Electron and ion dynamics in materials due to particle radiation and optical excitation

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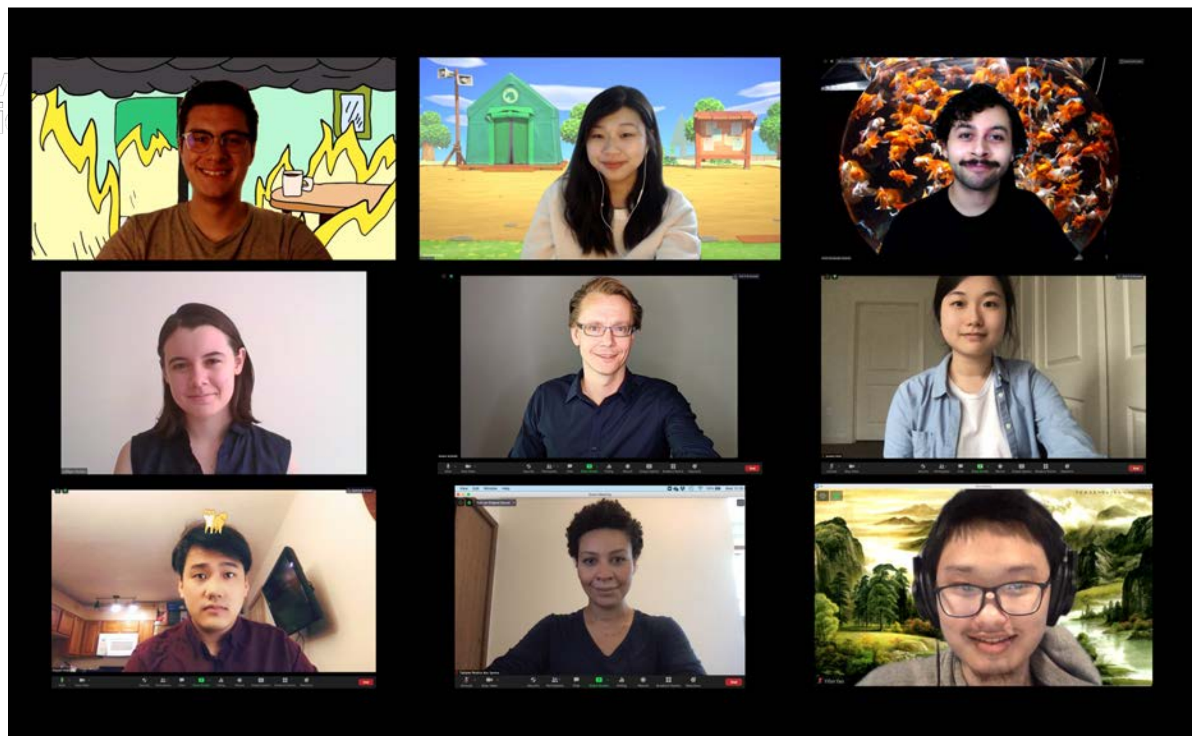
Vista Online Seminars, 4/14/2021



Schleife
Group
Department of Materials Science and Engineering

Acknowledgments

- **Cheng-Wei Lee**
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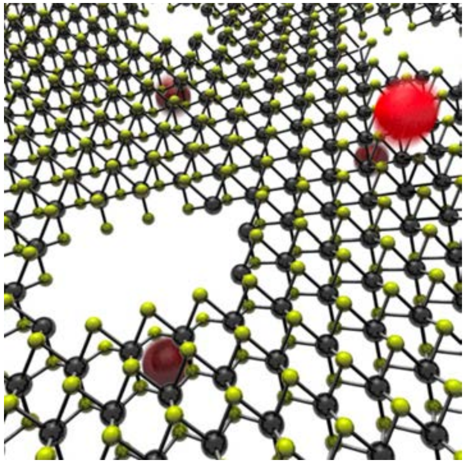
Motivation: Materials manipulation and characterization

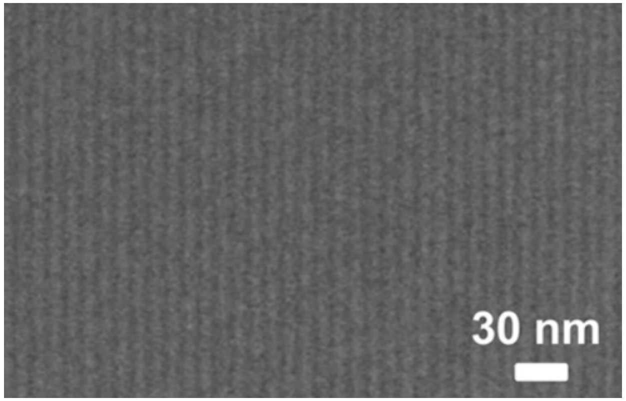
Precise defects:



- Swift heavy ions
- **Highly charged ions**
- Qbit applications

J. Phys. Chem. Lett. 2019, 10, 904−910

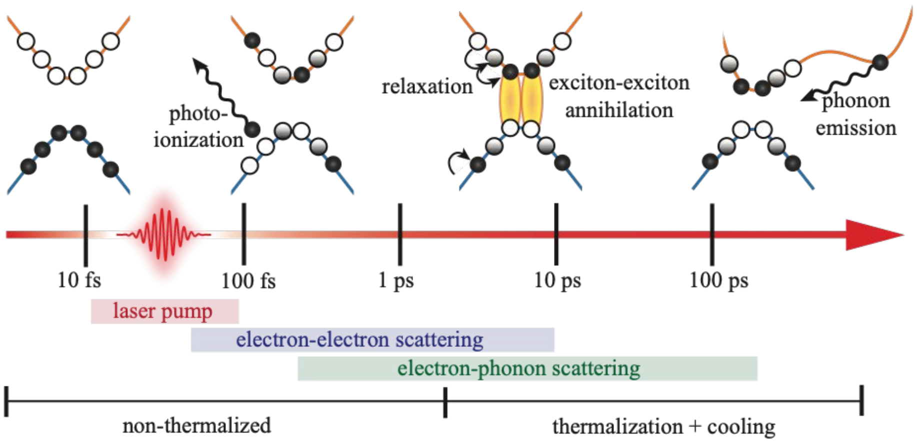
Helium microscopy:



- Insulating samples
- Secondary electrons
- Also: TEM

ACS Nano 2014, 8, 2, 1538–1546

Fundamental material properties:

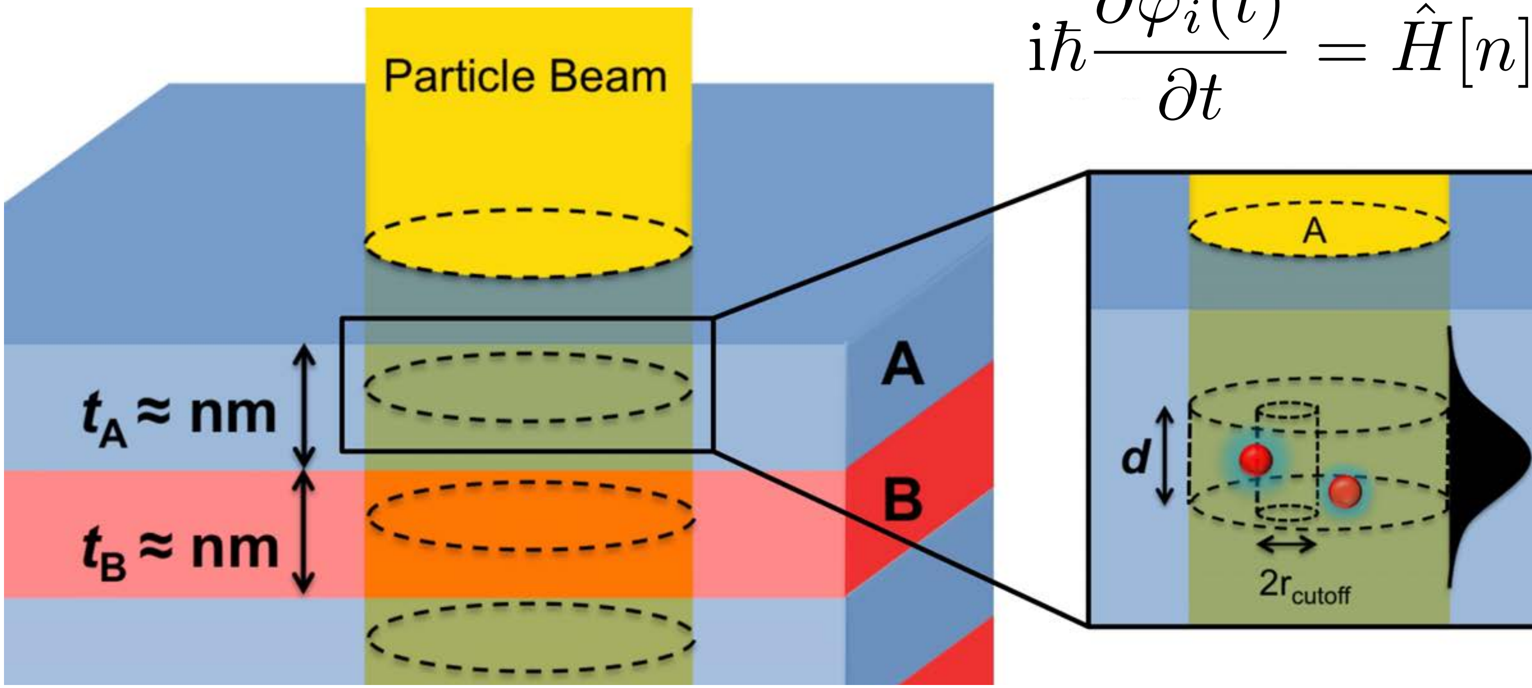


- Initial excitation triggers non-adiabatic electron-ion dynamics
- Early stages of radiation damage?
- Radiation hardness of materials

