# First-principles calculation of plasmonic resonances and electric field enhancement in metal-cluster dimers

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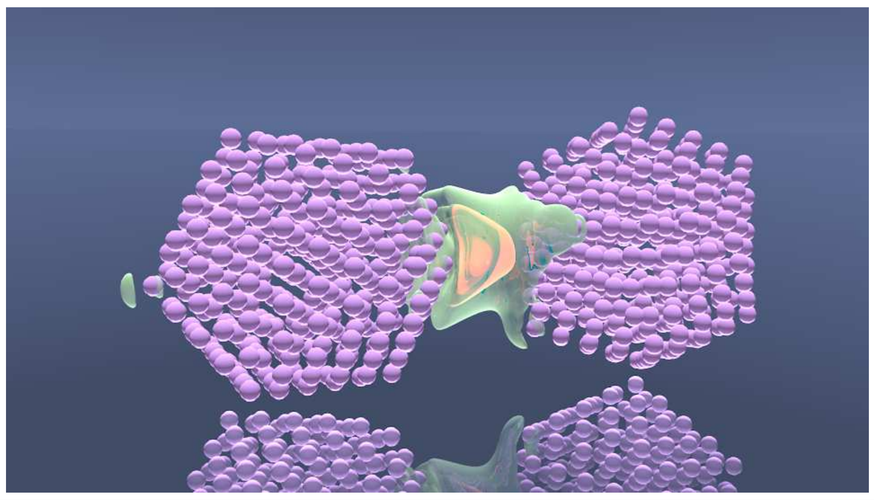
## Introduction

In this work[1], we present an ab-initio study of the optical absorption and electric field enhancement in the vicinity of metal cluster dimers. The approach is based on time dependent density functional theory (TDDFT) since only TDDFT allows a quantum-mechanical description of systems of several hundreds of atoms.



## Theory

In the framework of linear response TDDFT we obtain the action of the response operator $\chi = \frac{\delta n(\omega)}{\delta V_{\text{ext}}}$ on a given external perturbation $\delta n_\mu = \chi_{\mu\nu}\delta v^\nu$ iteratively[2]. The cross-section tensor $\sigma$ and the field enhancement $\mathbf{E}_{\text{ind}}$ reads

$$\sigma(\omega) \propto \text{Tr}\left(\text{Im}\left[\int \mathbf{r}_i \chi(\mathbf{r},\mathbf{r}',\omega)\mathbf{r}'_j d\mathbf{r} d\mathbf{r}'\right]\right), \quad (1)$$

$$\mathbf{E}_{\text{ind}}(\mathbf{r},\omega) = -\int \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}\delta n(\mathbf{r}',\omega) d^3\mathbf{r}'. \quad (2)$$

The calculation of the induced field was speed up by using fast Fourier transform techniques.

## Local field: Importance of atomic-scale geometric features

Figure 1 shows the induced local Field for one cluster containing 380 atoms calculated using our atomistic and a Jellium model (JM). We can observe that our atomistic model reveals the localization of the electric field at sharp edges and atomic-scale protrusions.

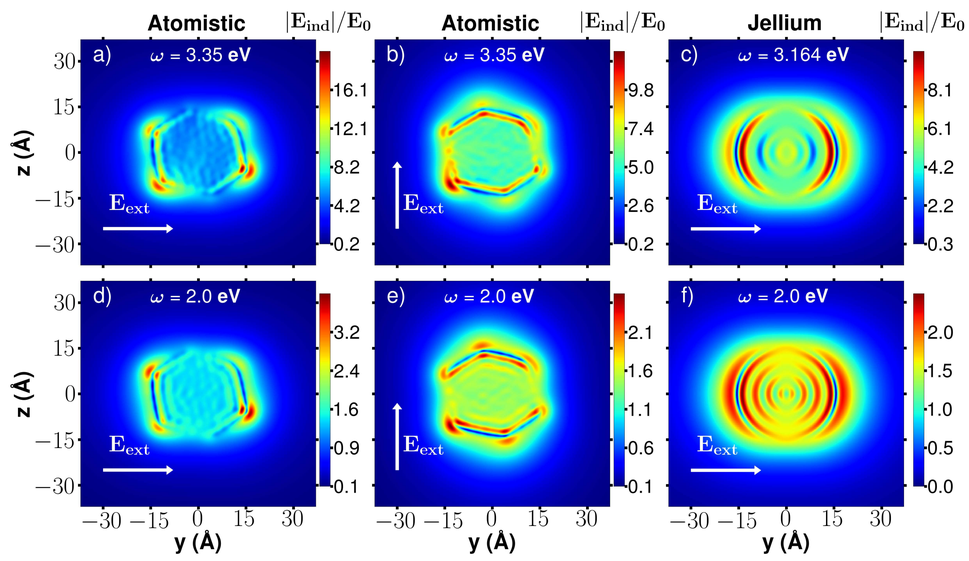



Figure 1 : The figure shows the induce field for only one $Na_{380}$ cluster with different conditions. The two graphics in the right column show the case of a JM.

