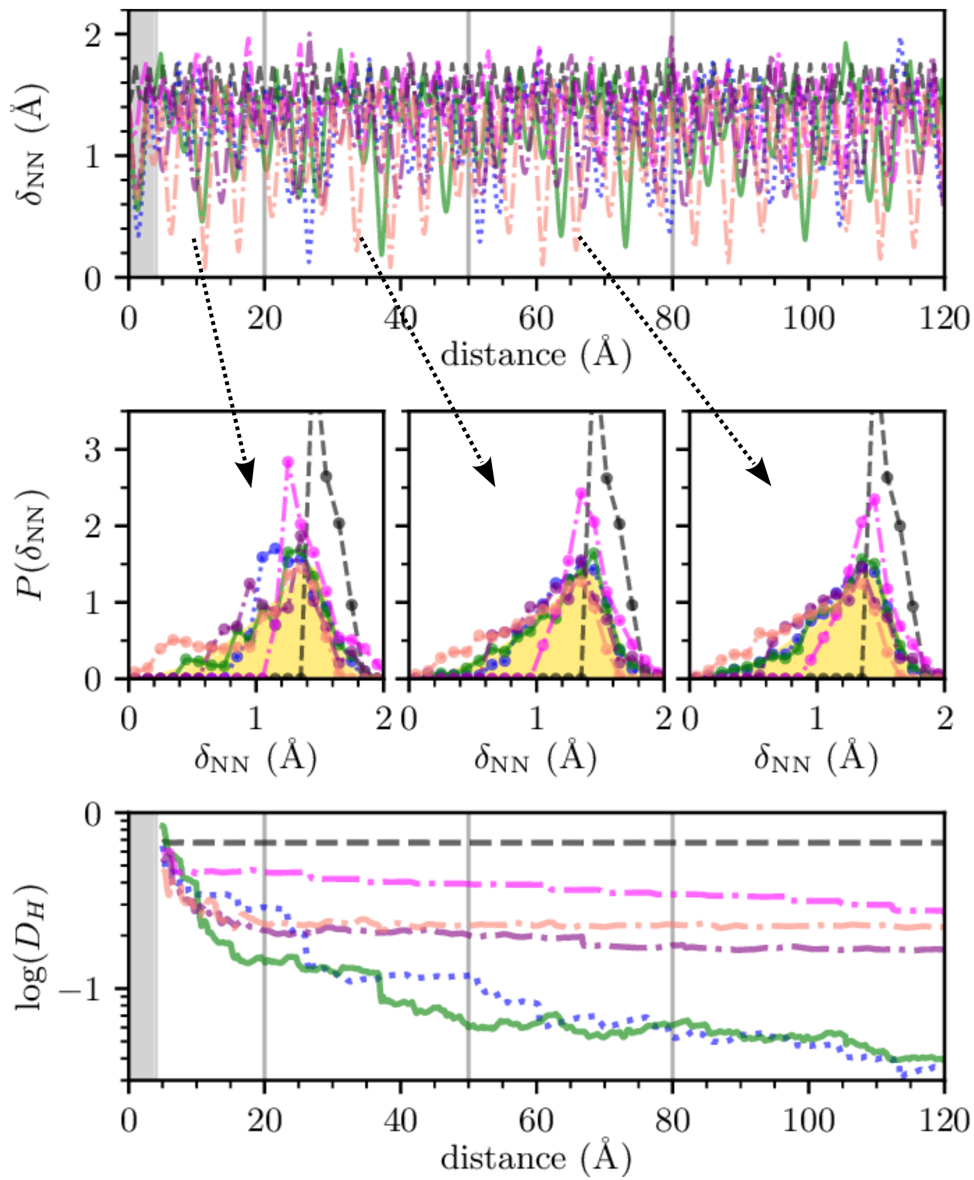
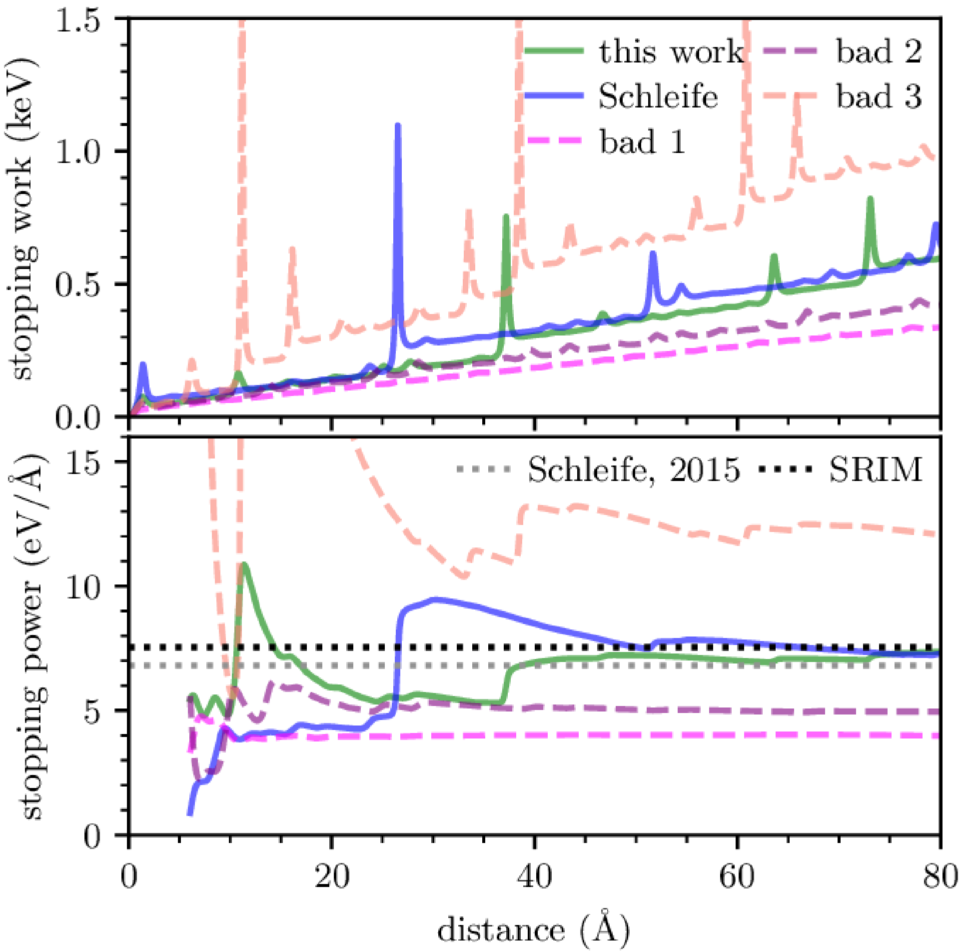
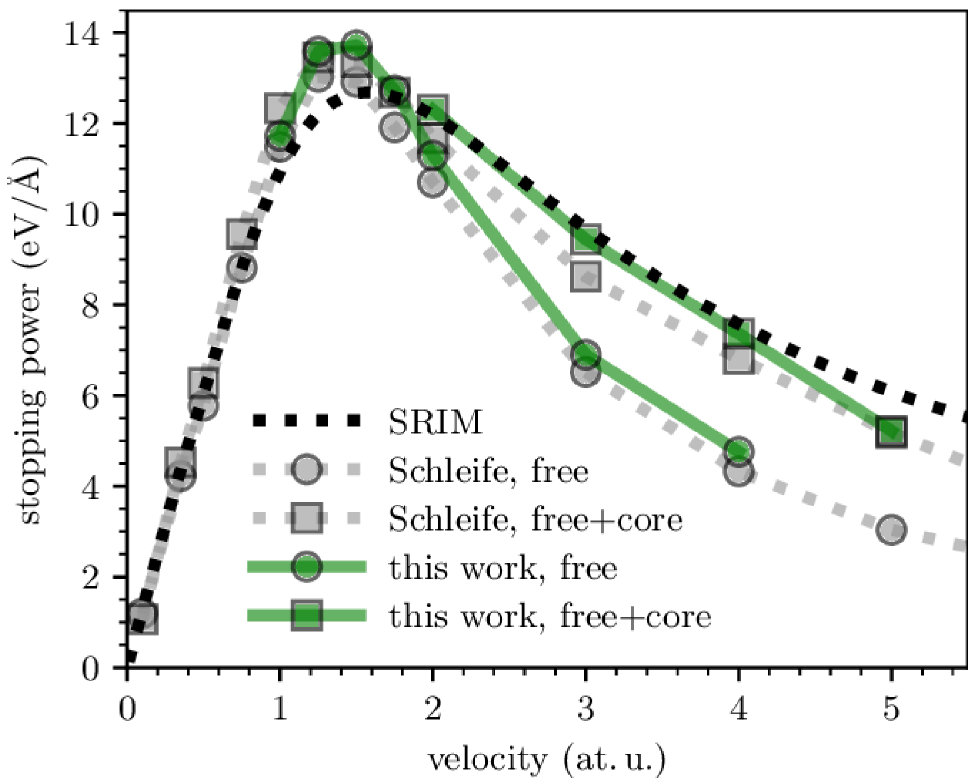


