Nanoplasmonics from large-scale ab initio calculations: opposite trends in Ag and Na clusters

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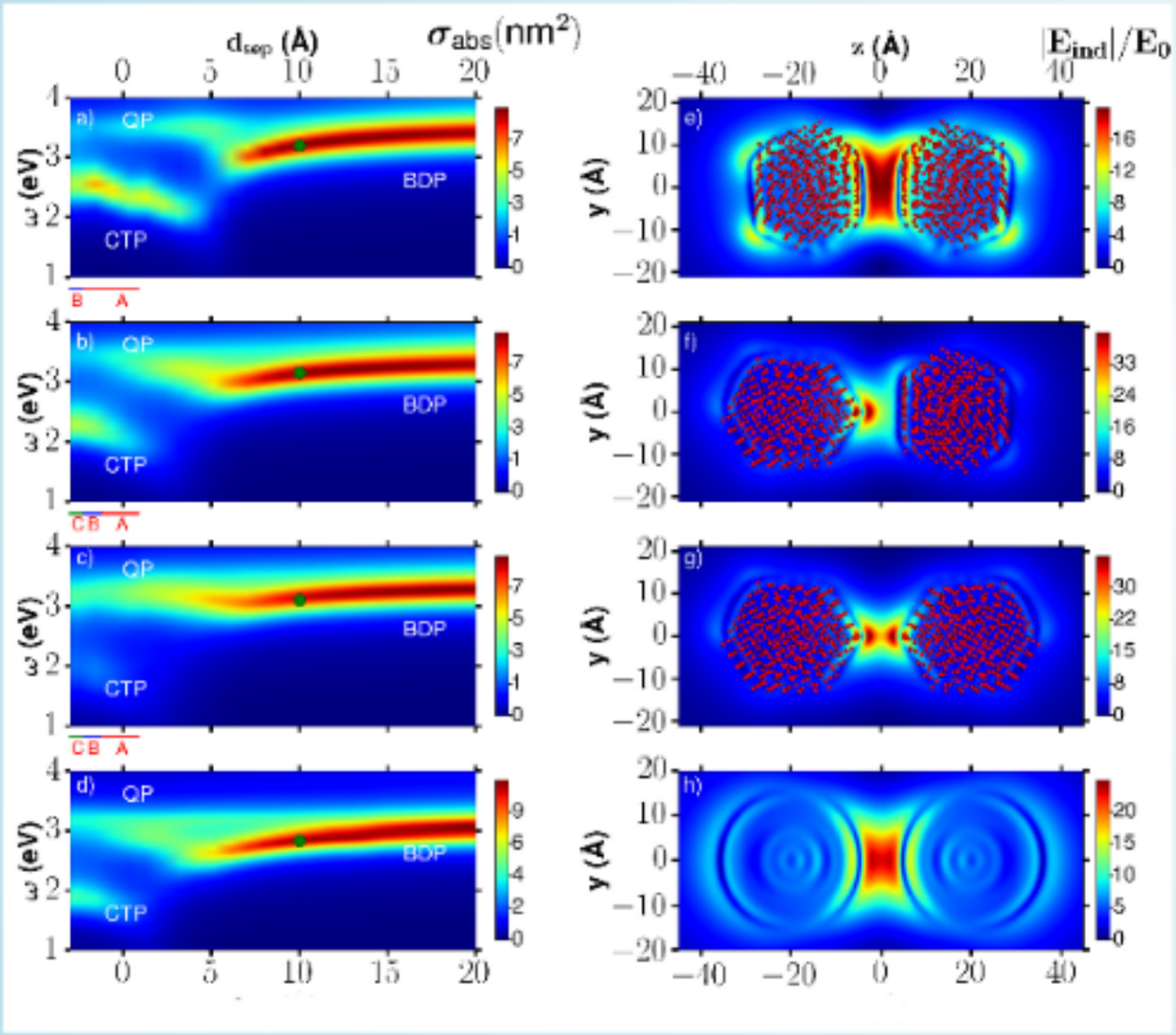
Nanoplasmonic with TDDFT

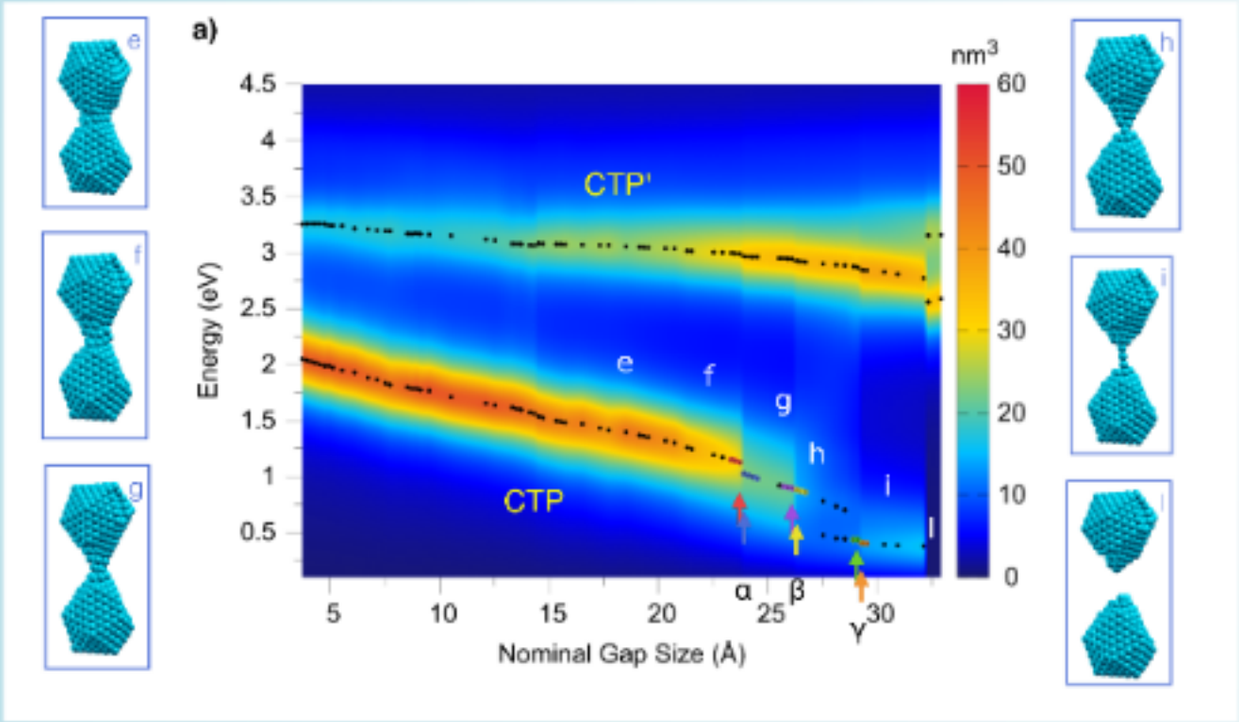


Electric Field enhancement in plasmonic nanostructures.

- Electric field enhancement inside the dimer.
- Field enhancement and polarizability geometry dependence.
- Up to 760 Na atoms.

