Electron Energy Loss Spectroscopy from ab-initio TDDFT Calculations: Proof-of-principles using Na Nanostructures

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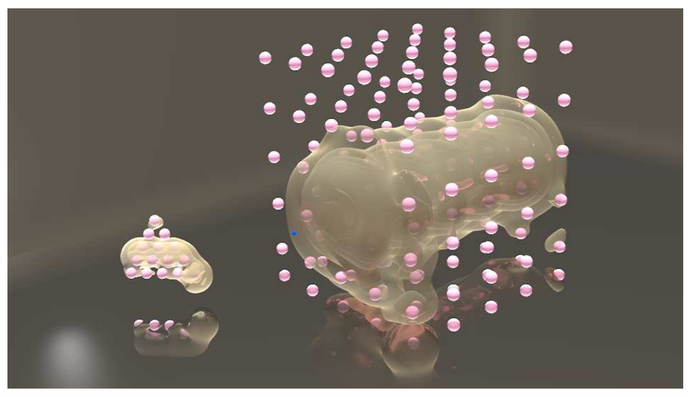
Introduction

Electron Energy Loss Spectroscopy (EELS) has reached in the last decades subnanometric spatial resolution[1]. However, accurate calculations of valence-band EELS with such resolution are scarce, and mostly based on simple models using dielectric functions. Recently, we succeed to map the local induced field associated with plasmonic resonances with atomic-scale resolution from first principles[2]. Based on this method, we present,

- an ab-initio study of the energy loss in the vicinity of metals Na clusters with arbitrary shapes,
- we use time-dependent density functional theory (TDDFT),
- TDDFT in the linear response regime [3], interface with SIESTA [4]



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. Here, we consider a charged particle moving along a line with a velocity **v**. Such a particle creates an electrostatic potential $\delta V_{\text{ext}}(\mathbf{r}, t) = \frac{1}{|\mathbf{r}-\mathbf{R_0}-\mathbf{v}t|}$. The energy loss ΔE and the field enhancement $\mathbf{E}_{\text{ind}}$ read

$$\Delta E = -\frac{1}{\pi}\int_0^{+\infty} \omega Im\left(\delta V_{\text{ext}}^{\mu *}(\omega)\chi_{\mu\nu}\delta V_{\text{ext}}^{\nu}(\omega)\right) d\omega \quad (1)$$

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

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

Electron passing close to a Na triangle

Here, we present the case of an electron shoots outside of the triangle in an orthogonal direction to the triangle plane.

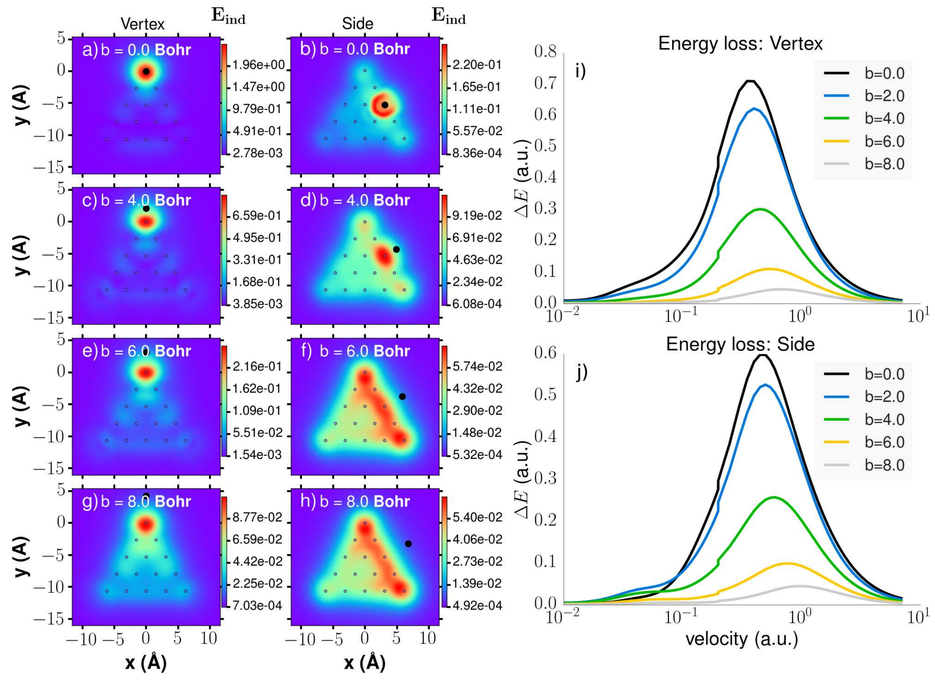


Figure 1 : The Figure shows on the left panel the induced field when the electron is close to a vertex of the triangle (left column) and close to the side of the triangle (right column) for several impact parameters. For short distances, the vertex present a stronger induced field than the side. The right panel shows the energy loss given by equation 1 as function of the electron velocity at the frequency of the maximum of the triangle's polarizability for both cases.