Quantitative Metric to Evaluate Trajectories

- Tests for v=4 at. u. proton in ambient aluminum
- “Good” trajectories agree within 1% and reproduce empirical data
- “Bad” trajectories off by up to 65% – incorrect sampling of close collisions





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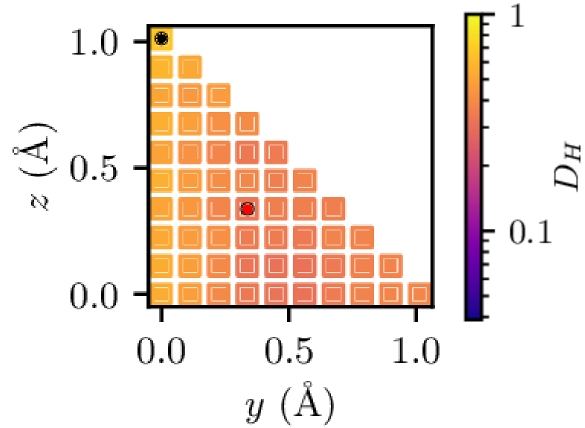
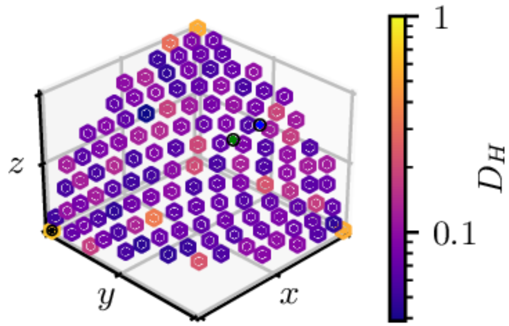
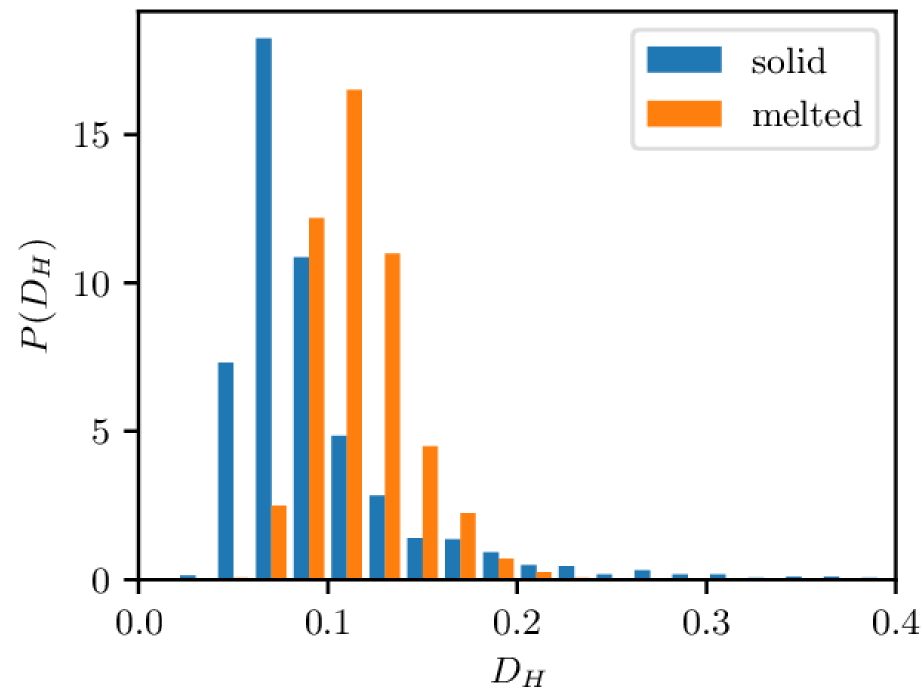
Trajectory Statistics

