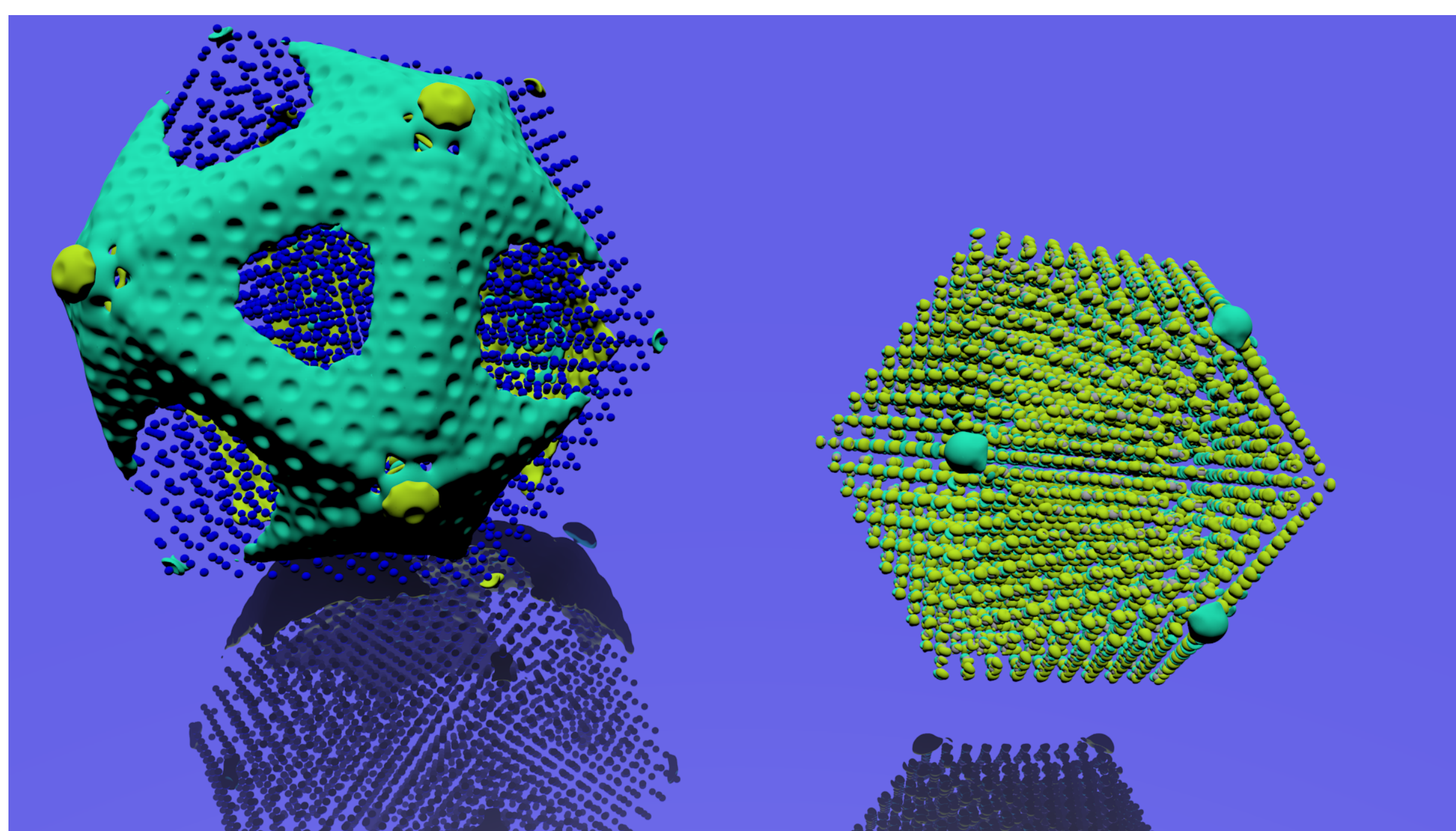


## Opposite trend in Na and Ag clusters revealed by ab-initio methods



We present large-scale atomistic ab-initio calculations of sodium and silver clusters counting up to 5083 atoms. To the best of our knowledge, this are the largest clusters to date for which the optical response have been explored using time dependent density functional theory (TDDFT). A comparison for these two materials is particularly interesting because experimentally, they show opposite behavior of the plasmonic frequency resonance as function of cluster size [1]. Analysis of our ab-initio calculations based on atomistic TDDFT reveals two competing phenomena - quantum size confinement and screening of the electron-electron interaction - determining the size dispersion of the plasmonic frequencies. Our calculations confirm the correlation of the induced density spill-out with the frequency of the plasmonic resonance in case of simple metals (like sodium), while we could not find similar relation in case of silver clusters.

