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

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Introduction

In this work, 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 $\chi = \frac{\nabla \rho}{\epsilon}$ on a given external perturbation $\epsilon$ iteratively[2]. The cross-section tensor $\sigma$ and the field enhancement $E_{\text{ind}}$ read:

$$
\sigma(\nu) \approx i \lim_{\delta \rightarrow 0} \left[ \int F \left( \frac{\nu}{\nu - \omega} \right) \frac{d\nu}{d\omega} \right],
$$

$$
E_{\text{ind}}(r) = \frac{\epsilon}{\epsilon - \sigma(\nu) \delta(\nu - \omega)}.
$$

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.

$\sigma_{\text{abs}}$ ($\text{nm}^2$)

Electron current in the gap

$|E_{\text{ind}}| / |E_0|

Figure 5: Amplitude of the electron current (in atomic units and normalized by the external field) flowing between the two $N_{\text{Na}}$ 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 the charge crossing a surface bisecting the gap by unit of time. As expected, in all the cases the currents grows steeply as the charge crossing a surface bisecting the gap by unit of time.

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