- No channeling trajectory achieves $D_H < 0.3$
- D_H very sensitive to trajectory angle (for finite path length)
- ~25% of random trajectories have $D_H > 0.1$ after 80 Å
- More likely to get unlucky in melted system!

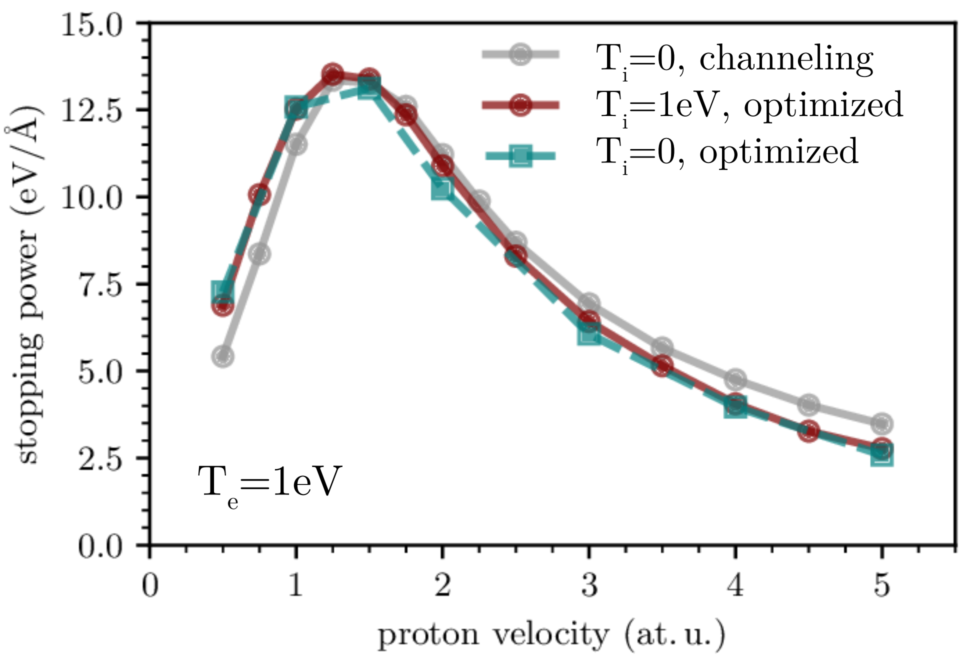


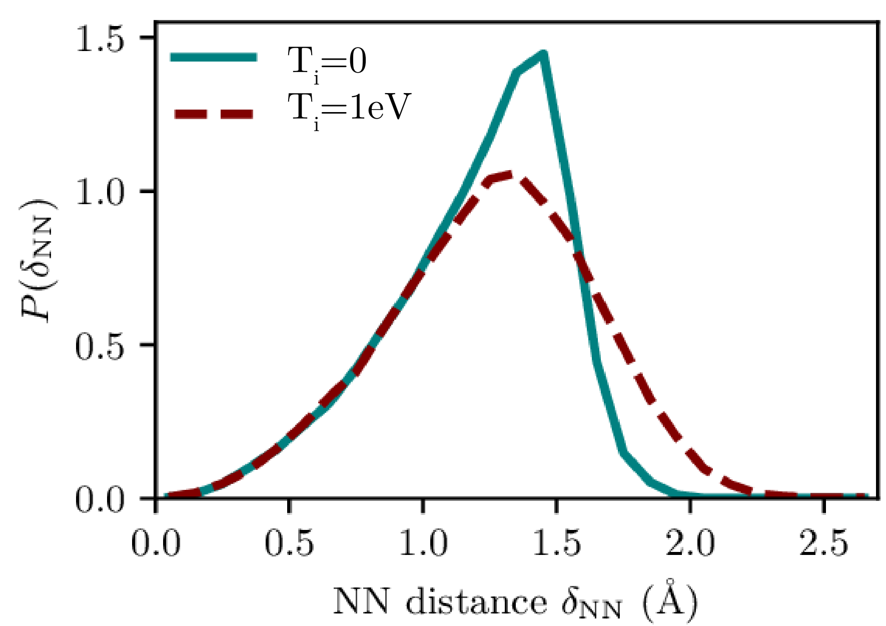




Proton Stopping in Aluminum: ion temperature

- Trajectory metric allows controlled comparisons in WDM
  - across different T
  - across different atomic configurations
  - thermalized vs. isochorically heated systems
- Free-electron stopping independent of ion temperature
  - slight variation with projectile trajectory
  - selecting similarly optimized trajectories important
- Verifying independence of core contribution