The 2021 Ultrafast Spectroscopic Probes of Condensed Matter Roadmap

Motivation: Materials manipulation and characterization

$$i\hbar \frac{\partial \varphi_i(t)}{\partial t} = \hat{H}[n]\varphi_i(t)$$



- Interesting physics: Non-adiabatic electron-ion dynamics
- Exciting applications: Materials modification, Ion implantation for Qbits

C.W. Lee and A. Schleife; Nano Lett. **19**, 3939-3947 (2019)

Real-time time-dependent density functional theory

Time-dependent Kohn-Sham equations:

$$i\hbar\frac{\partial\varphi_i(t)}{\partial t} = \hat{H}[n]\varphi_i(t) = \left[\hat{T} + v_{\mathrm{ext}}(\mathbf{r},t) + v_{\mathrm{H}}[n](\mathbf{r}) + v_{\mathrm{XC}}[n](\mathbf{r})\right]\varphi_i(t)$$

- Periodic systems: Plane-wave expansion of wave functions: $\psi_i(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} C_i(\mathbf{G},t)e^{i\mathbf{G}\cdot\mathbf{r}}$
- Electron-ion interaction: Norm-conserving pseudopotentials
- Exchange-correlation: Time-dependent local-density approximation
- Computationally challenging: Highly parallel implementation
- Excellent strong scaling: Qbox/Qb@ll code

- Compute forces at each time step and update positions of the atoms

→ Ehrenfest molecular dynamics

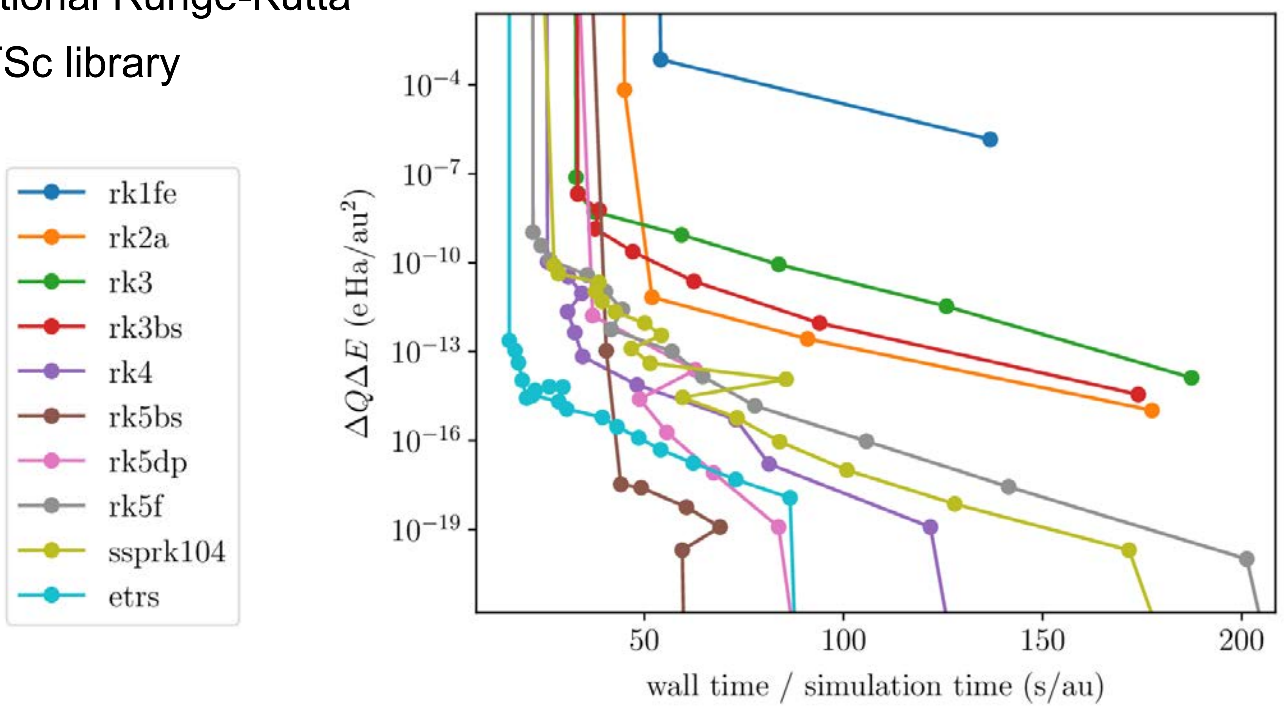
→ Problem: Integrating the equations of motion: Real-time TDDFT

Numerical Integrator and Parallel Scaling

- Enforced Time-Reversal Symmetry (ETRS) Method
- Implicit propagator: Depends on result of the equation (via density)

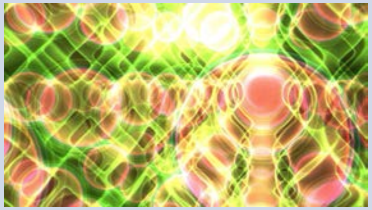
$$|\psi(t+\Delta t)\rangle = \left[\exp\left(-i\frac{\Delta t}{2}\hat{H}(n(t+\Delta t))\right) \times \exp\left(-i\frac{\Delta t}{2}\hat{H}(n(t))\right)\right]|\psi(t)\rangle$$

- Excellent conservation of energy and orthogonality
- Also tried variety of additional Runge-Kutta based schemes via PETSc library

