Atomic collisions with Time-Dependent Density Functional Theory

TDDFT without lasers

Guillermo Avendaño-Franco
guillermo.avendano@uclouvain.be
Bernard Piraux
Myrta Grüning
Xavier Gonze

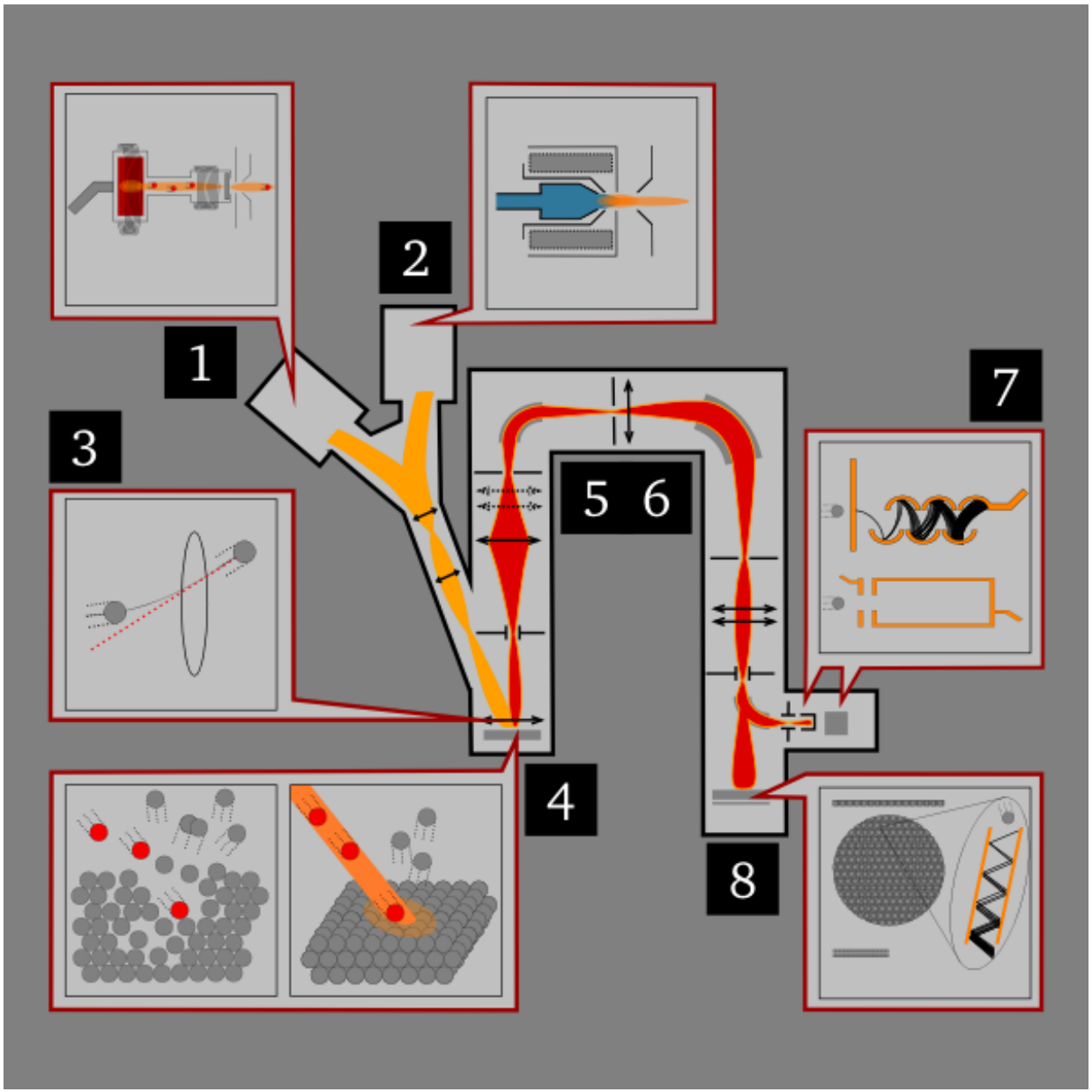
Université Catholique de Louvain (UCL)
Belgium

October 22, 2012

Purpose and Motivation

Time-of-Flight Secondary Ion Mass Spectrometry

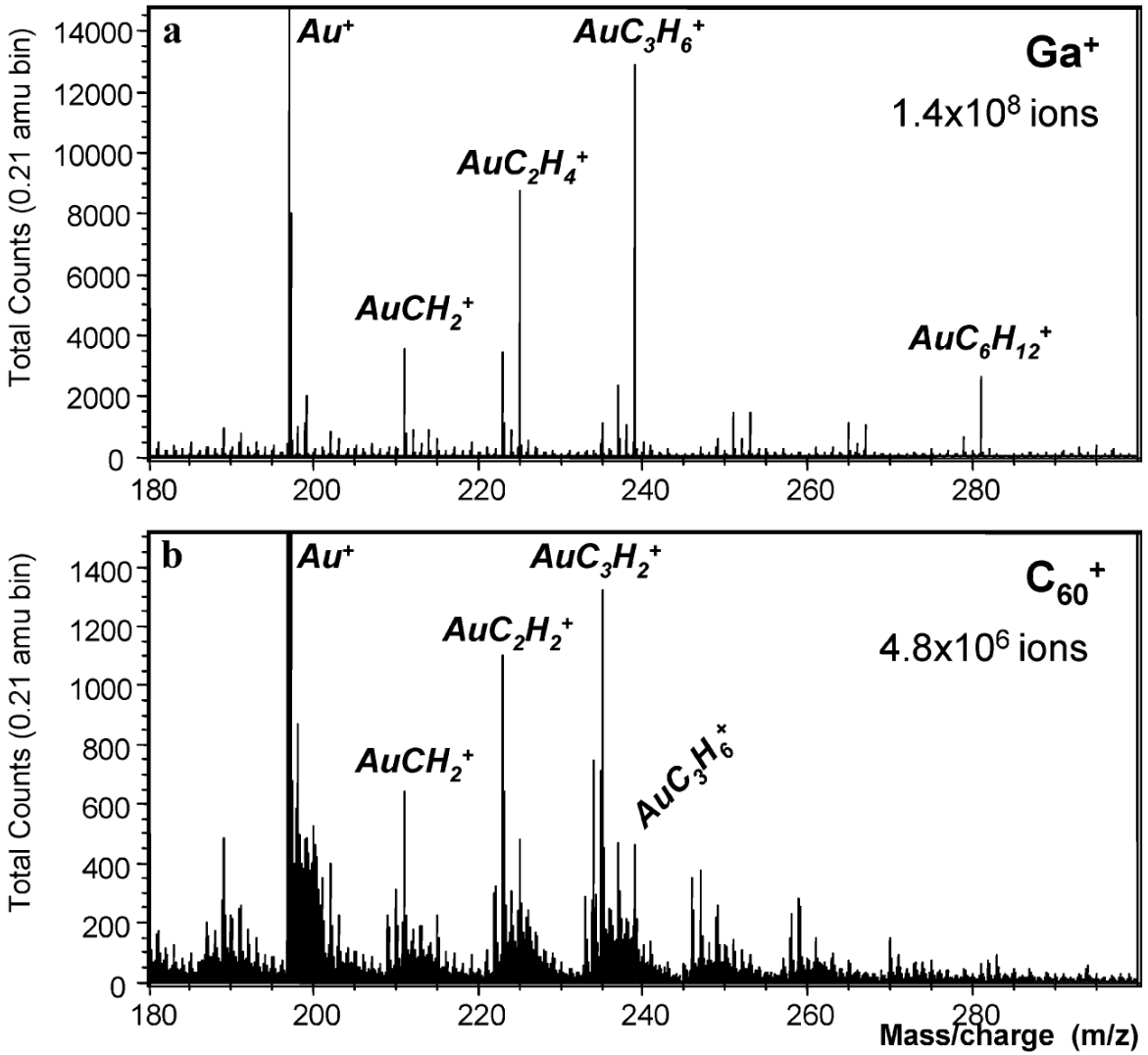
Purpose and Motivation



SIMS

1. Gun 1
2. Gun 2
3. Target sample
4. Sputtered atoms
5. Magnetic lenses
6. Collimator
7. Electron multiplier
8. CCD screen

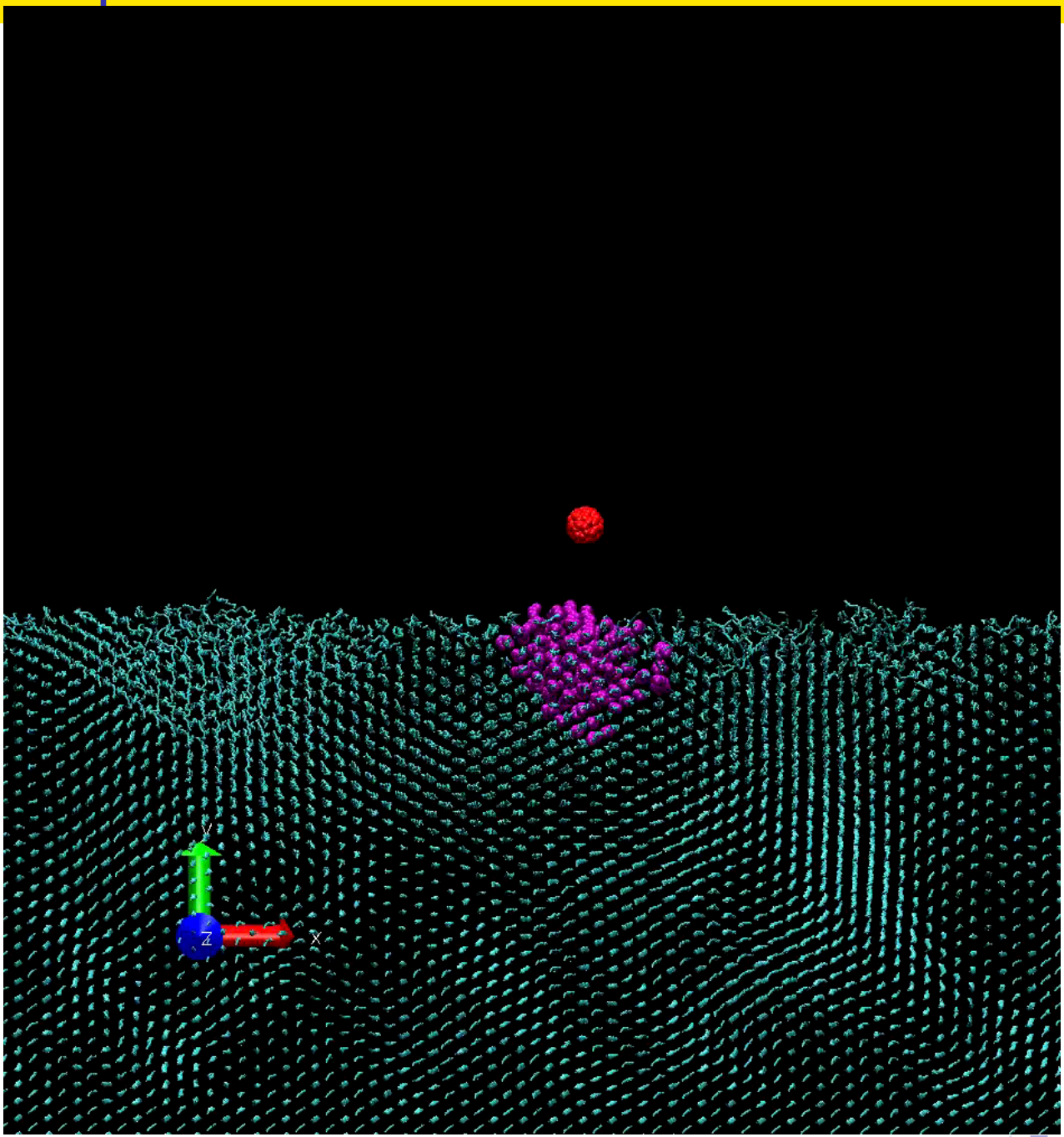
Purpose and Motivation



Positive SIMS

Partial positive secondary ion mass spectra ($180 < m/z < 300$) of Au-metallized PP samples upon
(a) 15 keV Ga+
(b) 15 keV C60+ bombardment.

Purpose and Motivation



CMD

Classical Molecular dynamics simulation of a C60 molecule impacting on a Au-metallized PP samples.

Outline

Proton impacting Helium

Why proton and Helium?

1. It is simple, only 2 electrons involved
2. Experimental data
3. Higher levels of Theory
4. Spin saturated system

How to model such collision?

1. TDDFT: Octopus
2. Initial kinetic energy
3. Parallelepiped (17Å,10Å,10Å)
4. Impact parameter

How to model such collision?

1. TDDFT: Octopus
   - Real-space grid discretization
   - Ehrenfest dynamics for the nuclei (Phys. Rev. Lett. 101, 096403 (2008))
   - Real-time TDDFT propagation (J. Chem. Phys. 121, 3425 (2004))
   - Norm-conserving pseudo-potentials
2. Initial kinetic energy
3. Parallelepiped (17Å,10Å,10Å)
4. Impact parameter

How to model such collision?

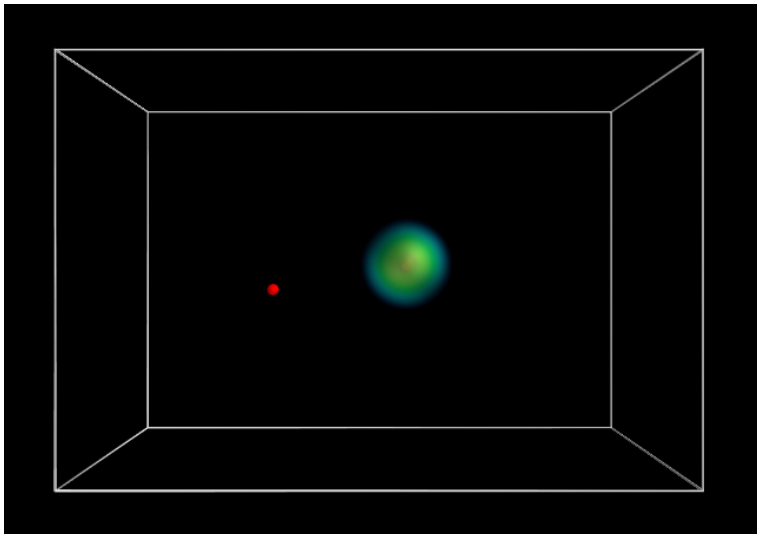
1. TDDFT: Octopus
2. Initial kinetic energy

From 10 keV to 500 keV

3. Parallelepiped (17Å,10Å,10Å)
4. Impact parameter

How to model such collision?