M. Barbry et al., Nanoletters, 15, 5 (2015)

Nanoplasmonic with TDDFT

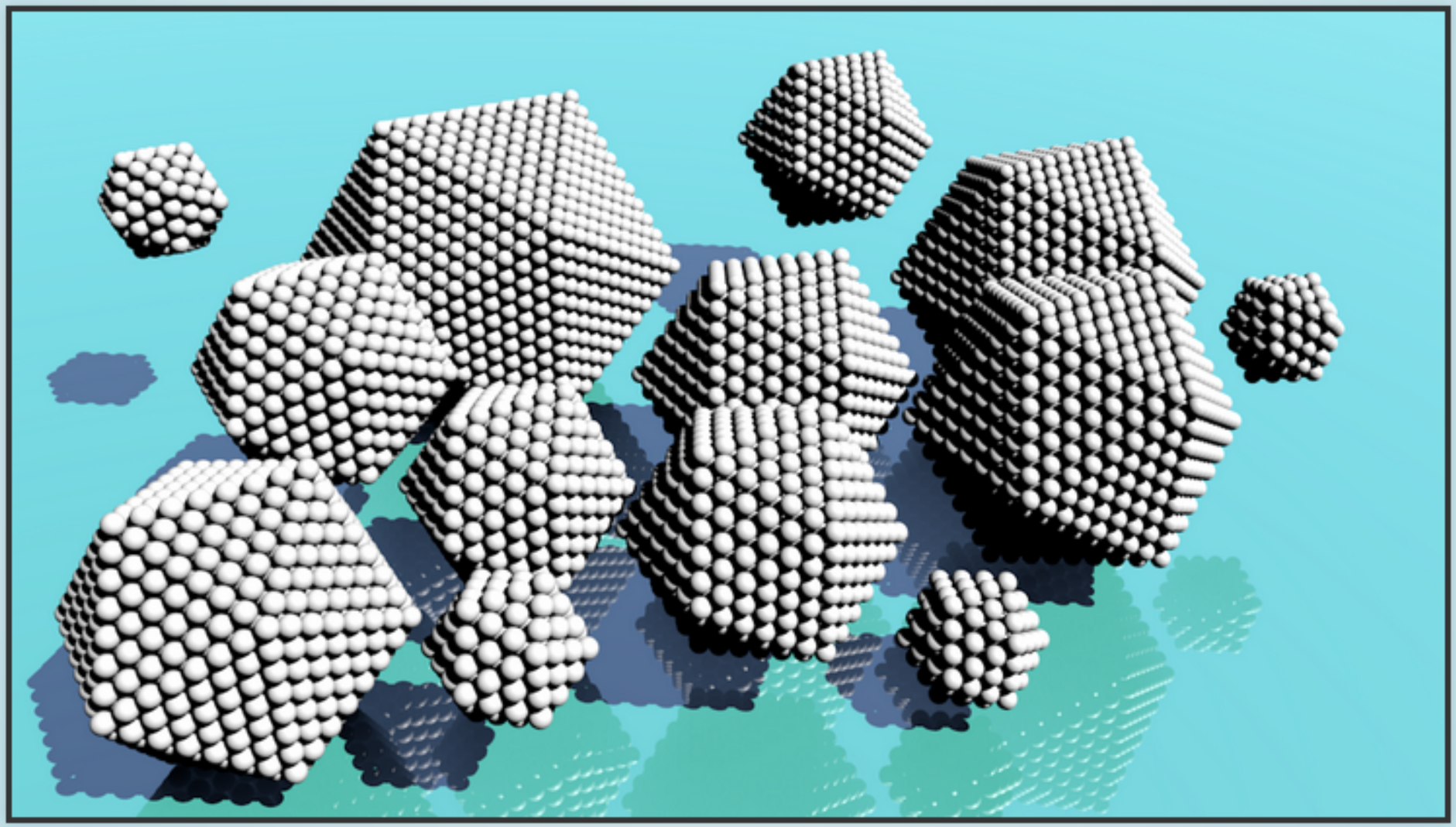


Optical response of metallic nanojunctions driven by single atom motion

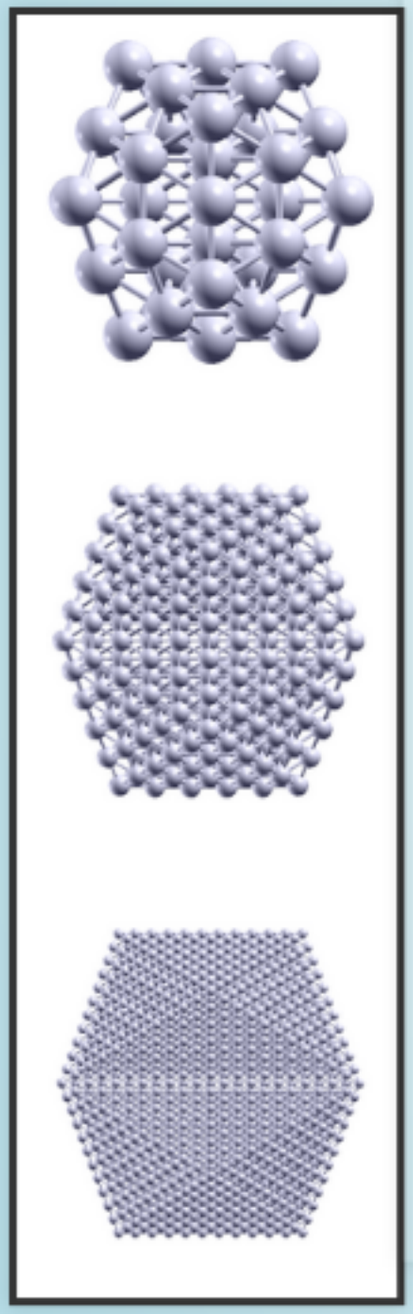
- Atomic Relaxation strongly influence polarizability.
- Polarizability quantization by single atom motion.

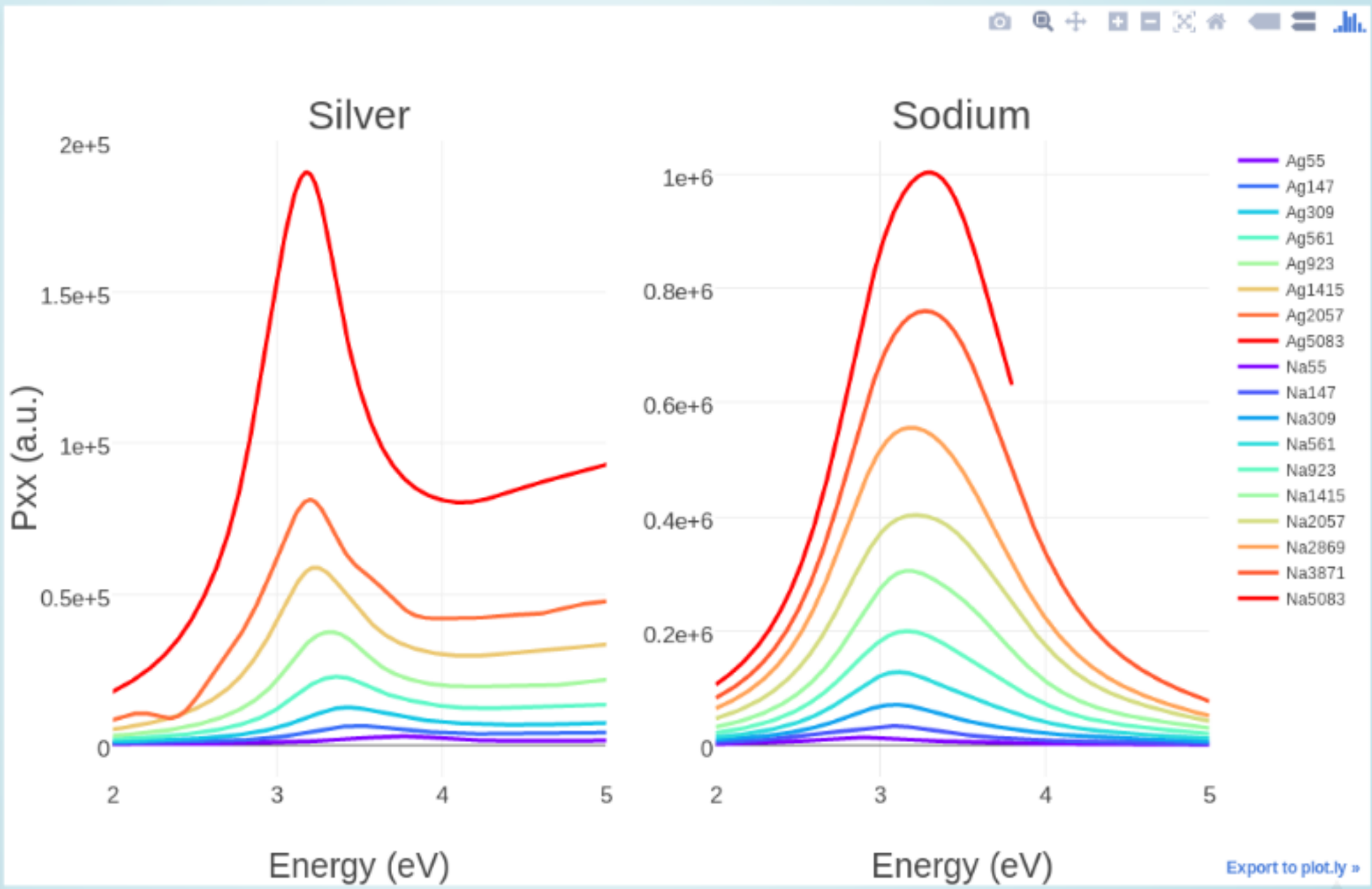
F. Marchesin et al., ACS Photonics, (2016)