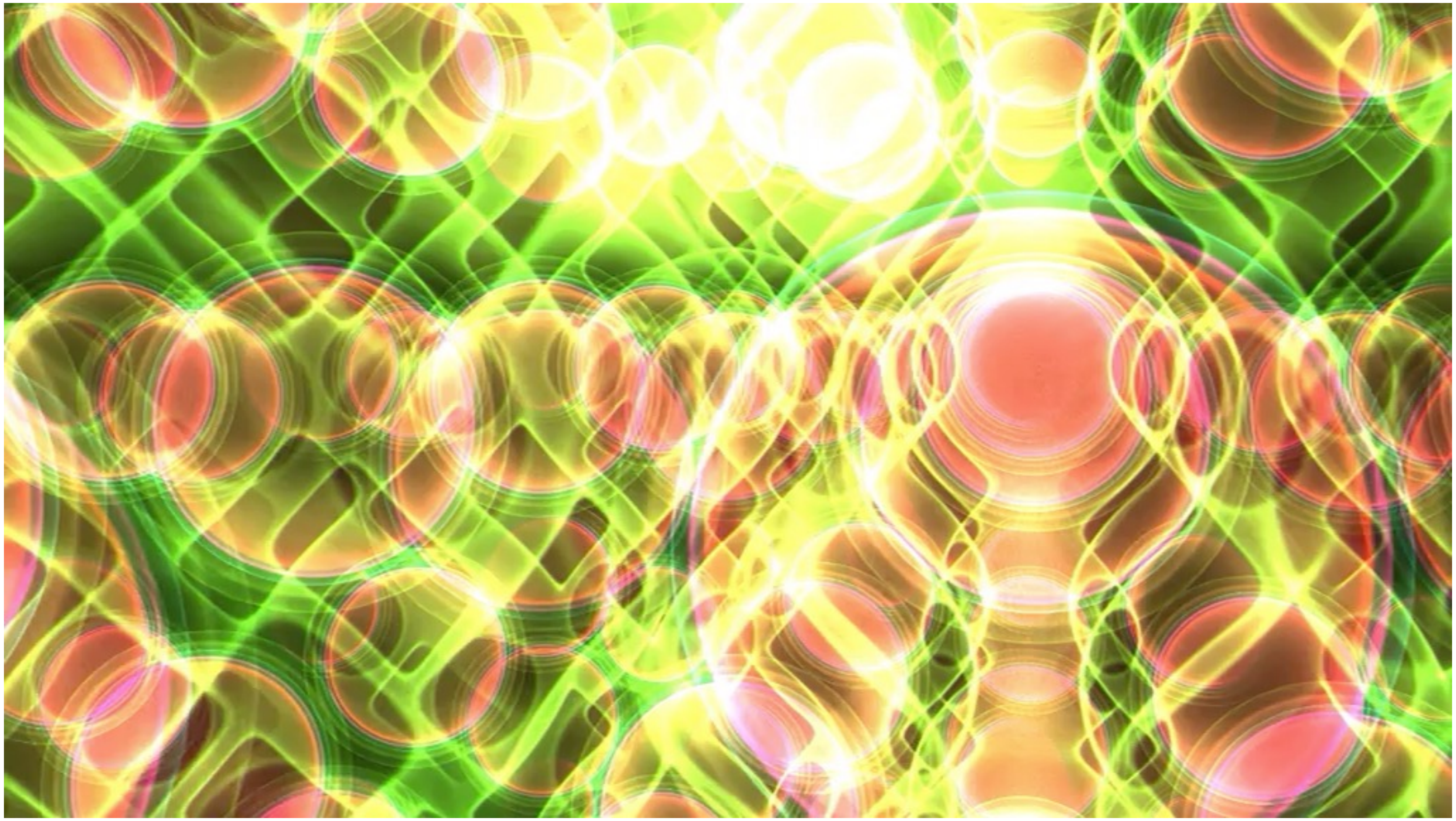


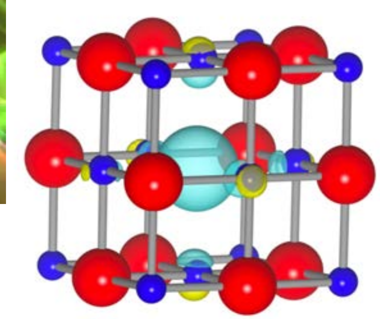
Kang, Schleife *et al.*; Comput. Mater. Sci. **160**, 207 (2019)

Plan/Outline

	Proton irradiation	Laser irradiation
Bulk target material (+defects)	MgO (Cheng-Wei) 	MgO (Yifan)
Surface target material	Aluminum (Alina)	Aluminum (Yifan)

Hot-electron mediated ion diffusion: Oxygen vacancies in MgO



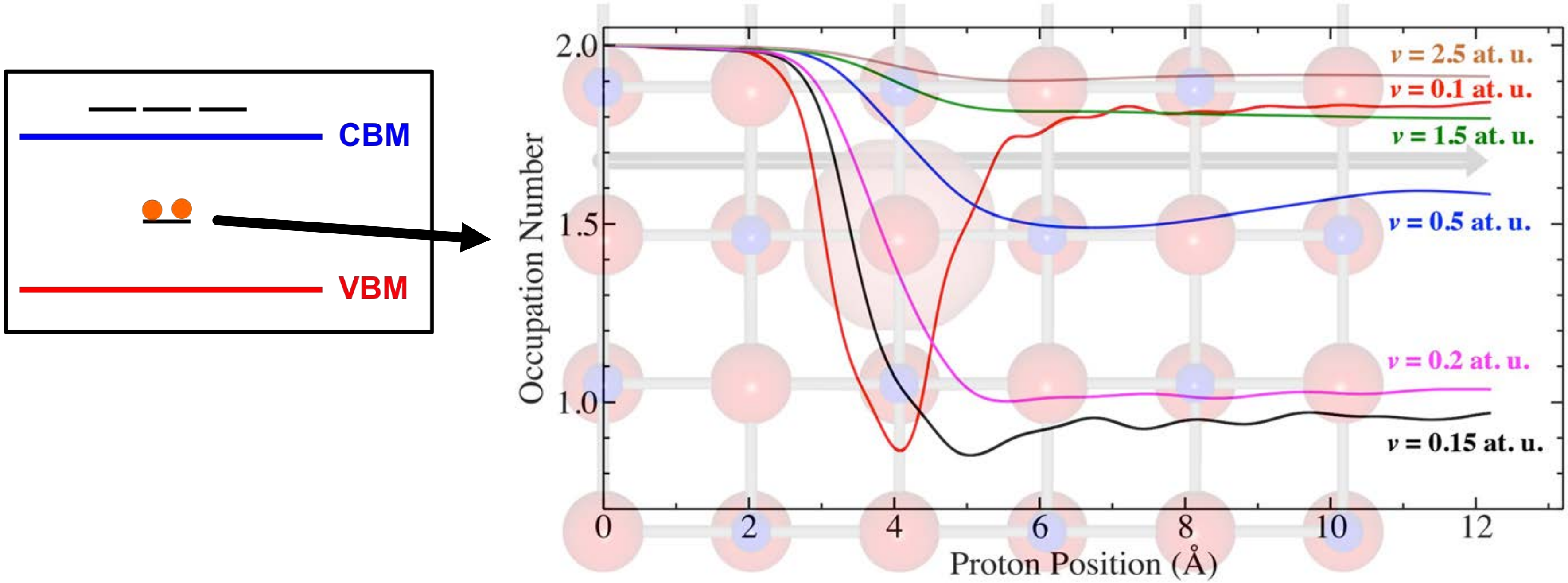


- Excited-electron contribution to diffusion?

C.W. Lee and A. Schleife; Mater. Today **21**, 925-927 (2018)

C.W. Lee and A. Schleife; Nano Lett. **19**, 3939-3947 (2019)

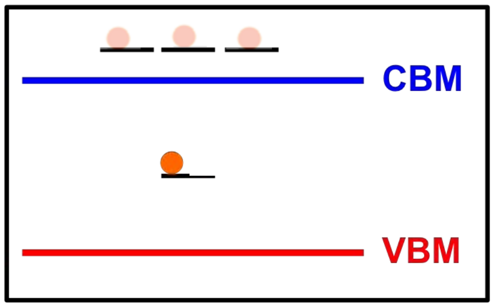
Excited electrons: Oxygen vacancy in MgO

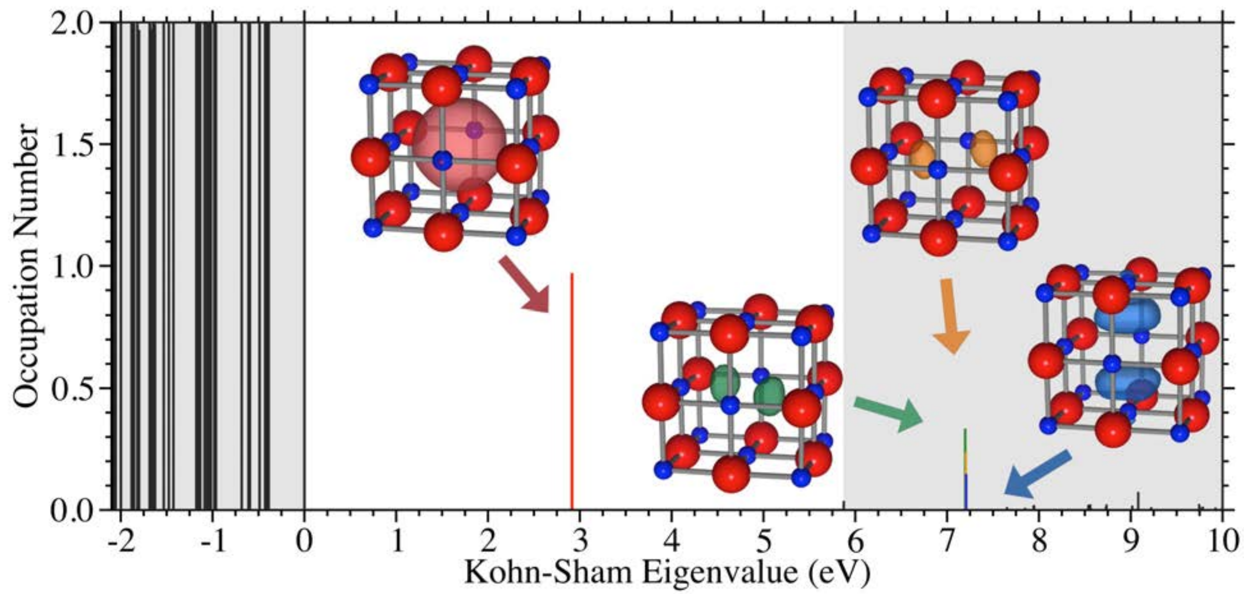


- Ultrafast electron dynamics and evolution of vacancy charge state
- Strong velocity dependence
- Largest number of electrons is excited for v=0.15 at. u.
- Distribution of excited electrons?

