Dispersion of the plasmon frequency in metallic clusters: ab-initio atomistic description

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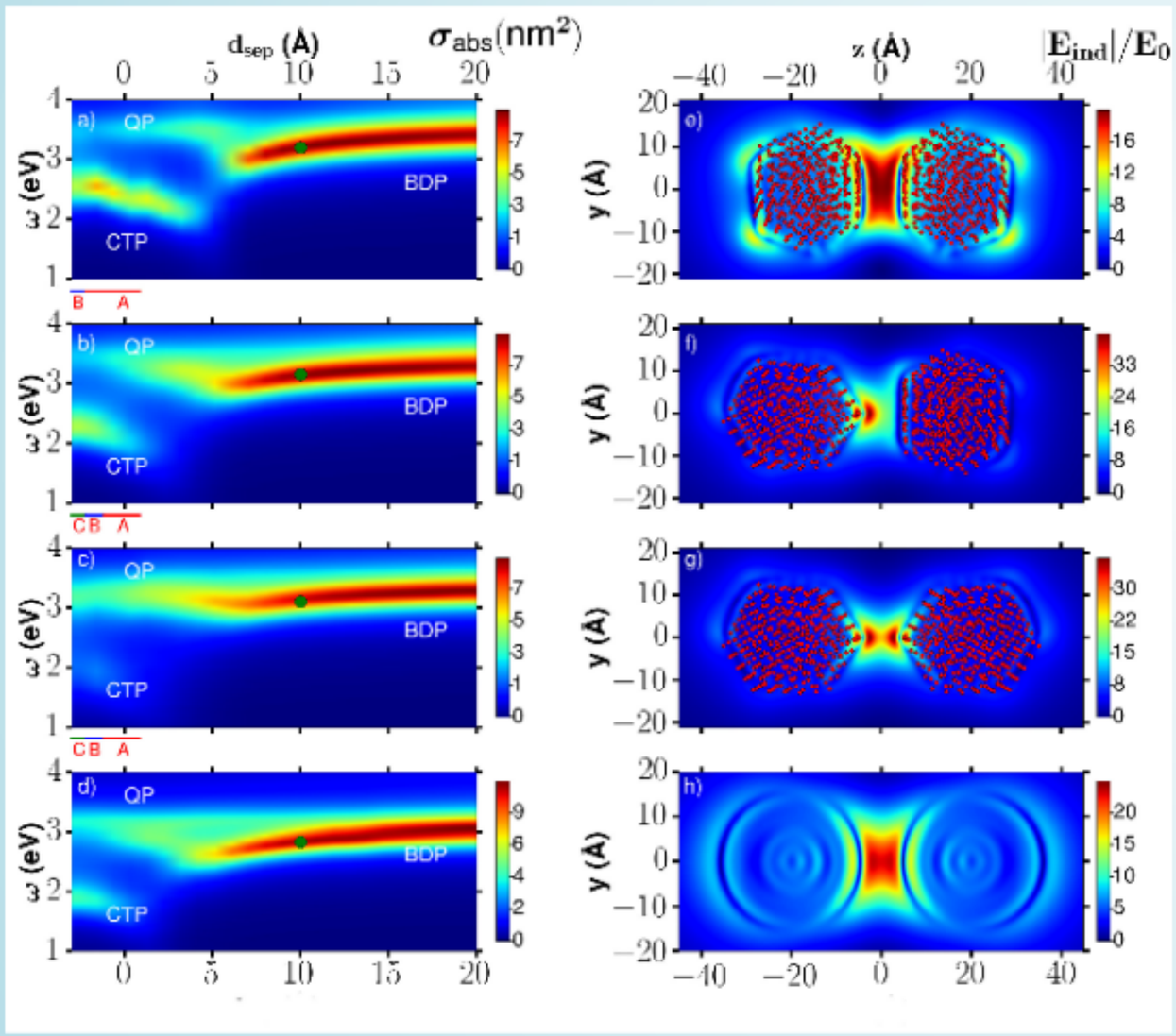
Nanoplasmonic with TDDFT

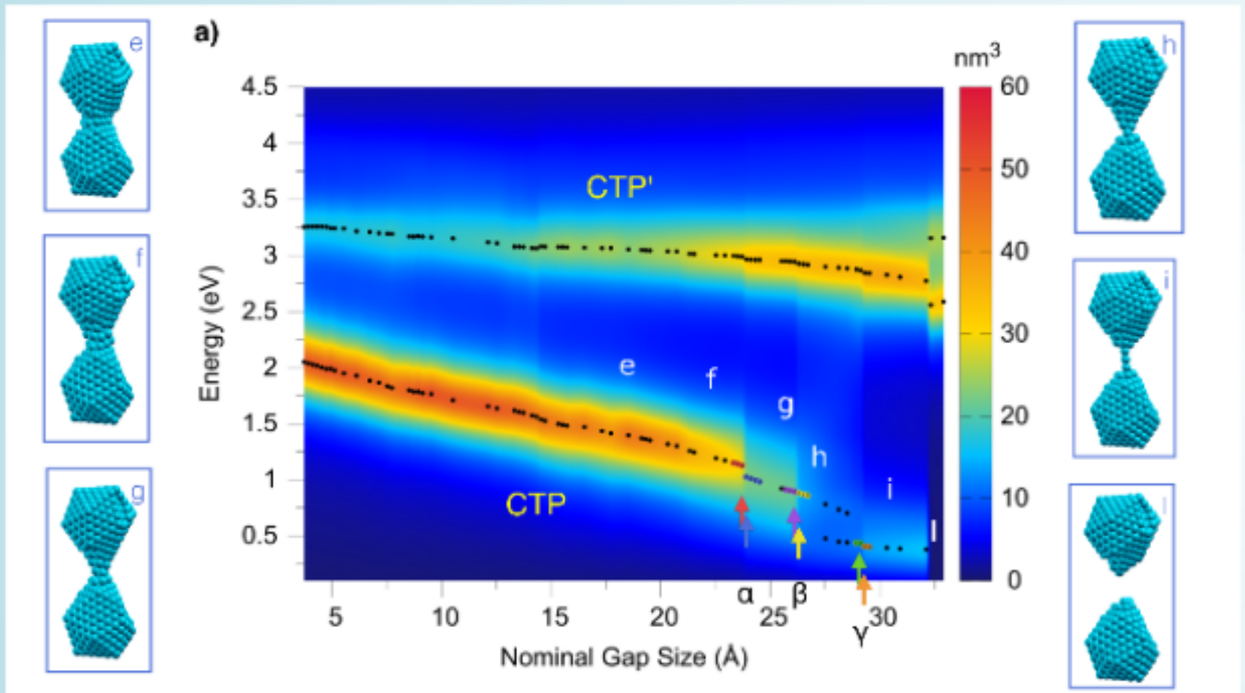


Electric Field enhancement in plasmonic nanostructures.