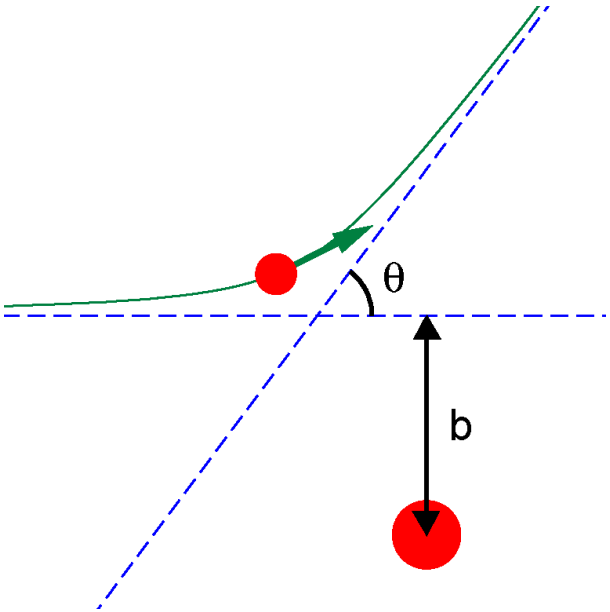
1. TDDFT: Octopus
2. Initial kinetic energy
3. Parallelepiped (17Å,10Å,10Å)



4. Impact parameter

How to model such collision?

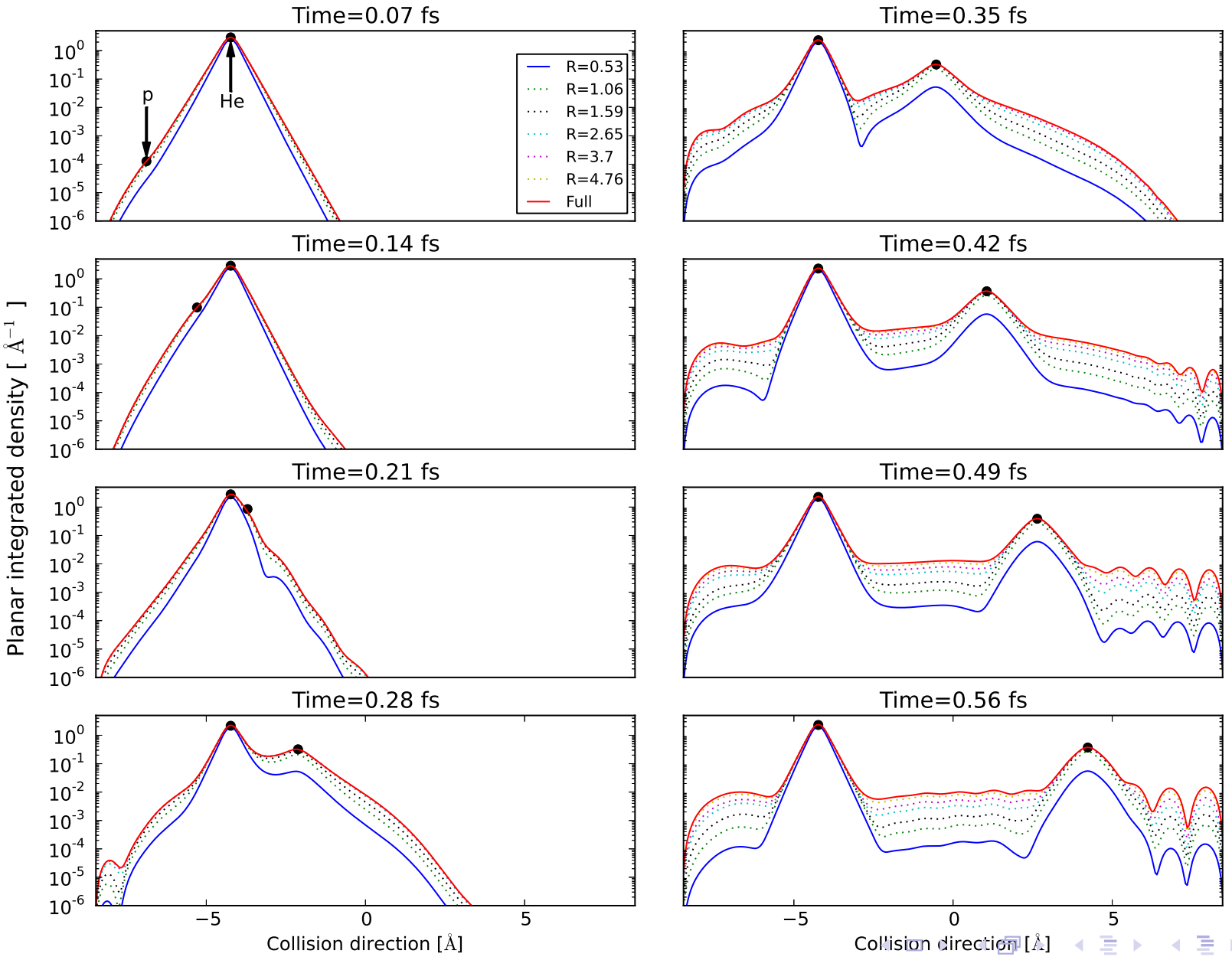
1. TDDFT: Octopus
2. Initial kinetic energy
3. Parallelepiped (17Å,10Å,10Å)
4. Impact parameter



The impact parameter b is defined as the perpendicular distance between the path of a projectile and the center of the field U(r) created by an object that the projectile is approaching *Wikipedia*

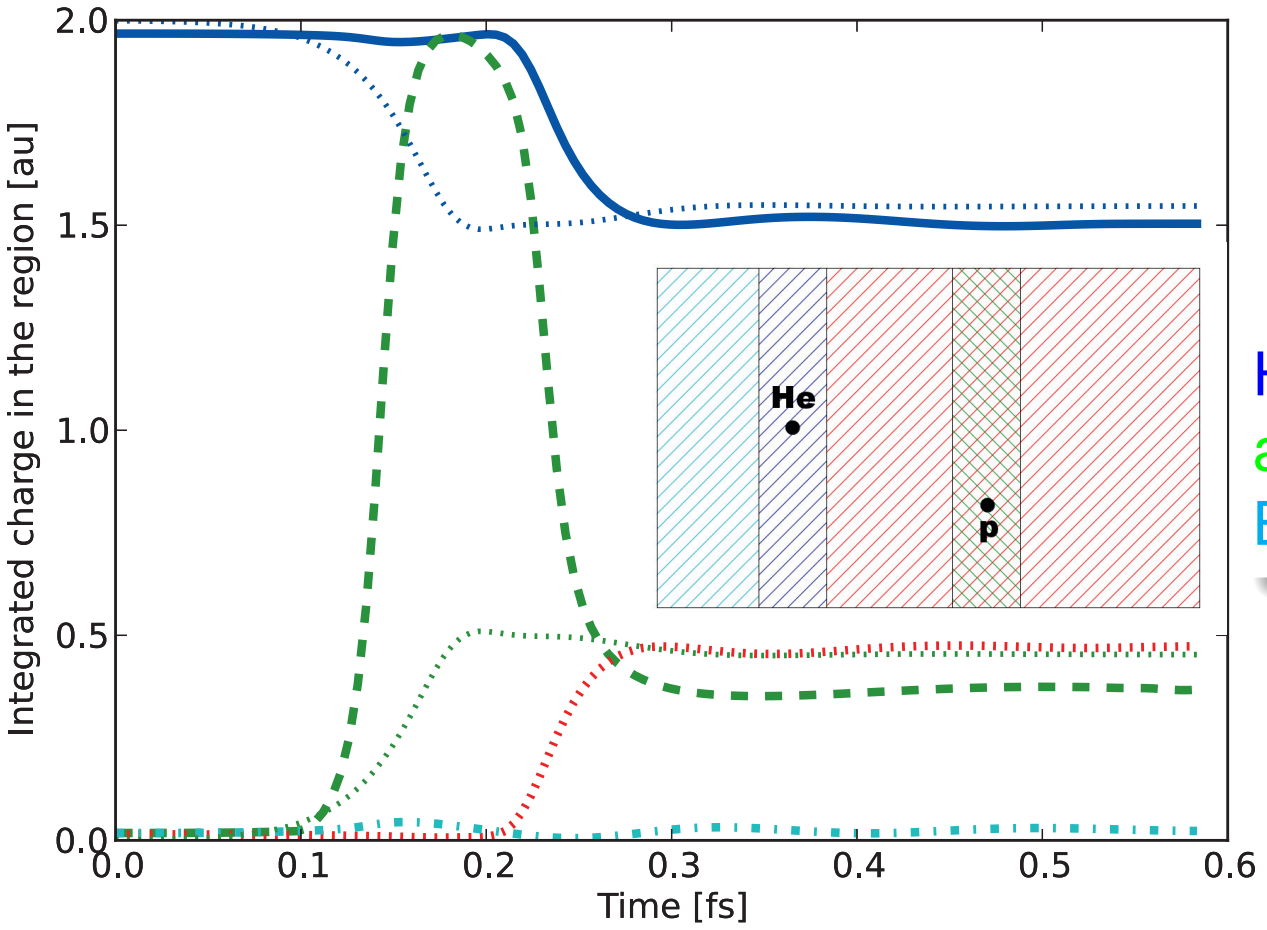
Charge transfer

Impact parameter is 0.74 Å, Initial kinetic energy of the proton is 26.8 keV.



Charge transfer

Impact parameter is 0.74 Å, Initial kinetic energy of the proton is 26.8 keV.



Helium atom Proton atom Forward region Backward region

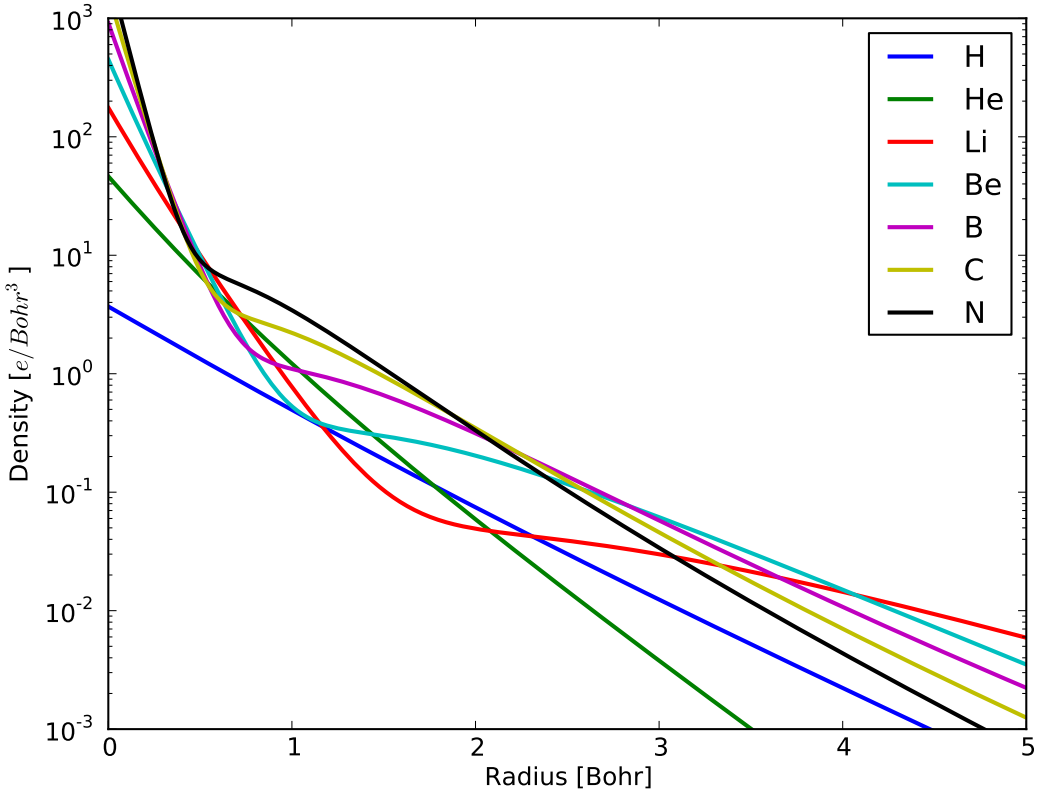
Hirshfeld analysis

Hirshfeld FL
Bonded-atom fragments for describing molecular charge densities
Theo Chim Acta 44:129 (1977)
Doi:10.1007/BF00549096

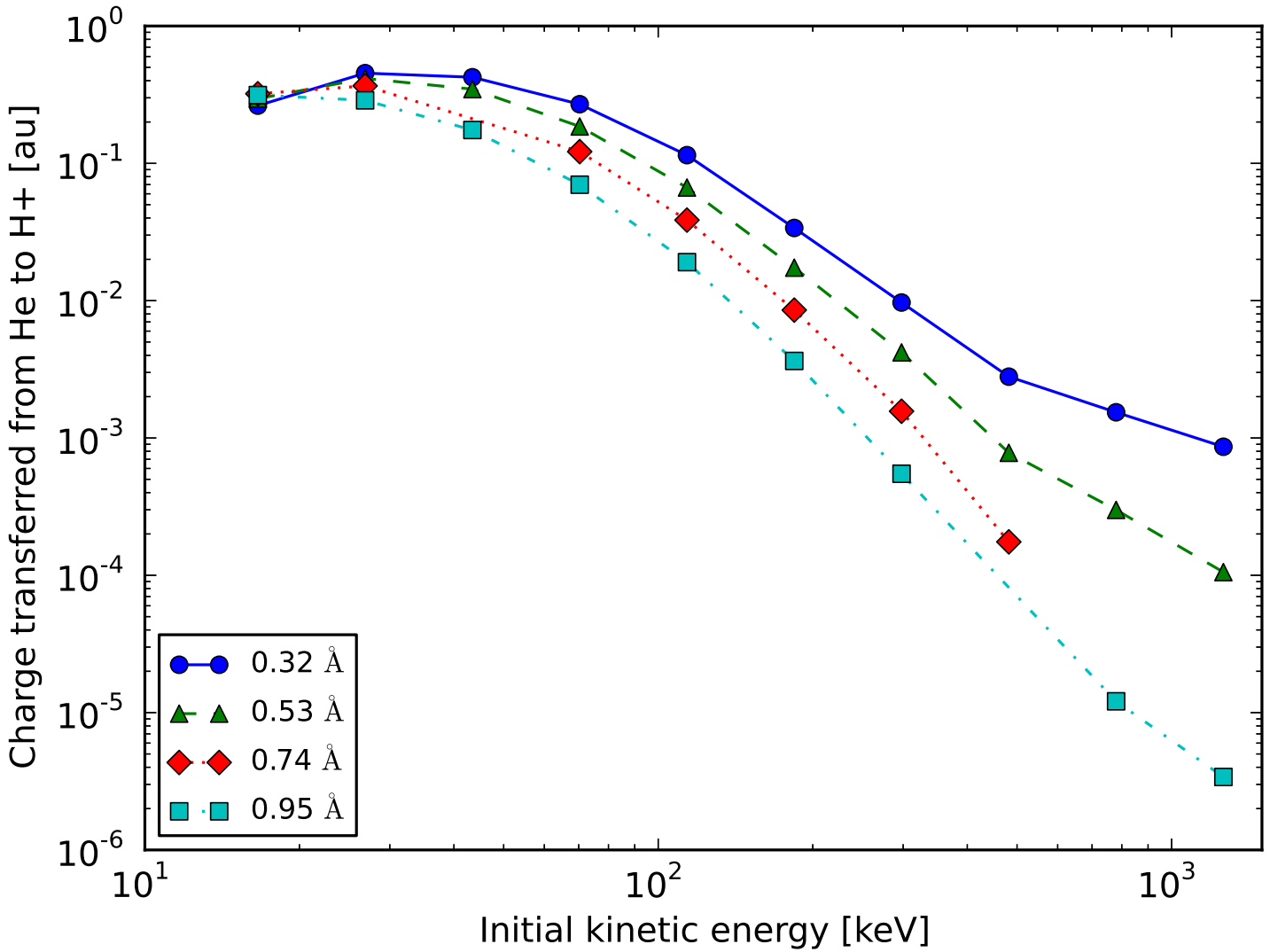
- Radial description of the density
- All the charge is associated to the atoms

