Applications of Ehrenfest dynamics: from excited state evolution of protected gold clusters to stopping of high-energy ions in graphene

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Background

- Shift of interest from ground state electronic structure calculations towards processes and phenomena
- Many processes, such as ion-atom collisions or electron transfer in biomolecules, are nonadiabatic
  - The process is not dictated by a single electronic state, but instead by two or more coupled states
- Ehrenfest dynamics (ED) + time-dependent DFT + PAW = a computationally affordable framework for studying nonadiabatic processes

Ehrenfest dynamics in GPAW

- Conservation of the total energy leads to Ehrenfest dynamics equations within the PAW method[1]

electrons $$i\tilde{S}\frac{\partial\tilde{\psi}_n}{\partial t} = (\tilde{H}+\tilde{P})\tilde{\psi}_n = (\tilde{H} - i\sum_a \dot{\mathbf{R}}_a \cdot \hat{\mathbf{D}}_a)\tilde{\psi}_n$$

nuclei $$M\ddot{\mathbf{R}}_a = -\nabla_{\mathbf{R}_a} E_{\mathrm{KS}} + \sum_n f_n \langle\tilde{\psi}_n|\hat{\mathbf{D}}_a^\dagger \tilde{S}^{-1}\tilde{H} + c.c|\tilde{\psi}_n\rangle$$

$\tilde{P}$ term accounts for the position-dependent augmentation operator, with

$$\hat{\mathbf{D}}_a = \mathcal{T}^\dagger \frac{\partial \mathcal{T}}{\partial \mathbf{R}_a} = (1+\hat{t}_a^\dagger)\frac{\partial \hat{t}_a}{\partial \mathbf{R}_a} \quad \text{and} \quad \hat{t}_a = \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle)\langle\tilde{p}_i^a|$$

- In practice, simultaneous solution using
  - Time propagator (SICN) for the electrons
  - Velocity Verlet for the nuclei

[1] A. Ojanperä, V. Havu, L. Lehtovaara, and M. Puska. JCP 136, 144103 (2012)

Excited state evolution of a protected gold cluster

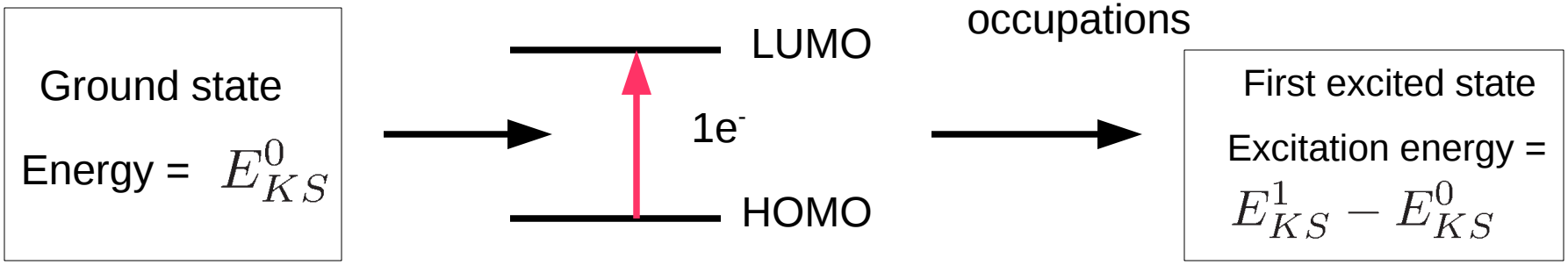
- Protected metal nanoparticles = a novel class of luminescent nanomaterials
  - Applications: medicine, imaging and catalysis
- Exact mechanism at the origin of the luminescence of gold clusters is not understood
  - Better knowledge of the interaction between the gold core and the surrounding ligands, and the photo-induced dynamics required!
- We investigated[1] the photo-induced dynamics of a protected Au2 cluster using Ehrenfest dynamics in conjuction with the Delta Self-Consistent-Field method