Figure 1 shows that for short distances between the electron and the triangle, the induced field as well as the energy loss are stronger when the electron is close to a vertex than to a side of the triangle.

Peaks shift

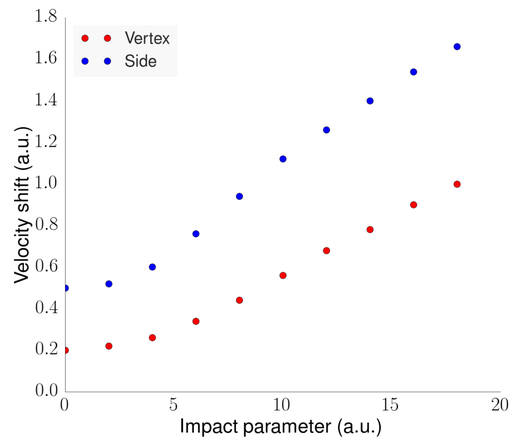


Figure 2 : The velocity shift observed on Figure 1 i) and j) are shown as function of the impact parameters.

Figure 2 shows the velocity peak shift of the Figure 1 i) and j) for the vertex and the side configurations. The peaks from the side configuration (Fig. 1 j) are at higher energies than the vertex ones. A somewhat similar effect is observed in Figure 5, while longer trajectories inside the Na triangle produce maxima of stopping at higher velocities. Column 1 and 2 of Figure 1 shows atomic scale resolution since the induced field of the vertex case is different than the induced field at the proximity of the side. Therefore, our results indicate that valence EELS can provide information on the electronic response and geometrical features of the target with subnanometric resolution.

Time evolution of the induced field

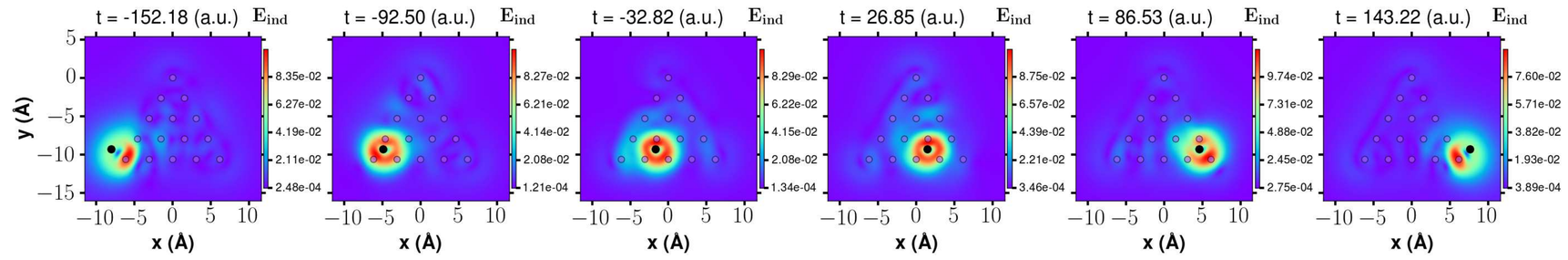


Figure 3 : The evolution of the induced field as function of the time. The black dot shows the position of the electron. Looking at the time evolution really show us the impact of the electron when it is moving through the system.

Electron traversing a Na triangle

In order to understand the density and field distribution induced by the moving electron, we decided to focus on a simple system with a well defined geometry. Therefore, we chose an artificial Na equilateral triangle constituted of 15 atoms and to shoot the electron following trajectories with different lengths inside the triangle. We can observe a clear influence of the distribution of the density change and the electric field with the trajectory of the electron.