The detailed analysis for the unprecedentedly large clusters was possible because of recent improvements in the iterative TDDFT code that we are using [2, 3, 4]

mail: [marc.barbry@mailoo.org](mailto:marc.barbry@mailoo.org), website: <https://mbarbry.pagekite.me>

## Opposite trend in Ag and Na clusters

The study of the dependence of the surface plasmon polariton frequency  $\omega_{sp}$  as function of the size of the clusters shows that sodium and silver have an opposite trend. We use icosahedral clusters with similar geometry for both Na and Ag.

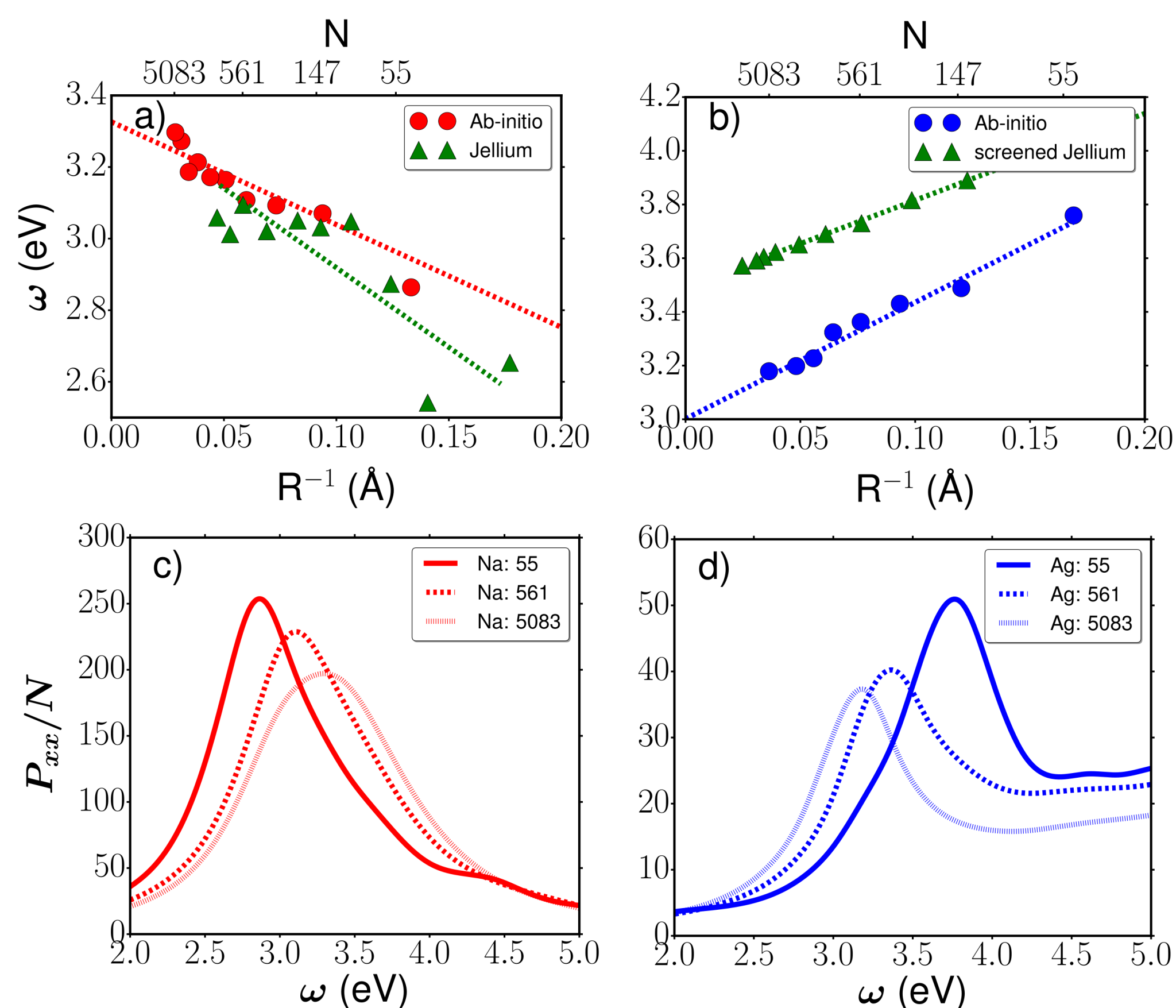


Fig. 2: Theoretical results on the size dispersion of sodium and silver icosahedral clusters. The size dispersion of the plasmonic frequency for Na and Ag clusters is shown on panels a) and b) correspondingly. The average polarizability per atom (ab-initio atomistic calculations) is shown for Na and Ag on panels c) and d) correspondingly.