1: A. Ojanperä, O. Lopez-Acevedo, and M. Puska, accepted to JPC C

The Delta-SCF+Ehrenfest method

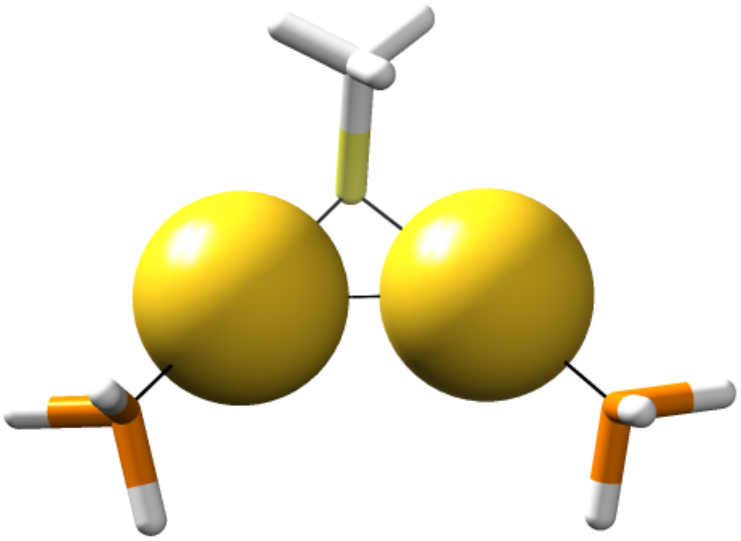
Delta Self-Consistent Field

Solving the Kohn-Sham equations with changed occupations



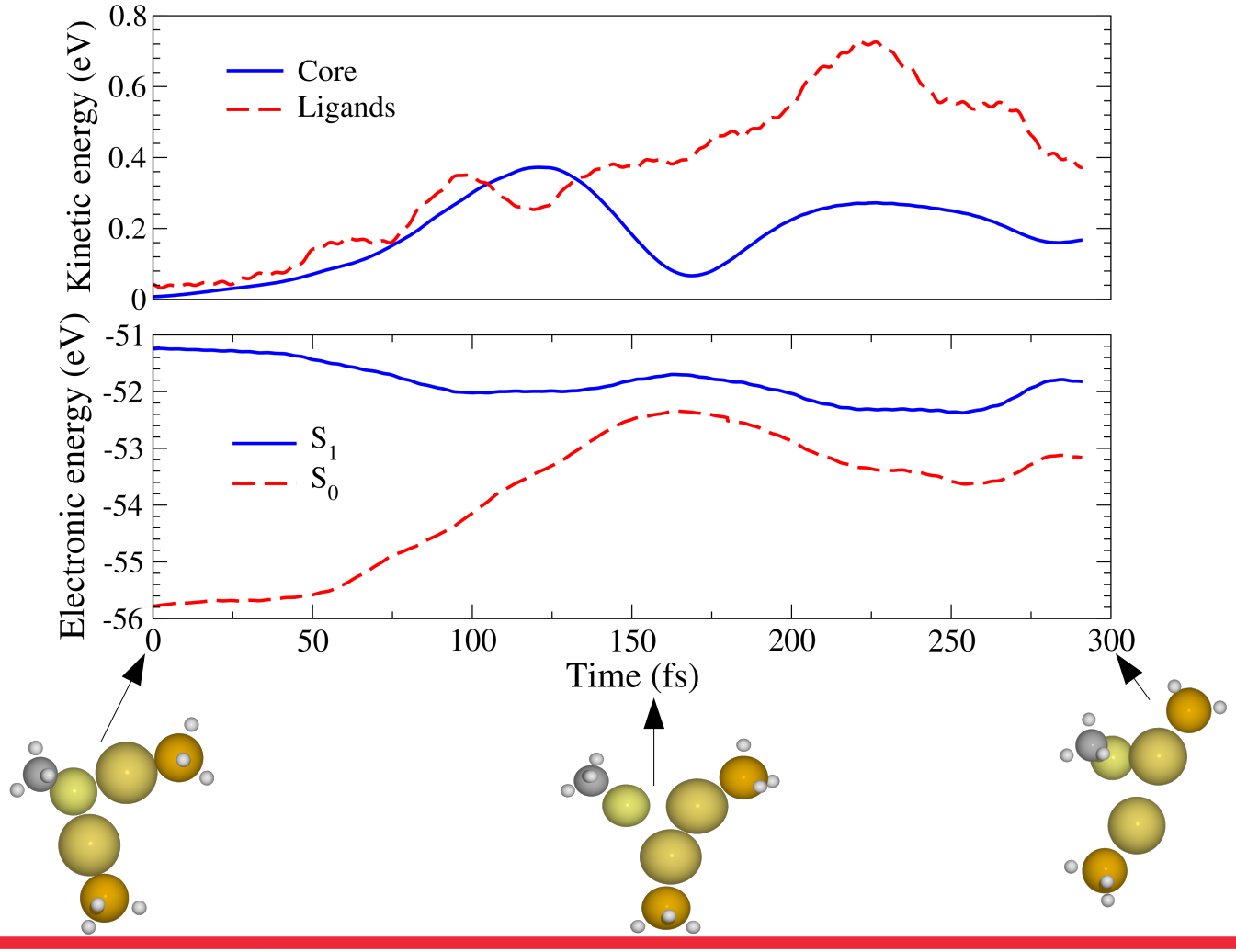
- Excitation energies from spin-unpolarized Delta-SCF often very close to linear-response TDDFT
- Initial state with Delta-SCF, photoexcitation dynamics from Ehrenfest dynamics