C.W. Lee and A. Schleife; Nano Lett. **19**, 3939-3947 (2019)

Excited electrons: Oxygen vacancy in MgO

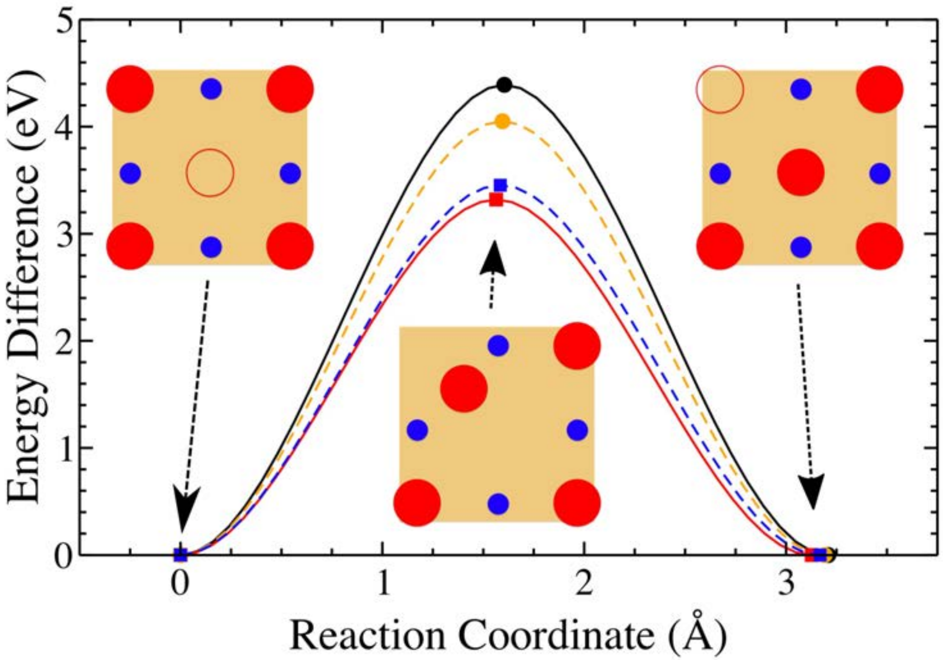




- Occupation numbers after proton has passed cell once
- Increase of electronic stopping when defect is present (v=0.15 at. u.)
- Found clear influence of the mid-gap oxygen-vacancy related level
- About one electron removed due to excitation
- 0.72 electrons in three localized vacancy-related states
- Influence on ion dynamics? (Problem: Time scale much slower)

C.W. Lee and A. Schleife; Nano Lett. **19**, 3939-3947 (2019)

Hot-electron mediated ion dynamics



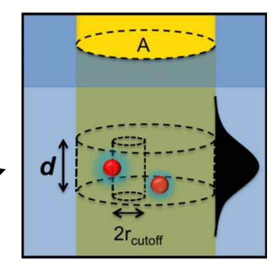
$$D = \frac{1}{6} f\, Z_f Z_m l^2 C_d \Gamma$$

geometry

fixed

$$\Gamma = \nu^* e^{-\Delta E_m / k_B T}$$

- Compare: **Ground-state DFT (black)**, Mermin DFT (orange, T=9211 K), fixed charge state (red), and **Ehrenfest MD (blue)**
- Small effect of change in attempt frequency (less than 20 percent)
- Significant reduction of barrier by about 0.94 eV
- Example: For T=900 K, increase of D by about 10^5
- Estimate: Enhance diffusion within depth of 117 - 156 nm



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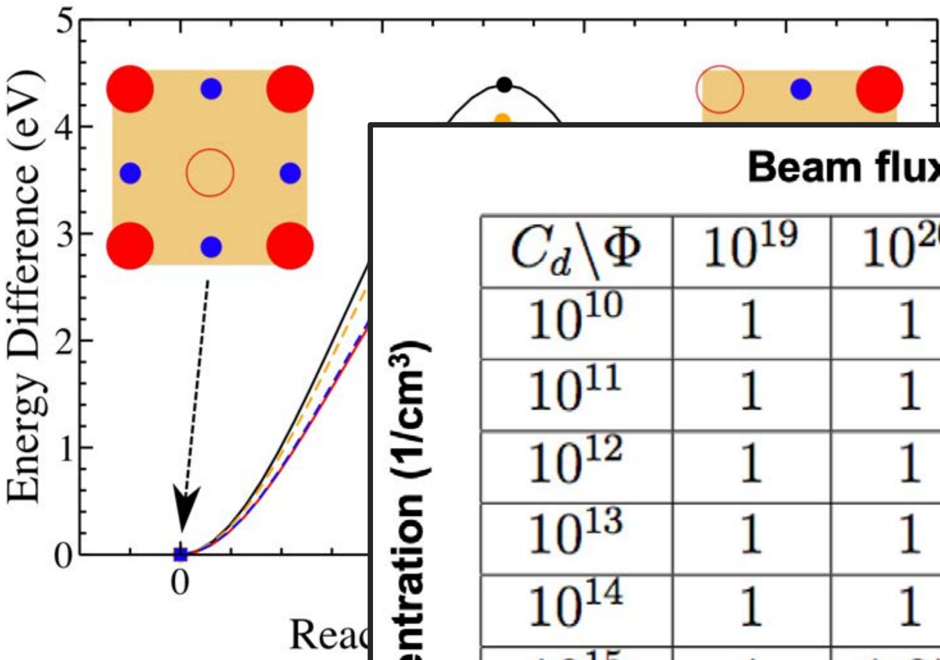
Hot-electron mediated ion dynamics



Beam flux ($m^{-2} s^{-1}$)

Defect Concentration ($1/cm^3$)

$C_d \backslash \Phi$	10^{19}	10^{20}	10^{21}	10^{22}
10^{10}	1	1	1	1
10^{11}	1	1	1	1
10^{12}	1	1	1	1
10^{13}	1	1	1	1
10^{14}	1	1	1.05	1.50
10^{15}	1	1.05	1.50	6.03
10^{16}	1.05	1.50	6.03	51.2
10^{17}	1.50	6.03	51.2	501
10^{18}	6.03	51.2	501	4790
10^{19}	51.2	501	4790	33500

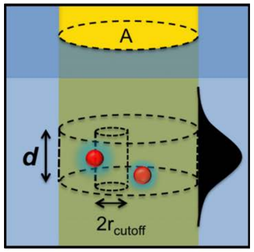
Achieved by thermochemically reduced MgO

$Z_m l^2 C_d \Gamma$

ry fixed

$E_m/k_B T$

- Compare: **Gro** ... K), fixed charge state (red), an...
- Small effect of
- Significant red
- Example: For T
- Estimate: Enhance diffusion within depth of 117 - 156 nm



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Plan/Outline

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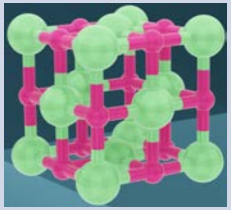
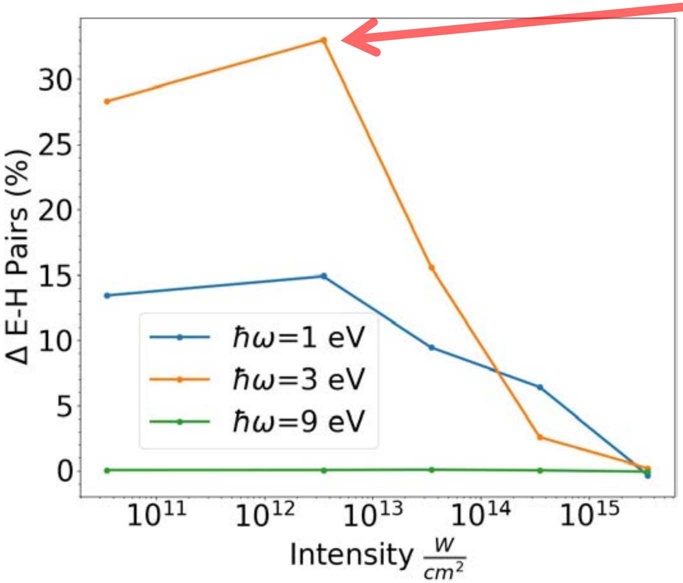
Bulk target material (+defects)	MgO (Cheng-Wei)	MgO (Yifan) 
Surface target material	Aluminum (Alina)	Aluminum (Yifan)

Laser excitation: Oxygen vacancy in MgO

$$\Delta\text{E-H} = \frac{\text{E-H}_{\text{Oxygen Vacancy}} - \text{E-H}_{\text{Perfect Bulk}}}{\text{E-H}_{\text{Perfect Bulk}}}$$



Low Intensity: ΔE-H is most significant at 3 eV.