Ab-Initio calculations for very larger clusters!

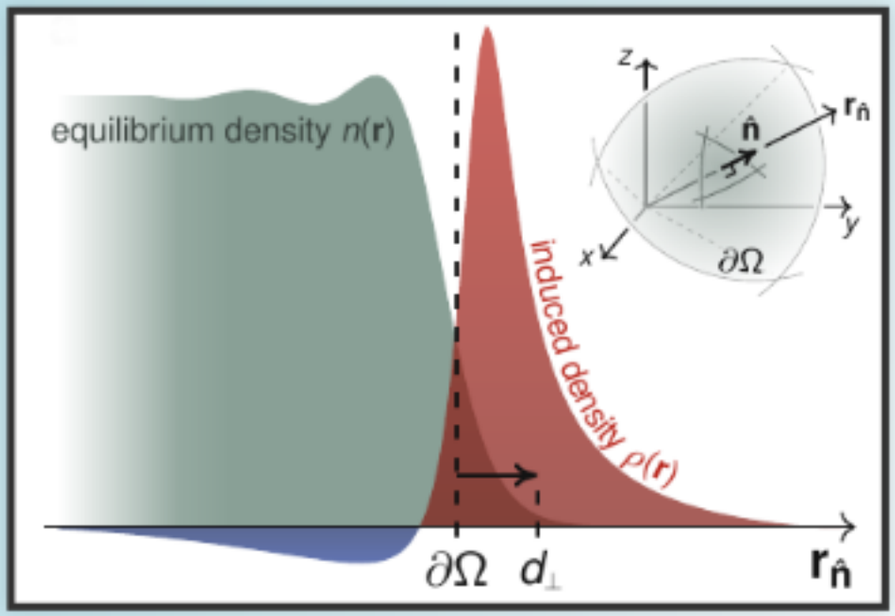


Clusters Polarizability





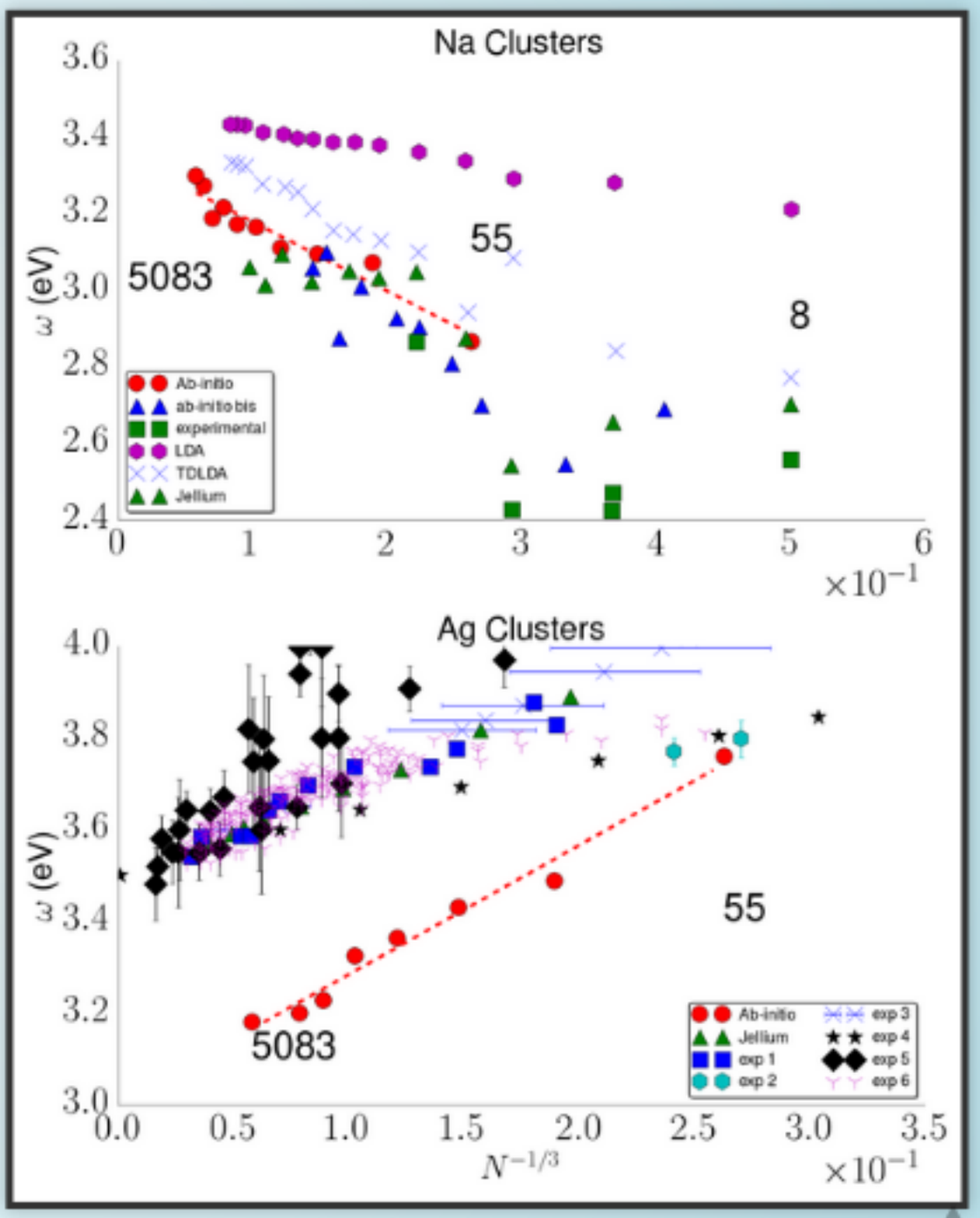
Frequency shift: opposite trend



$$\omega_{sp} = \omega_\infty(1 + \frac{3d}{(2+\varepsilon_b)r_s N^{1/3}})$$

$$\Longrightarrow d = \frac{k(2+\varepsilon_b)r_s}{3\omega_\infty}$$

$$\Longrightarrow d_{Ag} = 7.0 \text{ Bohr and}$$
$$d_{Na} = -2.20 \text{ Bohr}$$