- 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

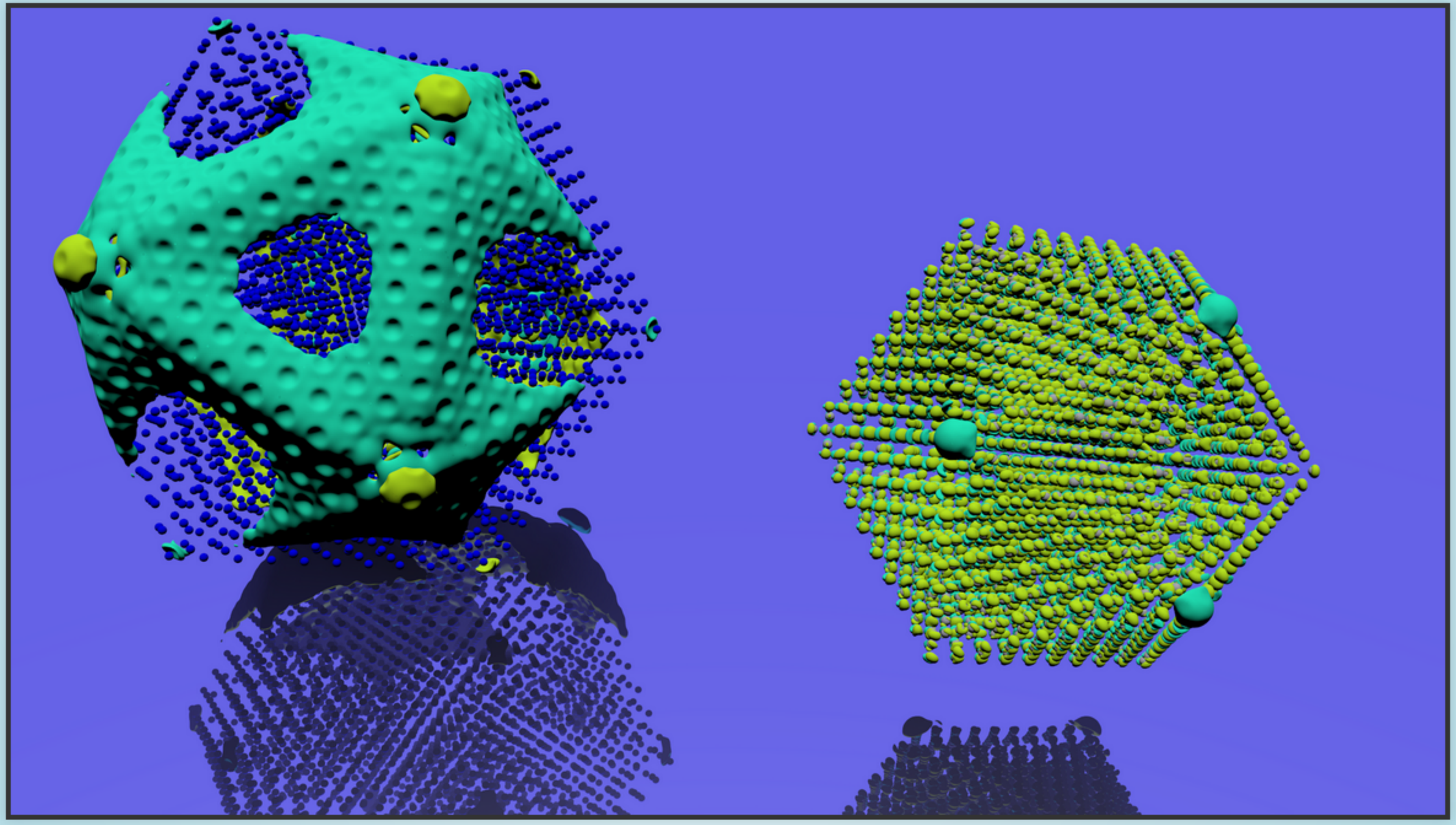


Optical response of metallic nanojunctions driven by single atom motion

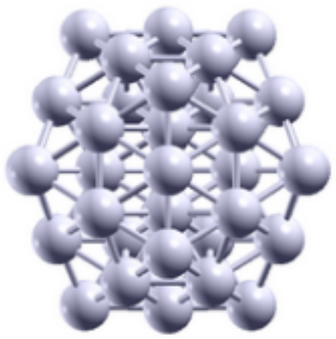
- Atomic Relaxation strongly influence polarizability.
- Polarizability quantization by single atom motion.

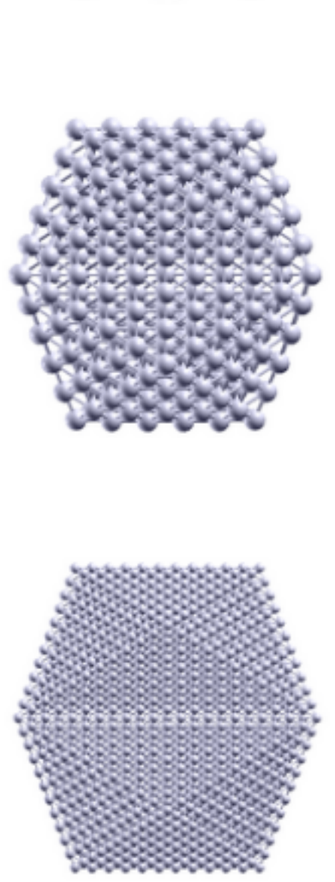
F. Marchesin et al., ACS Photonics, (2016)