- Single photon excitation from the mid-gap defect state

Definition of electron-hole pair: $n_{eh}(t) = 2\sum_{i}^{occ.}\left(1 - \sum_{j}^{occ.} |< \phi_j|\psi_i(t) >|^2\right)$

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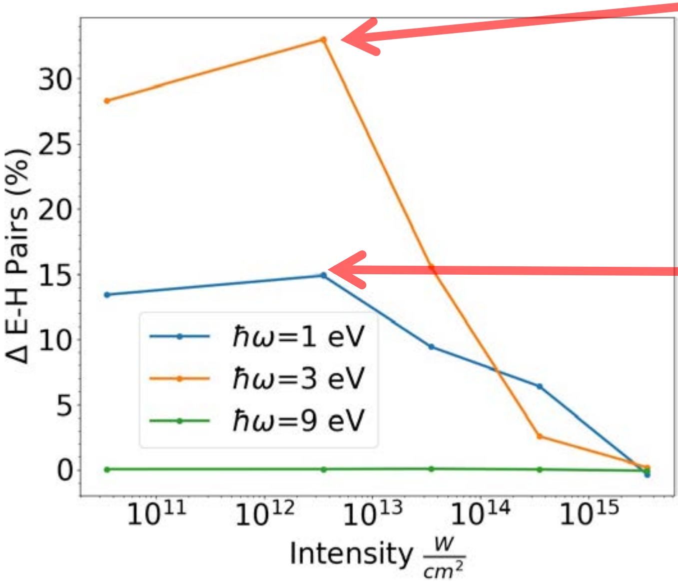

Low Intensity: ΔE-H is most significant at 3 eV.

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ΔE-H is reduced compared to $\hbar\omega$=3eV:

- Multiphoton excitation is needed for mid-gap defect state as well

Definition of electron-hole pair: $n_{eh}(t) = 2\sum_{i}^{occ.}\left(1 - \sum_{j}^{occ.} |< \phi_j|\psi_i(t) >|^2\right)$

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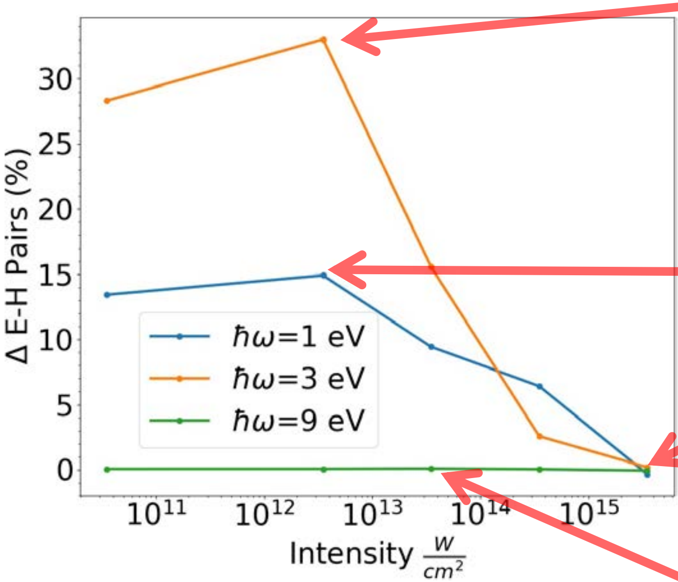


Low Intensity: ΔE-H is most significant at 3 eV.

- Single photon excitation from the mid-gap defect state

ΔE-H is reduced compared to $\hbar\omega$=3eV:

- Multiphoton excitation is needed for mid-gap defect state as well

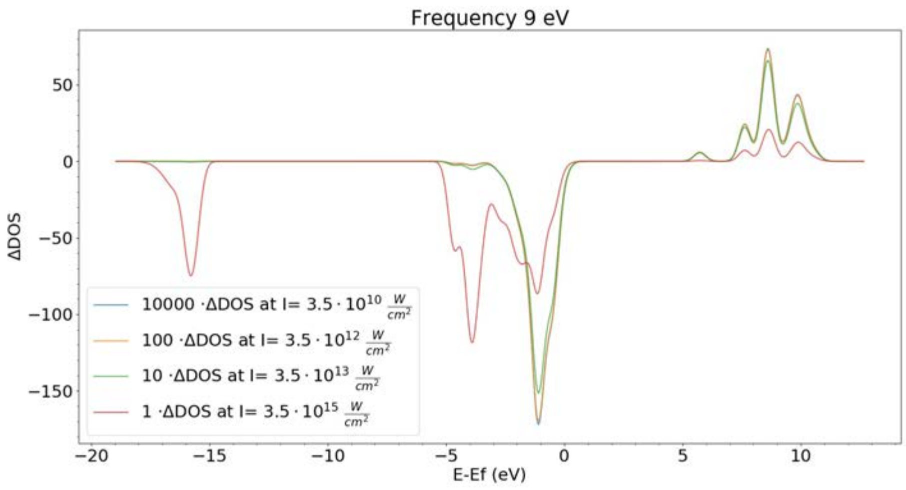
High Intensity: ΔE-H is insignificant for all frequencies

High Frequency: ΔE-H is insignificant for all intensities

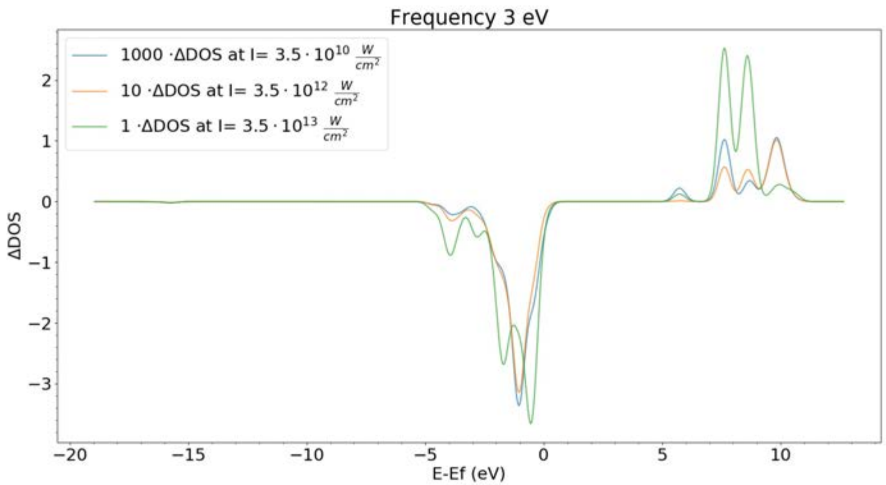
Definition of electron-hole pair: $$n_{eh}(t) = 2\sum_{i}^{occ.}\left(1 - \sum_{j}^{occ.} |< \phi_j|\psi_i(t) >|^2\right)$$

Laser excitation: Oxygen vacancy in MgO

Occupation change: 9 eV laser excitation



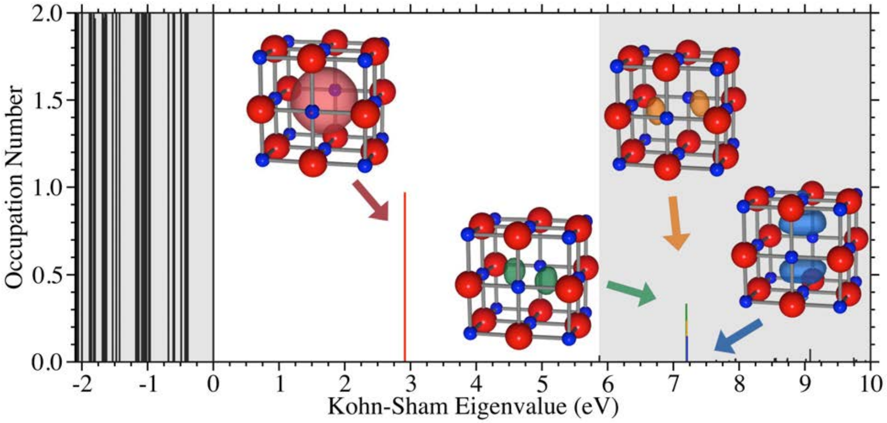
Occupation change: 3 eV laser excitation



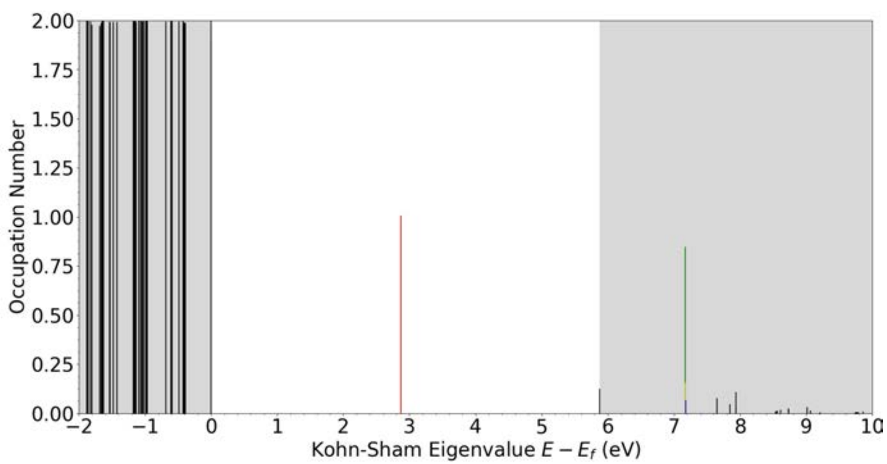
- Comparison with ground state at the end of first laser period
- Non-linear effects disappear if intensity decreases
- Strong dependence on frequency