Hirshfeld analysis

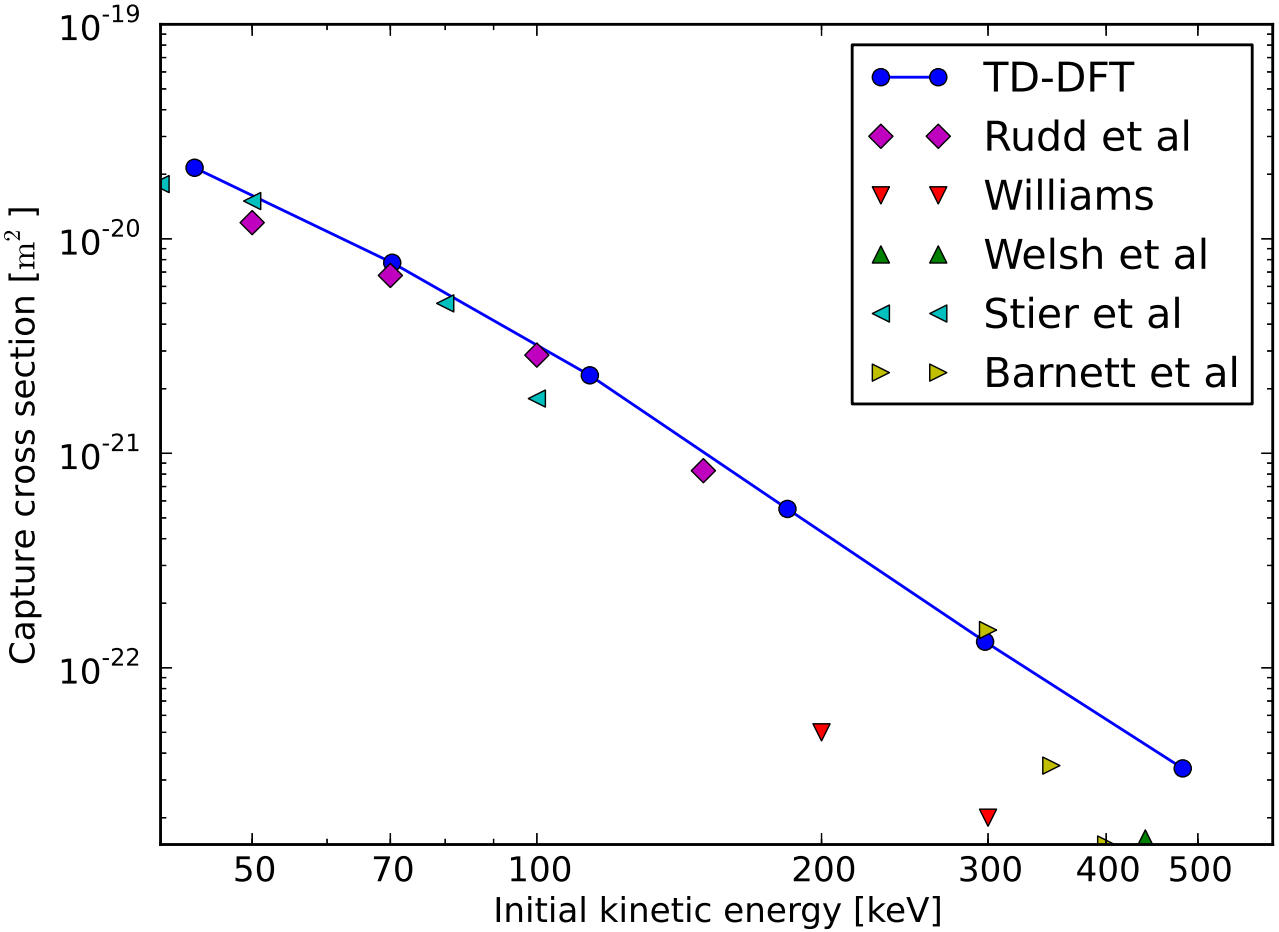
Hirshfeld FL
Bonded-atom fragments for describing molecular charge densities
Theo Chim Acta 44:129 (1977)
Doi:10.1007/BF00549096



Charge transfer

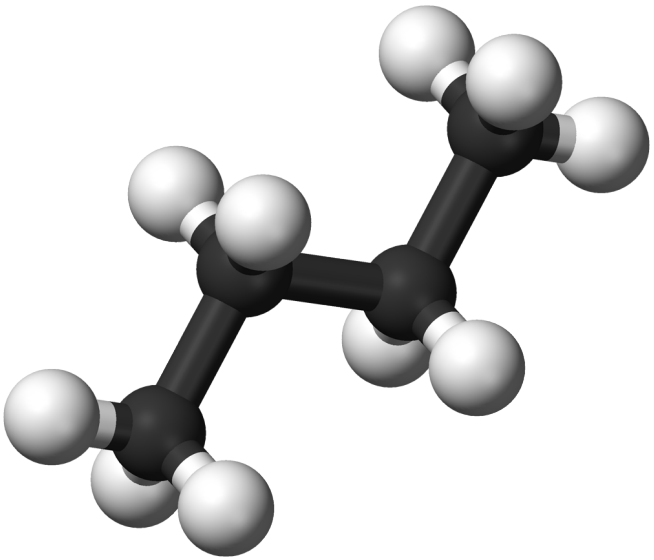


Capture cross section



Satisfactory agreement with experimental data.

Gold-Butane collision



1. Challenging (113 electrons instead of 2)
2. Beyond the reach of WFT methods
3. Motivated by Secondary Ion Mass Spectrometry

Gold-Butane collision

1. Challenging (113 electrons instead of 2)

Using norm-conserving pseudo-potentials the number of electrons treated explicitly can be reduce to 37
The dimension of the parameter space is 5

2. Beyond the reach of WFT methods
3. Motivated by Secondary Ion Mass Spectrometry

Gold-Butane collision

1. Challenging (113 electrons instead of 2)
2. Beyond the reach of WFT methods

Atomic physics WFT methods are cumbersome for 37 electrons.

3. Motivated by Secondary Ion Mass Spectrometry

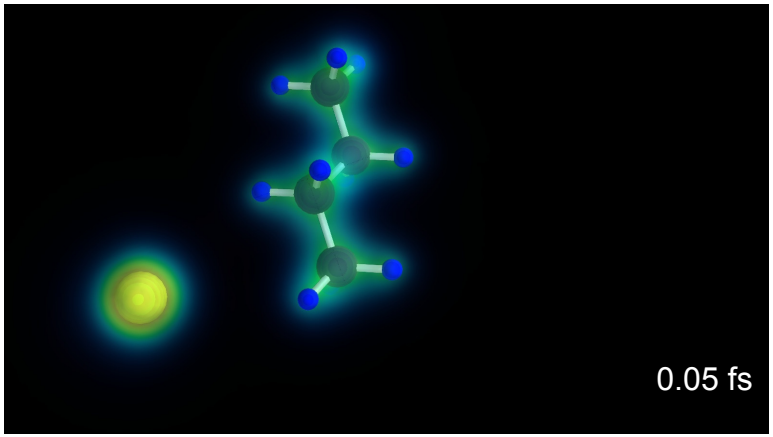
Gold-Butane collision

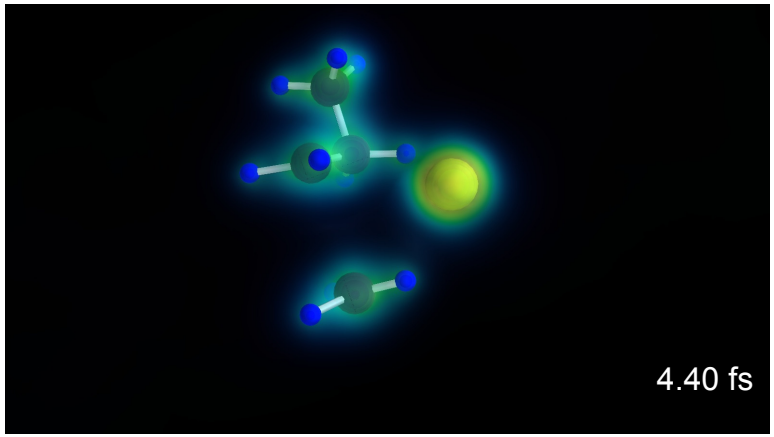
1. Challenging (113 electrons instead of 2)
2. Beyond the reach of WFT methods
3. Motivated by Secondary Ion Mass Spectrometry

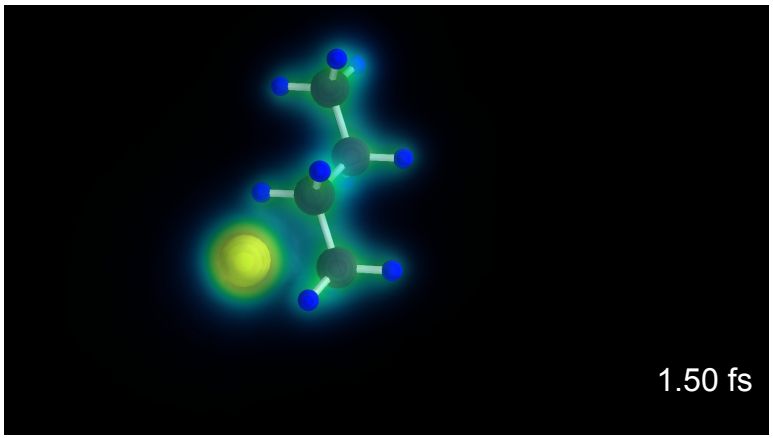
The fragmentation should be similar to those occurring in organic polymers due to secondary collision of the atoms from a gold deposit seuface as in metal-assisted SIMS

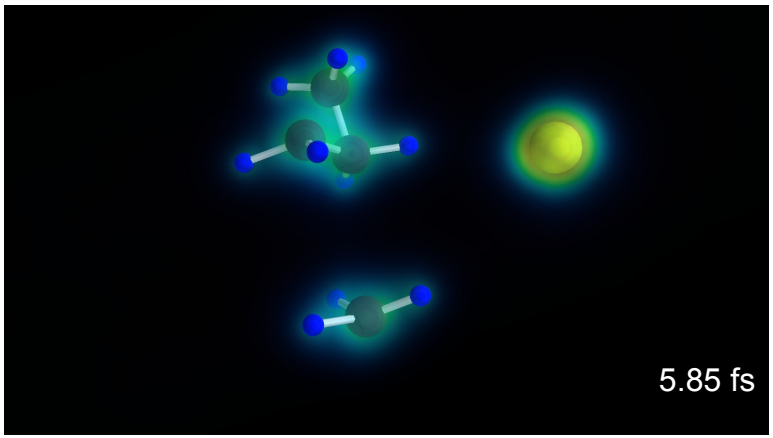
Gold-Butane collision (Ionization and fragmentation)

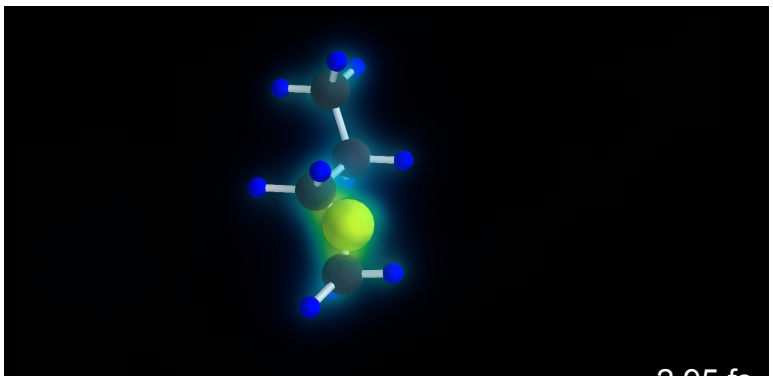
Gold 23.9 keV directed to a C-C bond

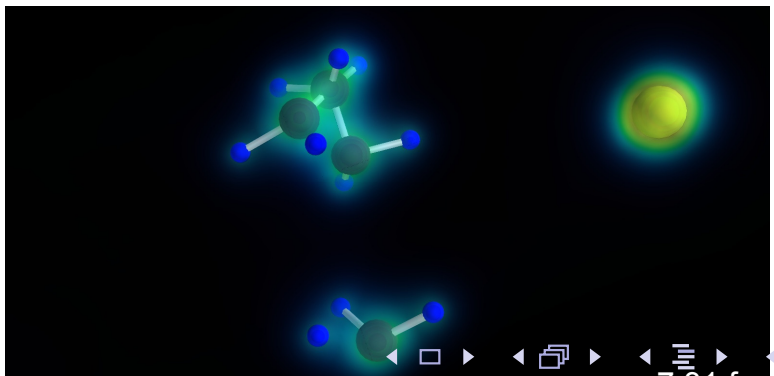






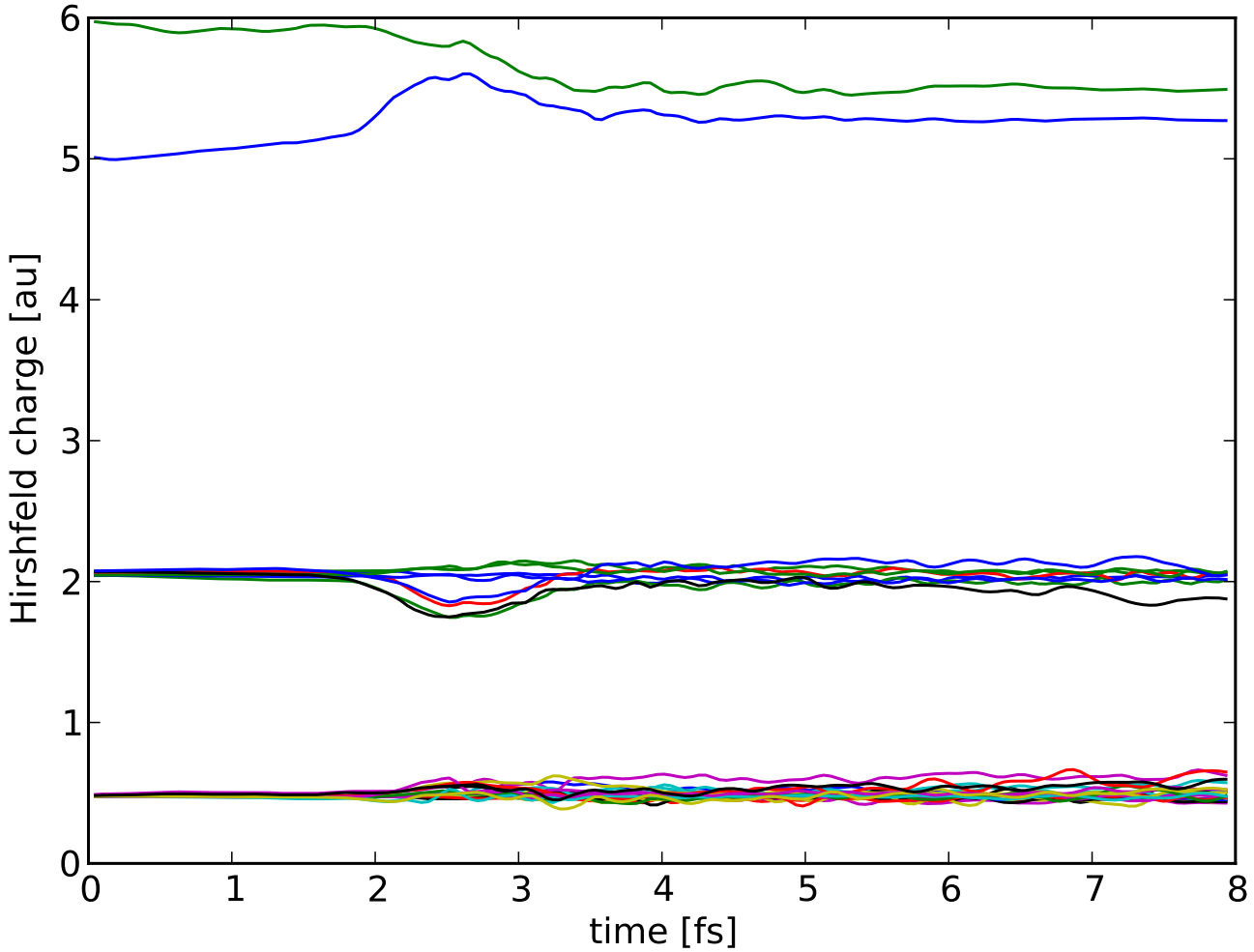






Gold-Butane collision (Ionization and fragmentation)