Simulation details



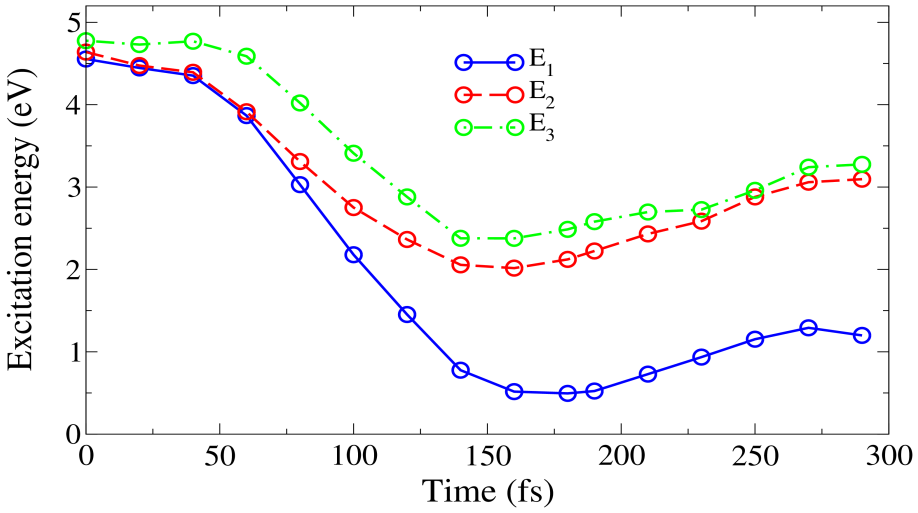
- Au_2 cluster protected by one SCH_3 and two PH_3 groups
- 300 fs long calculations with a small initial kinetic energy
- Grid spacing h = 0.2 Å, 5 Å vacuum around the ligands, PBE XC functional