In the case of the dimers, the induced near-field $\mathbf{E_{ind}}$ as well as optical cross-section $\sigma_{\text{abs}}$ of metallic cluster dimers depend on the inter-cluster separation, as shown in Figure 2 where 3 different dimers geometries as well as the Jellium model are studied.

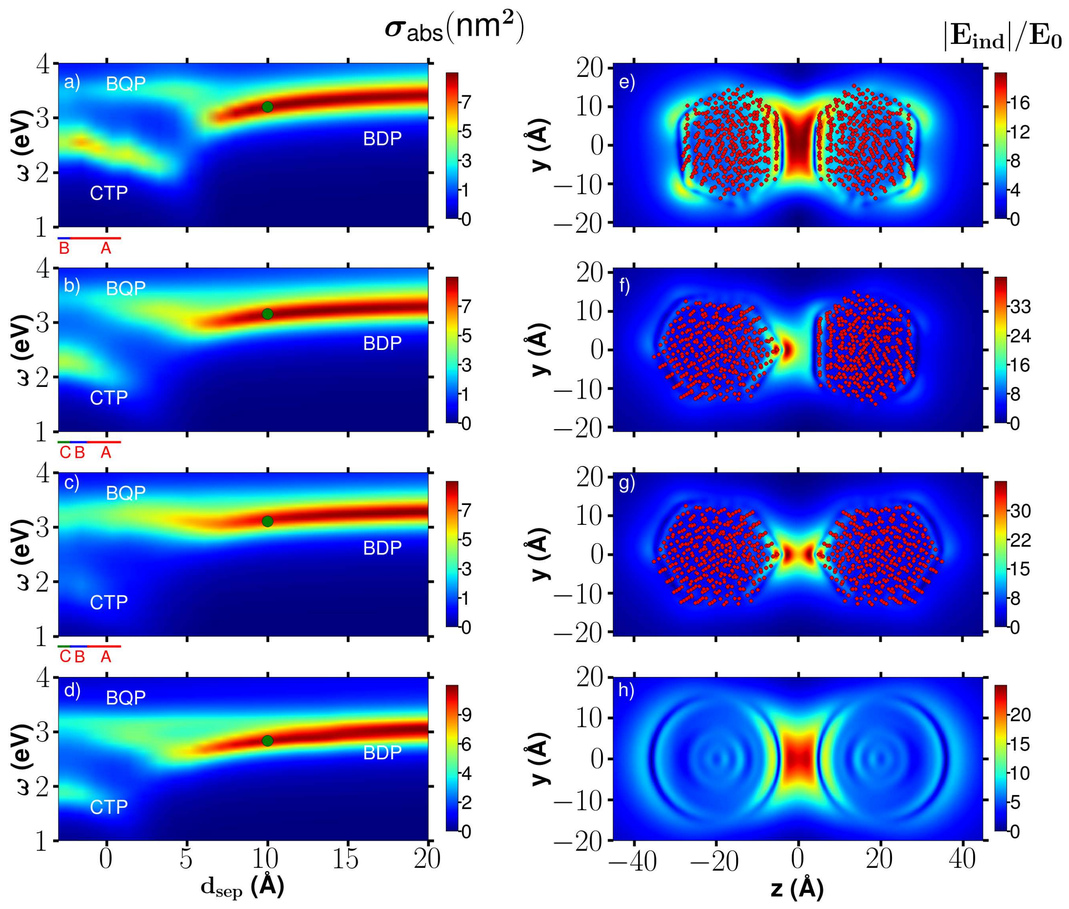



Figure 2 : The left panel shows the dependence of $\sigma_{\text{abs}}$ on the inter-cluster distance for 3 different geometries and a JM of the $Na_{380}$ dimers. While the right panels show the induced field in a plane containing the dimers axis for a distance of 10Å between the two clusters. The energy of the fields in the right panels correspond to the main resonances of the cross-section (green dots in right panel). a) and e) facet to facet, b) and f) tip to facet, c) and g) tip to tip and d) and h) JM.

One can observe the strong influence of the cluster geometry on the field localization. The sharpest the surface, the stronger the enhancement and localization of the induced field will be. The atomistic model makes possible to investigate atomic-scale details that other models as Jellium or classical can not give. The effects of the atomistic description can also be observed in the $\sigma_{\text{abs}}$. For small distances, the intensity of the CTP is directly related to the *contact* surface between the 2 clusters.