T. Christensen et al., arXiv:1608.05421v2

d parameter from centroid of charge

- The parameter d gives a distance between the edge of the system and the mean position of the oscillating density change
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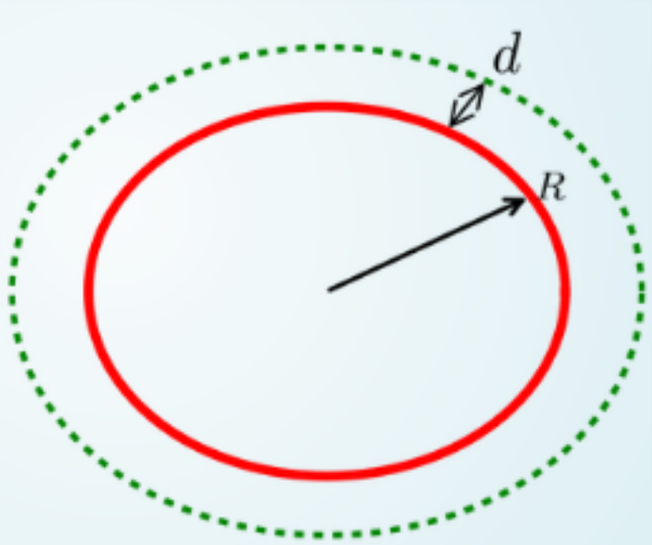
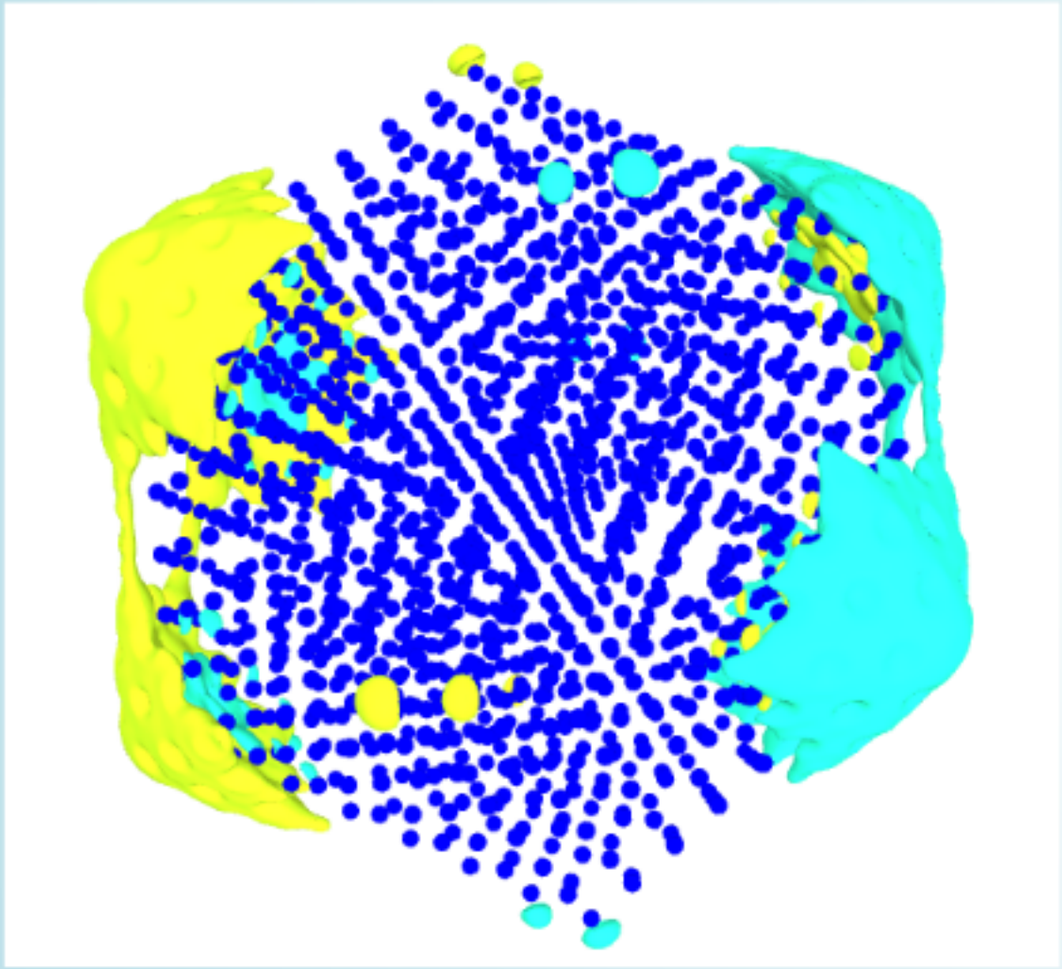
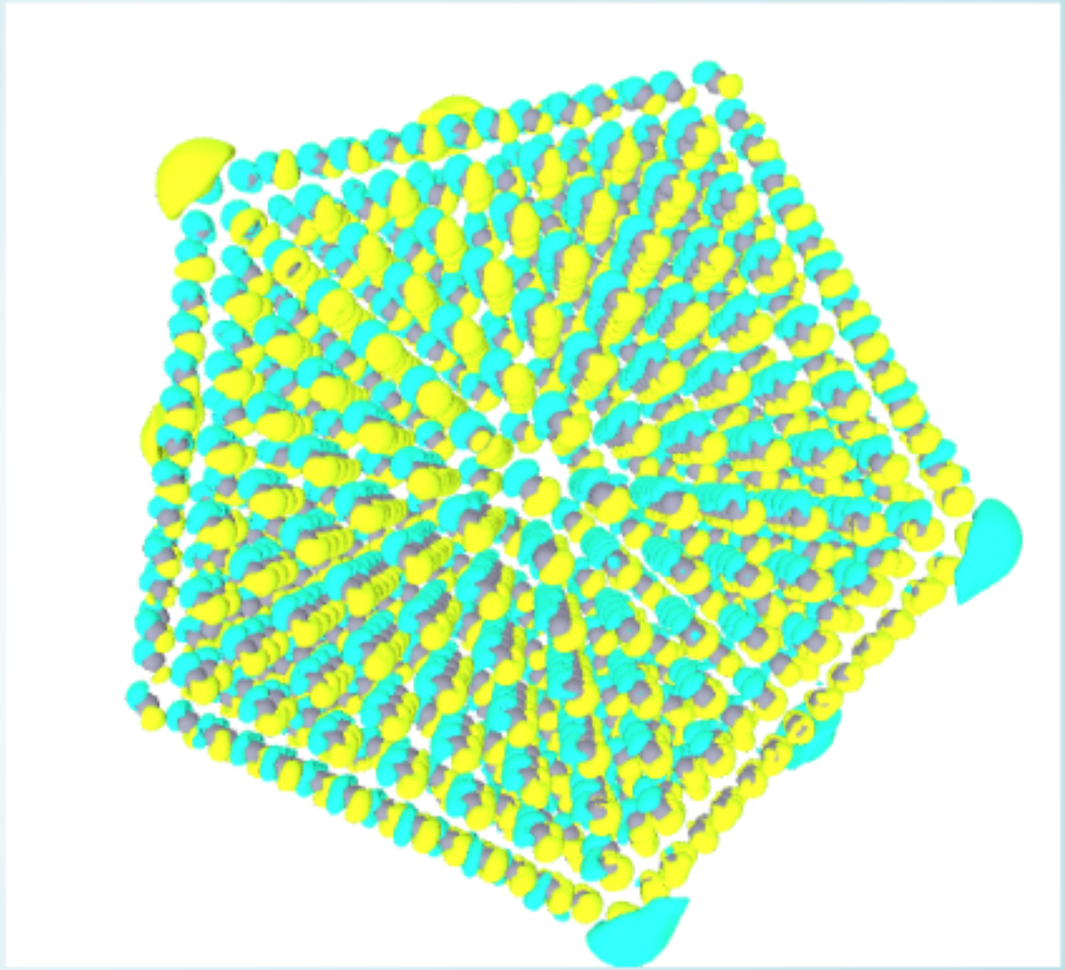
$$d = R - \frac{\int_{V/2} r\delta n(r,\omega)dV}{\int_{V/2} \delta n(r,\omega)dV}$$