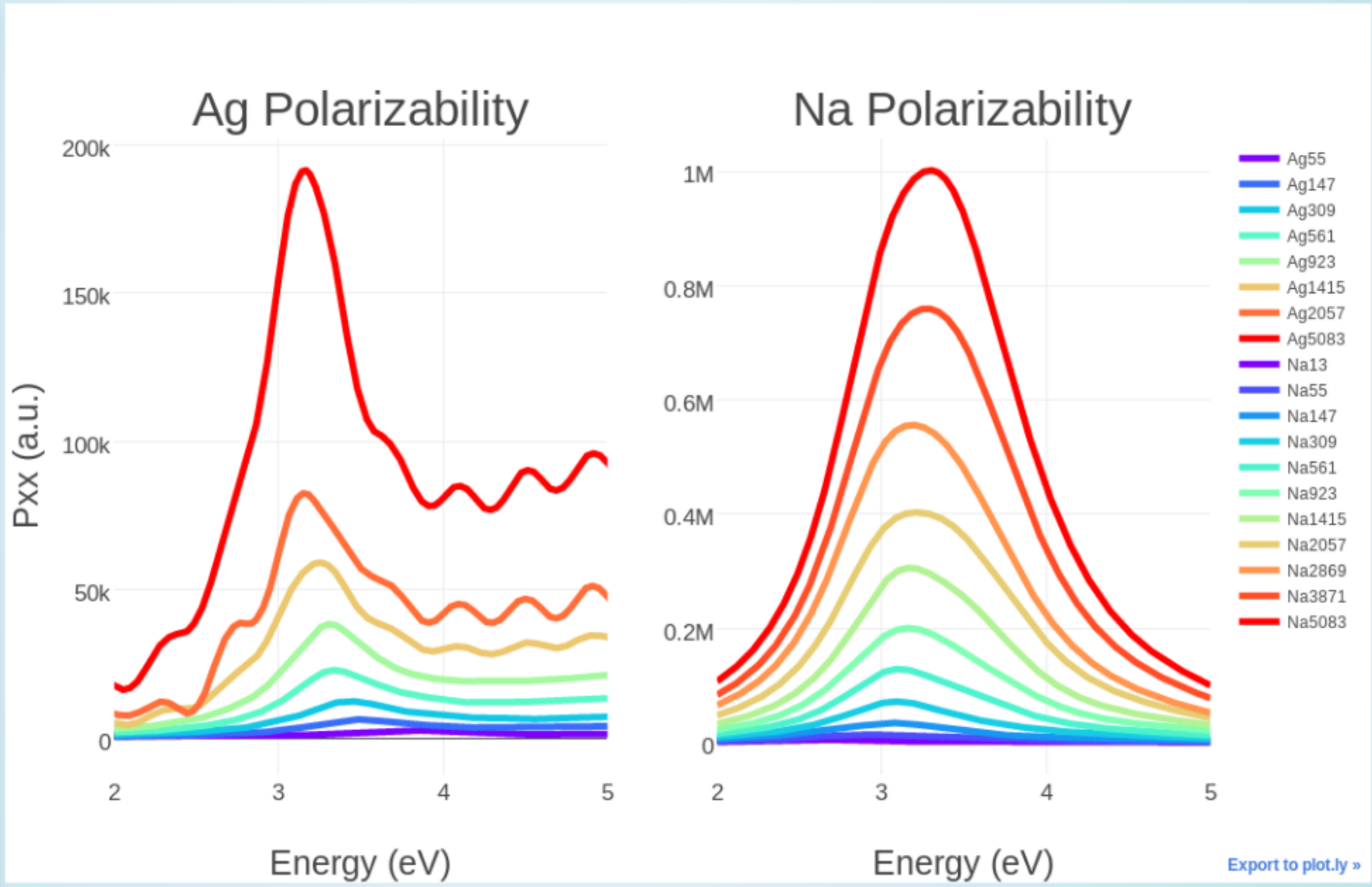
Ab-Initio calculations for very larger clusters!