Evolution of the nuclei and electrons

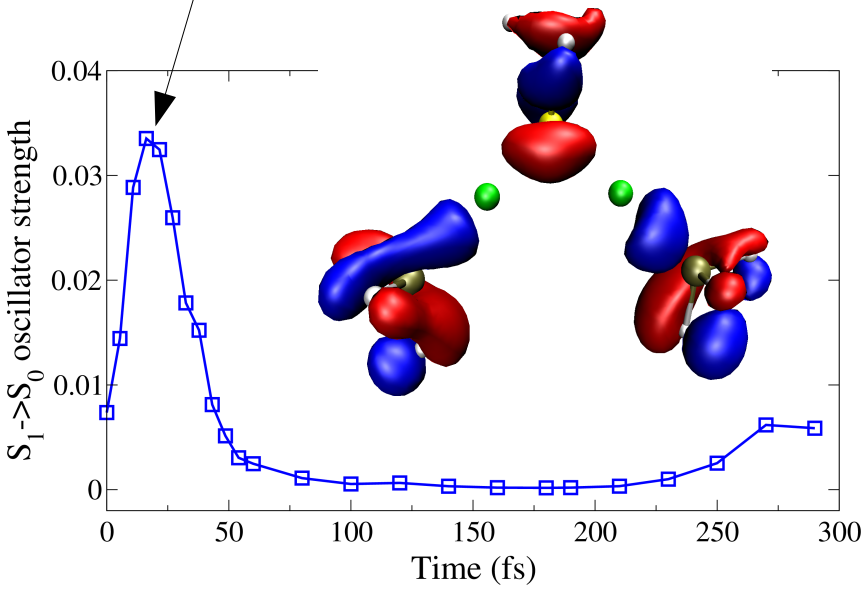


Linear-response TDDFT results

- for the trajectory obtained with Ehrenfest dynamics

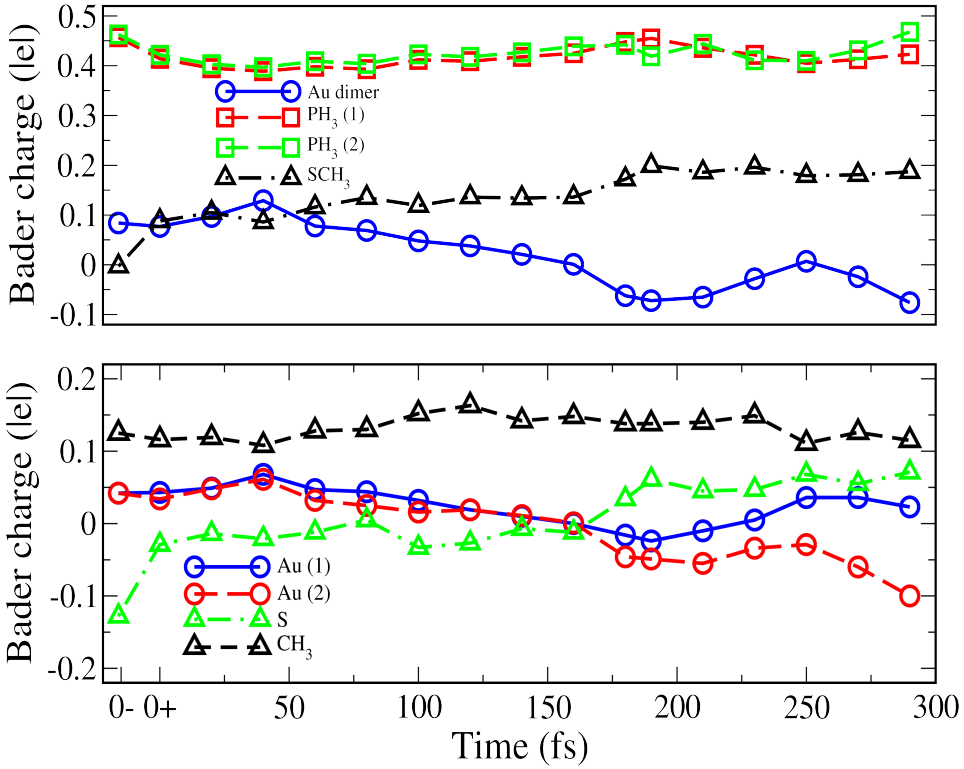


LUMO(t = 25 fs) – LUMO(t =0)



Increased oscillator strength at the beginning and at the end of the simulation

Charge transfer analysis



- Excitation (0- → 0+) localized in the ligands
- Metal-to-ligand charge transfer (first 50 fs), ligand-to-metal thereafter
- Asymmetric charge distribution in the gold core at the end

Au2 cluster: conclusions

- Complex dynamics in spite of the simple core
- Metal-to-ligand charge transfer during first 50 fs, reversed thereafter
  - Increased oscillator strength coupled to accumulation of charge around the P atoms, suggesting use of stronger electron-accepting groups in the phosphine ligands to enhance emission
- Asymmetric charge distribution in the core at the end
  - Coupled to increased oscillator strength
  - This mechanism might be present in the excited state dynamics of larger protected cluster

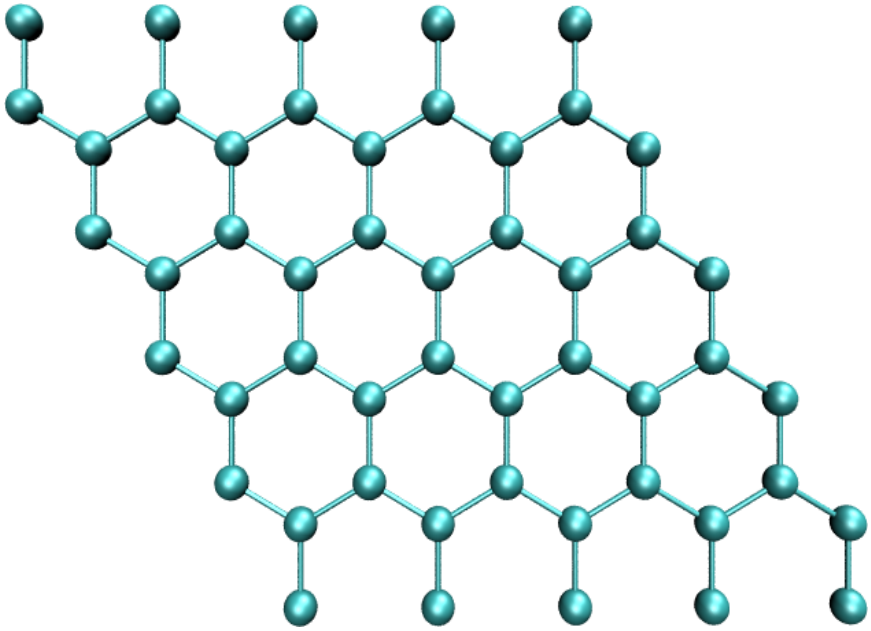
Stopping of high-energy ions in graphene