The frequency shift is linear with  $R^{-1}$ ,

$$\omega_{sp} = \frac{\omega_p}{\sqrt{2 + \epsilon_b}} \left( 1 + \frac{3}{2 + \epsilon_b} \frac{d}{R} \right), \quad (1)$$

where  $R$  is the radius of the cluster and according to several authors the parameter  $d$  should correspond to the so-called centroid of charge.

## Electron interaction and frequency shift

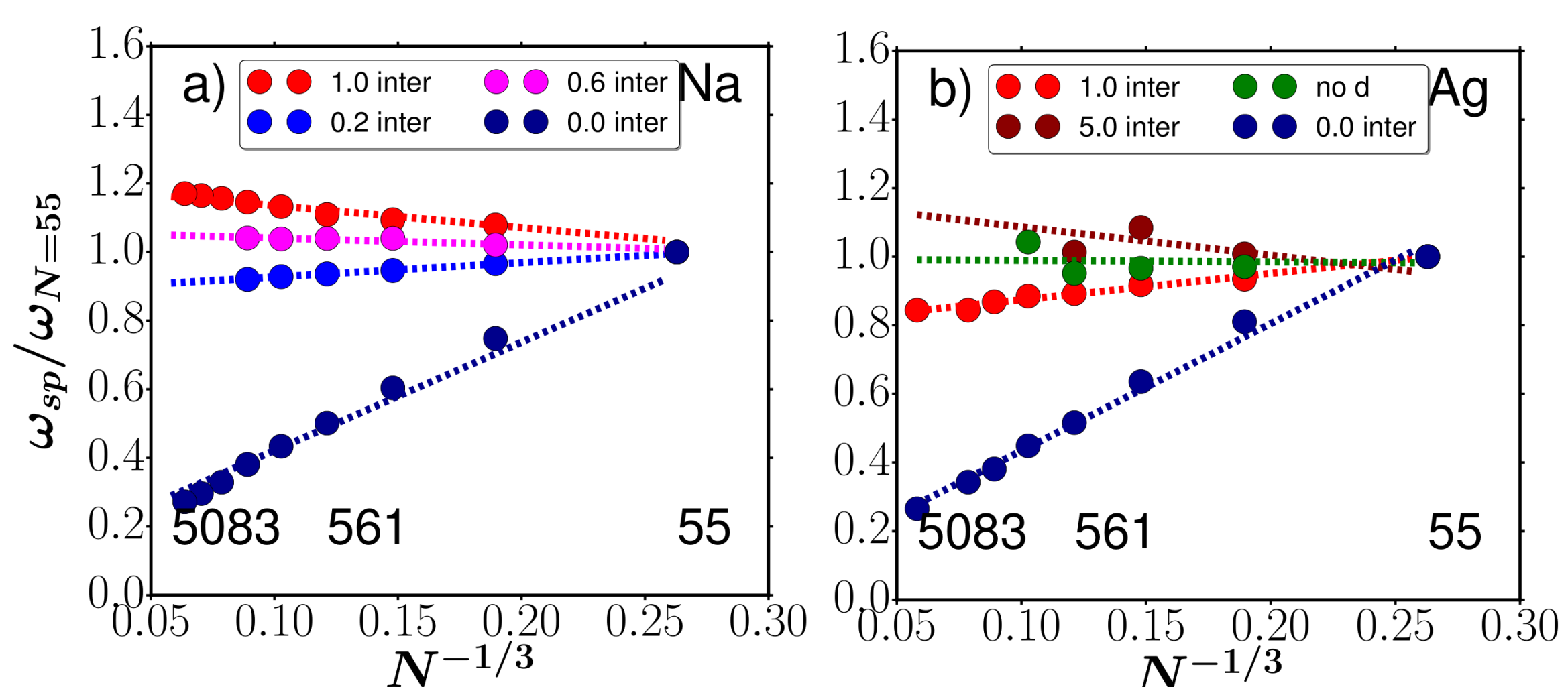


Fig. 3: Frequency shift for different impact of the kernel.

