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

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Abstract

Recent progress in fabrication of nanodevices has made possible the production of nanoobjects of controlled composition and shape down to atomic precision. Metallic clusters of Ag, Cu, Au have been used to amplify Raman spectroscopy signal [1]. One of the mechanism that leads to amplification of Raman signal is the enhancement of the electromagnetic field in the nanoscale [2]. Namely, if a metal cluster locates in the vicinity of a molecule, then the electromagnetic field induced by the cluster response can be much larger than the driving laser field.

In this work, we present an *ab-initio* study of the polarizability and electric field enhancement in the vicinity of metal cluster dimers. The approach is based on time-dependent density functional theory (TDDFT) because only TDDFT offers a feasible quantum-mechanical description for systems of several hundred of atoms. TDDFT reproduces the basic features of experimental absorption spectra and it allows to examine the spatial- and frequency-dependence of the field enhancement in nano-cavities of different sizes and shapes [3].

For our calculations, we employ an original implementation of TDDFT in the linear response regime [4]. This implementation is optimized for utilizing locality of operators in order to construct an algorithm of low computational complexity. Our TDDFT code is interfaced with SIESTA: an efficient density functional theory implementation [5]. The low complexity algorithms employed in SIESTA and in our TDDFT code made possible to address electric field enhancement between sodium cluster dimers composed of several hundreds of atoms. We perform a detailed analysis of the density change and the induced electric field distribution. From the calculations, we demonstrate that the atomic structure plays a crucial role for the absorption cross-section and the electric field enhancement, especially for small dimer separations. In the Figure 1, we show the electric field enhancement and the polarizability for a $2xNa_{380}$ dimer.

References

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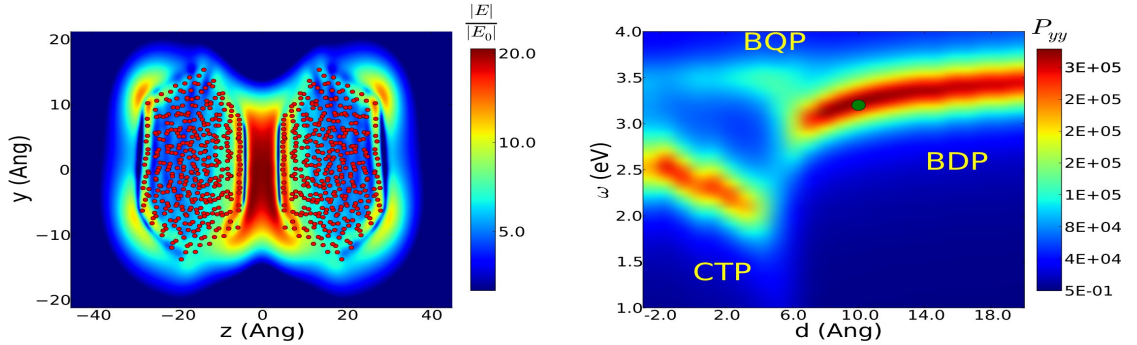

Figure 1: Left panel shows the electric field enhancement for the face to face geometry of Na380 dimers. Right panel shows the corresponding contour plot of the polarizability as function of separation distance d and frequency. The green dot marks parameters at which the electric field enhancement is plotted on the right panel.