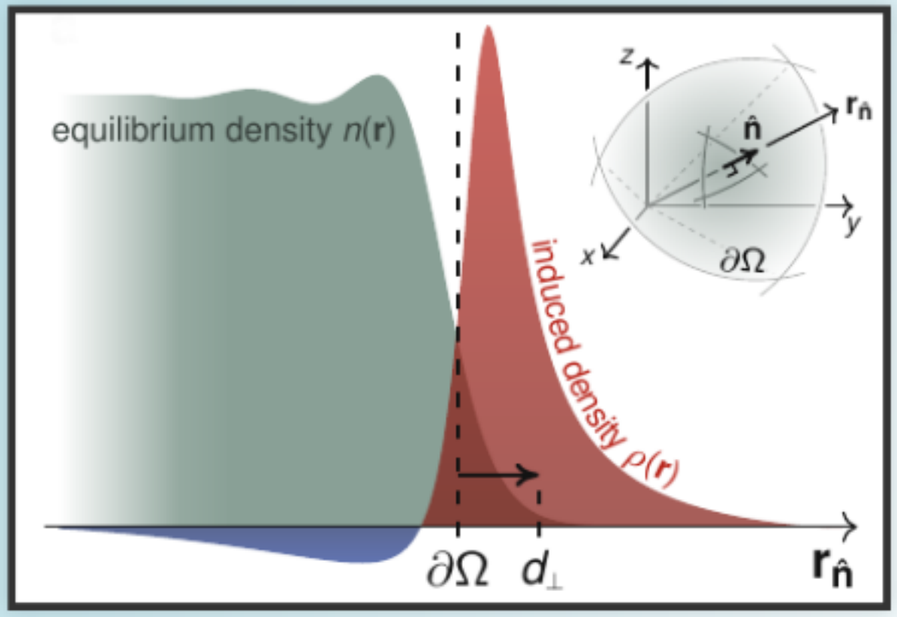
Clusters Polarizability







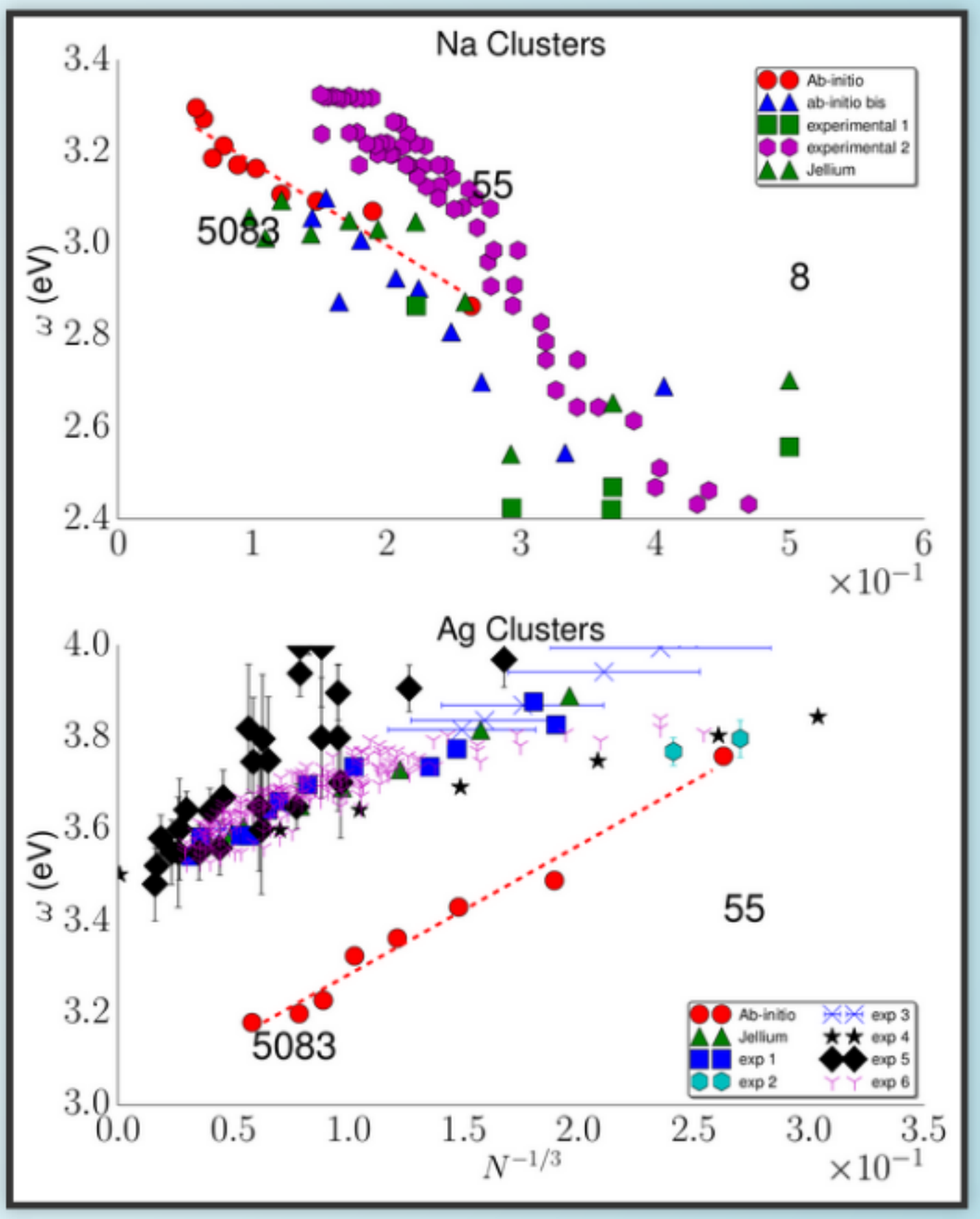
Frequency shift: opposite trend



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

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

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

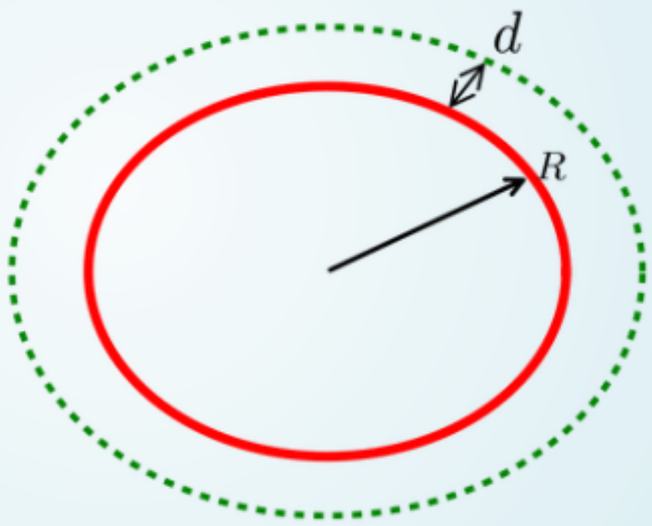