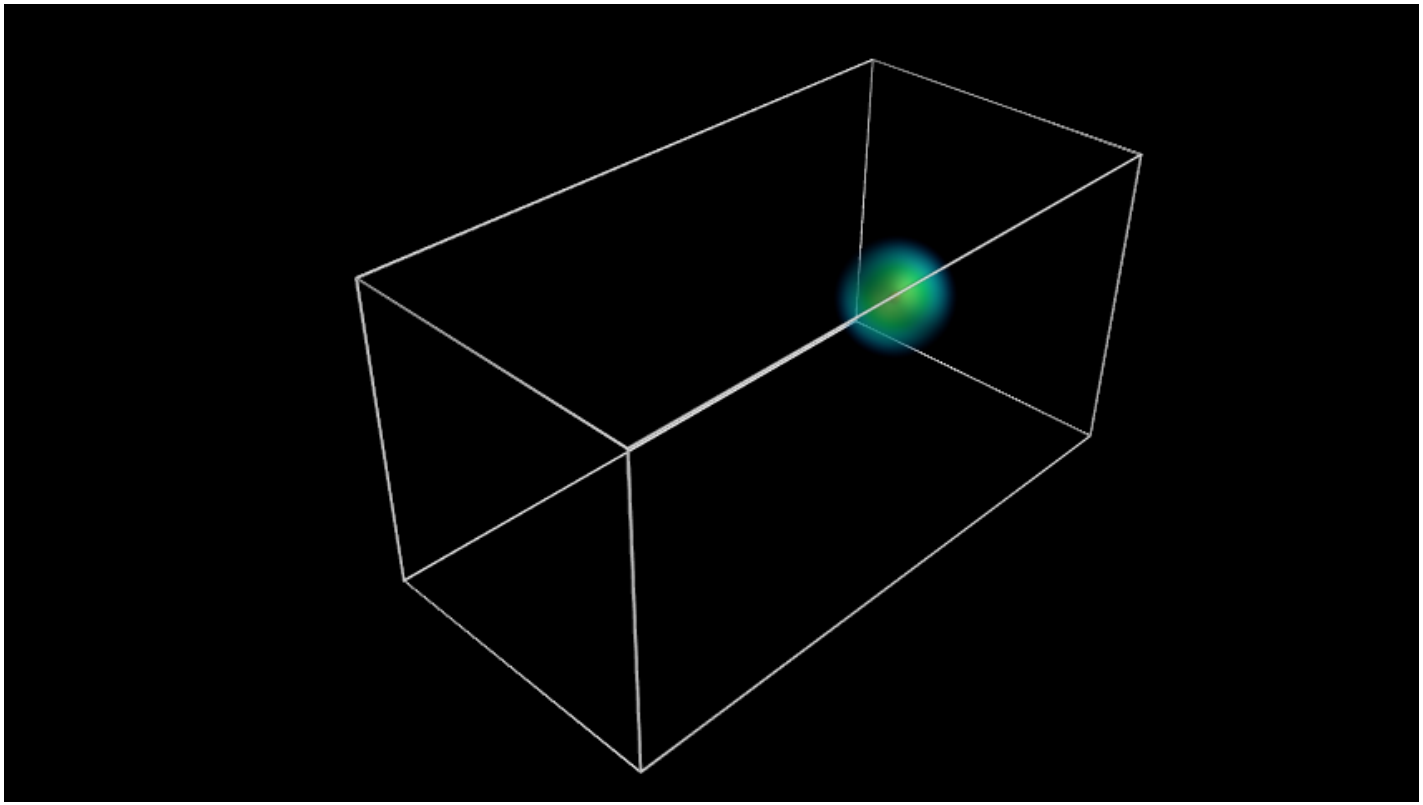
Hirshfeld charges during the simulation



Theo. Phys. Acc (2012)

Velocity phase correction

What happens when you compute the GS of an light atom (H) and after you propagate with a kinetic energy of 10 keV?



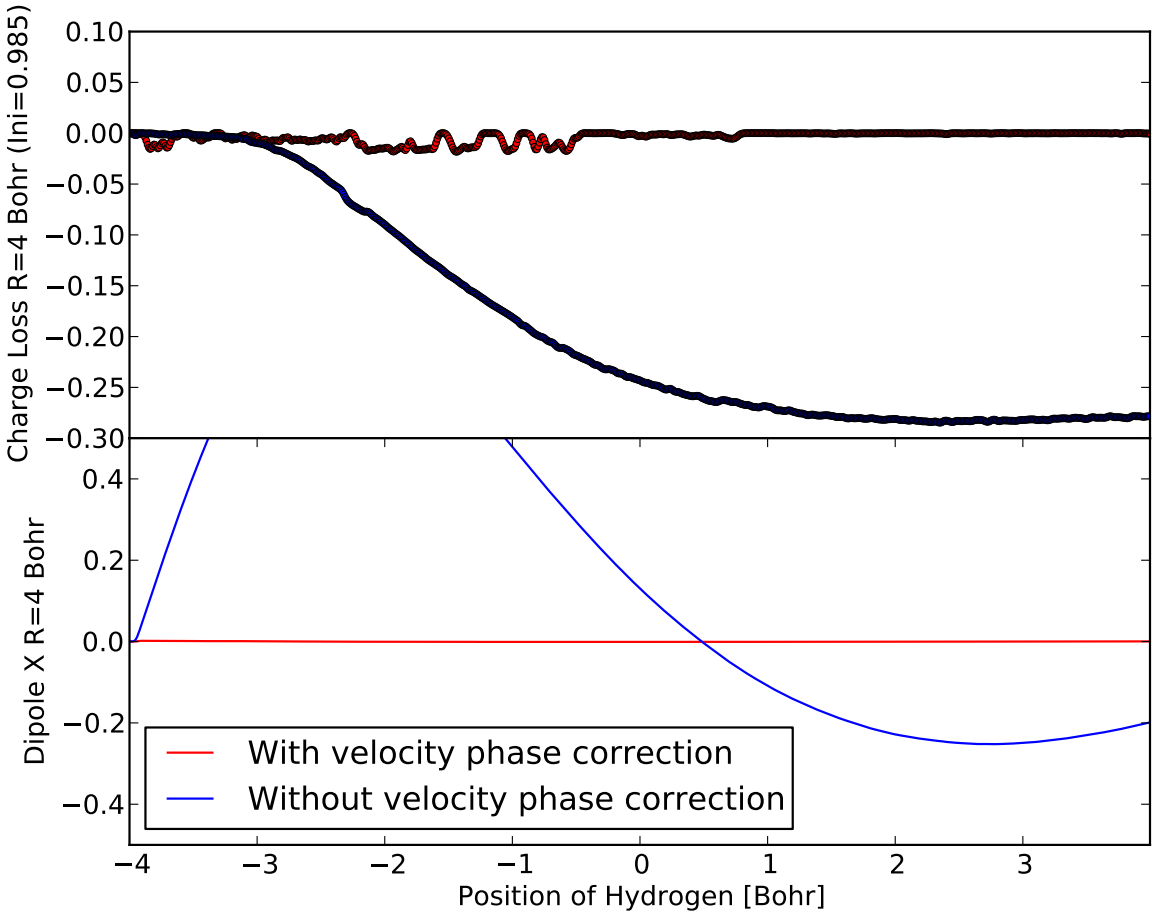
Electronic Ground State of a moving particle

The electronic ground-state of a inertial frame of reference (under Galilean Transformations) can be found from the electronic ground-state of the same particle at rest.

$$\psi_{\vec{v}}(\vec{r}, t = 0) = \varphi_{\vec{v}=0}(\vec{r}) e^{i\vec{v}\cdot\vec{r}}$$