- In ion bombardment, the projectile loses kinetic energy to
  - collisions with the nuclei (nuclear stopping)
  - electronic excitations in the target or in the projectile (electronic stopping)
- Ab initio description of electronic stopping difficult
  - Especially at high impact energies, at which core electron excitations start to contribute to the stopping process
- By bombarding graphene with high-energy ions, we studied[1] the capability of Ehrenfest dynamics for modeling electronic stopping from first principles

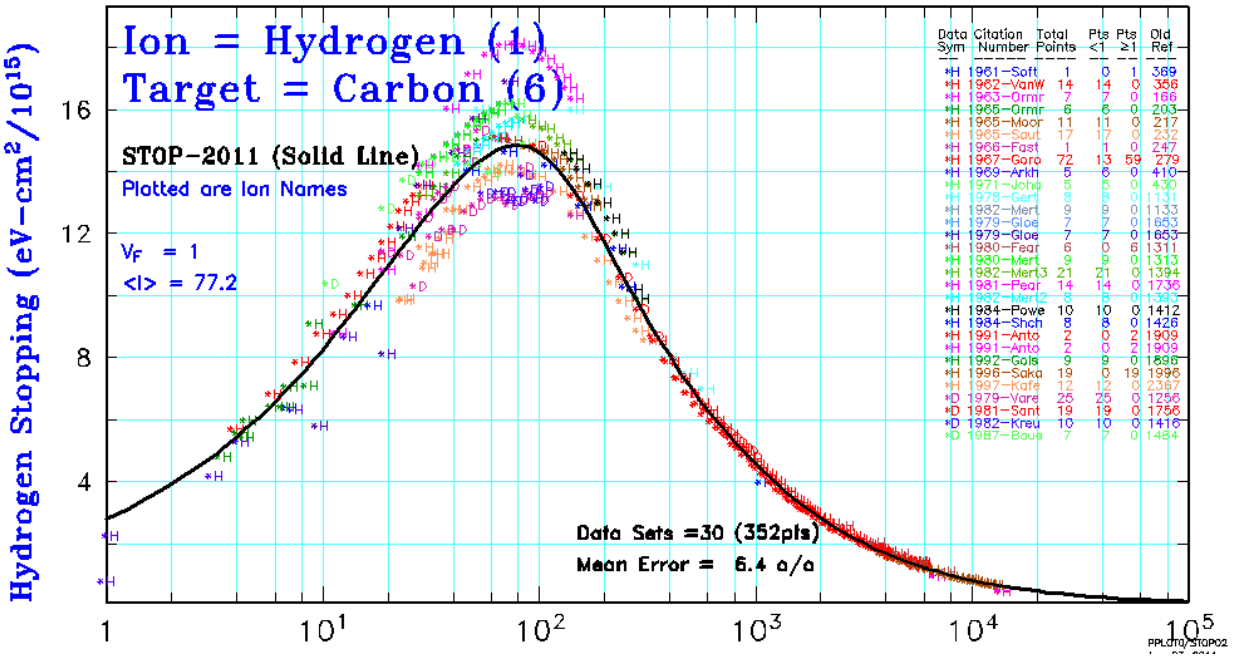
1: A. Ojanperä, A. V. Krasheninnikov, and M. Puska, submitted

Simulation details

- Main quantity of interest: energy deposited into the electrons of the target and the projectile
  - Can be converted into stopping power S_e if the thickness if the target is known
- Slabs composed of up to 6 layers of graphene, 50 atoms in each layer
- Periodic boundary conditions in all directions, singly ionized projectiles
- Spacing h = 0.2 Å, LDA XC