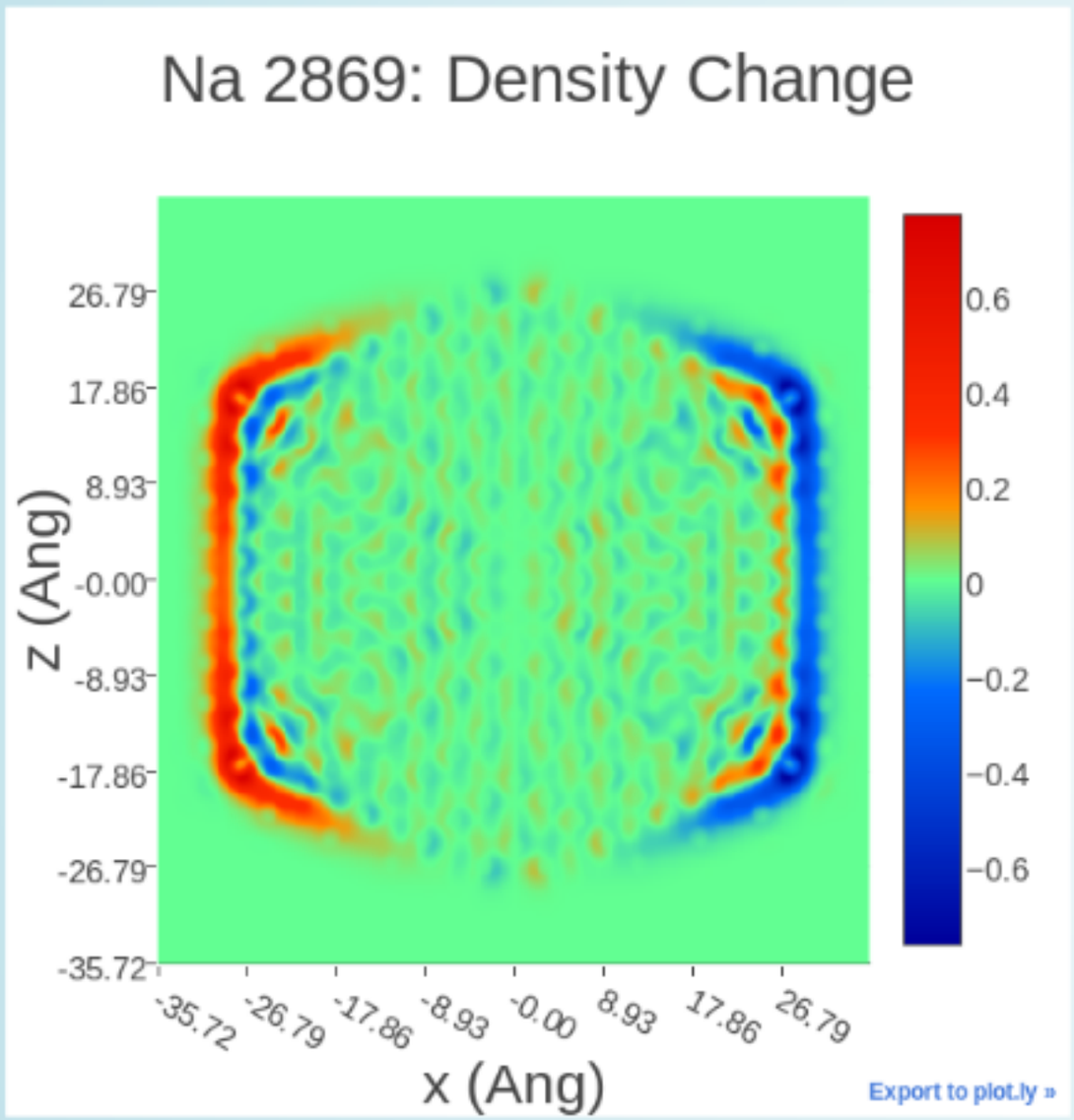
- And the surface plasmon is proportional to d
- $\omega_{sp} = \omega_{\infty}(1 + \frac{3d}{(2+\varepsilon_b)r_s N^{1/3}})$