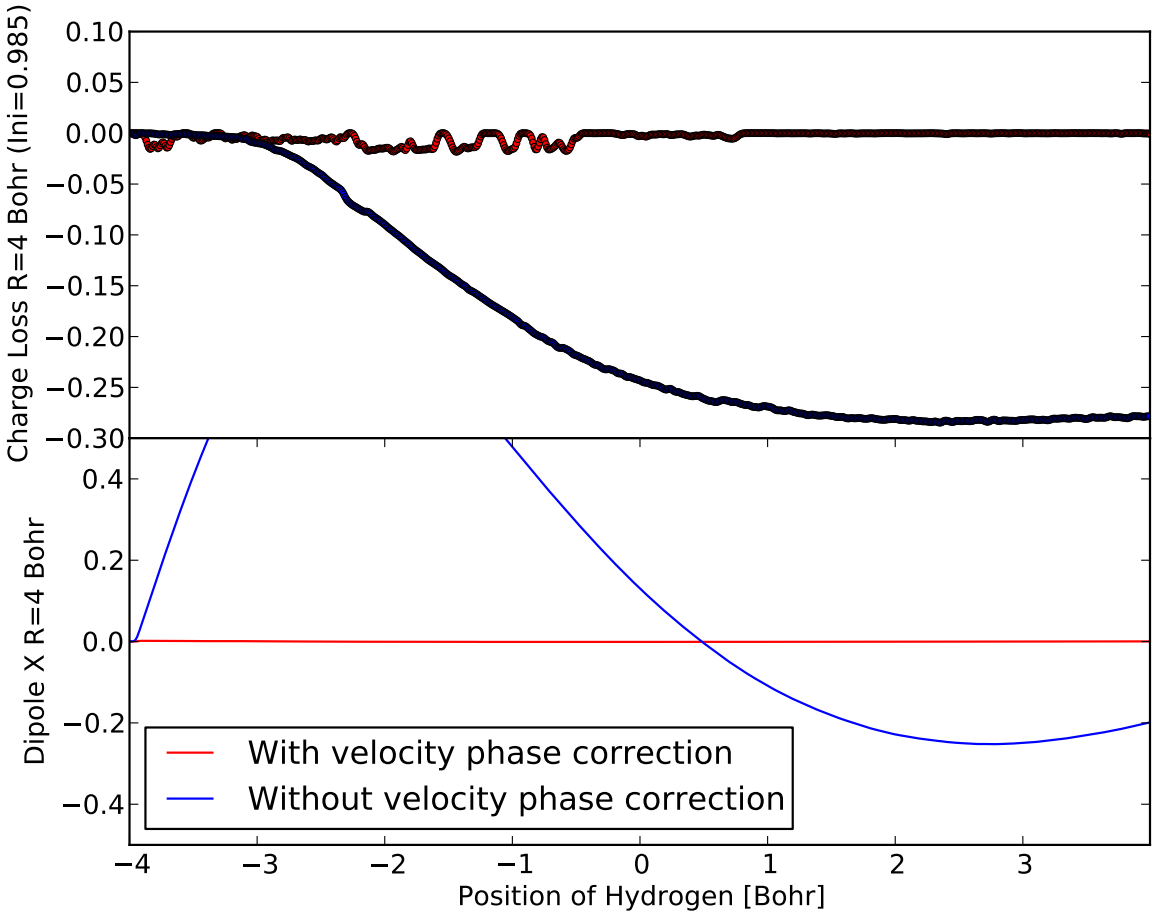
Hydrogen moving in a box

Kinetic energy: 10 keV



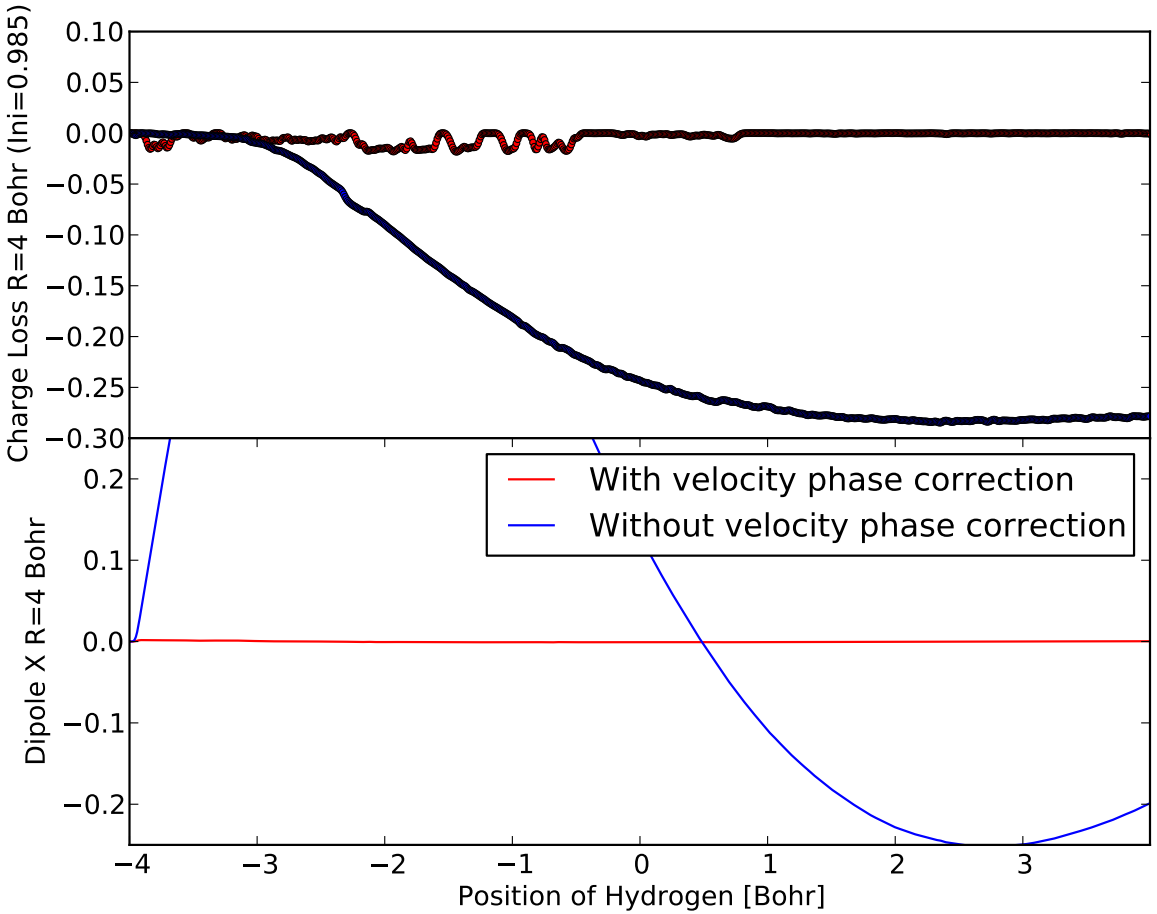
Hydrogen moving in a box

Kinetic energy: 10 keV



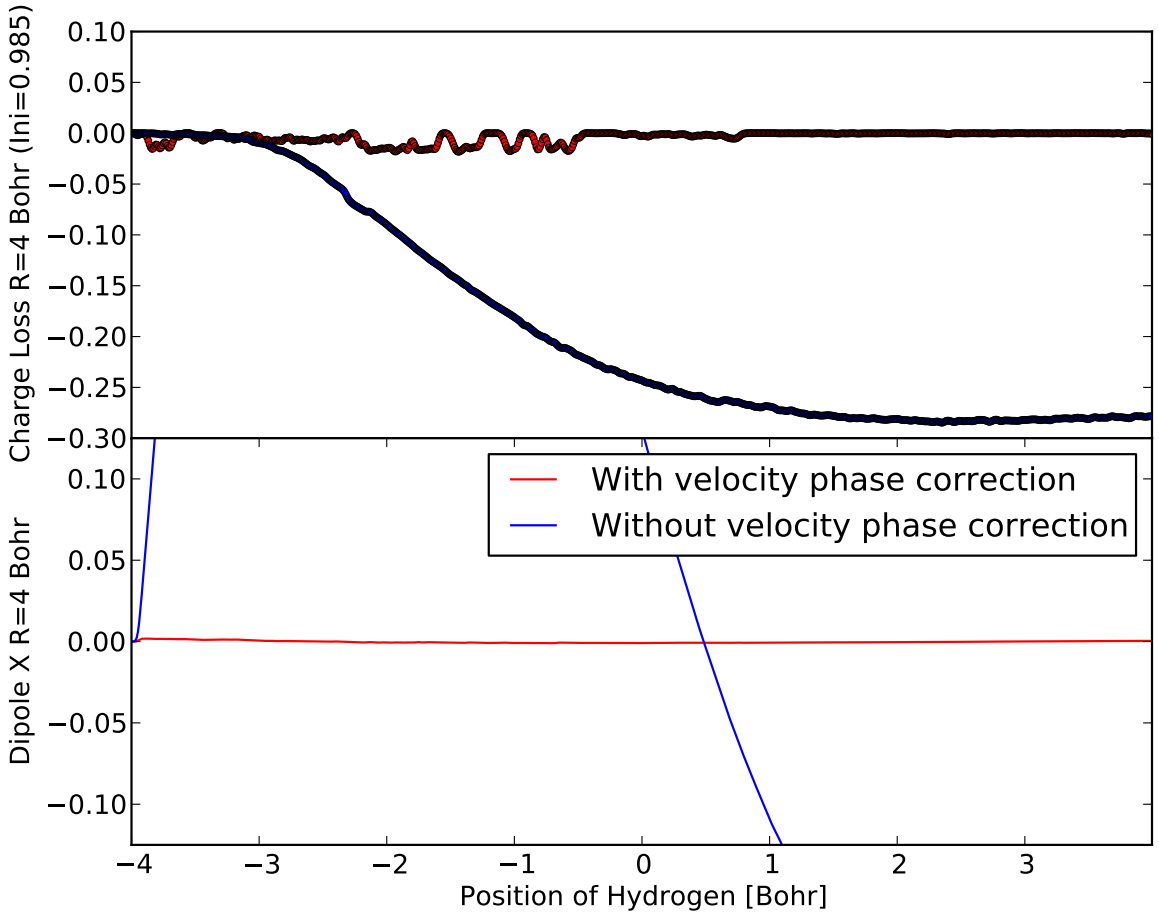
Hydrogen moving in a box

Kinetic energy: 10 keV



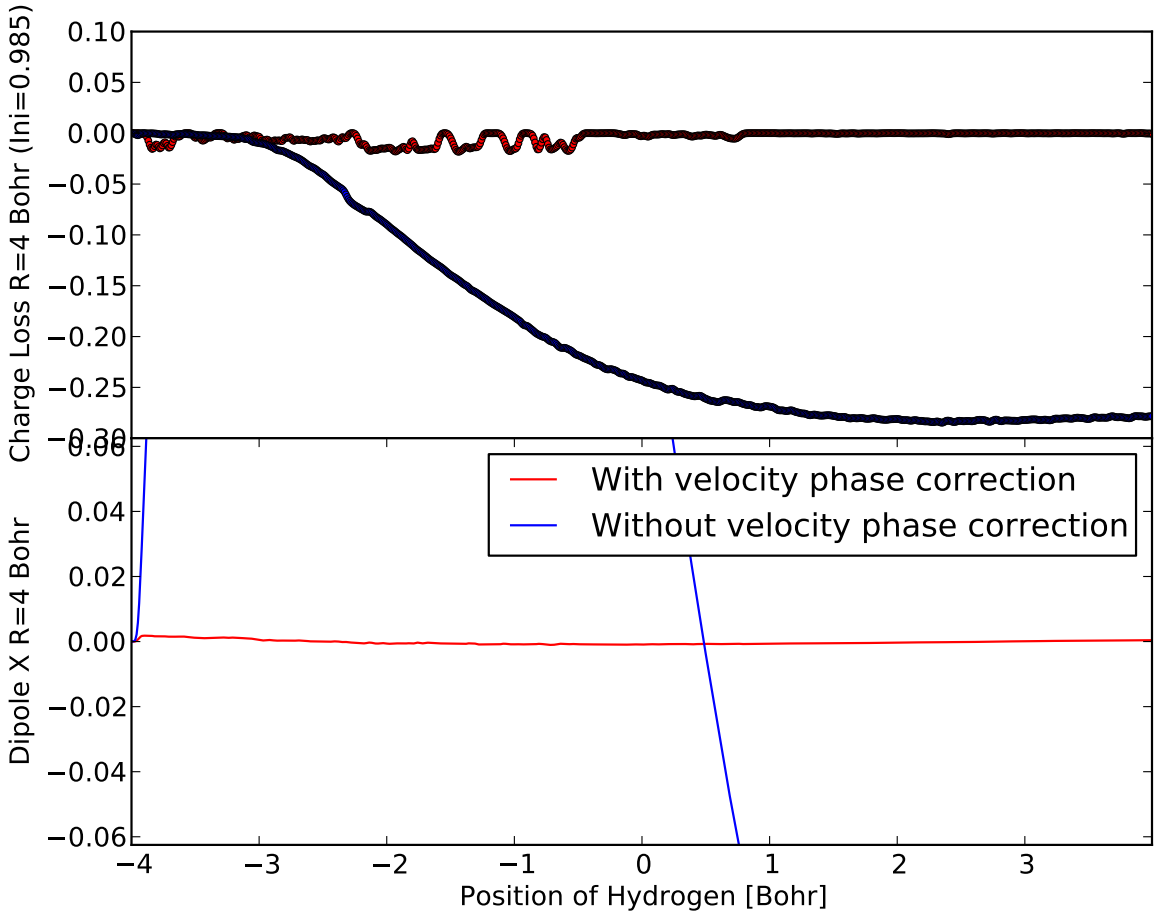
Hydrogen moving in a box

Kinetic energy: 10 keV



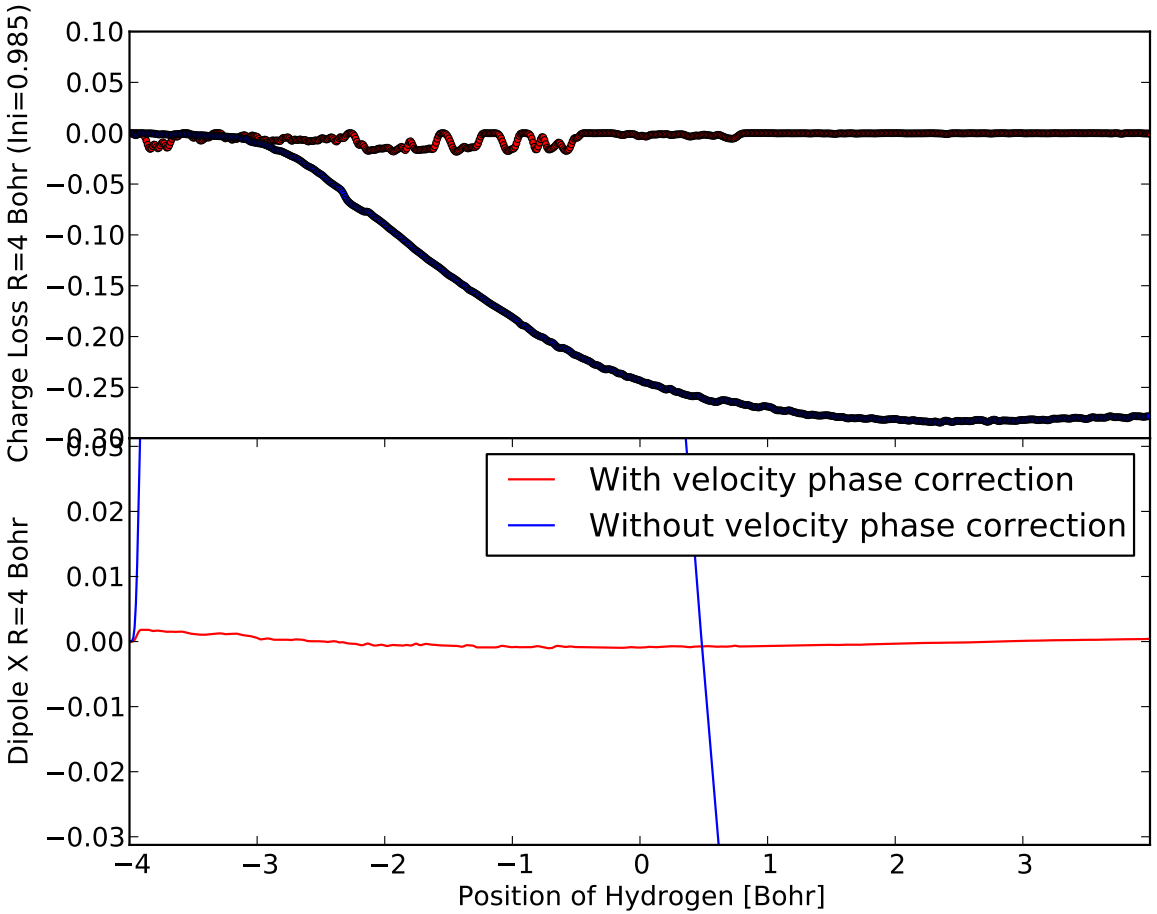
Hydrogen moving in a box

Kinetic energy: 10 keV



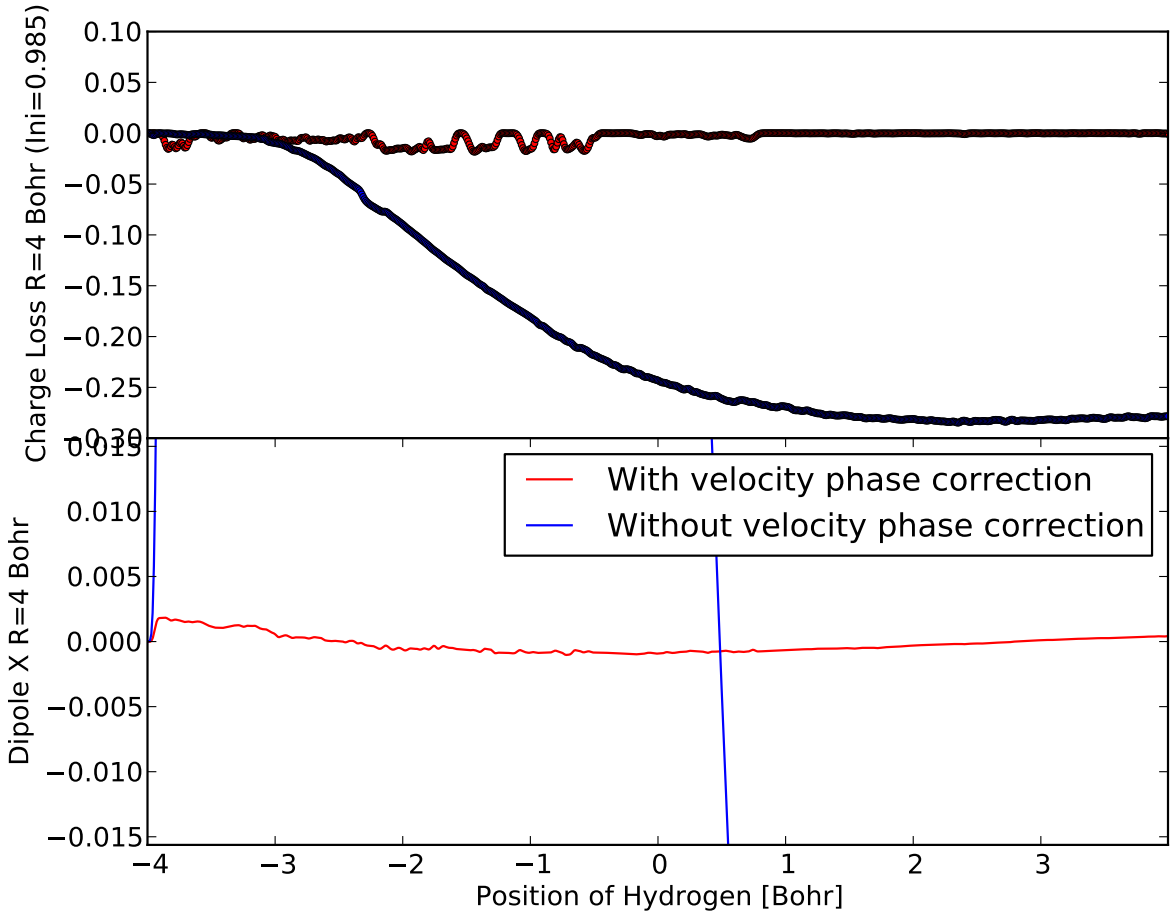
Hydrogen moving in a box

Kinetic energy: 10 keV



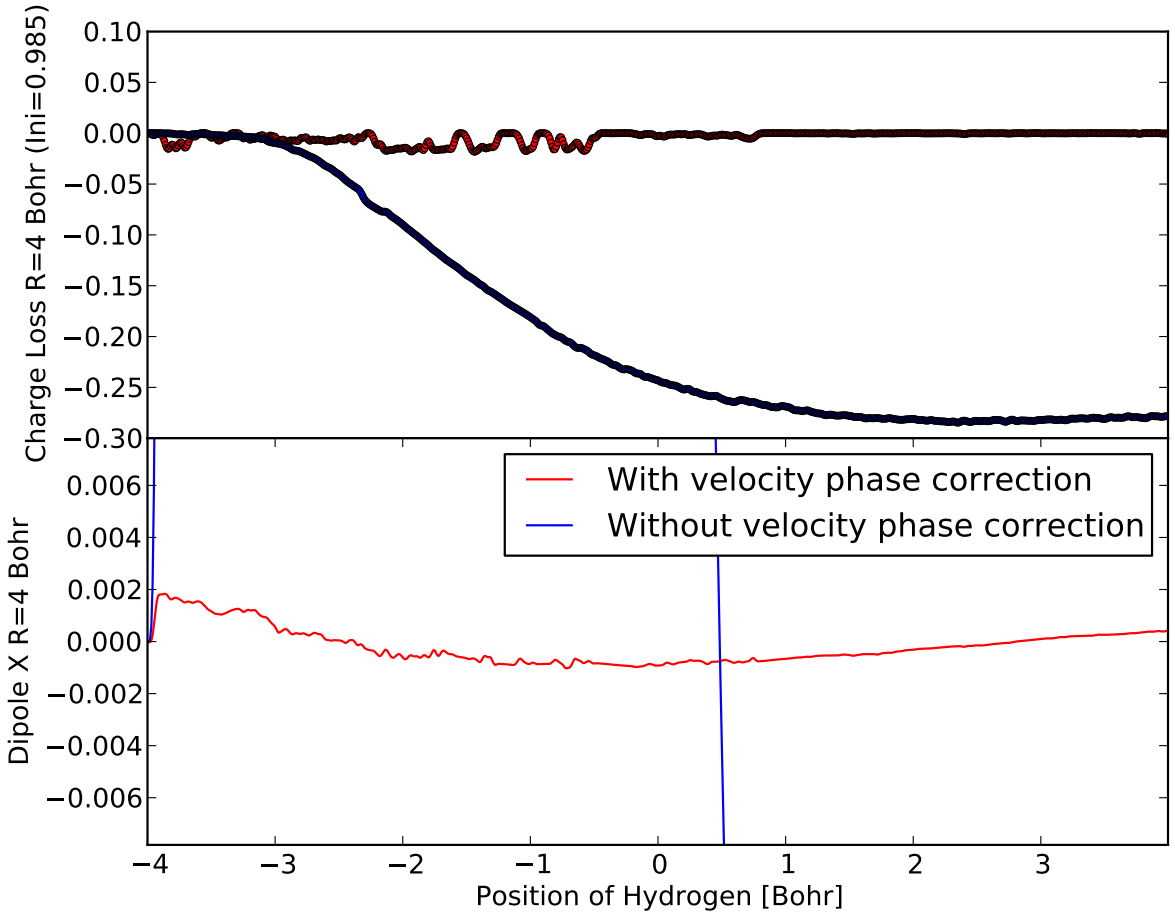
Hydrogen moving in a box

Kinetic energy: 10 keV



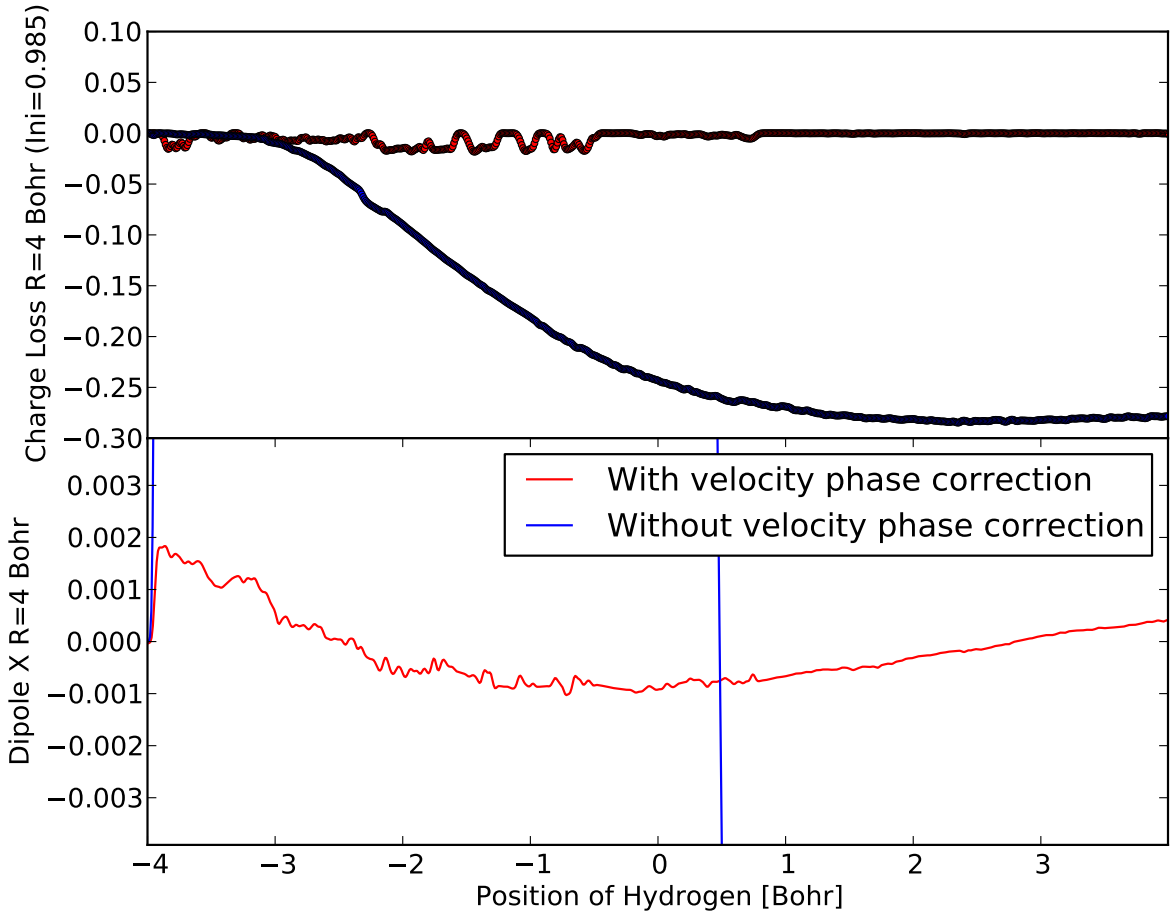
Hydrogen moving in a box

Kinetic energy: 10 keV



Hydrogen moving in a box

Kinetic energy: 10 keV

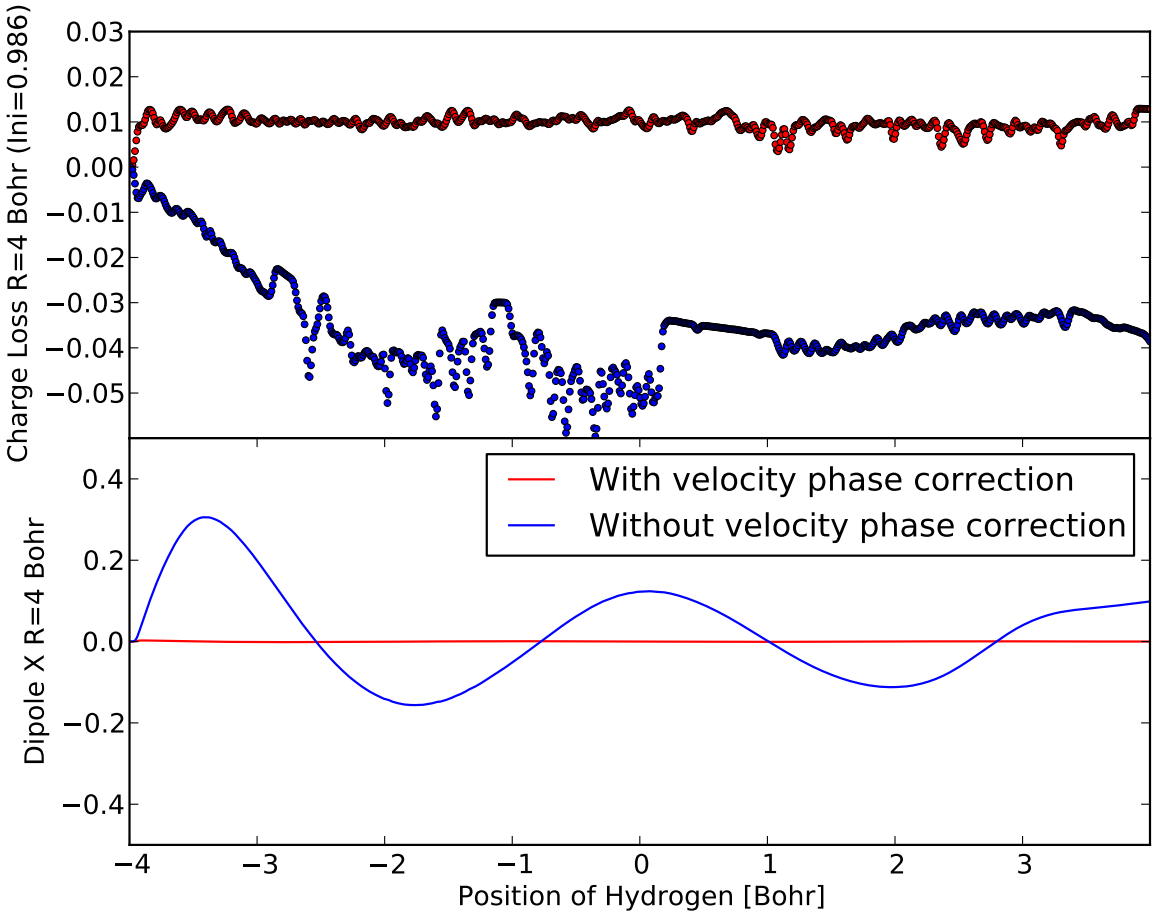