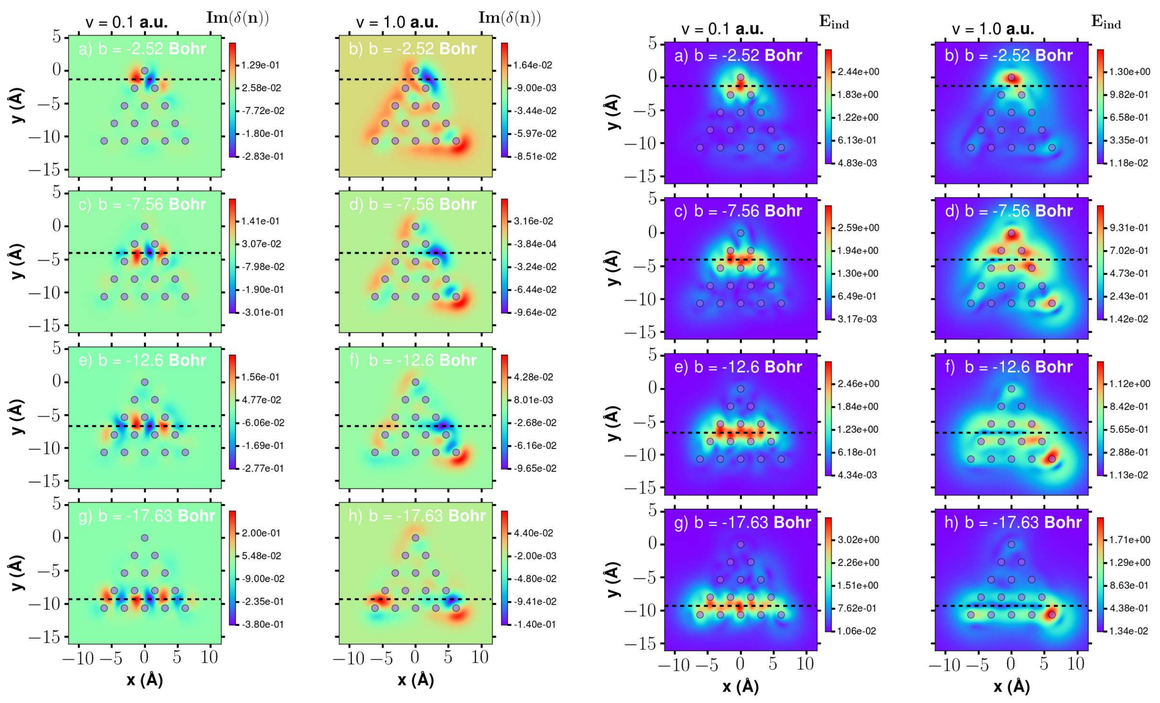


Figure 4 : The Figure shows the imaginary part of the density change in the two right columns and the induce field in the two left columns for one Na_{15} triangle. The electron is shot along the x axis (dashed black lines) with a velocity of 0.1 a.u. and 1.0 a.u. at the frequency of the maximum of the polarizability (2.06 eV).

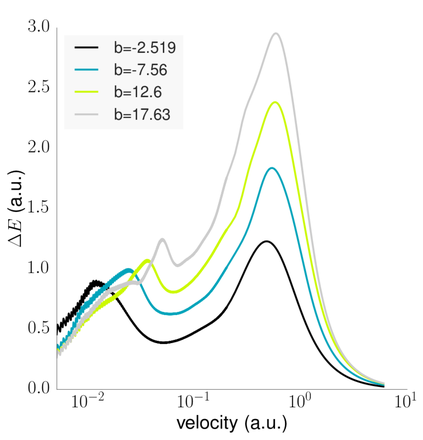


Figure 5 : This Figure shows the change of energy loss as function of the velocity of the electron for the impact parameters shows in Figure 4.

Obviously, the amount of energy lost by the projectile increases with the path length. A less obvious effect, however, is the shift of the maximum of the energy loss versus velocity curves as shown in Figure 5. From equation 1 one can get the energy loss of the electron when it goes through the system for the considered trajectories as function of the velocity of the electron. As one can see in Figure 5 two peaks are present. One at high energy ($\sim$ 10 eV) and another one at lower energy ($\sim 10^{-2} - 10^{-1}$ eV). We observe a blue shift of the lower energy peak as we increase the length of the trajectory within the Na triangle. As expected for longer trajectories inside the Na triangle the energy loss increases. This increase is approximately linearly proportional to the path length at high impact velocity, but shows a more complex dependence on the path length for smaller electron velocities.

3D cubic Na cluster

We study as well a much bigger system than the Na_{15} triangle: a Na cube with 64 atoms. We are mainly interested on this system because at small velocity the energy loss should be linear as function of the electron speed.