Figure 3 shows the strength of the electron-electron interaction. We can then deduce that the electron-electron interaction is at the origin of the opposite trend in sodium and silver.

## Density change and centroid of charge

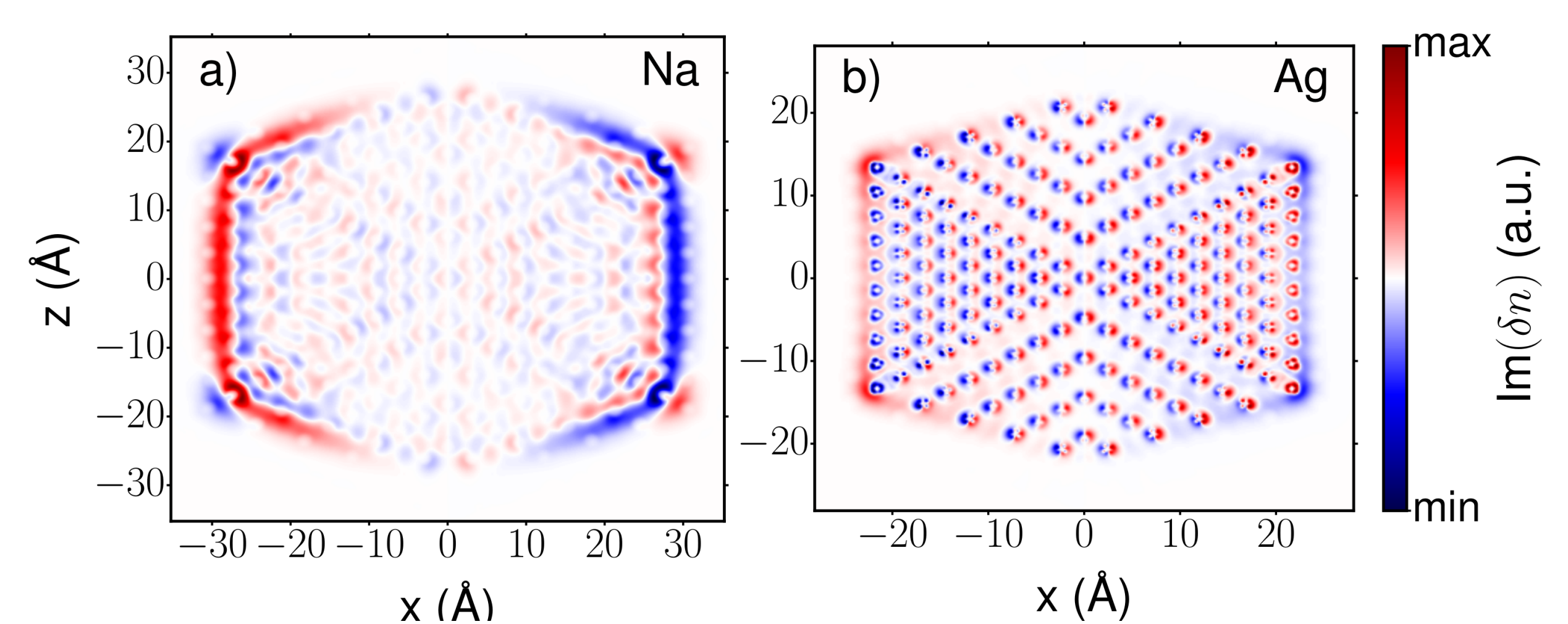


Fig. 4: Distribution of induced electron charge  $\delta n$  for a) sodium and b) silver.

The differences in the electronic structure of sodium and silver are reflected in the distribution of induced density. In case of sodium (plasmonically active) valence electron  $3s^1$  are well separated in energy from the  $2s^2p^6$  electrons, while the  $4d^{10}$  electrons in silver are energetically close from the  $5s^1$ . This difference results in a largely polarizable 4d shell, giving rise to a large screening (weakening) of the electron-electron interaction in the case of silver, leading to a domination of the quantum size confinement effect over the electron-electron interaction in order to determine the size scaling of the plasmon resonance.