## Local field distribution: sub-nanometer localization

The dependence of the near-field enhancement on the inter-cluster distance and relative orientations were computed for the $Na_{380}$ dimers

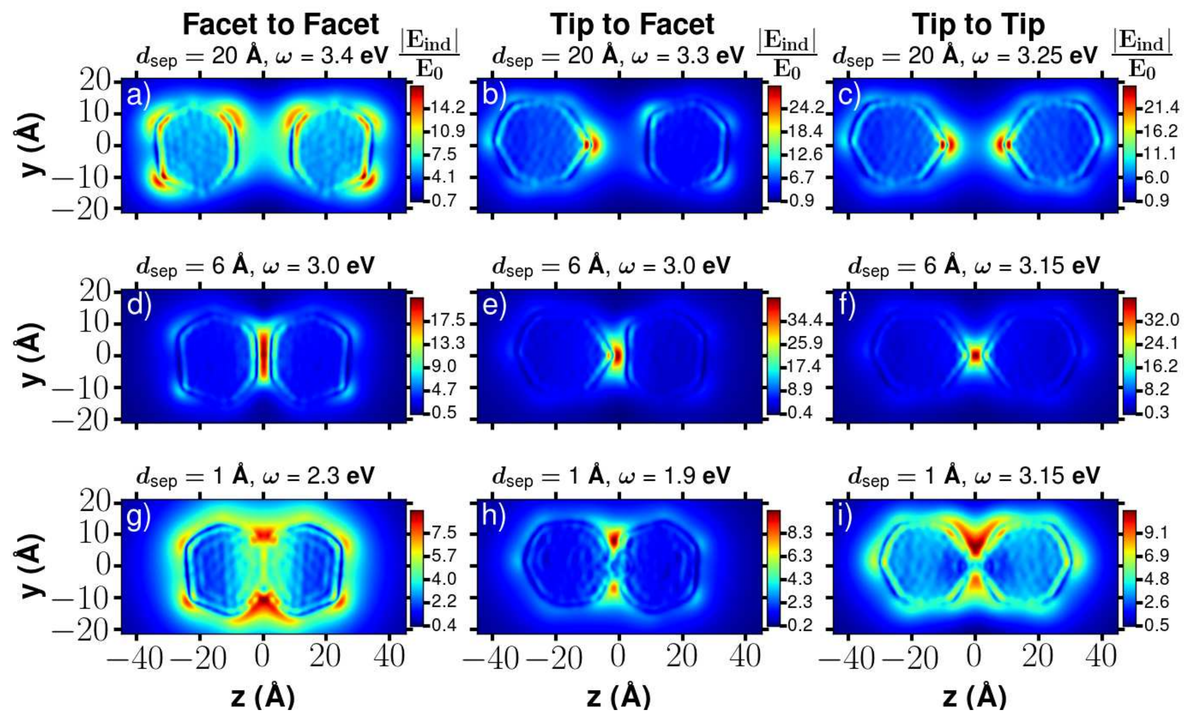



Figure 3 : The electric field enhancement dependence is shown for 3 geometries (facet to facet (left column), tip to facet (central column) and tip to tip (right column)) at 3 inter-cluster distances along the dimer axis.

Figure 4 shows the dependence of the electric field enhancement as function of the inter-cluster distances for the three geometries and the field distributions in the middle plane between the two clusters.