Laser excitation: Oxygen vacancy in MgO

Previous figure: Proton irradiation



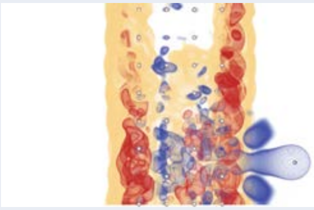
Comparison: Laser irradiation



- By tuning laser parameters, we obtain the distribution of occupation number comparable to proton irradiation: $I=7.3\times10^{12}$ W/cm^2 and $\hbar\omega$=4.5 eV

- Currently: Estimate the change of migration barrier during the laser irradiation
- Currently: Keldysh analysis

Plan/Outline

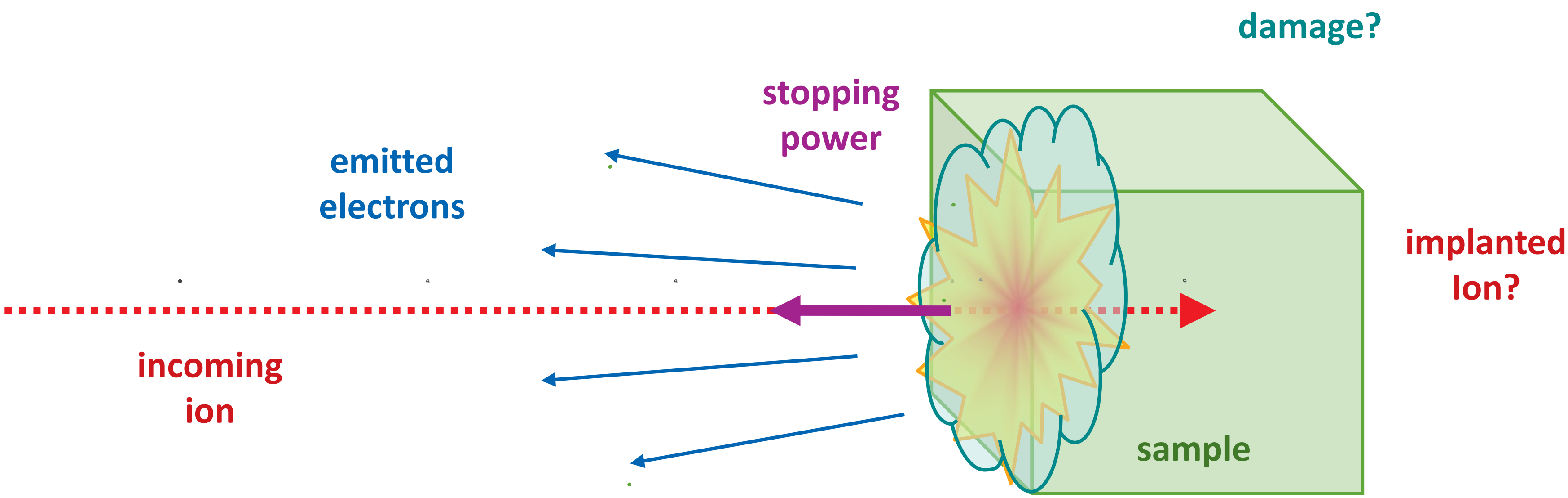
	Proton irradiation	Laser irradiation
Bulk target material (+defects)	MgO (Cheng-Wei)	MgO (Yifan)
Surface target material	Aluminum (Alina) 	Aluminum (Yifan)

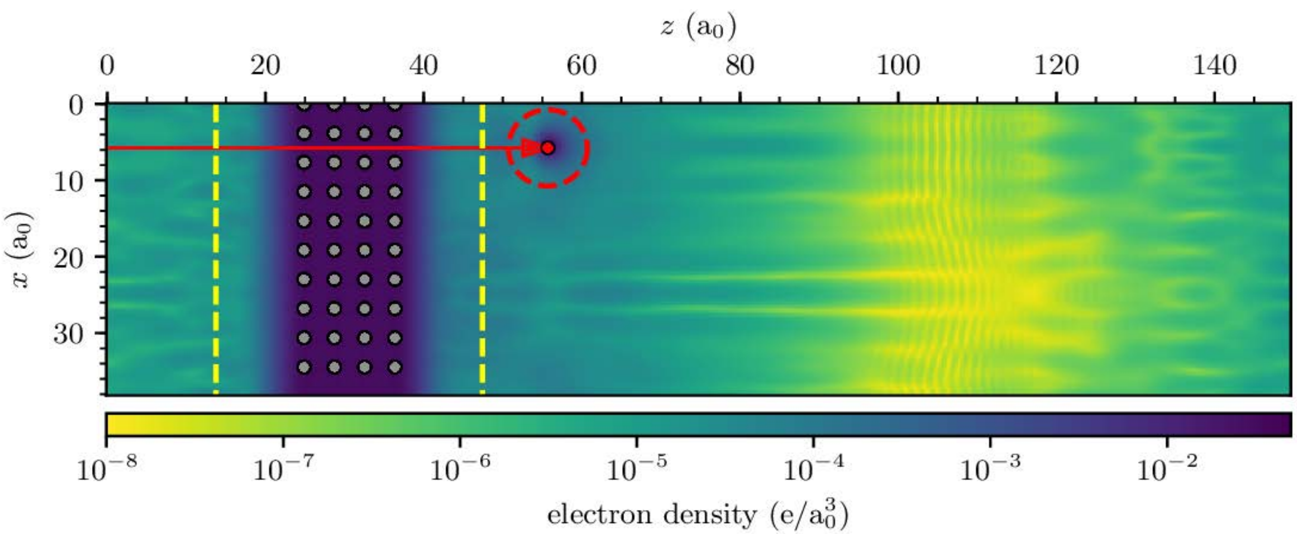
What happens near the surface?

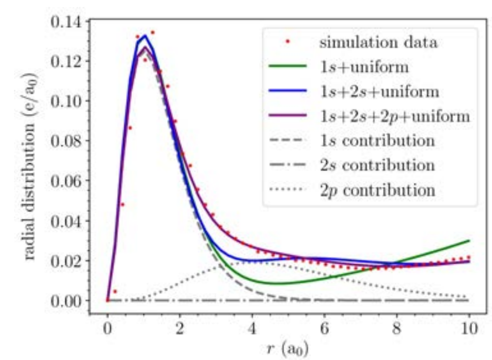
- Interesting physics: Pre-equilibrium regime near surface poorly understood, Extreme case of 2D materials largely unexplored
- Exciting applications: Materials modification, Defects for Qbits

Kononov, Schleife, PRB **102**, 165401 (2020)

Proton irradiation of aluminum Sheets



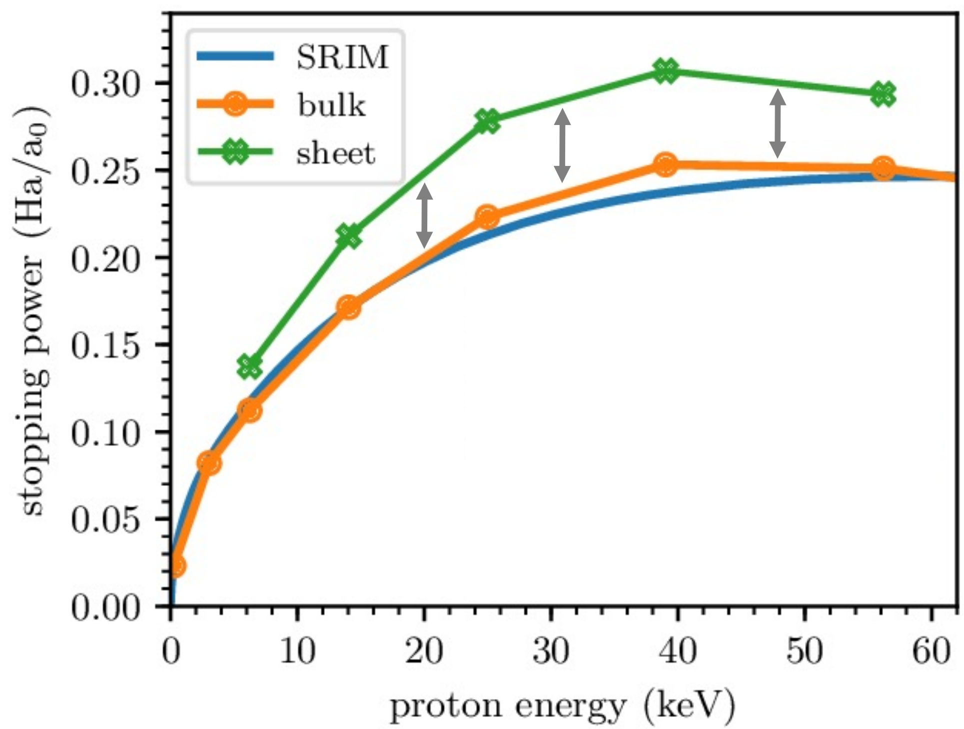




Kononov, Schleife; PRB **102**, 165401 (2020)