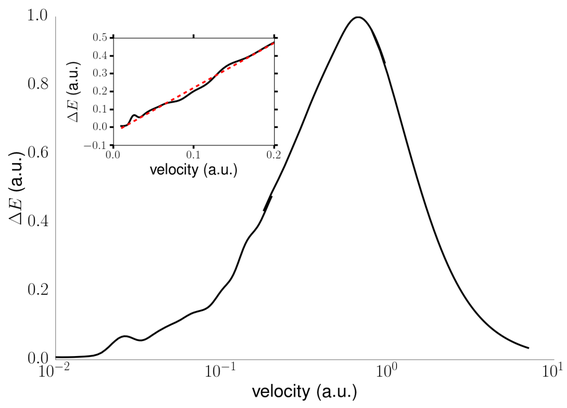


Figure 6 : This figure shows the energy loss of the electron as function of the velocity for a cube of 64 atoms.

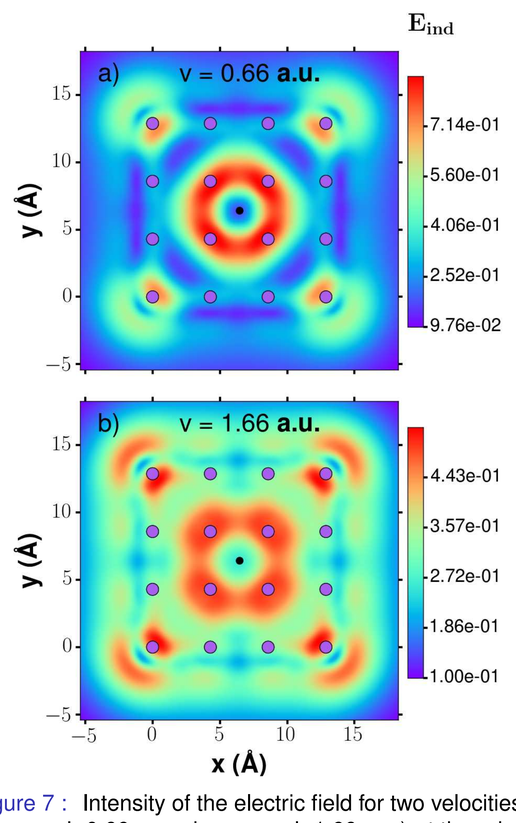


Figure 7 : Intensity of the electric field for two velocities (top panel: 0.66 a.u., down panel: 1.66 a.u.) at the edge of the cube at the the frequency of the maximum of the polarizability (2.216 eV). The electron moves along the perpendicular direction of the plan.

Cubic Na: induced field

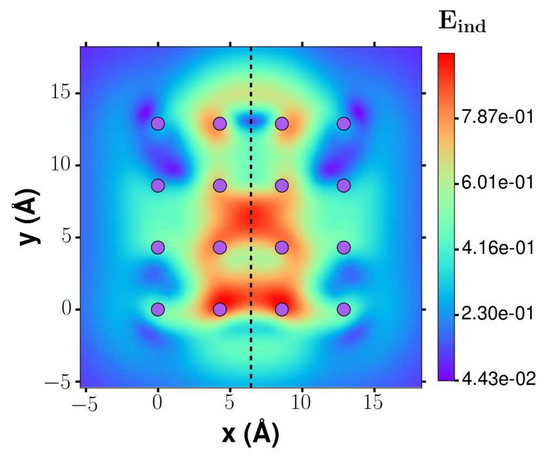


Figure 8 : Intensity of the electric field for a velocity of 0.66 a.u. at the the frequency of the maximum of the polarizability (2.216 eV). The electron is going along the y axis indicated on the Figure.

Conclusion

Our proof-of-principles calculations using simple systems with different geometries and dimensionalities allowed us to understand the dependence of EELS, as well as associated distribution of the induced density and field on such parameters. It is a necessary step before to go to more realistic models. Similarly to the case of the field enhancement in plasmonic nanostructures, where we recently found subnanometric hot spots dependent on the atomic-scale details of the structure [2], here, we show that the energy loss and the corresponding induced density and field strongly depend on the impact parameter and fine structural details of the target. Having a quite good understanding of our method for systems with artificial geometries, we wish now to look at more realistic models of nanoparticles and plasmonic antennas. We believe that this method will provide a good understanding of the valence-band EELS at subnanometric scale.

References

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