100X smaller

Than without the correction

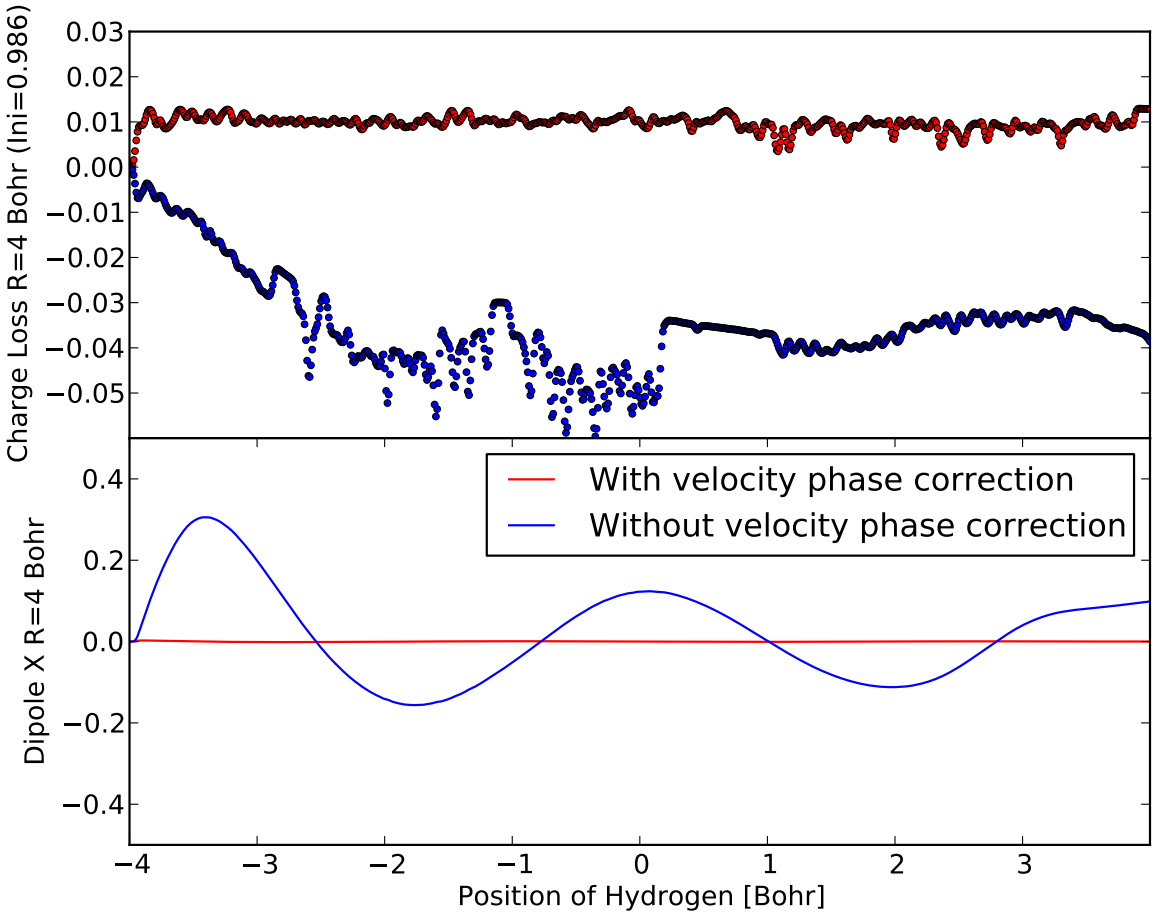
Hydrogen moving in a box

Kinetic energy: 1 keV



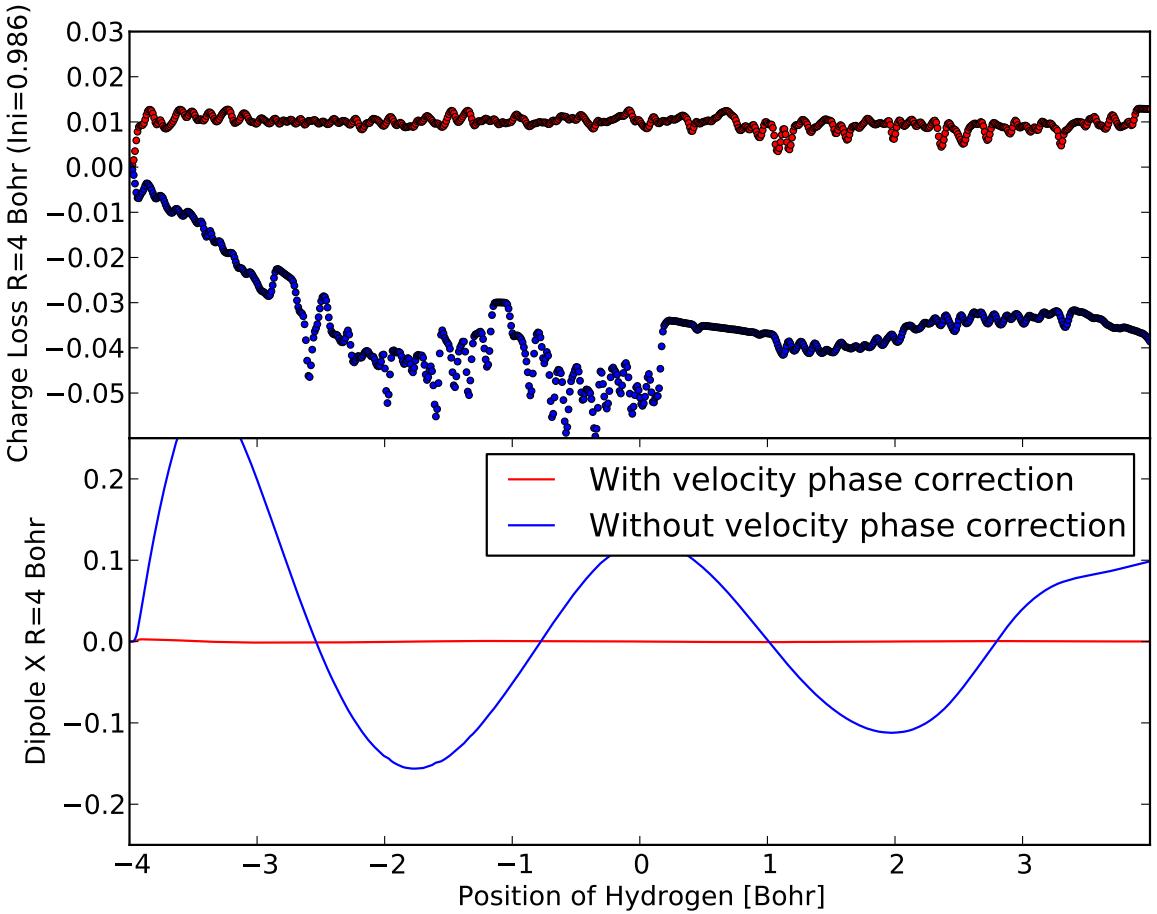
Hydrogen moving in a box

Kinetic energy: 1 keV



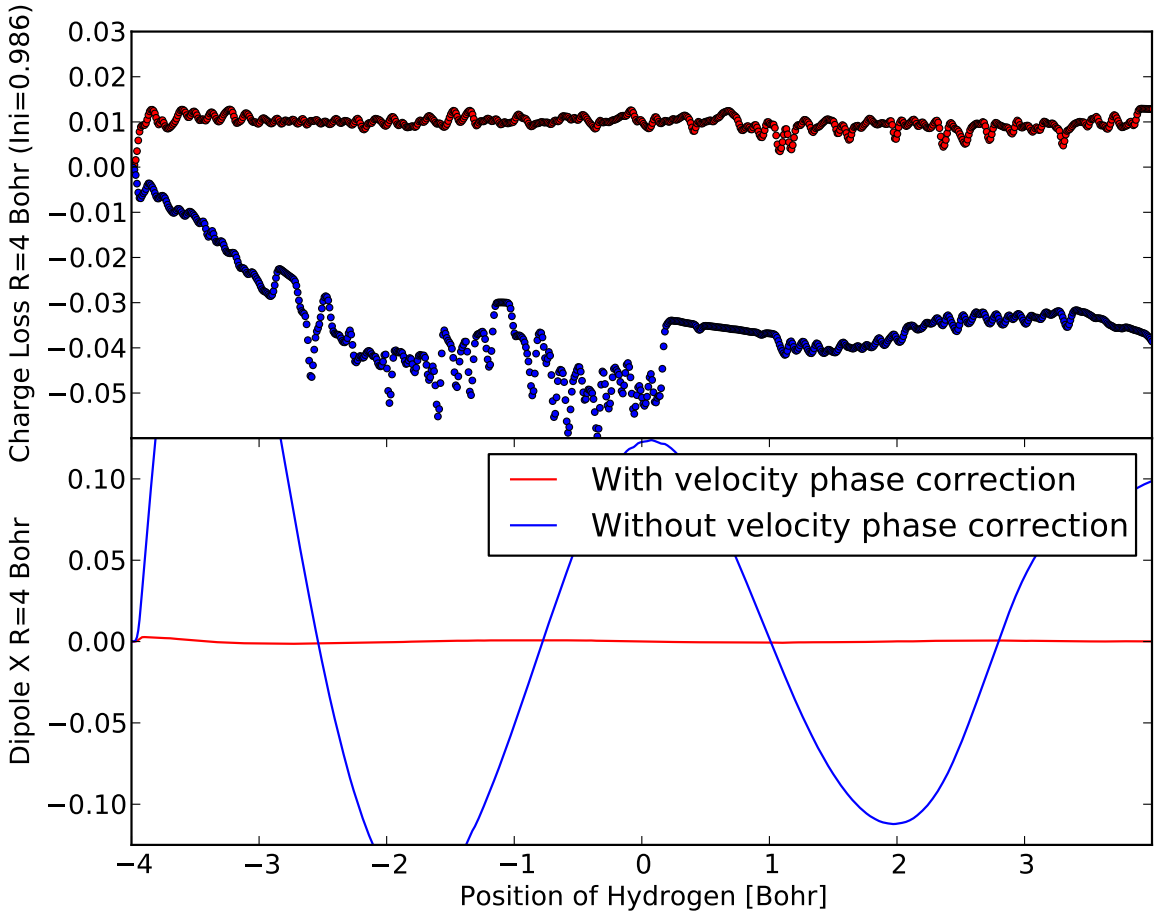
Hydrogen moving in a box

Kinetic energy: 1 keV



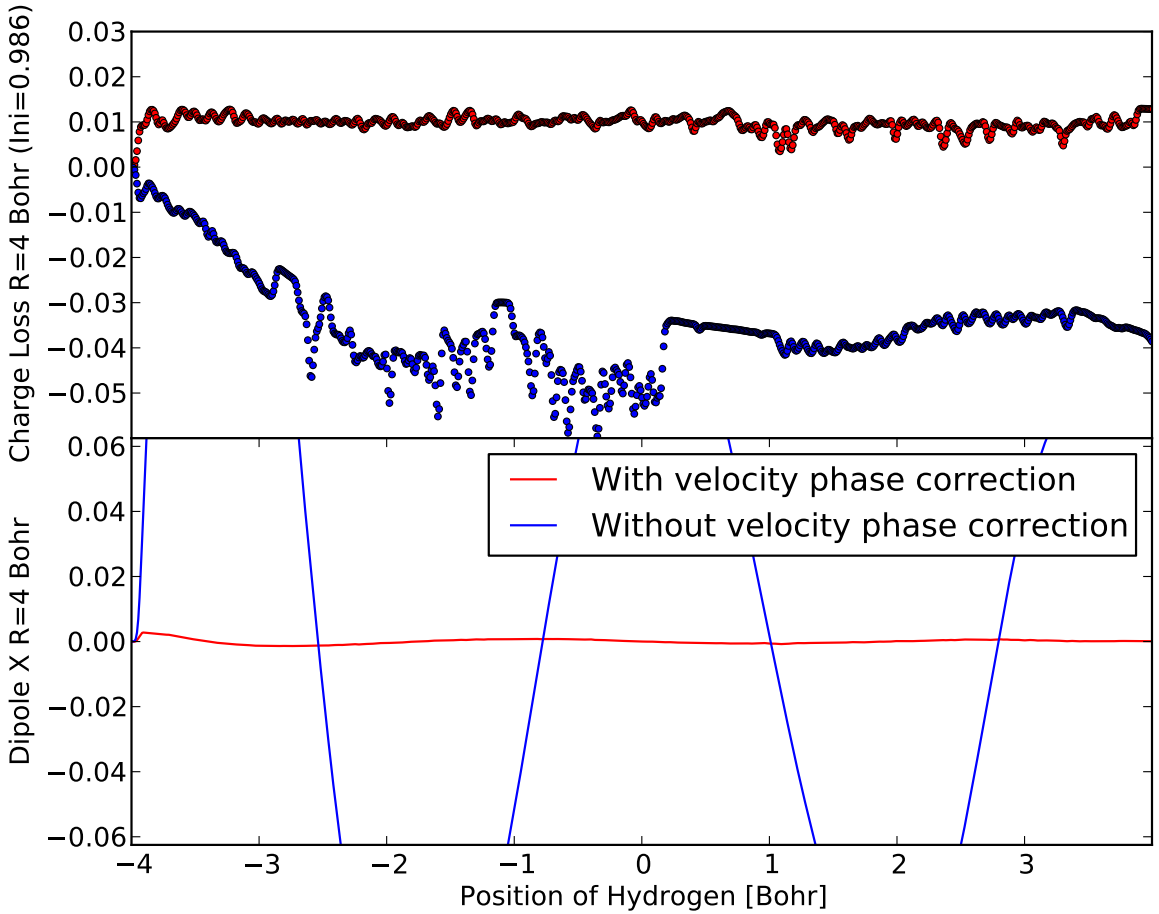
Hydrogen moving in a box

Kinetic energy: 1 keV



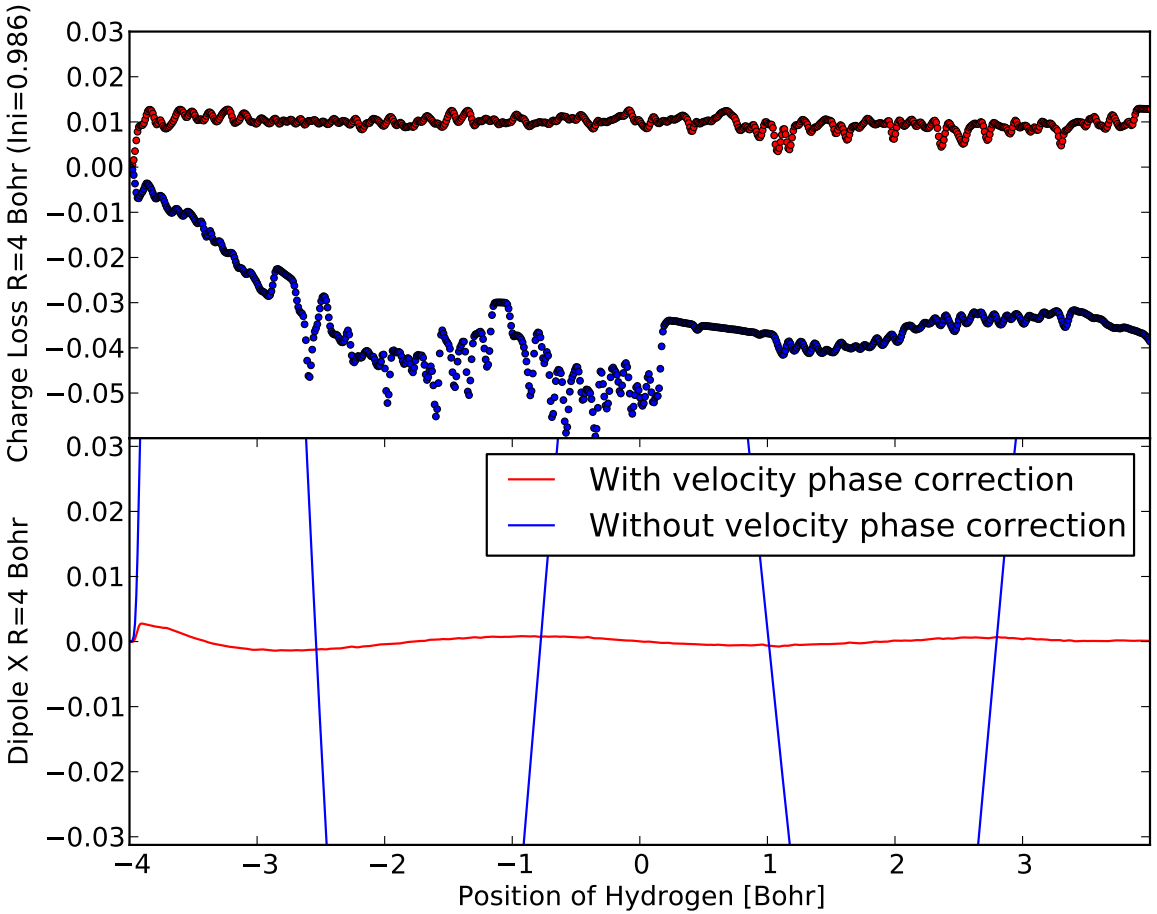
Hydrogen moving in a box

Kinetic energy: 1 keV



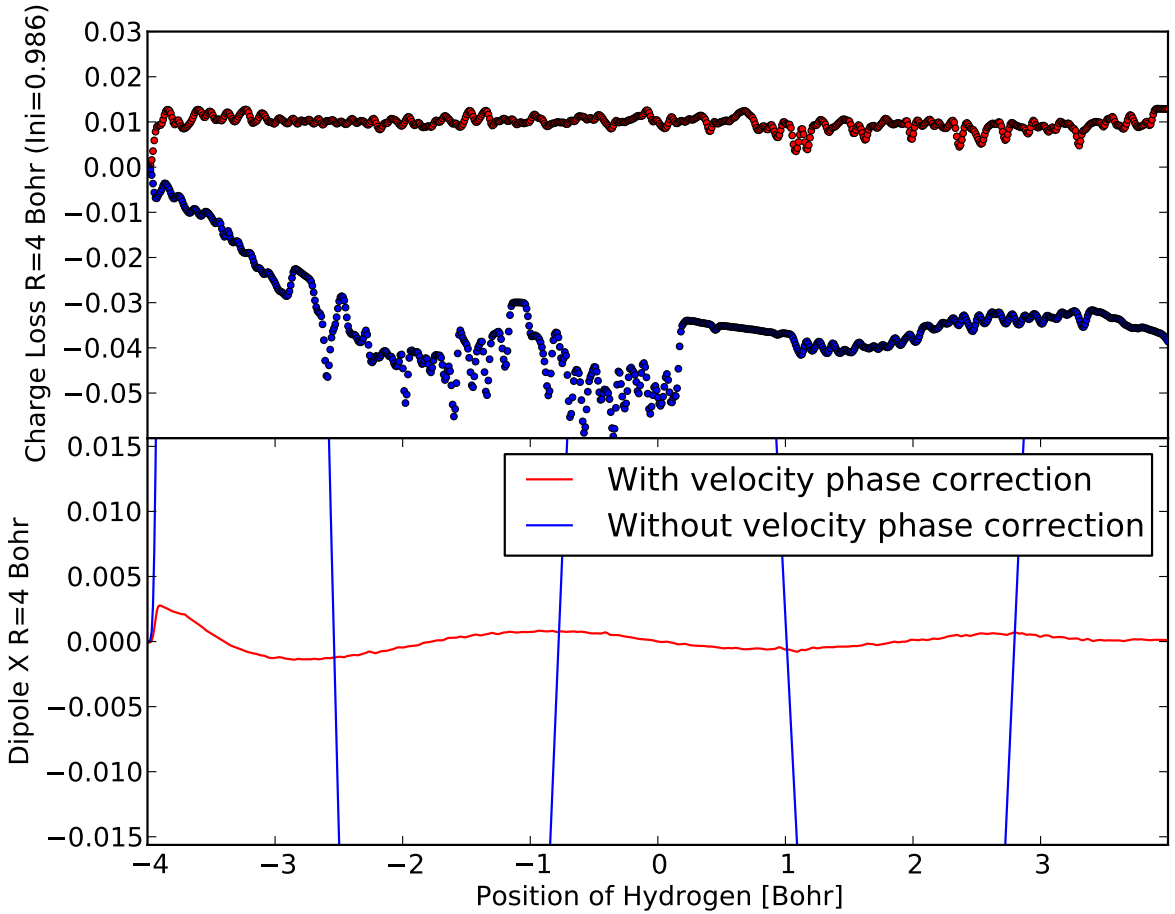
Hydrogen moving in a box

Kinetic energy: 1 keV



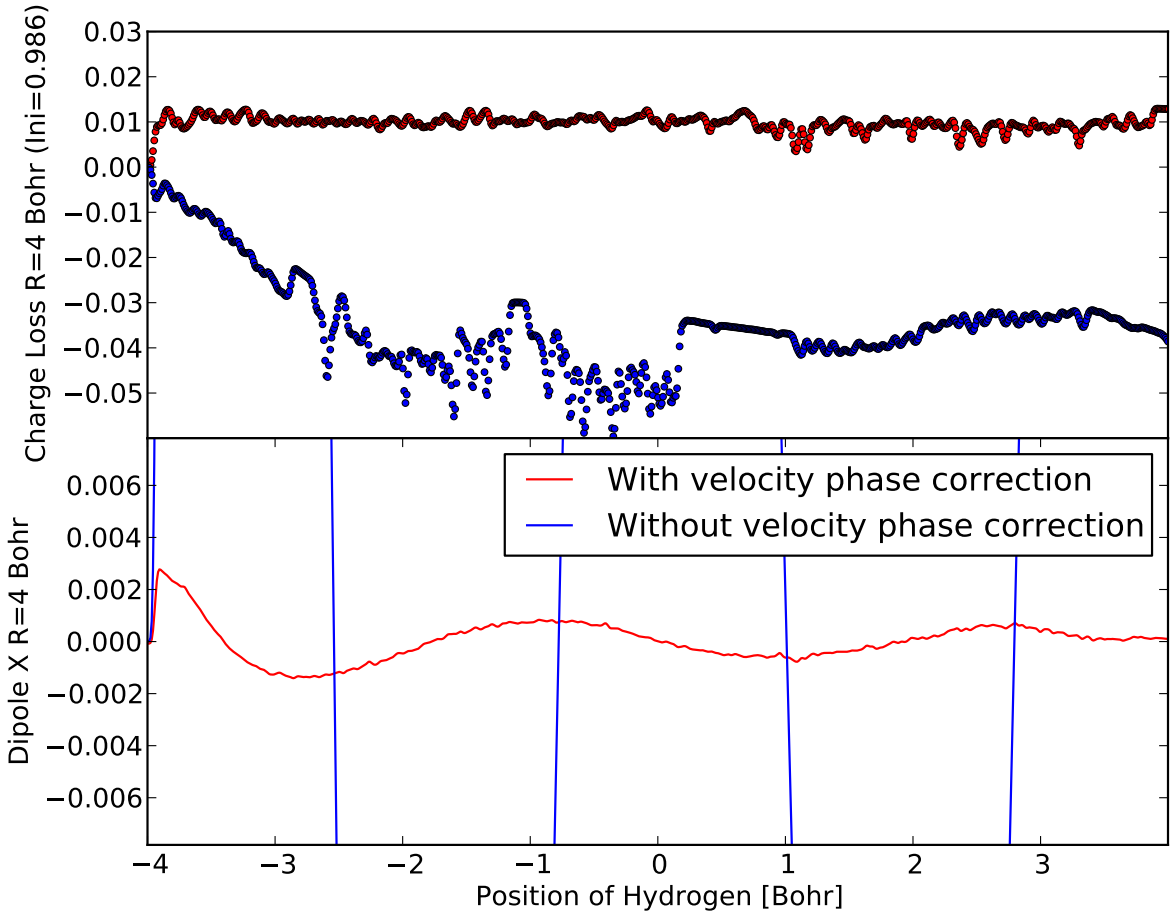
Hydrogen moving in a box

Kinetic energy: 1 keV



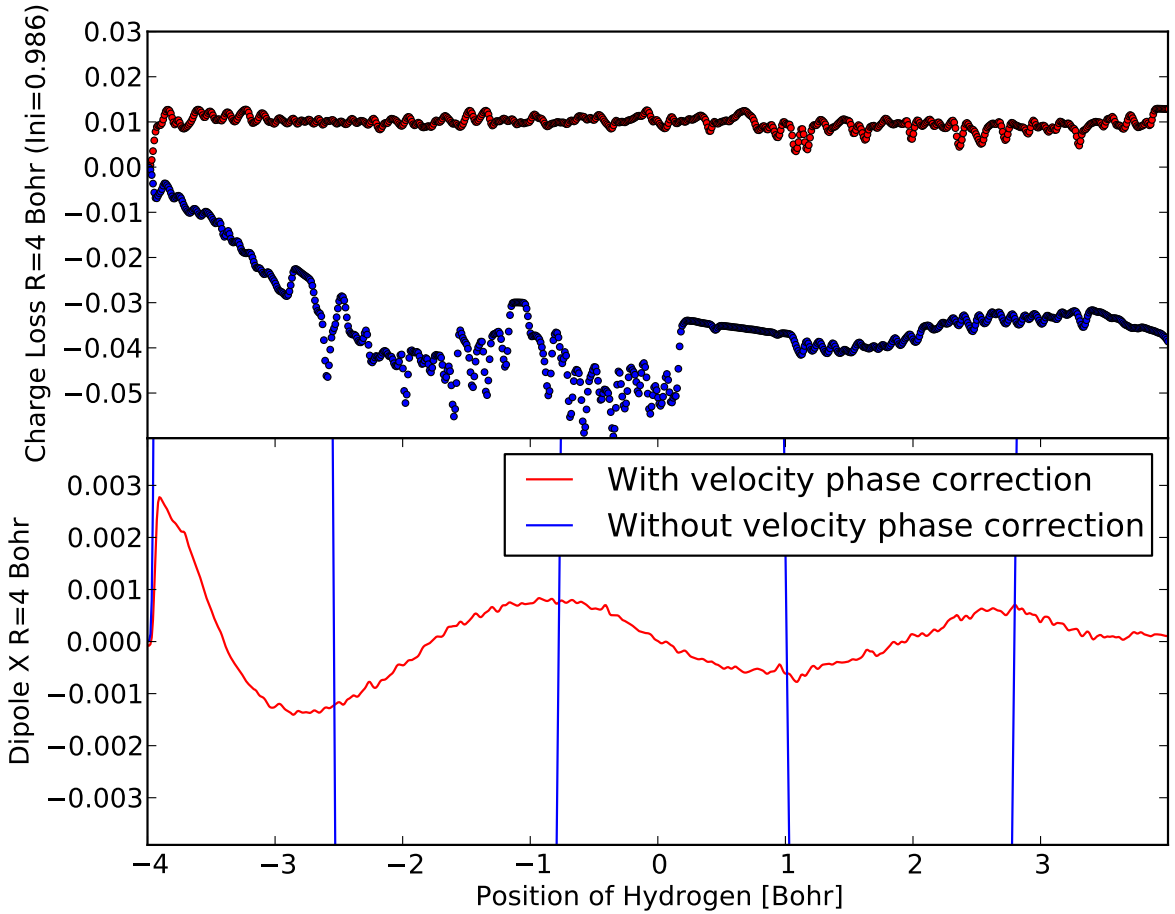
Hydrogen moving in a box

Kinetic energy: 1 keV



Hydrogen moving in a box

Kinetic energy: 1 keV