Aluminum Sheets: Pre-equilibrium stopping

Stopping power $S = dE/dz$
- energy transfer per depth
- drag force on projectile

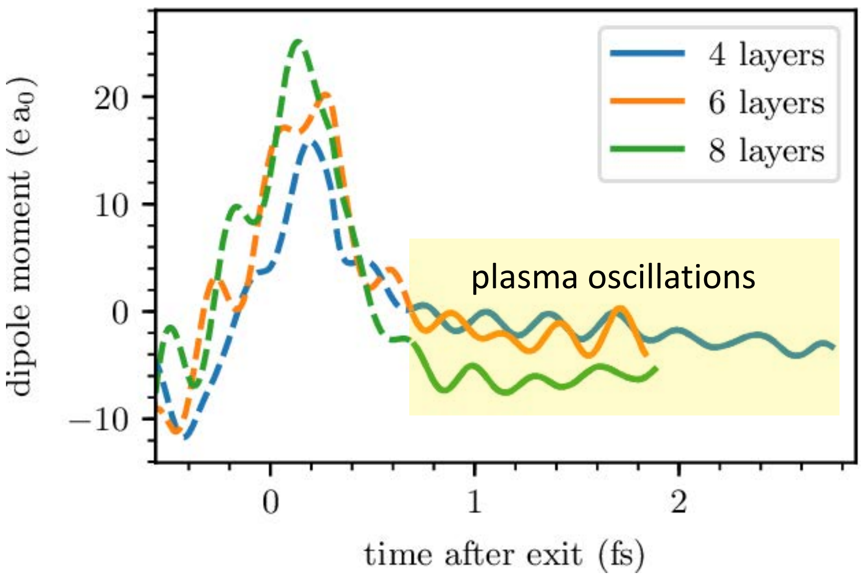


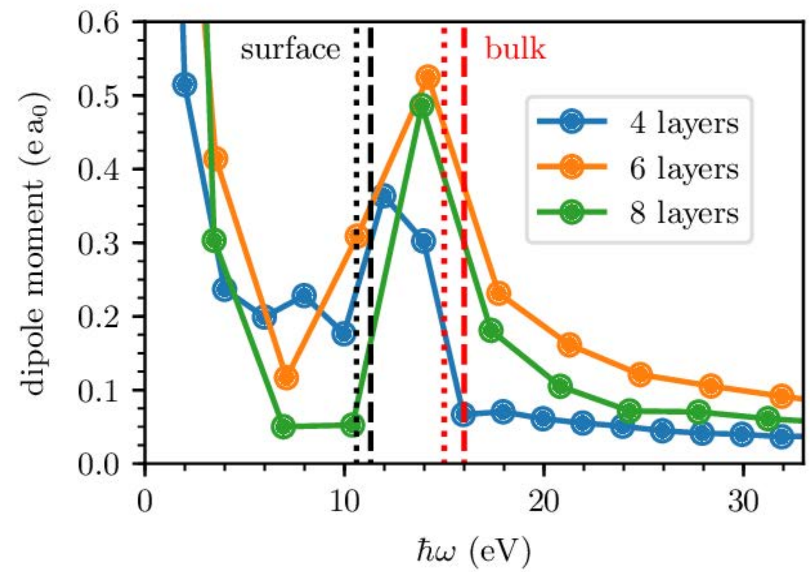
Higher in sheets than bulk!
- even for thicker sheets

Cause of pre-equilibrium stopping?
- projectile charge? $S \propto Z^2$
- polarized sheet? $S \propto n$
- surface plasmons? $S = \frac{dE_\mathrm{e}}{dz} + \frac{dE_\mathrm{bp}}{dz} + \boxed{\frac{dE_\mathrm{sp}}{dz}}$

Kononov, Schleife, PRB **102**, 165401 (2020)

Aluminum Sheets: Pre-equilibrium stopping

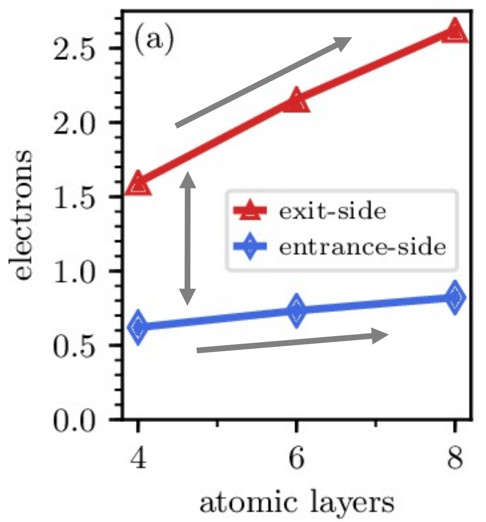




- Surface plasmon modes: most likely source of enhanced stopping power in sheets
- Analyzed plasmonic behavior in out-of-plane dipole moment
- Density oscillations below bulk plasma frequency

Kononov, Schleife, PRB **102**, 165401 (2020)

Proton irradiation of aluminum Sheets



- More secondary-electron emission from exit-side
- Emitted electron yields increase with sheet thickness
- Extrapolated to thick foils by fitting to model:

$$\gamma(d) = \gamma_{\mathrm{eq}}(1 - e^{-d/\lambda})$$

- Extrapolated entrance-side yield of 0.92 agrees with 1.09 from experiment
- Determined escape depth λ

	entrance-side	exit-side
γ_{eq}	0.92	4.5
λ (nm)	0.73	1.8

Kononov, Schleife; PRB **102**, 165401 (2020)

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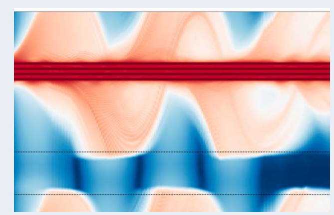
Surface target material	Aluminum (Alina)	Aluminum (Yifan) 

Aluminum Sheets: Laser excitation

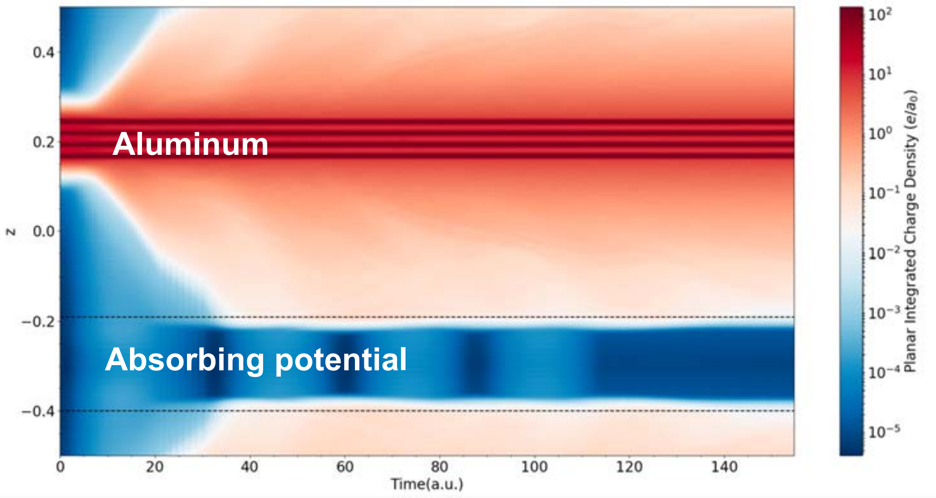
- Electron emission?
- Coulomb explosion?
- Dependence on laser parameters?