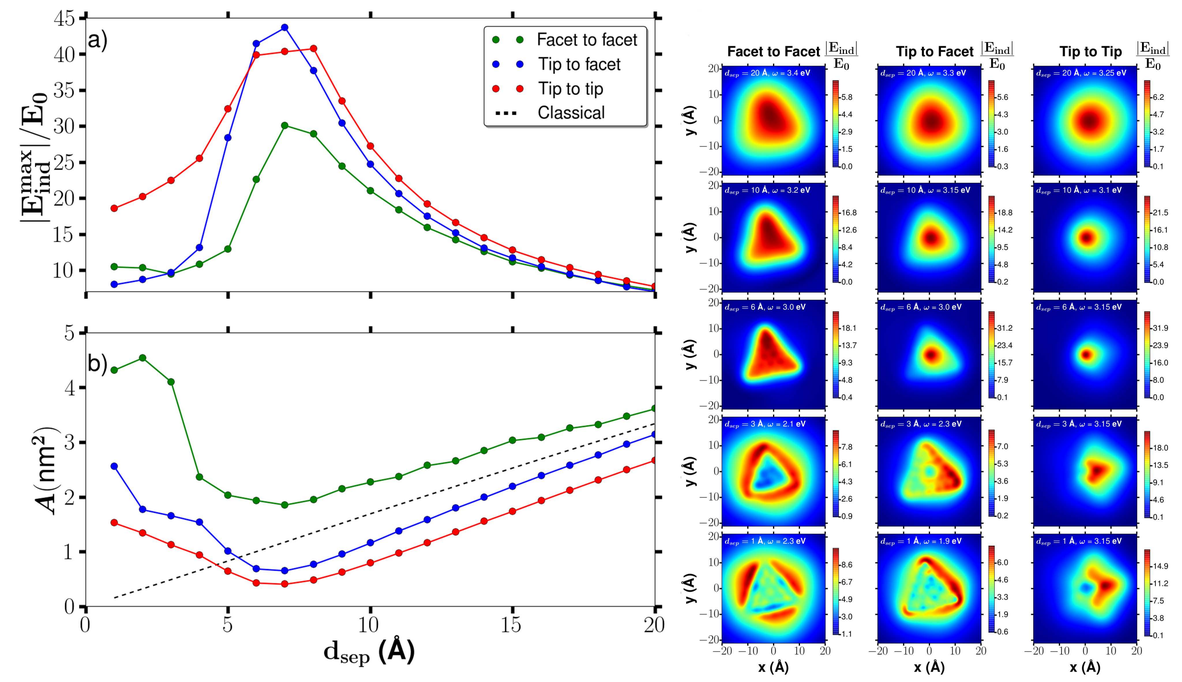



Figure 4 : The right panel shows the dependence of the electric field as function of the inter-cluster distances in the plane perpendicular to the dimer axis. The top left graphic represent the maximal field in the plane $y = 0$ perpendicular to the dimer axis. and the bottom left graphics represent the confinement of the field in the same plane given by equation 3.

The confinement of the electric field in the plan $y_0$ shows in Figure 4 is given by

$$A = \int_S \frac{|E_{enh}(x, y_0, z)|^2}{|E_{enh}^{max}|^2} dxdz \quad (3)$$

## Electron current in the gap

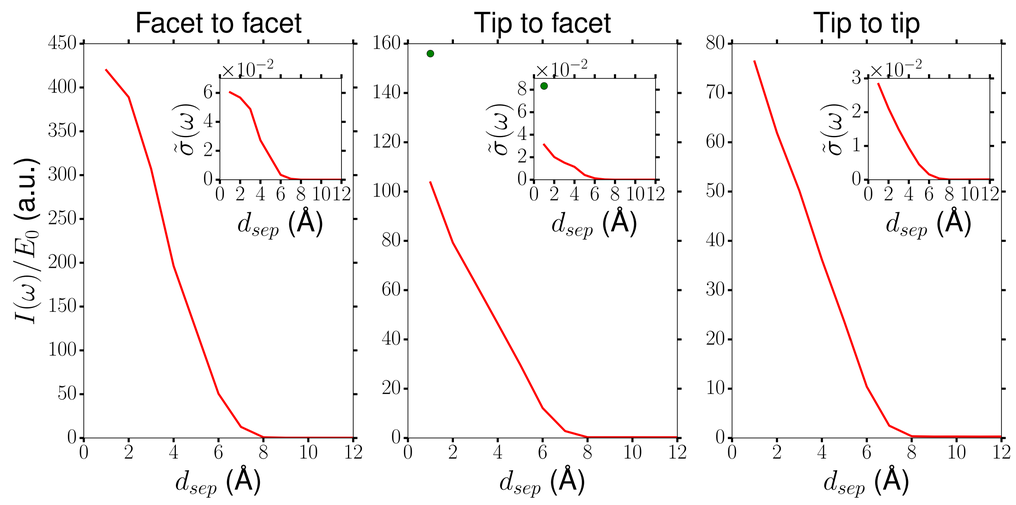



Figure 5 : Amplitude of the electron current (in atomic units and normalized by the external field) flowing between the two $Na_{380}$ clusters as a function of the interparticle separation $d_{\text{sep}}$ for the three plasmonic gap considered.

The currents show in Figure 5 are calculated, using the induced electron-density at a given frequency, as the charge crossing a surface bisecting the gap by unit of time. As expected, in all the cases the currents grows steeply as $d_{\text{sep}}$ is reduced.

## Conclusion

- Our model provides atomic-scale resolution of the electric field enhancement in contrast to classic spheres[3], Jellium spheres[4] and quantum corrected[5] models.
- Thanks to this resolution we demonstrate a large dependence of the electric field enhancement on the geometrical details of the nanogap.
- With this model we wish now to look toward time dependence and EELS calculations . In order to get closer from the reality, the relaxation of the dimers is also a crucial forward step.

## References

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