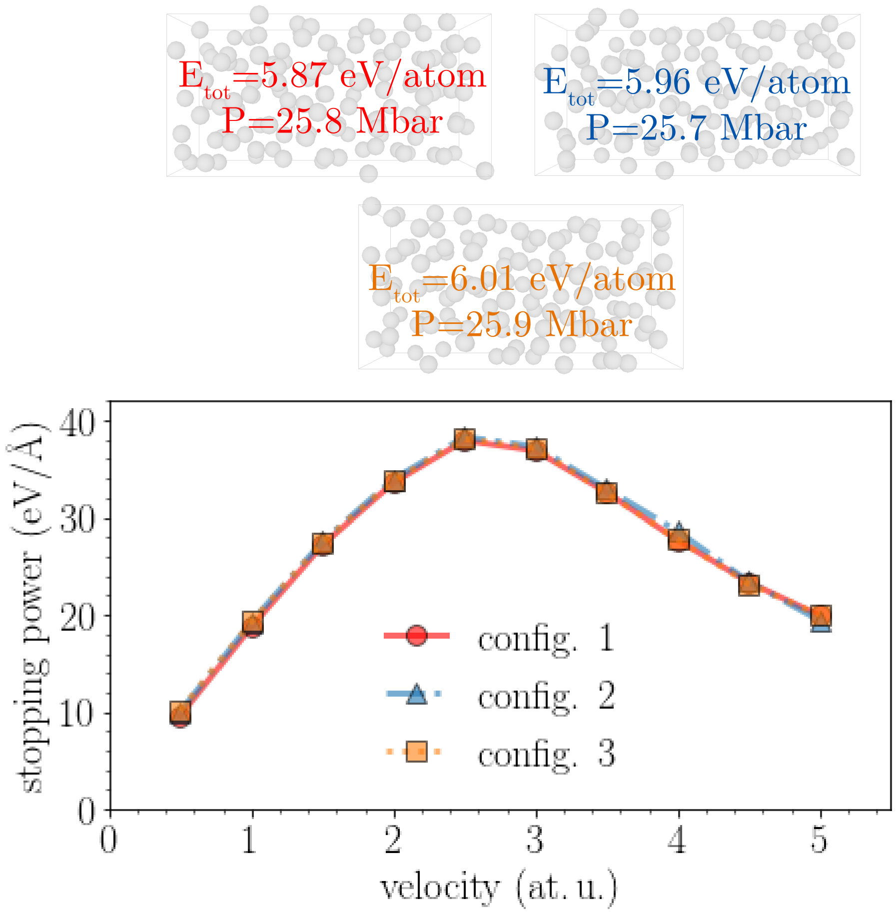




Proton Stopping in Liquid Carbon: atomic configurations

- Thermal fluctuations may affect stopping
- Separately optimized trajectory for several MD snapshots
- Little variation across atomic configurations
- Trajectory metric may eliminate need for configurational averaging

10g/cc, 1eV



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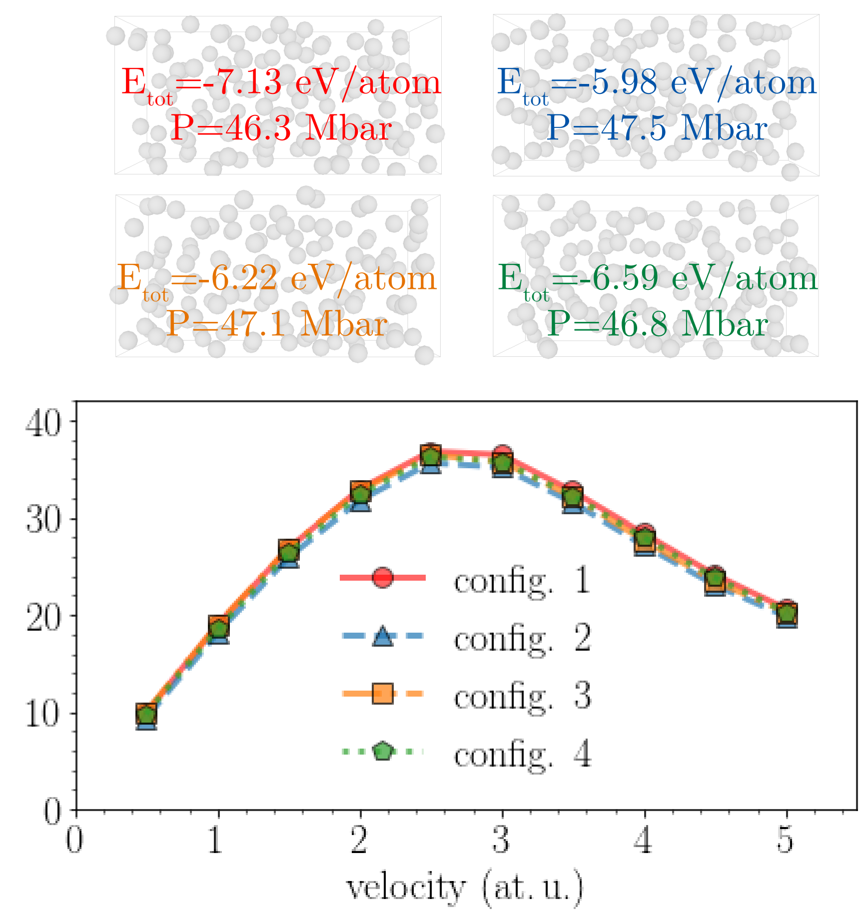
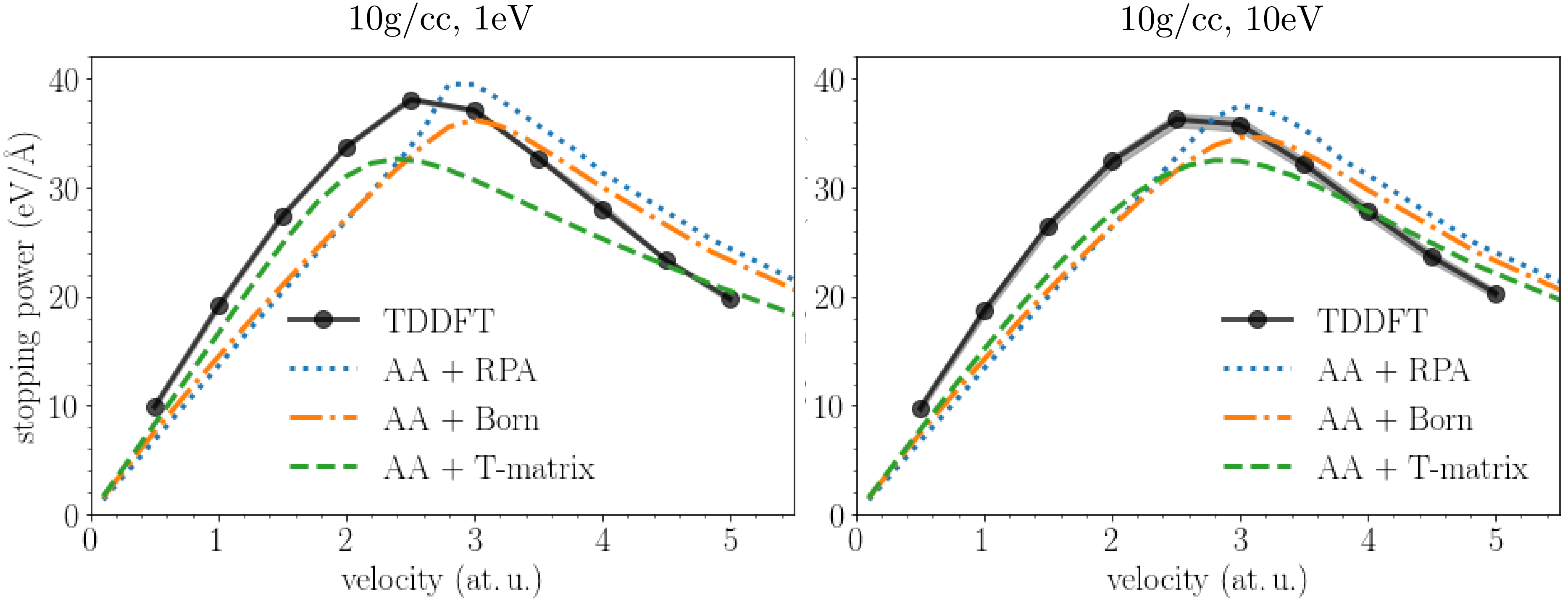