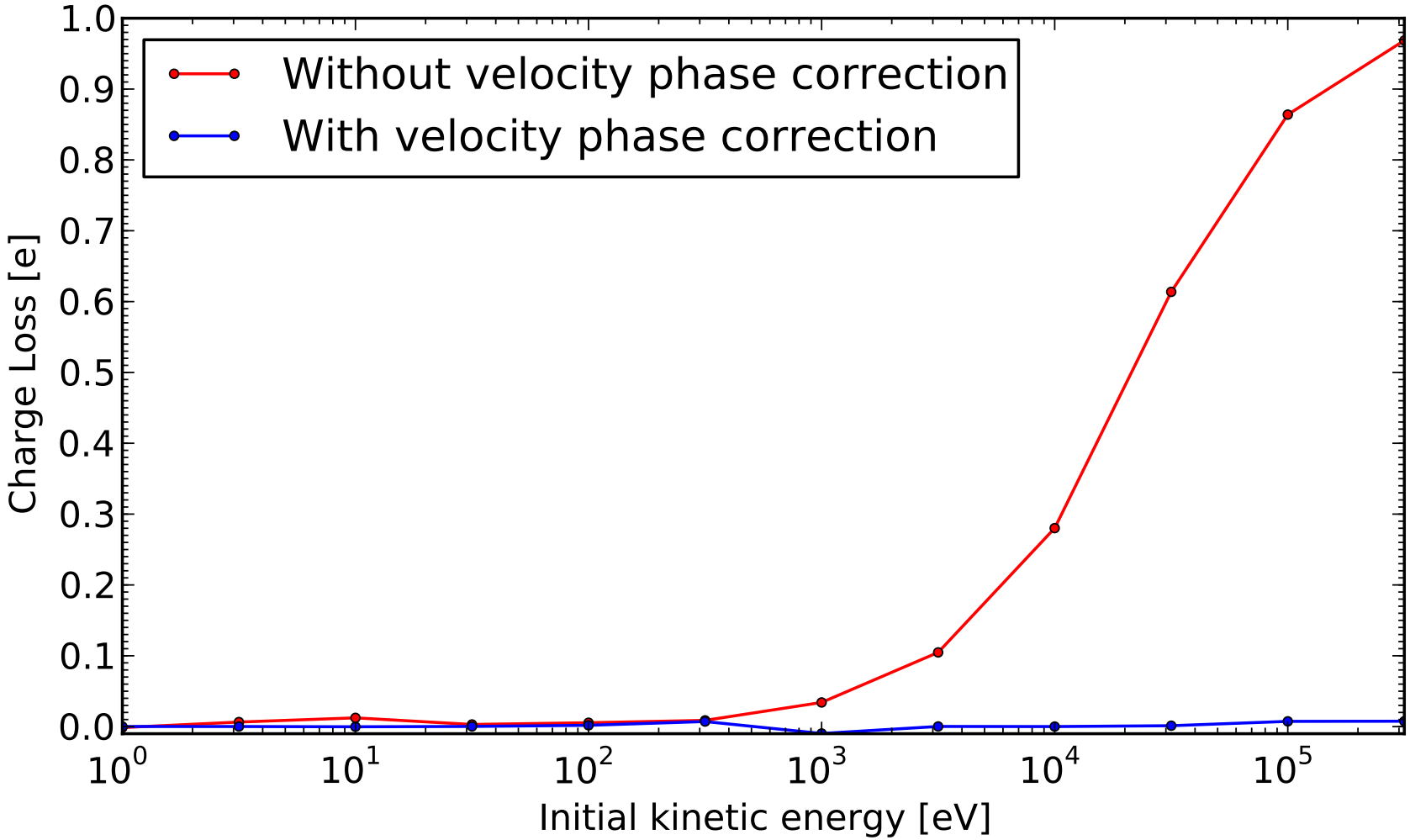


100X smaller

Than without the correction

Hydrogen moving in a box

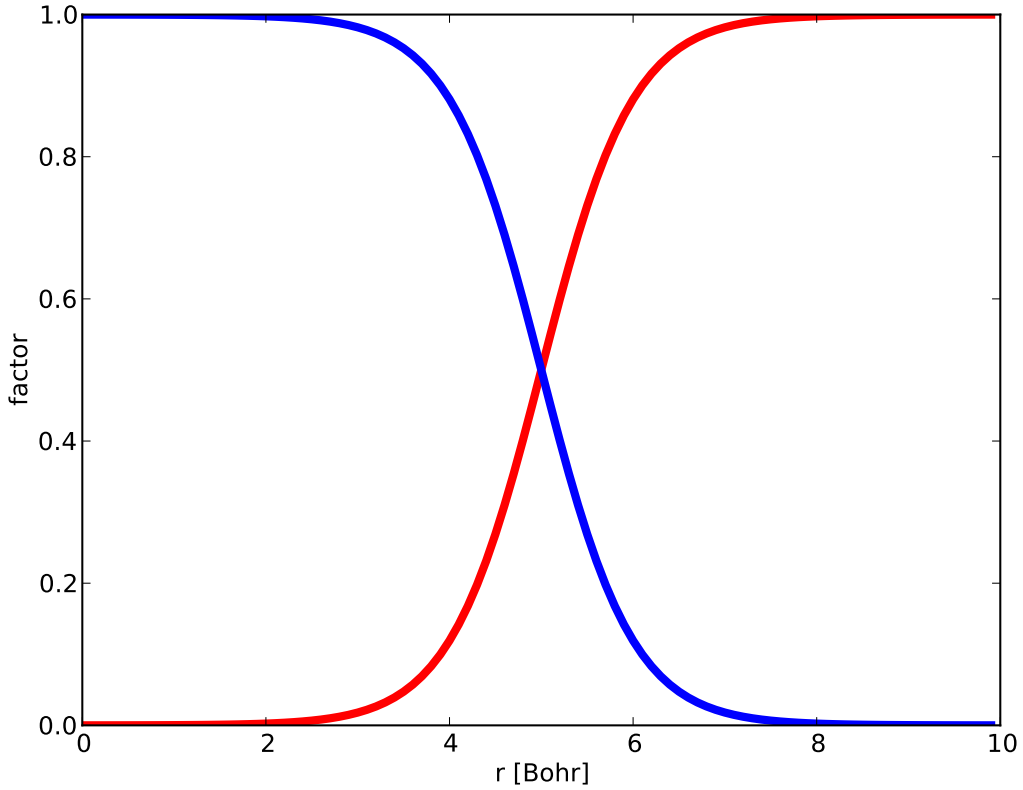
Charge loss after displacement (8 Bohr)



When several particles are moving

We introduce a sigmoid function to weight the phase

$$S(r) = -\frac{1}{1 + e^{-\alpha(r - r_c)}}$$



When several particles are moving

We introduce a sigmoid function to weight the phase

$$S(r) = -\frac{1}{1 + e^{-\alpha(r - r_c)}}$$

- The moving particle must be suficiently differentiated
- The parameters α and r_c must be tune to avoid an important overlapping between regions

Conclusions

1. Capture cross sections can be computed within the TDDFT approach with reasonable agreedment with experimental results.
2. Computation within TD-DFT of Ionization and fragmentation of molecules are computationally challenging but feasible.
3. A velocity phase correction should be introduced for light projectiles with large kinetic energies (keV) when those projectiles carry some charge described explicitly.

Perspectives

1. Going to bigger but symmetrical molecules
2. Explore the reliability of transfer of charge and fragmentation under a broader range of kinetic energies

Acknowledgements

1. Octopus developers for create a nicely coded piece of software.
2. A. Delcorte and O. Restrepo related with secondary ion mass spectrometry.
3. Y. Popov concerning the proton-Helium collision.
4. Communauté française de Belgique, through the Action de Recherche Concertée 07/12-003 “Nanosystèmes hybrides metal-organiques”, and by the FRS-FNRS Belgium (FRFC Grant 2.4.589.09.F).

Thank you for your attention.