T. Christensen et al., arXiv:1608.05421v2

d parameter from centroid of charge

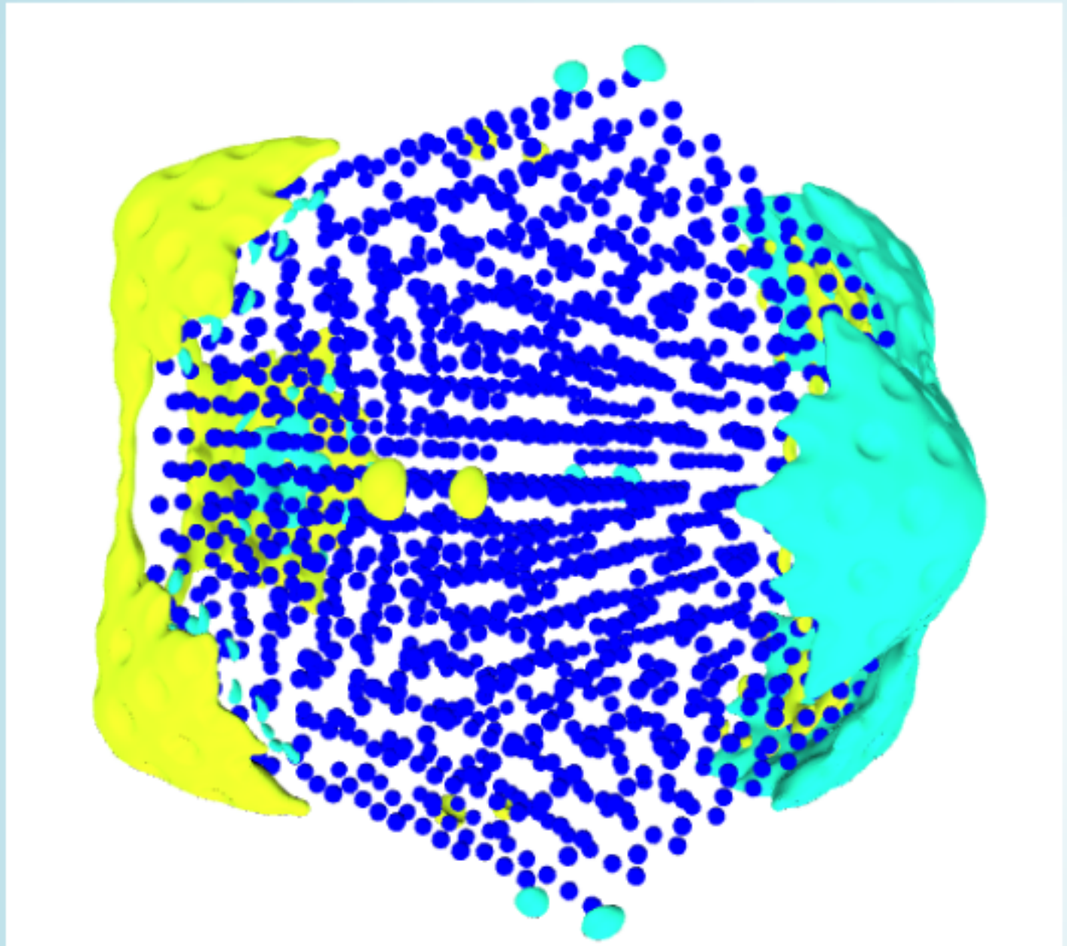
- The parameter d gives a distance between the edge of the system and the mean position of the oscillating density change
-

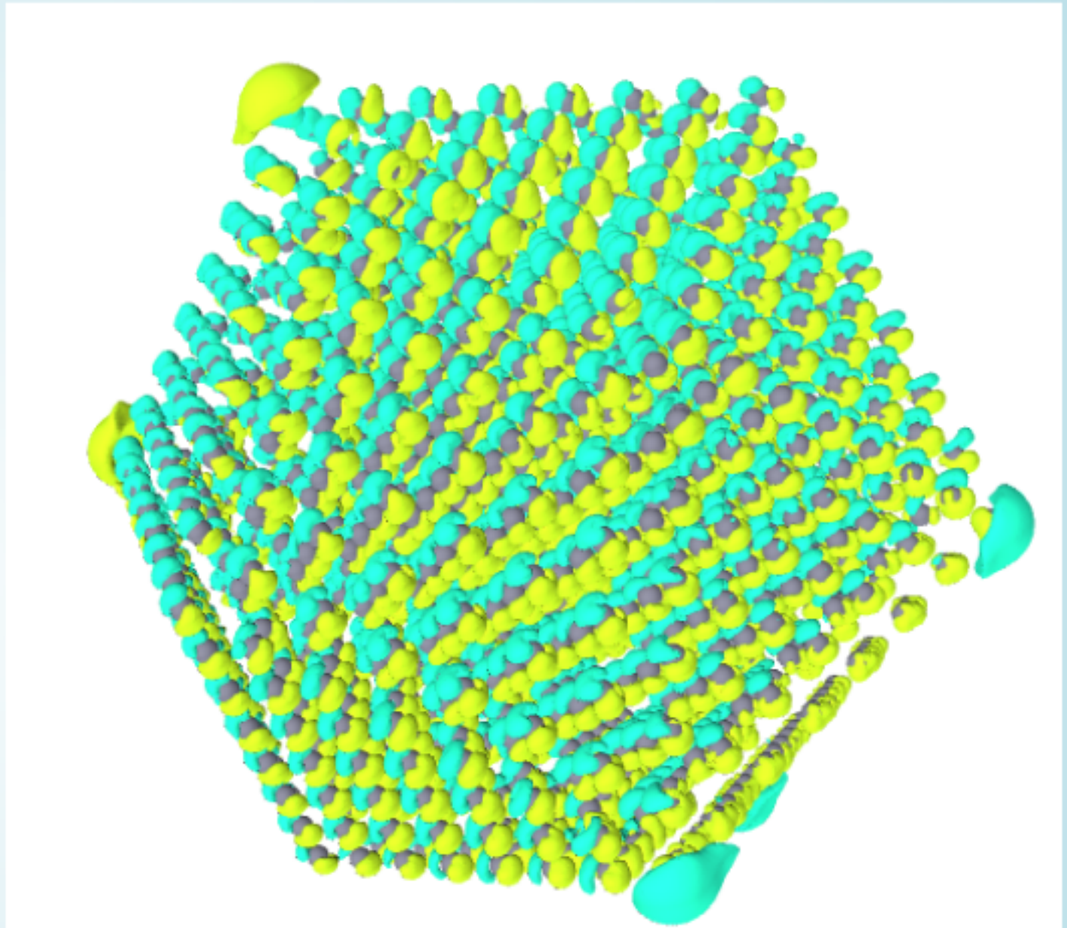
$$d = R - \Re \frac{\int r \delta n(r,\omega) dV}{\int \delta n(r,\omega) dV}$$