Proton Stopping in Liquid Carbon: comparing to AA

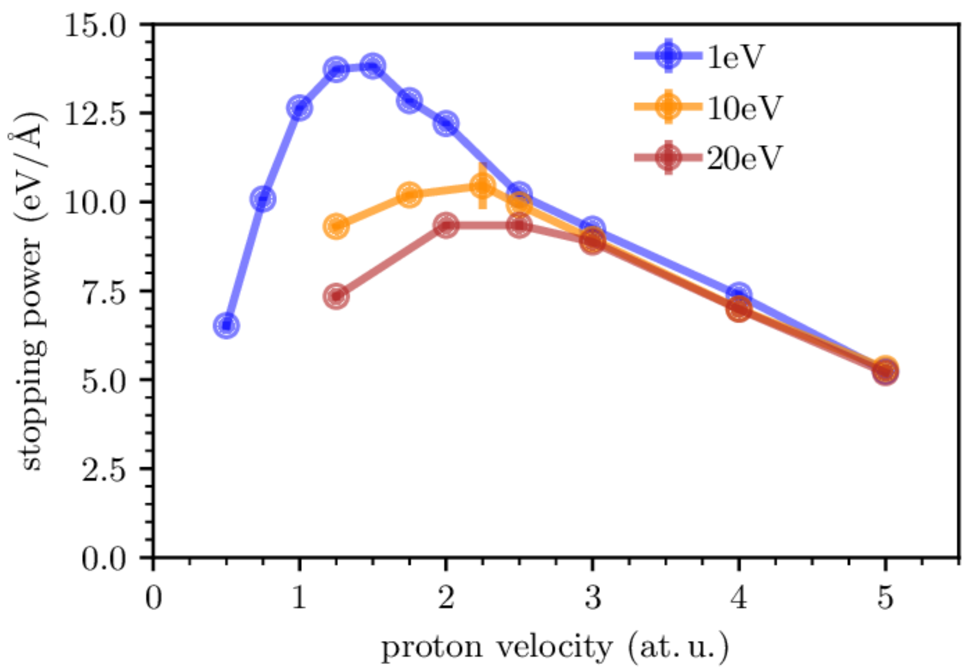
- AA parameterizes dielectric models entering into stopping power
- Significant discrepancies with all models

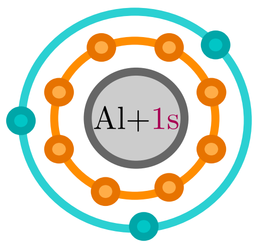
$$S(v) = \frac{2Z_I^2}{\pi v^2} \int_0^\infty \frac{dk}{k} \int_0^{kv} d\omega\, \omega\, \mathrm{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right] \qquad \epsilon_{\mathrm{MA}}(k,\omega) = 1 + \frac{(\omega + i\nu)[\epsilon_{\mathrm{RPA}}(k,\omega+i\nu) - 1]}{\omega + i\nu \frac{\epsilon_{\mathrm{RPA}}(k,\omega+i\nu)-1}{\epsilon_{\mathrm{RPA}}(k,0)-1}}$$



Proton Stopping in Aluminum: electron temperature

- At high T_e, Bragg peak lowers and shifts to higher velocities
- Different pseudizations offer rough insight:
  - 11e PP: total stopping