## Problems with the centroid of charge

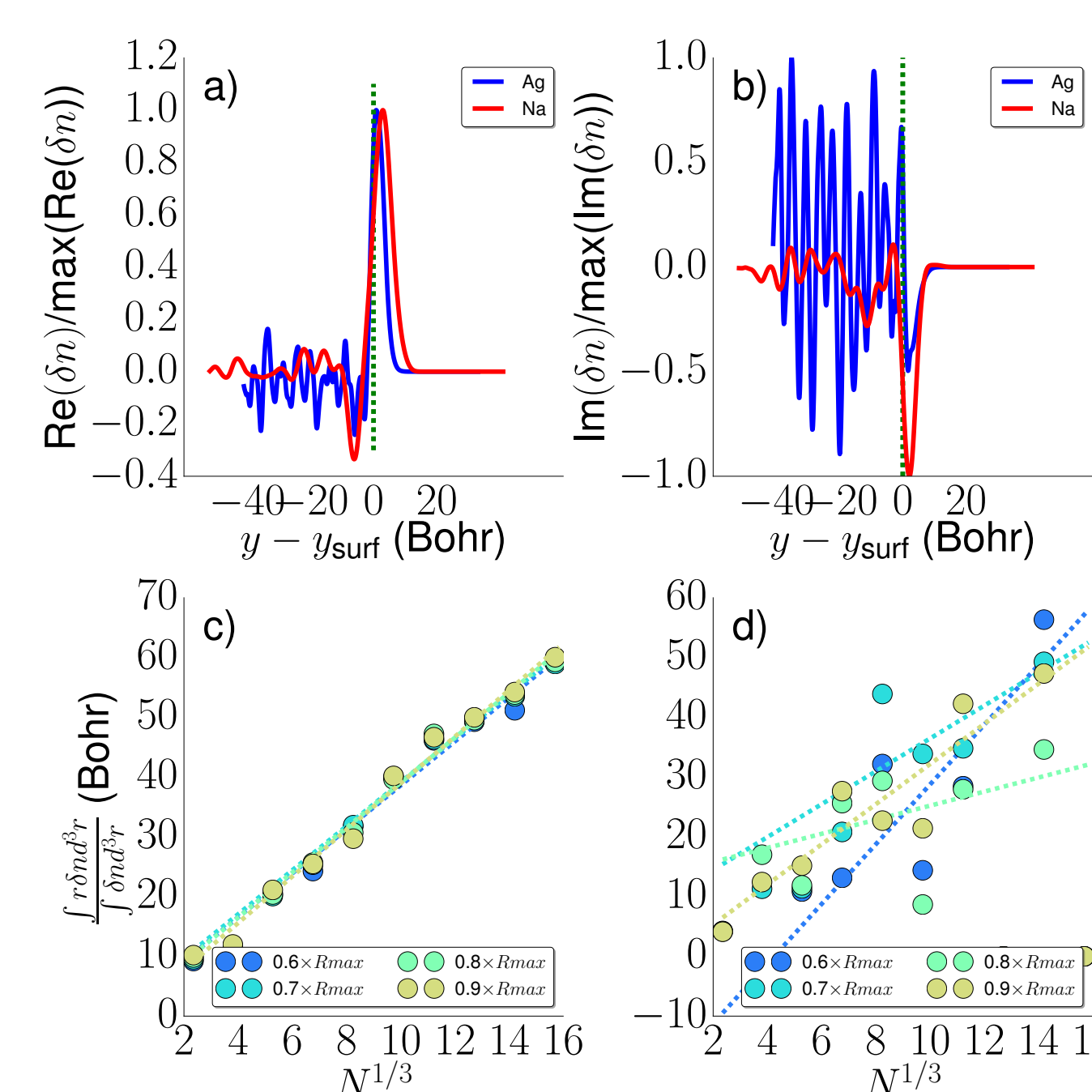


Fig. 5: Distribution of induced electric charge  $\delta n$  along the cylinder axis a) real part b) imaginary part. Centroid of density change as function of the size of the cluster c) sodium d) silver.

In order to get the centroid of charge, we integrated the density change in a cylinder which axis is parallel to the external field and perpendicular to a cluster facet.

$$\mathfrak{R} \int_0^{+\infty} x \delta n(x) dx = r_s N^{1/3} - d \quad (2)$$

The position of the centroid of charge relative to the surface is then given by the value of the above expression at  $N = 0$ .

## Conclusion

- Ab-initio calculations for very large clusters with low resources (32 CPU, 512 GB).
- Ab-initio picture of the plasmon frequency dispersion.
- Competition of quantum size confinement and electron-electron interaction determines the size dispersion trends of the plasmonic frequency.

Ref: [1] K.P. Charl Crystal Research and Tech. 33 (1998). [2] P. Koval, et al. J. Chem. Theory Comput. 6 (2010). [3] M. Barbry et al. Nano lett. 15 (2015). [4] P. Koval et al. J. Phys.: Cond. Matter 28 (2016).