Electronic stopping: experiments

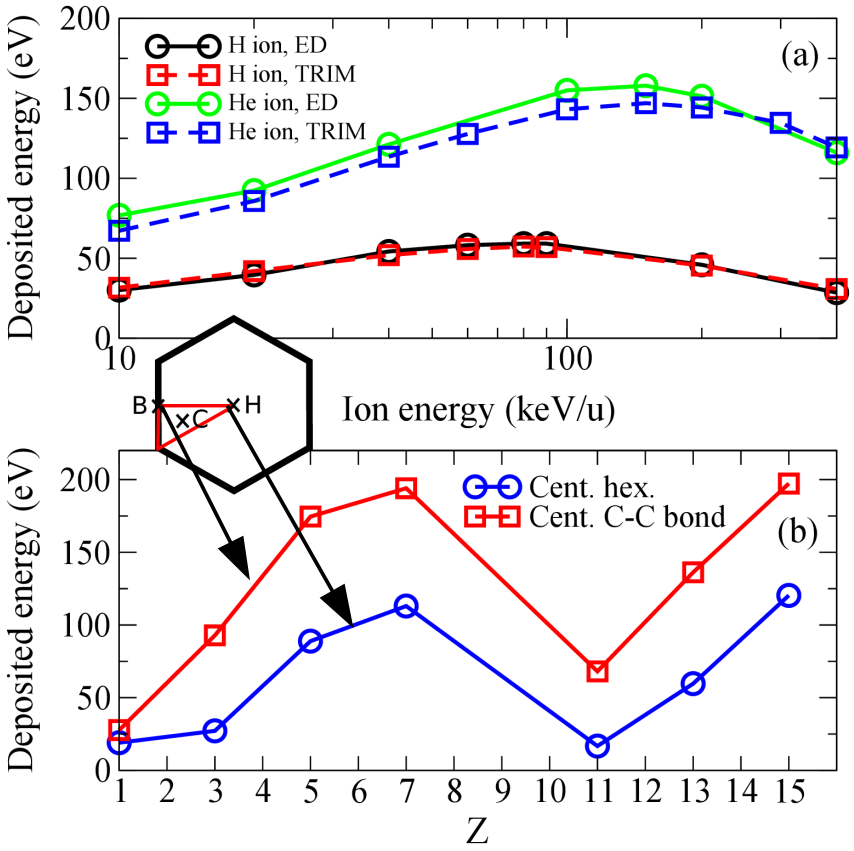


'Experiments' = best fit to a large amount of experimental data for carbon, obtained from the semi-empirical code TRIM (black line)

In order to do the comparison, we calculate the average stopping over the graphene surface (requires several trajectories / energy)

Stopping of light ions

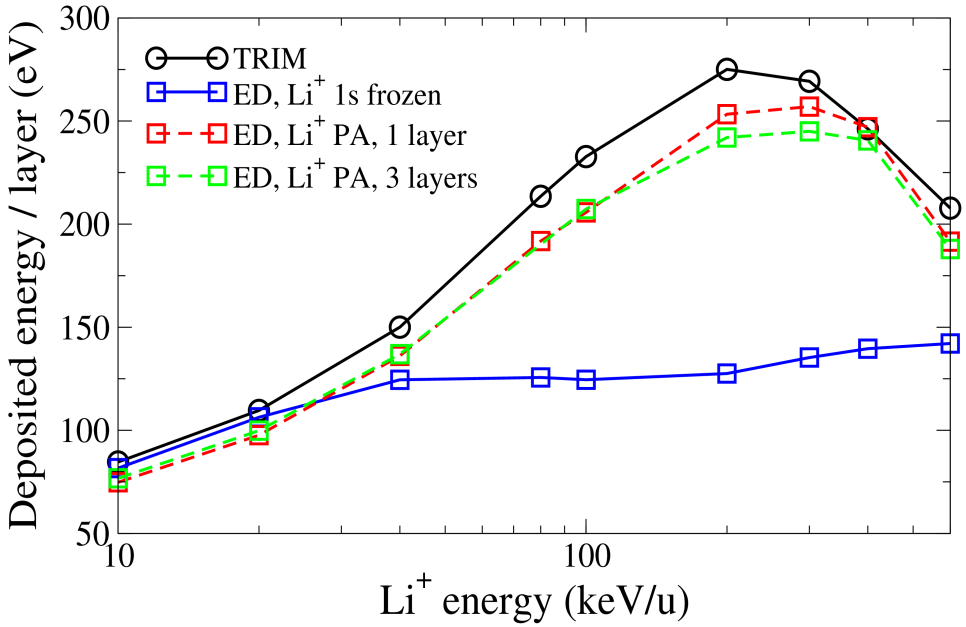
Top figure: ED results represent an estimated average over the graphene surface