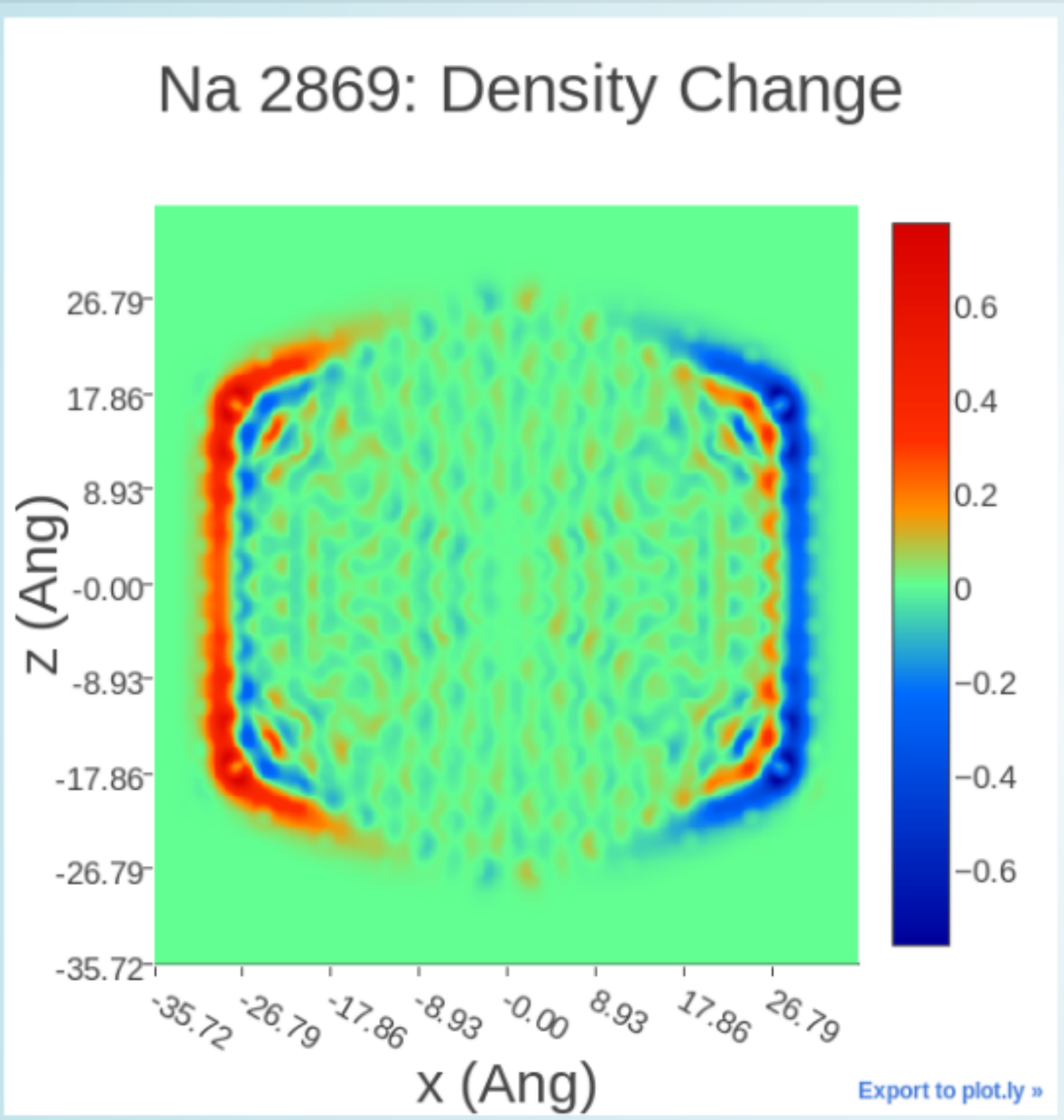
- And the surface plasmon is proportional to d
- $\omega_{sp} = \omega_{\infty}(1 + \frac{3d}{(2+\varepsilon_b) r_s N^{1/3}})$