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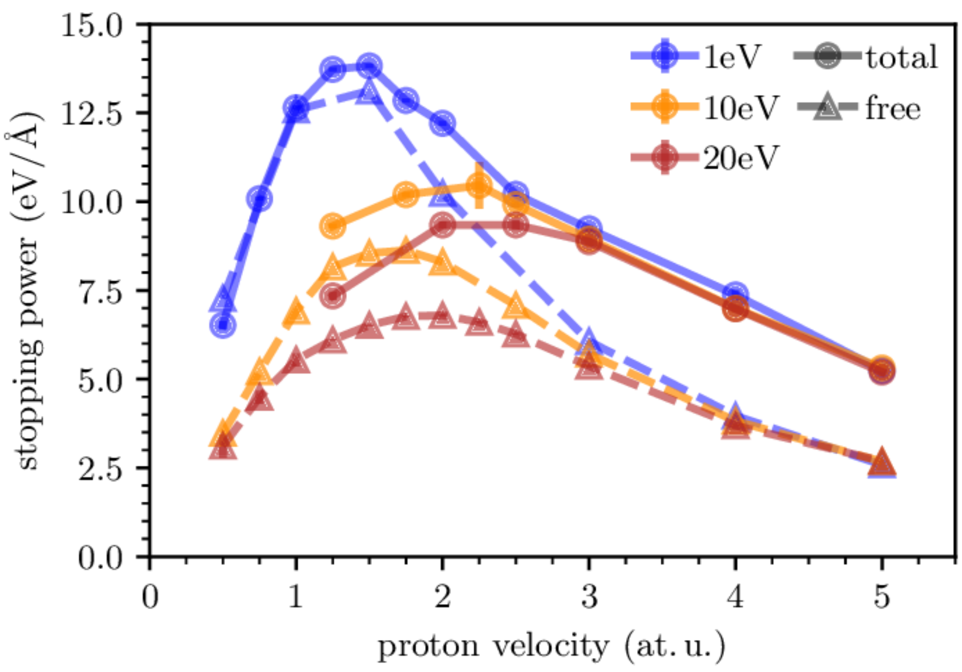

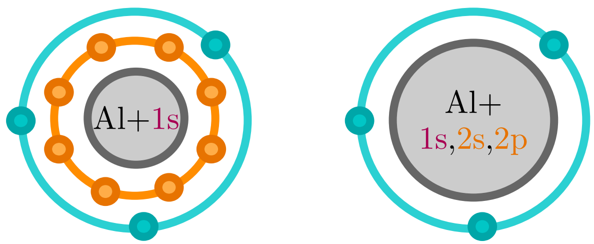

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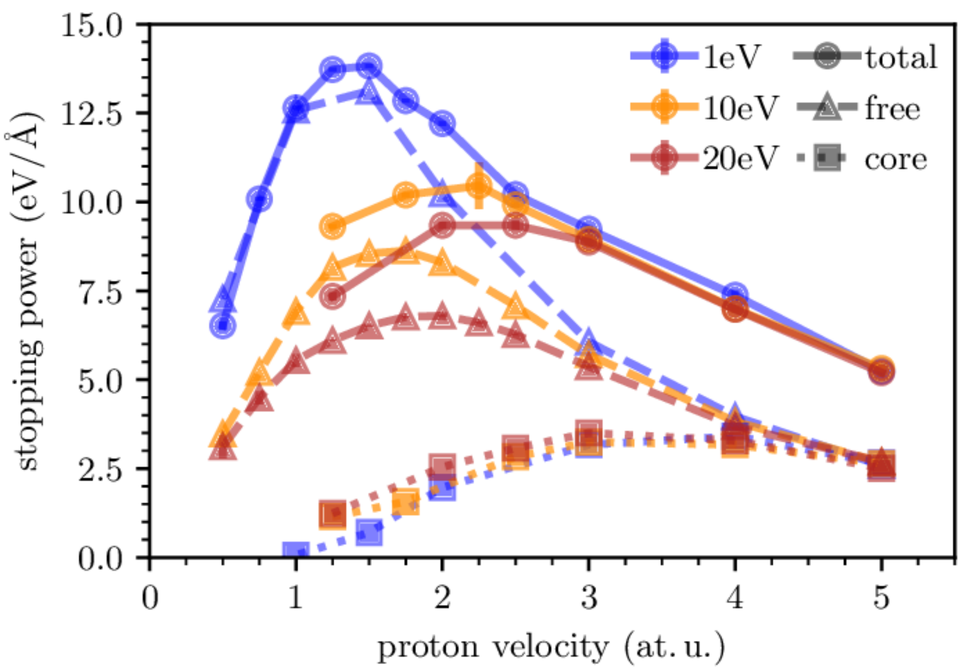
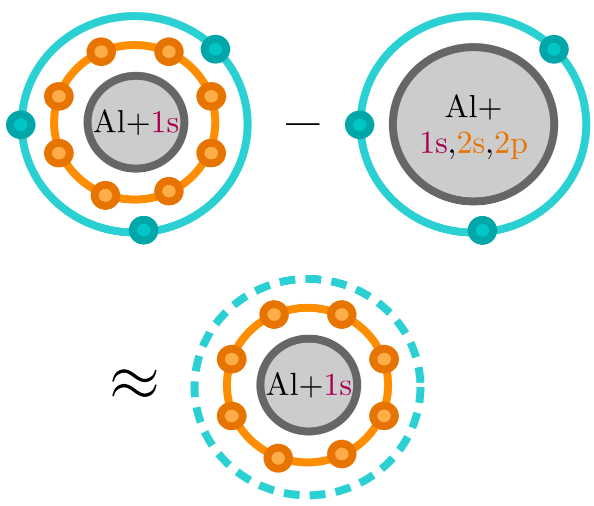
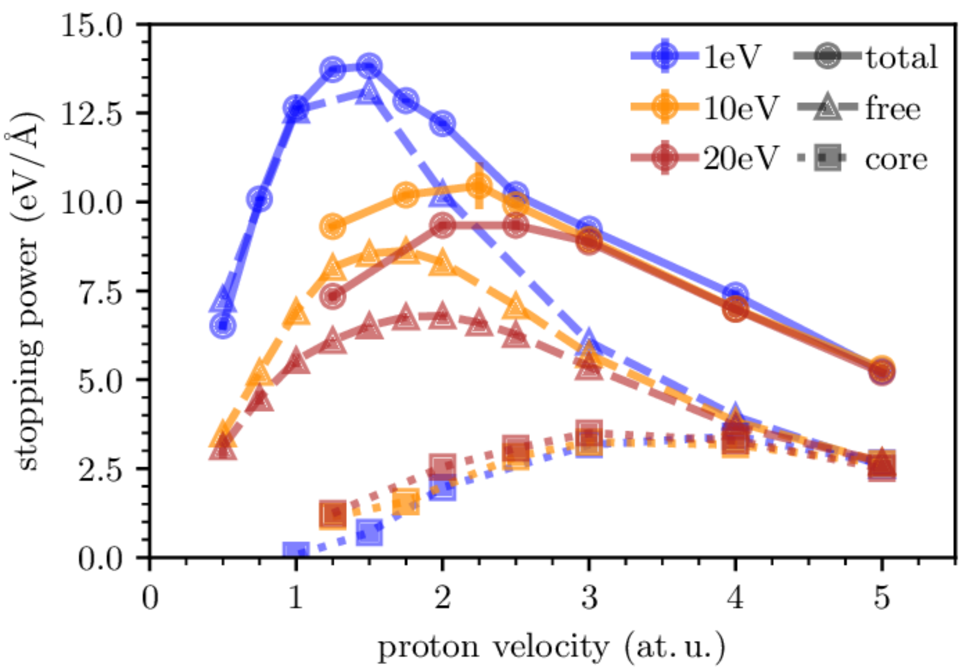
- Different pseudizations offer rough insight:
  - 11e PP: total stopping
  - 3e PP: ~free-electron contribution follows same trend as total
  - 11e PP – 3e PP: ~core contribution not sensitive to T_e, but accounts for increasing fraction of total