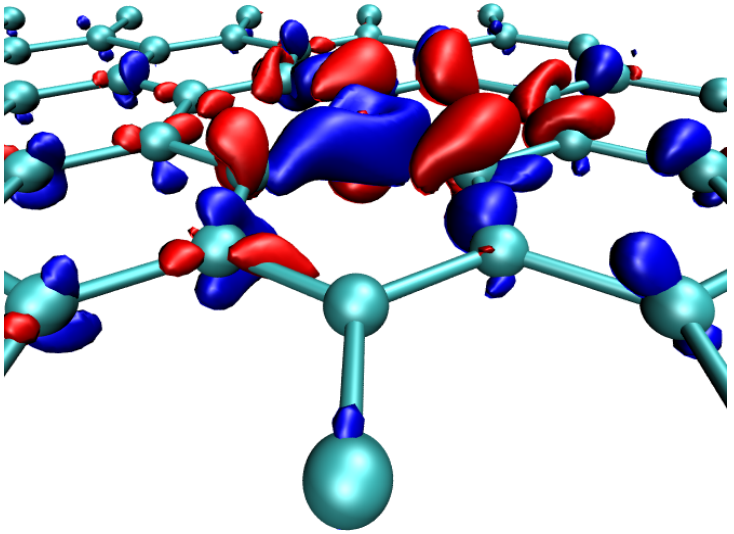
- Good agreement between ED results and experiments (TRIM) for H and He ions
- Stopping power oscillates as a function of nuclear charge Z, in agreement with earlier experimental observations

High-energy stopping for Li

Li “pseudoatom” (PA): core electrons treated as valence electrons within the PAW scheme



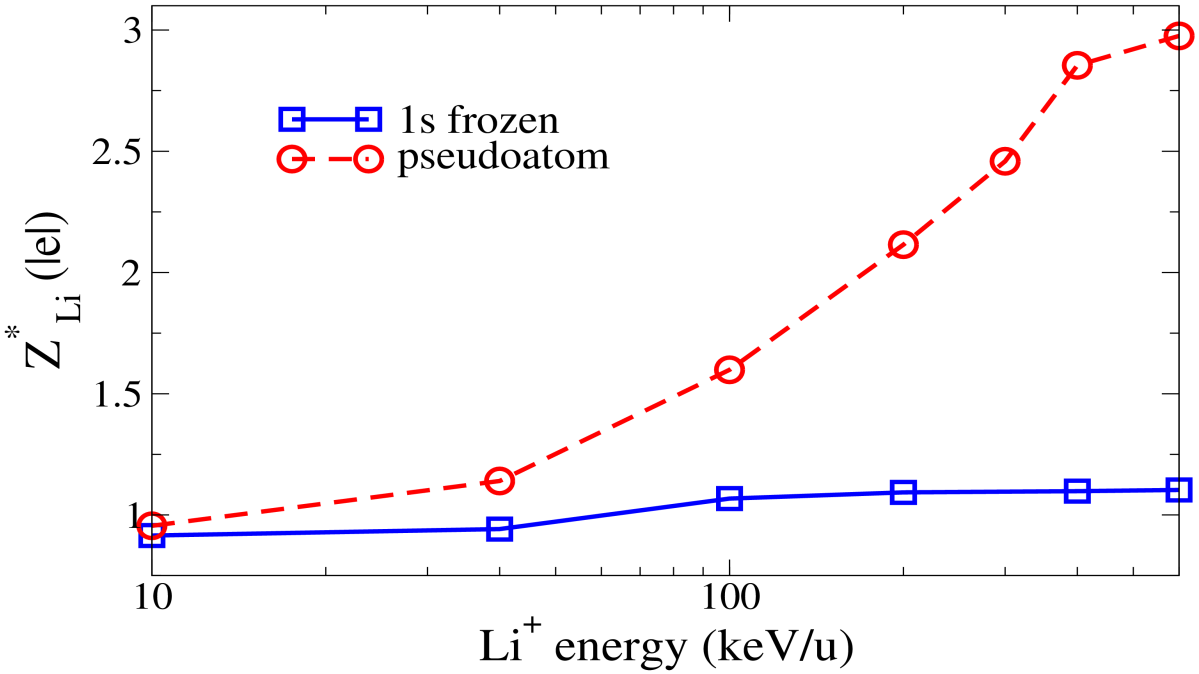
200 kev/u: difference between densities obtained using PA-Li and Li with 1s frozen



Huge improvement at high energies with the 3-electron setups!