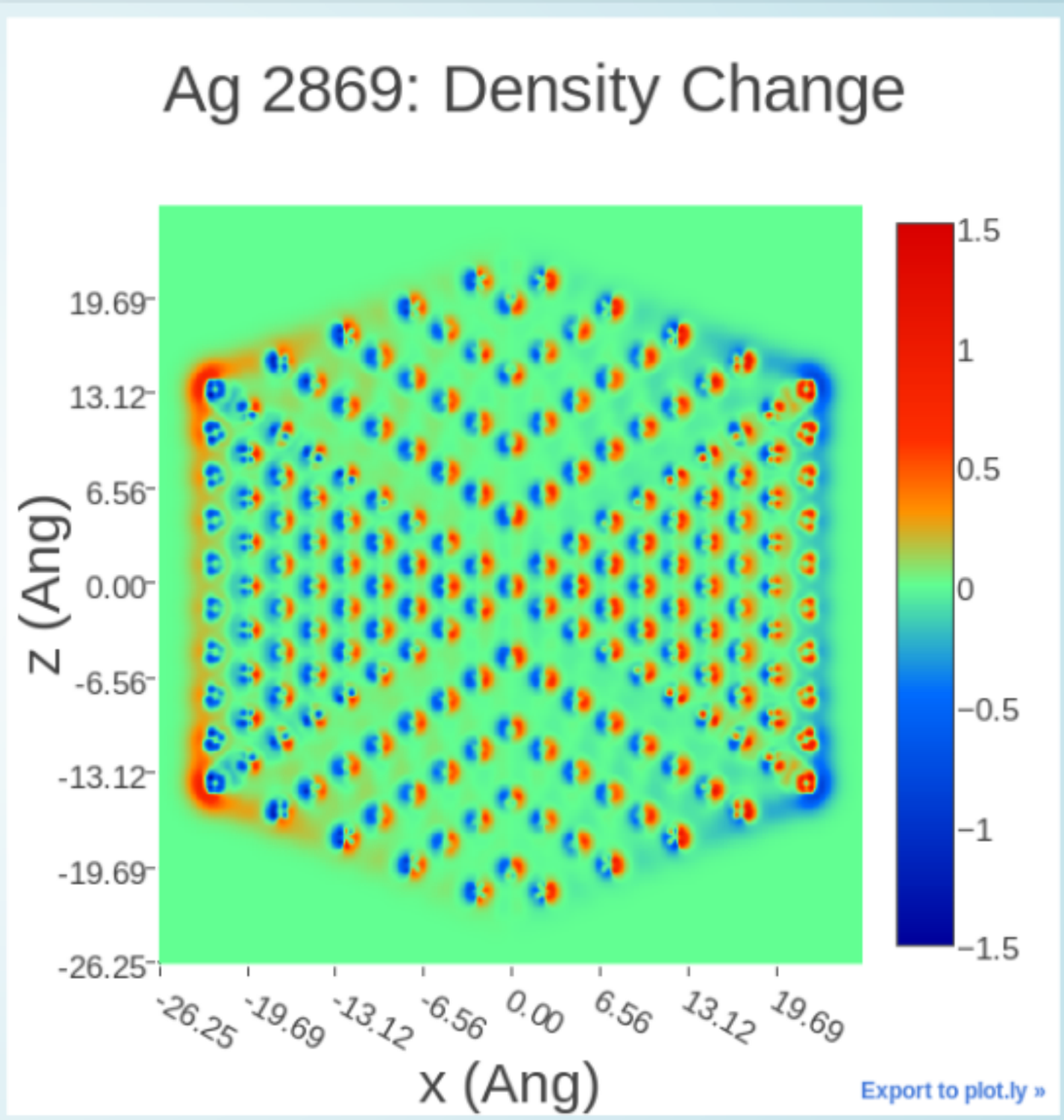
Density change Na and Ag 1415



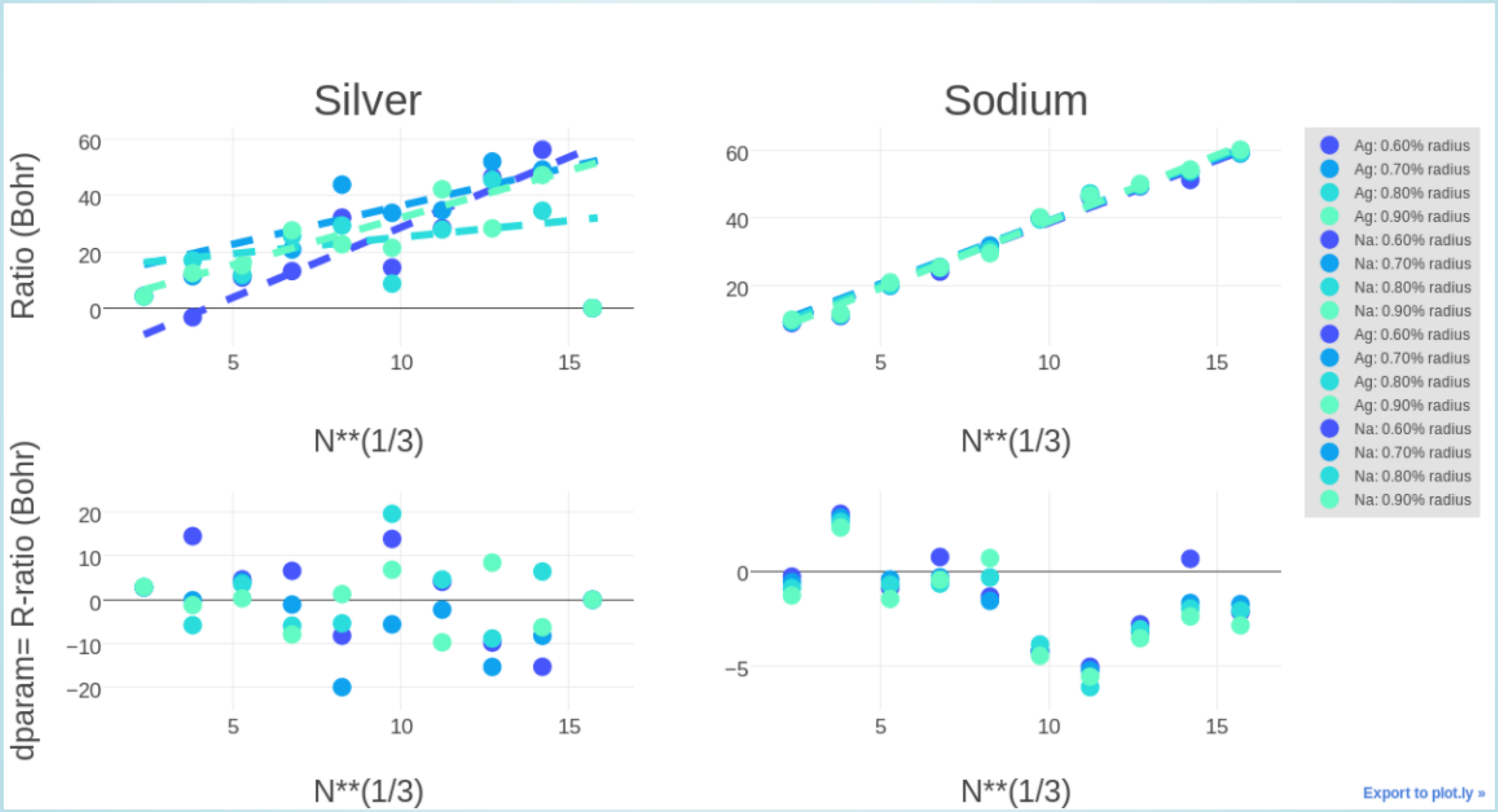


Density change: Imaginary part



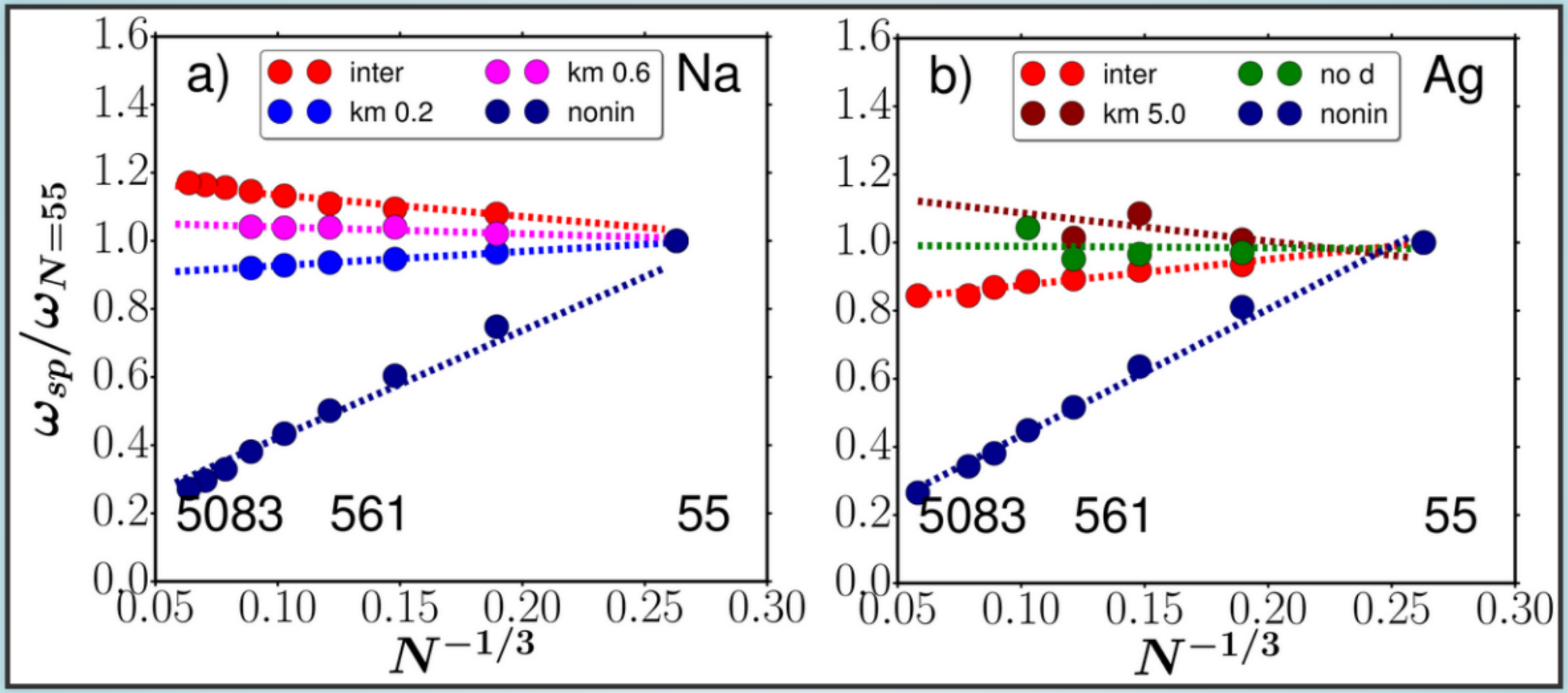


$$\text{d parameter:} \Re \frac{\int x \delta n(x) dx}{\int \delta n(x) dx} = r_s N^{1/3} - d$$



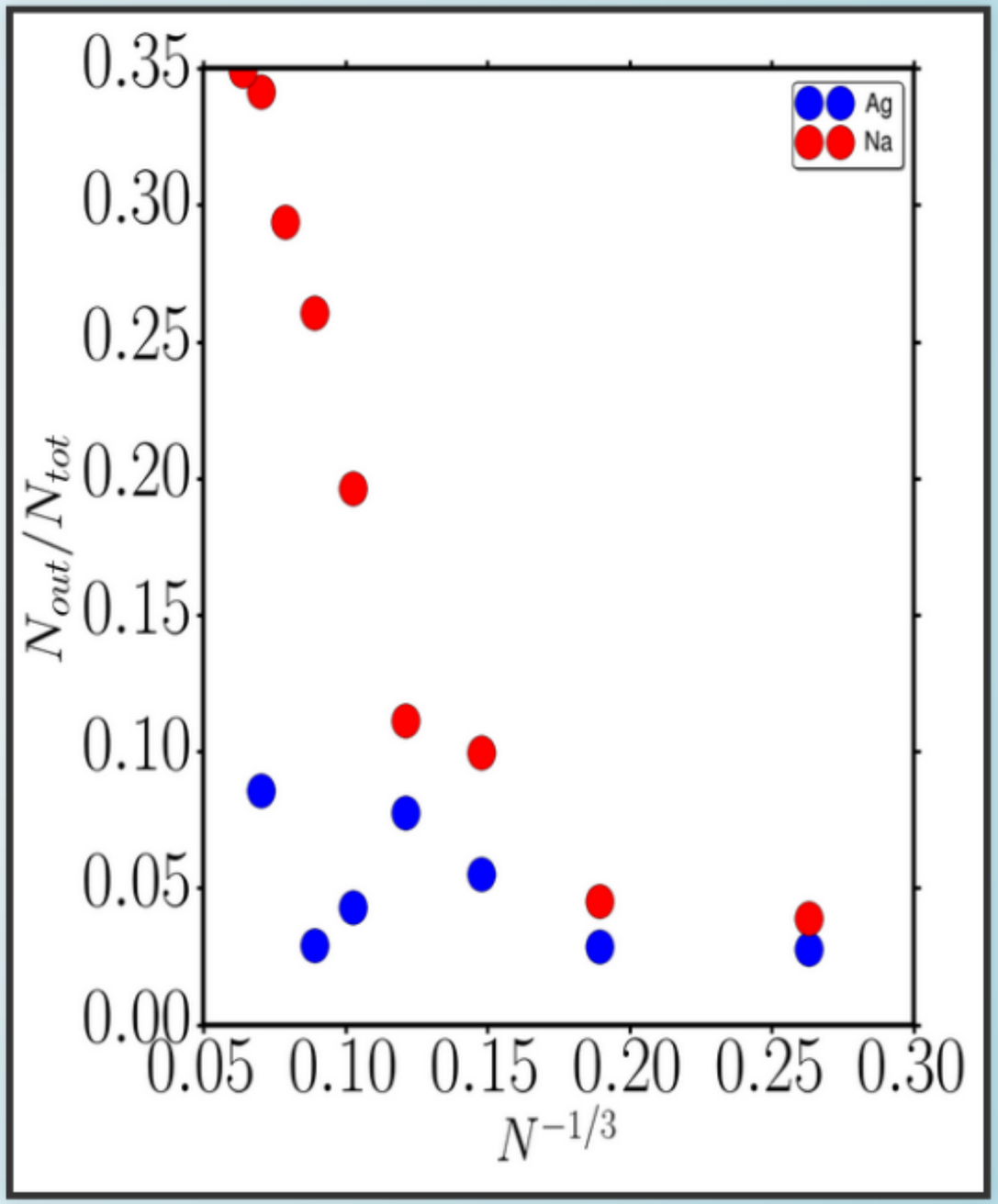
Electron interaction: at the origin of the problem?

Kernel impact



Electron at the cluster surface

- Concentration of electron at surface increase for Na but not for Ag.
- Thus electron interaction increases for Na when cluster growth but not for Ag.
- Therefore, ω_{sp} is red shift for sodium when the cluster size decrease, while it blue shift for silver because of the quantum confinement.



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.
- We could demonstrate that it is the electron interaction that is at the origin of the red shift in the case of sodium.

THANK YOU

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