- Used a smaller cell of 72 atoms
- Absorbing boundary/potential: $V_{cap} = -i \cdot \eta sin^2\left(\frac{(x-R)\cdot\pi}{2\cdot dR}\right)$
- 150 a_B vacuum (absorber 53 a_B from either surface)
- Vector potential for electric field (implemented with Xavier Andrade)

10.1140/epjb/e2015-50808-0

Aluminum Sheets: Laser excitation

Electric field in Al plane (x direction)



- Field: I=10^{15} W/cm^2, 3 eV

Aluminum Sheets: Laser excitation

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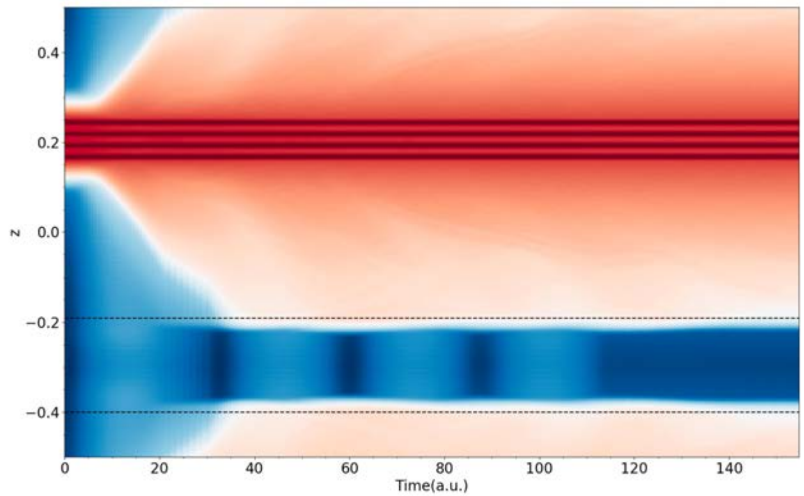
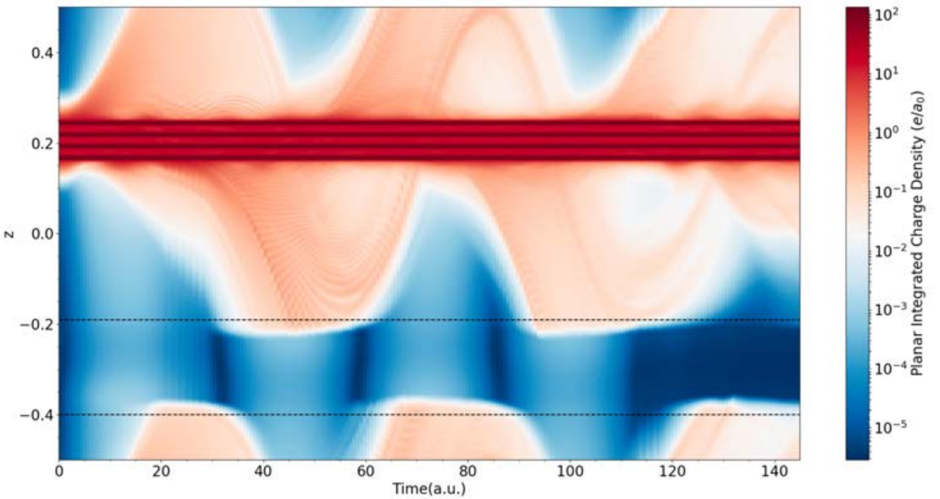
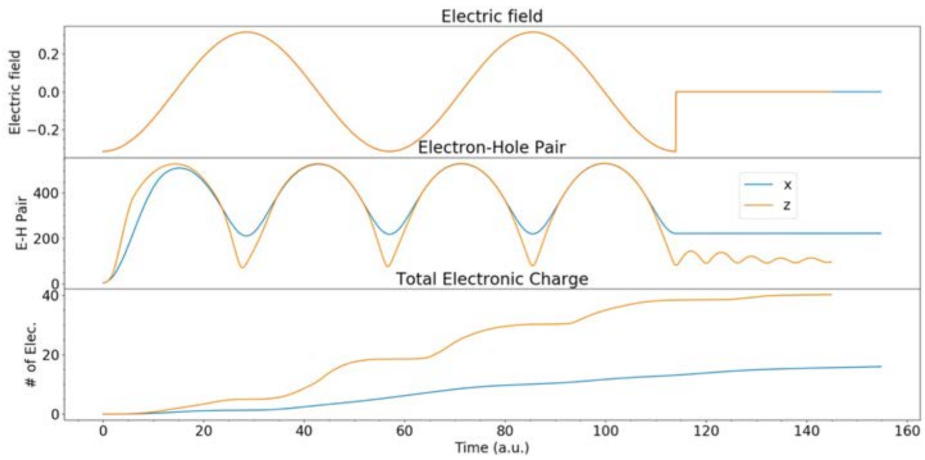


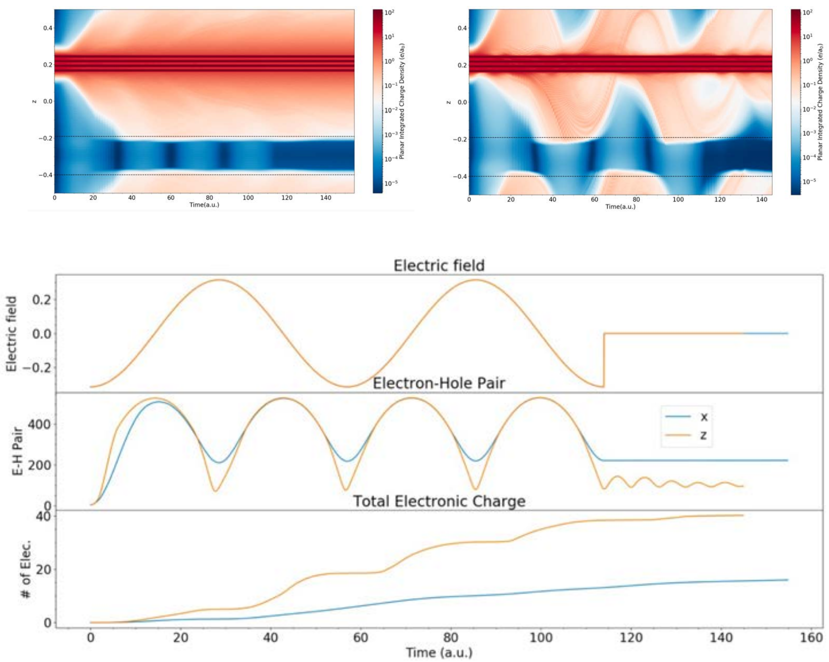
Electric field perpendicular to Al plane (z direction)

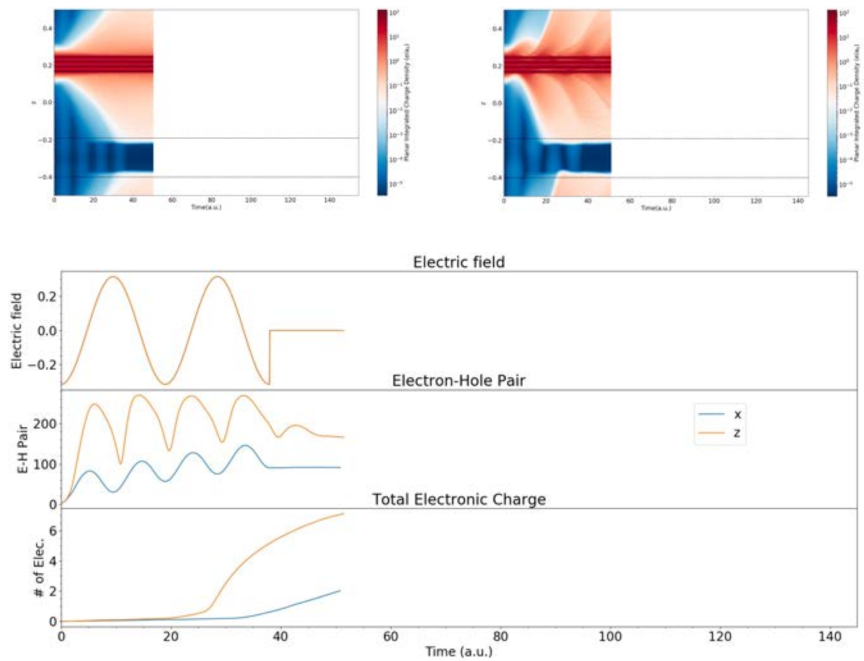




- Field: I=10^{15} W/cm^2, 3 eV

Aluminum Sheets: Laser excitation





- higher laser frequency leads to emission of fewer electrons
- more materials response for laser along z
- Force for field along z follows electric field
- Force for field along x: possible indication for Coulomb explosion

- Field: I=10^{15} W/cm^2, 3 eV (left), 9 eV (right)

Summary

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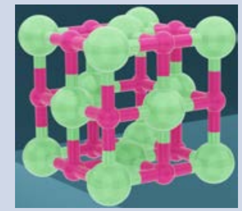
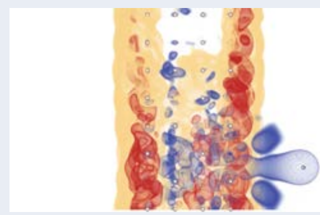
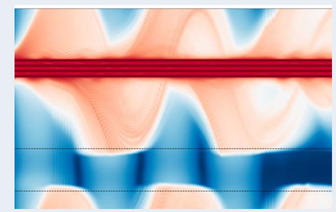
Bulk target material (+defects)	MgO (Cheng-Wei) 	MgO (Yifan) 
Surface target material	Aluminum (Alina) 	Aluminum (Yifan) 

C.W. Lee and A. Schleife; Nano Lett. **19**, 3939-3947 (2019)

C. Lee, J. A. Stewart, R. Dingreville, S. M. Foiles, and A. Schleife, Phys. Rev. B **102**, 024107 (2020)

A. Kononov, A. Schleife, Phys. Rev. B **102**, 165401 (2020)

- Accurate parameter-free description achievable
- Accuracy vs. computational cost vs. parameter space
- Fully exploit modern trends in high-performance computing
- Exciting potential for materials manipulation and characterization