Li stopping: ionization

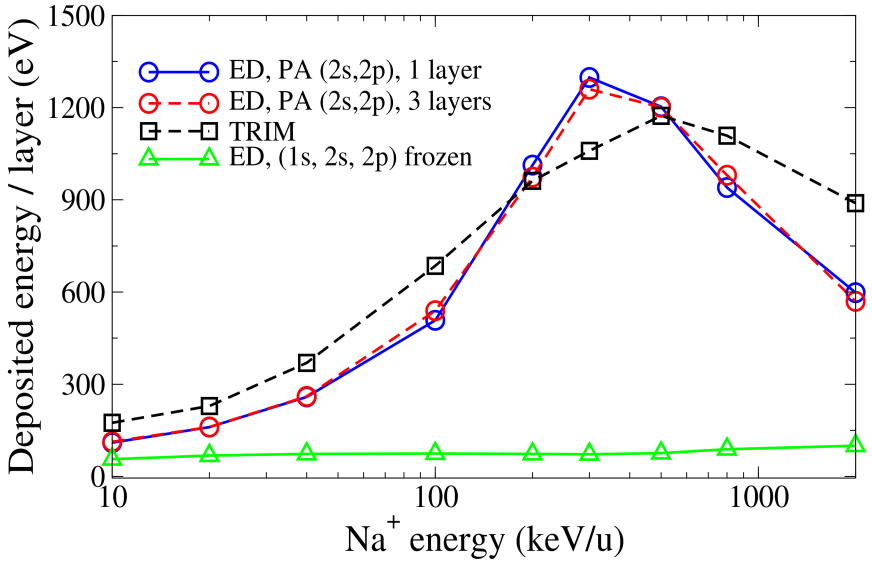
- Z^* = integrated all-electron density around the projectile just after passing through the target



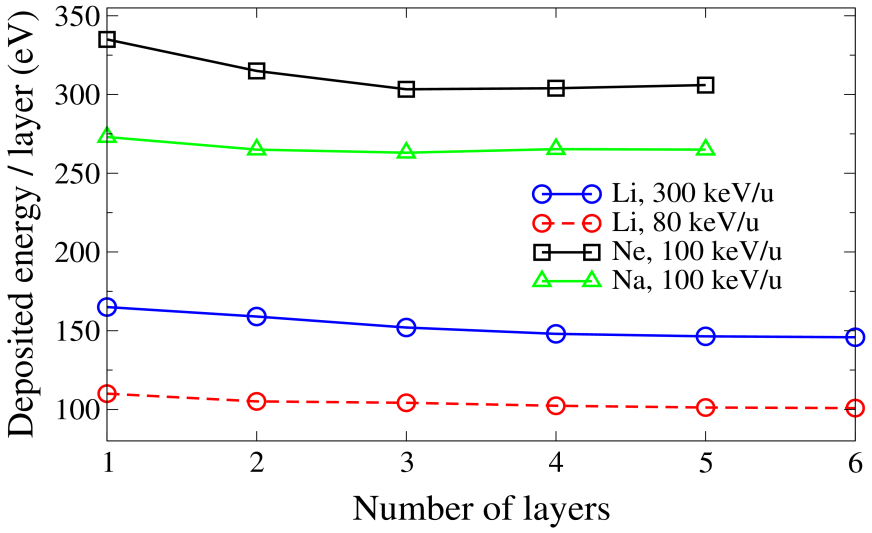
Increase in projectile charge coupled to increase in stopping power!

Results for sodium projectile and multiple graphene layers

Na (2s, 2p included) vs frozen-core



Li, Na as before, Ne (1s frozen)



High-energy stopping: conclusions

- Ehrenfest dynamics provides a quantitatively accurate description of electronic stopping for light projectiles
- Decent agreement between ED+pseudoatom results and experiments for higher-mass projectiles at high energies
  - Excellent result since core electron excitations are generally difficult to model!
- Our computational setup can also be used for simulating the impact of ions with a high charge state
  - The projectile can be ionized in the collision with an intermediate target

Thank you!

...and big thanks to CSC and the Triton cluster of the Aalto University for the computational resources!