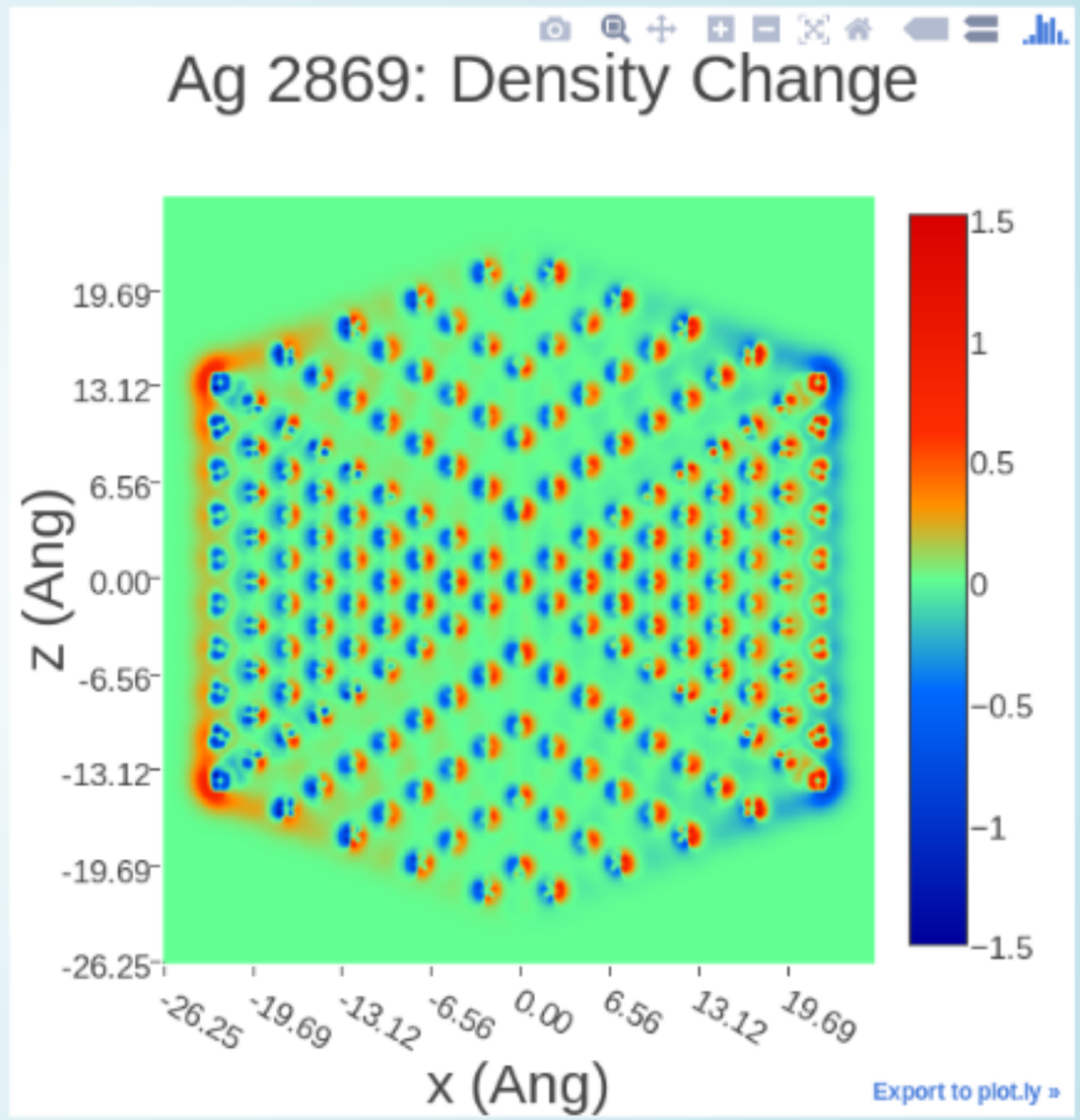
Density change Na and Ag 1415



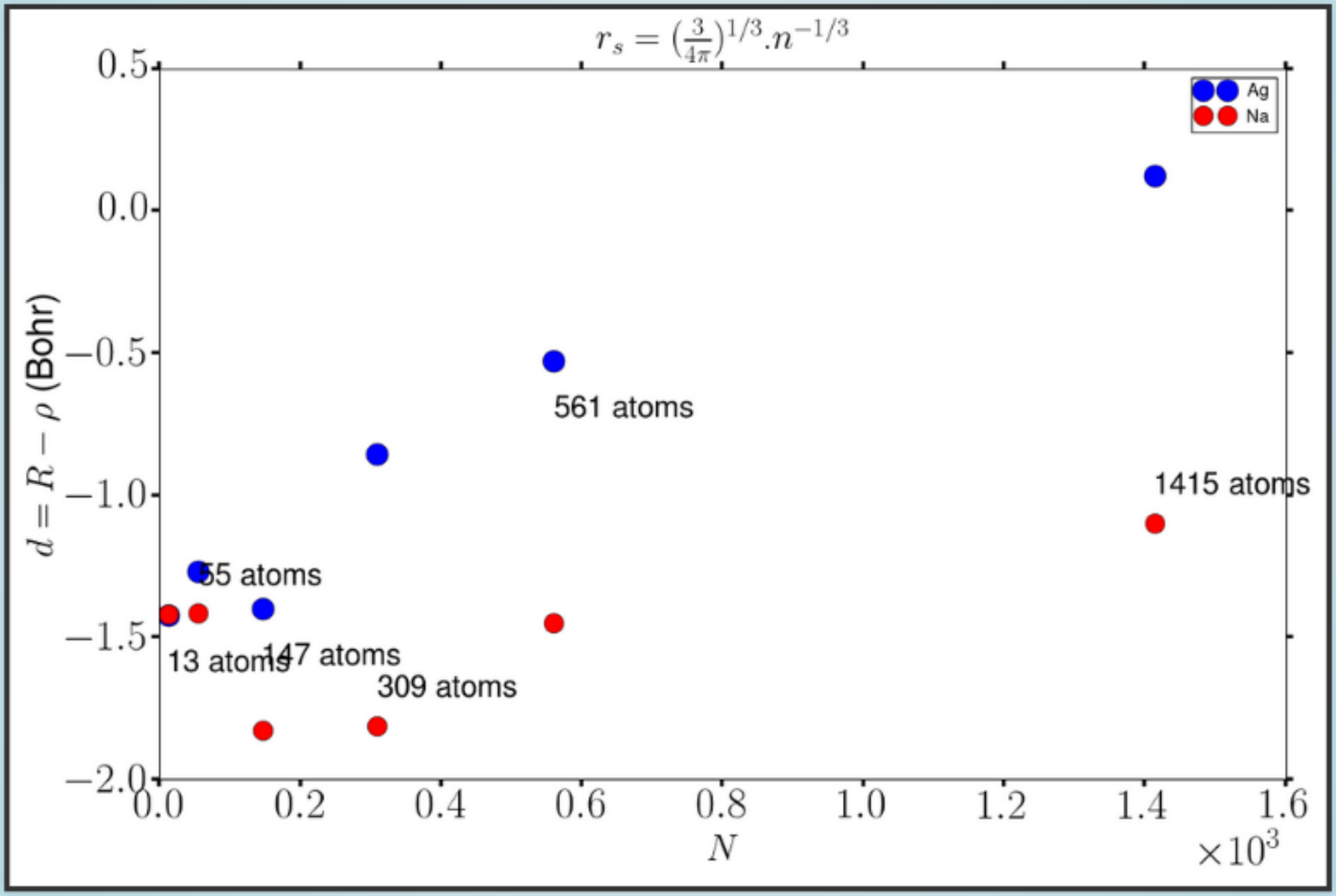


Density change: Imaginary part



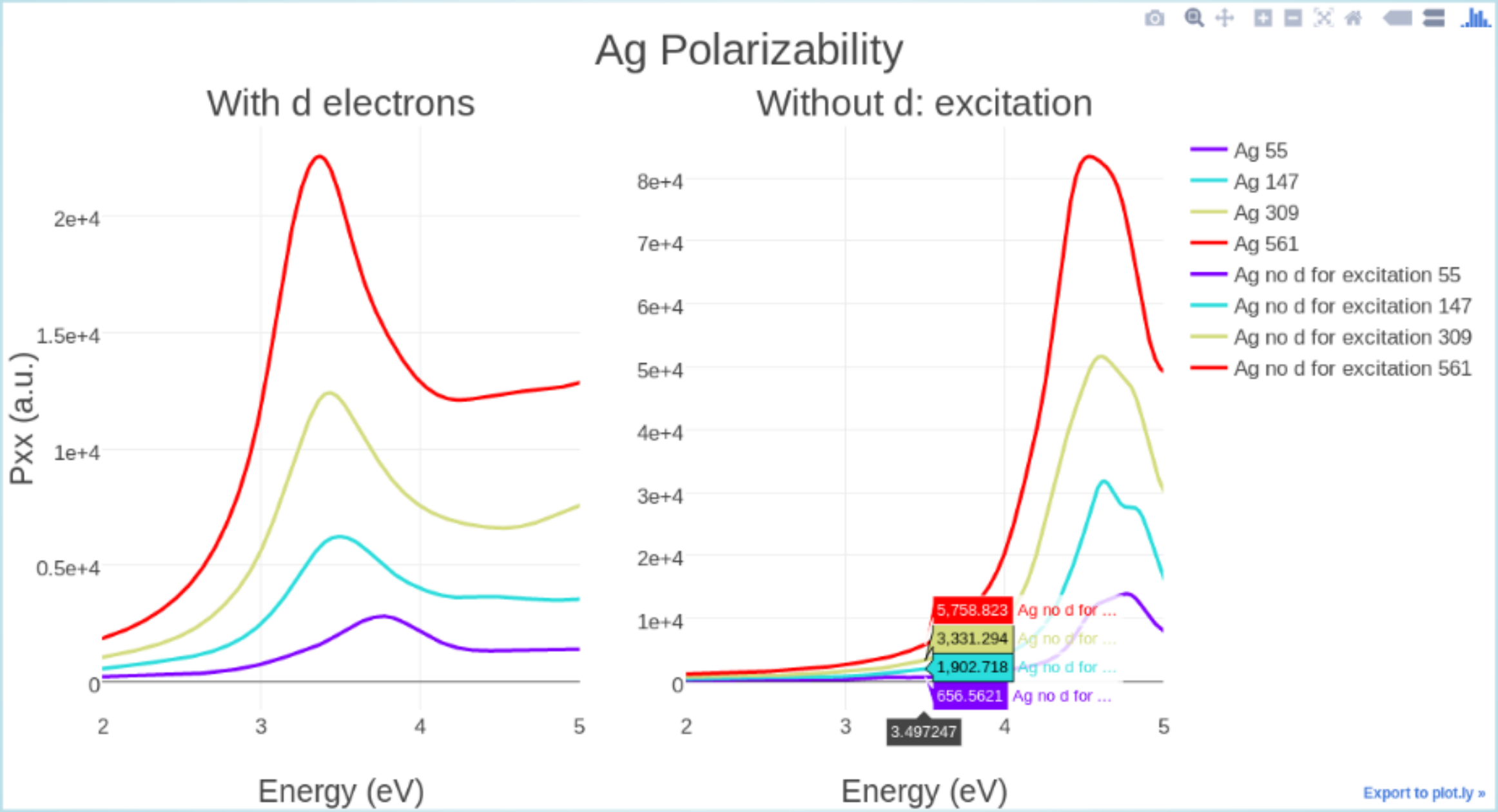


d parameter

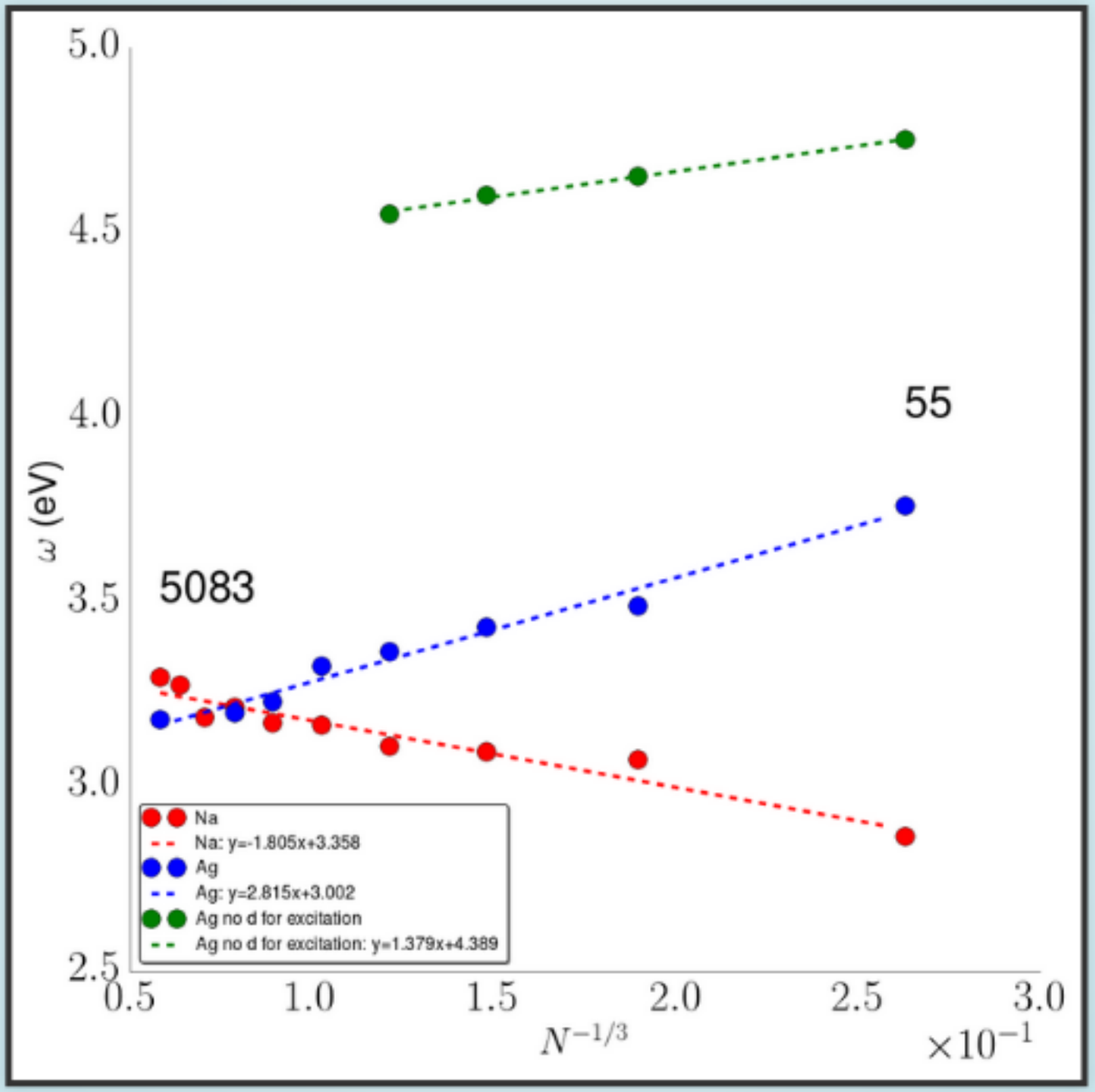

$r_s = (\frac{3}{4\pi})^{1/3}.n^{-1/3}$
$d = R - \rho$ (Bohr)
N
$\times 10^3$
Ag
Na
561 atoms
1415 atoms
55 atoms
13 atoms
147 atoms
309 atoms
0.5
0.0
−0.5
−1.0
−1.5
−2.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