Proton Stopping in Aluminum: electron temperature

- Competing effects obfuscated!
- Thermal excitations increase free-electron density
  - 3ePP underestimates free-electron contribution at 20eV



	1eV	10eV	20eV
free electrons per atom	3.00	3.02	3.61

Proton Stopping in Aluminum: electron temperature

- Competing effects obfuscated!
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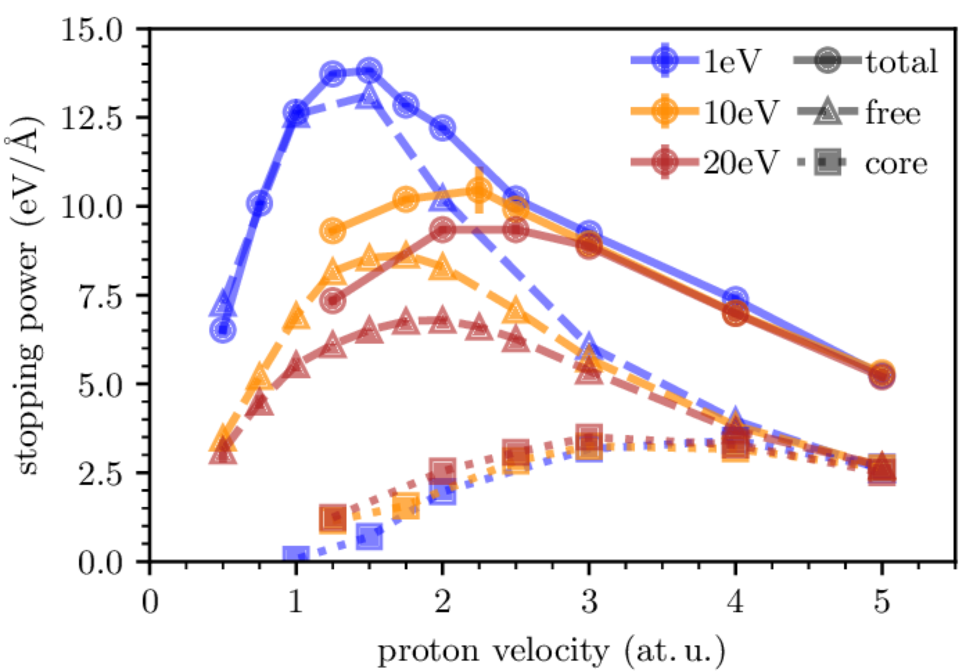

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2p – free energy difference (eV)	65	55	62.5

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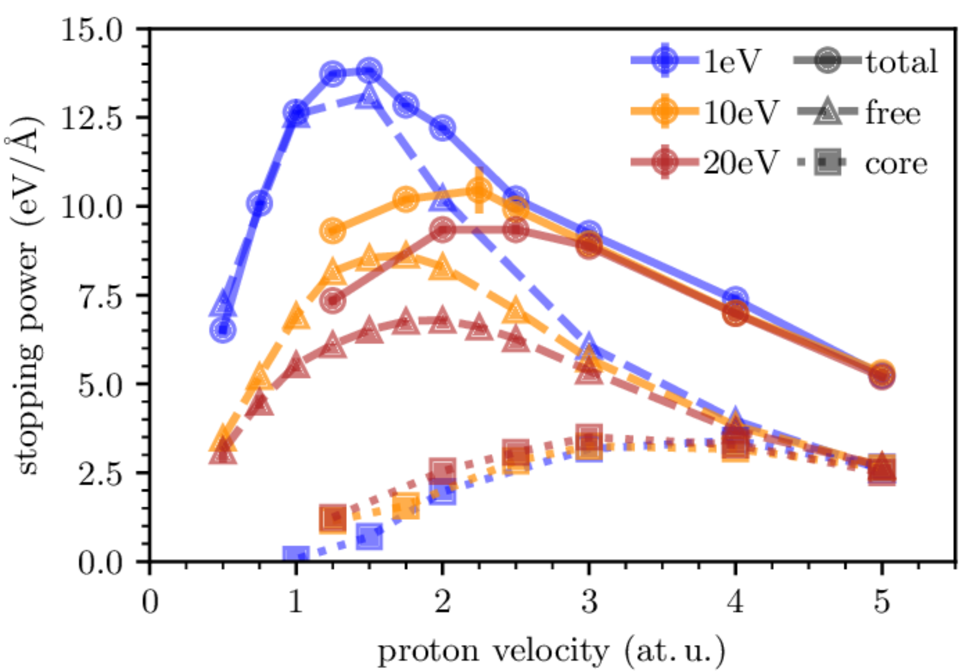
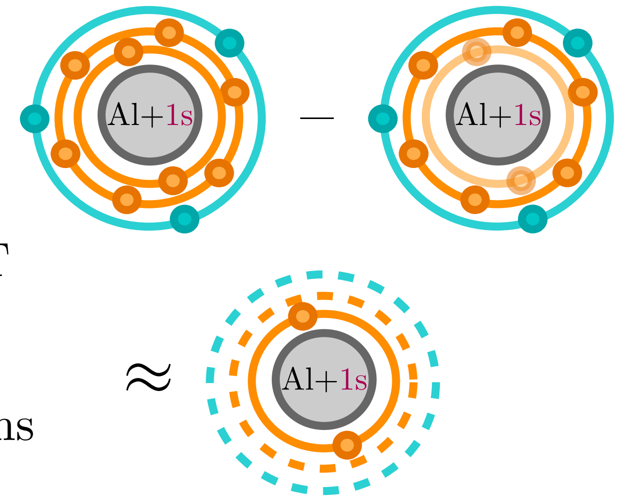
- Thermal depletion of 2p allows 2s $\rightarrow$ 2p at 20eV
- Working to disentangle these processes

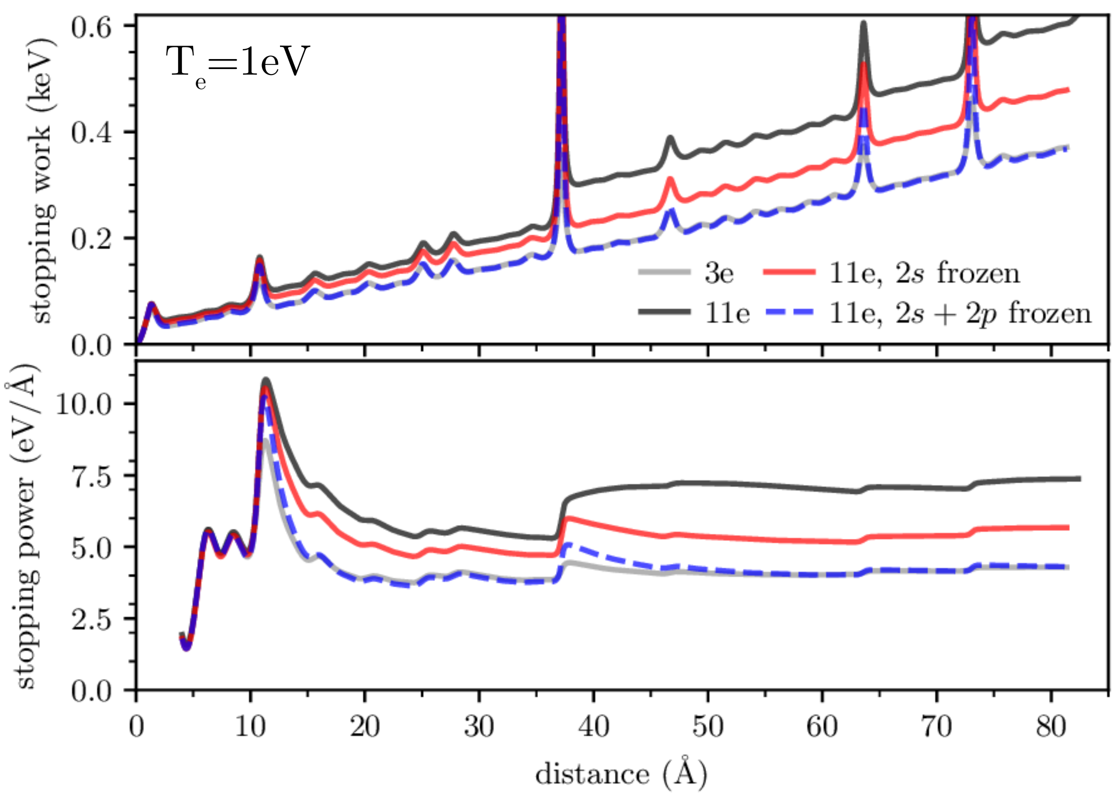


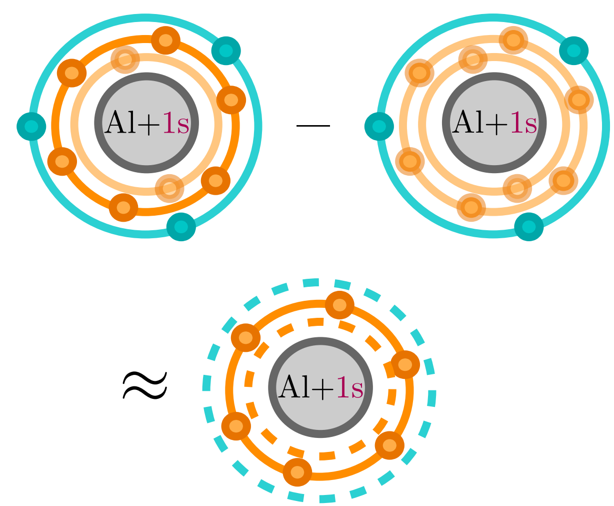
	1eV	10eV	20eV
free electrons per atom	3.00	3.02	3.61
2p – free energy difference (eV)	65	55	62.5
2p vacancy (%)	0	0.5	9.6

Isolating 2s and 2p contributions

- Besides changing the PP, we can freeze shells!
- 11e PP with 2s and 2p frozen
  - reproduces 3e PP result at low T
  - will give true free-electron contribution at high T
- 11e PP with 2s frozen ~ 9e PP
  - allows separate analysis of 2s and 2p contributions







Summary and Outlook

- Developed cost-reducing trajectory metric for stopping calculations
- Found negligible T_i, configurational effects
- Studying core electron mechanisms at high T
- Informing improvements to efficient AA models
- Ultimately interested in mixtures / heterogeneous systems