The impact of the d electrons

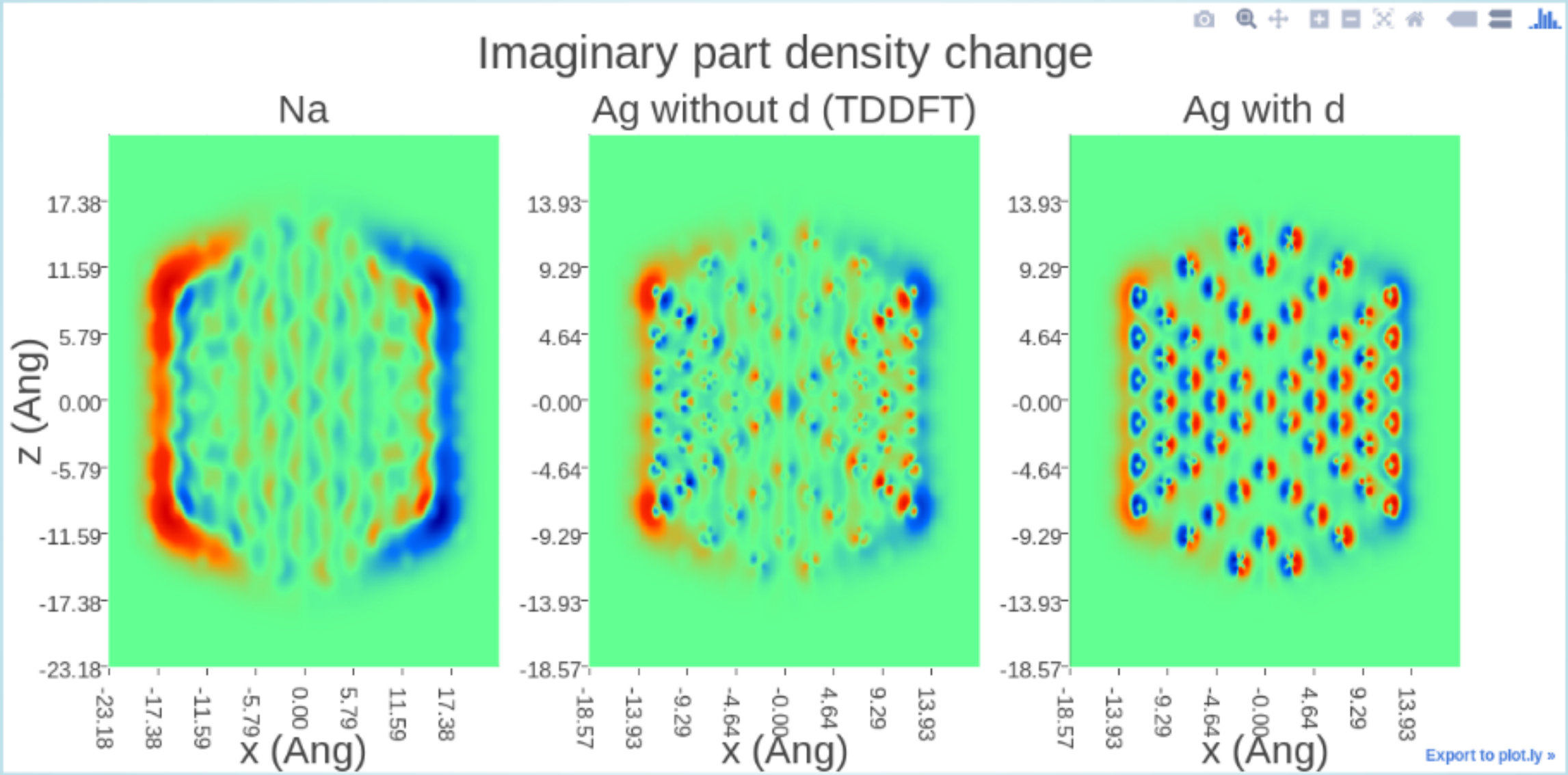
Ag polarizability d electrons



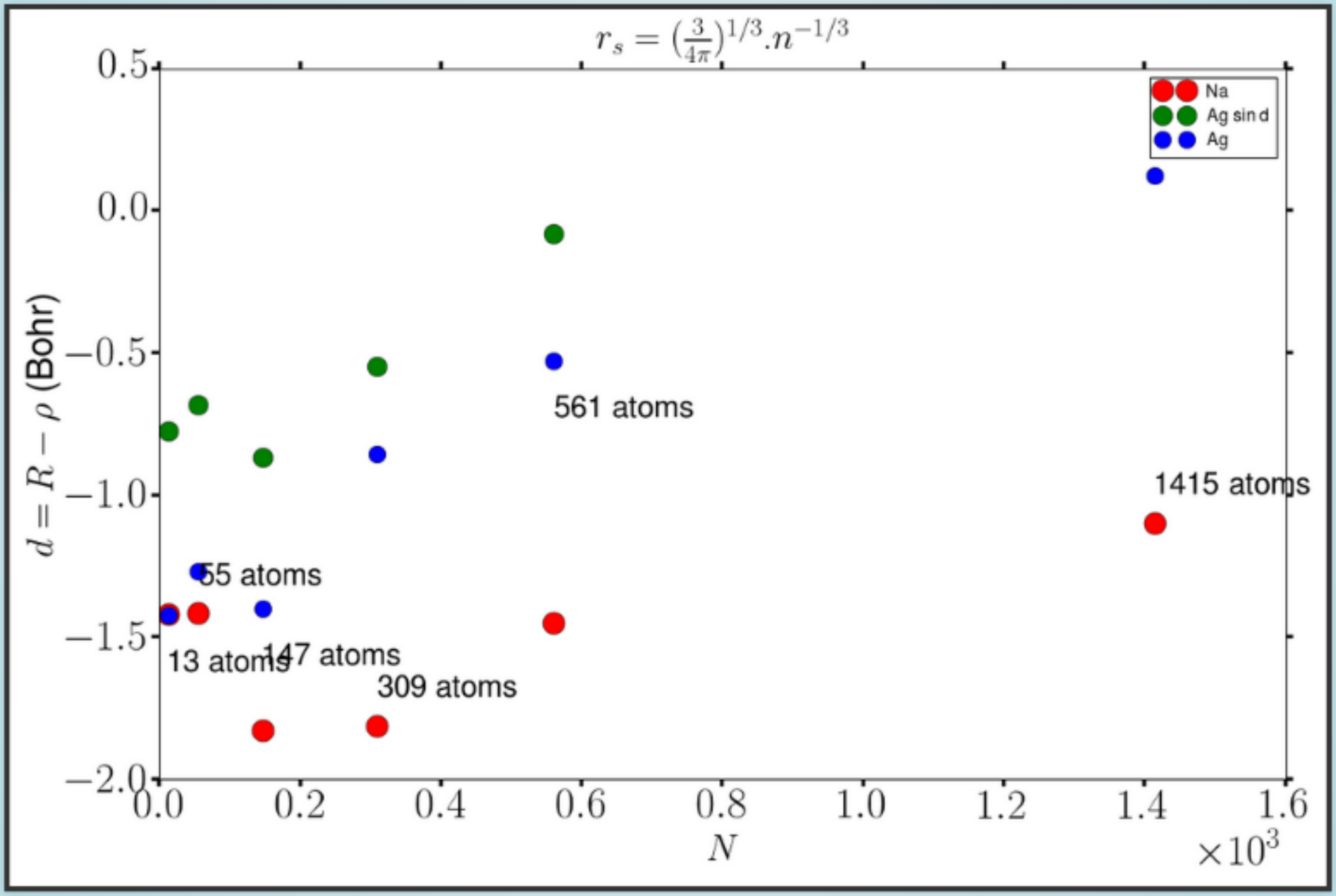
Frequencies shift not clear



Density change without d electrons



d parameter larger than with d electrons



Conclusions

- The new improvements in the implementation of the mbpt_lcao code allowed us to perform TDDFT calculations for systems up to 5083 atoms.
- Thanks to this, we could study the electron spill out in Ag and Na clusters from an ab-initio point of view with huge clusters.
- This study showed us different trends in Na and Ag clusters and we could get a size dependence of the spill-out.
- The d electron strongly impact the behavior of silver cluster. But them presence does not explain the different trend between Na and Ag.

THANK YOU

Questions

- $d = R - \rho$
- $\rho = \frac{\int_{V/2} r\delta n(rdV)}{\int_{V/2} \delta n(r)}$
- $r_s = \left(\frac{3}{4\pi}\right)^{1/3} n^{-1/3}$
- $n = \frac{1}{V.n_{\text{val}}} \int n(r)dV$

Centroid of charge and Wigner-Seitz radius