Unveiling atomic-scale features in plasmonic nanoparticles using electron beams

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Introduction and motivation

Scanning Transmission Electron Microscope (STEM):

Subnanometric spatial resolution [1].
Offers an alternative way to charaterize plasmon modes [2].

- Small nanoparticles: typically considered as spherical in most theoretical studies.
- Electron energy loss (EEL) spectra: significant **dependence** on the target's **shape**.

Our **aim** is to study the dependence of the **electron energy loss** on the atomistic structure and faceted shape using **classical** and **quantum** models.

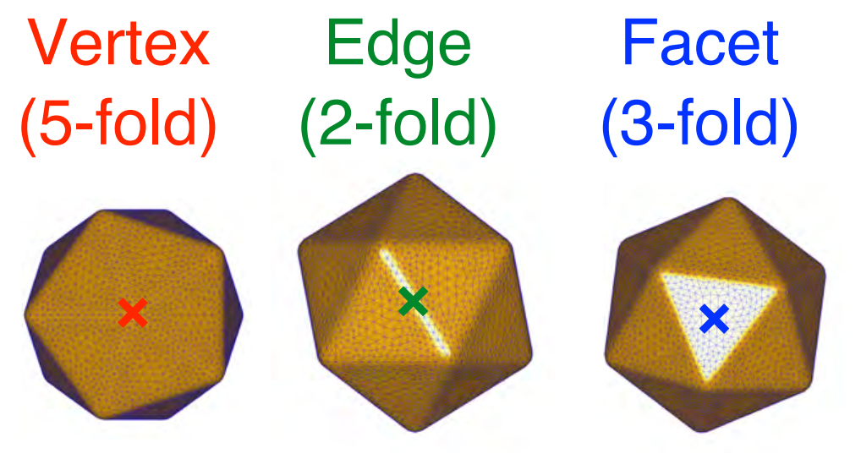
Methods

- **Quantum: Time Dependent Density Functional Theory (TDDFT)**
  Atomistic ab initio calculation [3].
  Electron energy loss probability: $\Gamma_{\mathrm{EELS}}(\omega) = -\frac{1}{\pi}\Im \int d^3r\, \delta V^*_{ext}(\mathbf{r},\omega)\delta n(\mathbf{r},\omega)$
  External potential: $\delta V_{ext}(\mathbf{r},\omega) = |\mathbf{r}_{\mathrm{e}}(t) - \mathbf{r}|^{-1}$
  Induced charge density: $\delta n(\mathbf{r},\omega)$
- **Classical: Boundary Element Method (BEM)**
  Maxwell's equations solver - homogeneous dielectric function & abrupt interfaces [4].
  MNPBEM Matlab Toolbox [5].
  Total energy loss W of q charged particle: $W = -q\int dz \left\{\frac{\partial \phi_{ind}}{\partial z}\right\} = \int_0^\infty \omega\,\Gamma_{\mathrm{EELS}}(\omega)\,d\omega$
  Bulk losses introduced by hand: $\Gamma_{\mathrm{EELS}}(\omega) = \Gamma_{surface}(\omega) + \Gamma_{bulk}(\omega)$

Subnanometric features in NPs

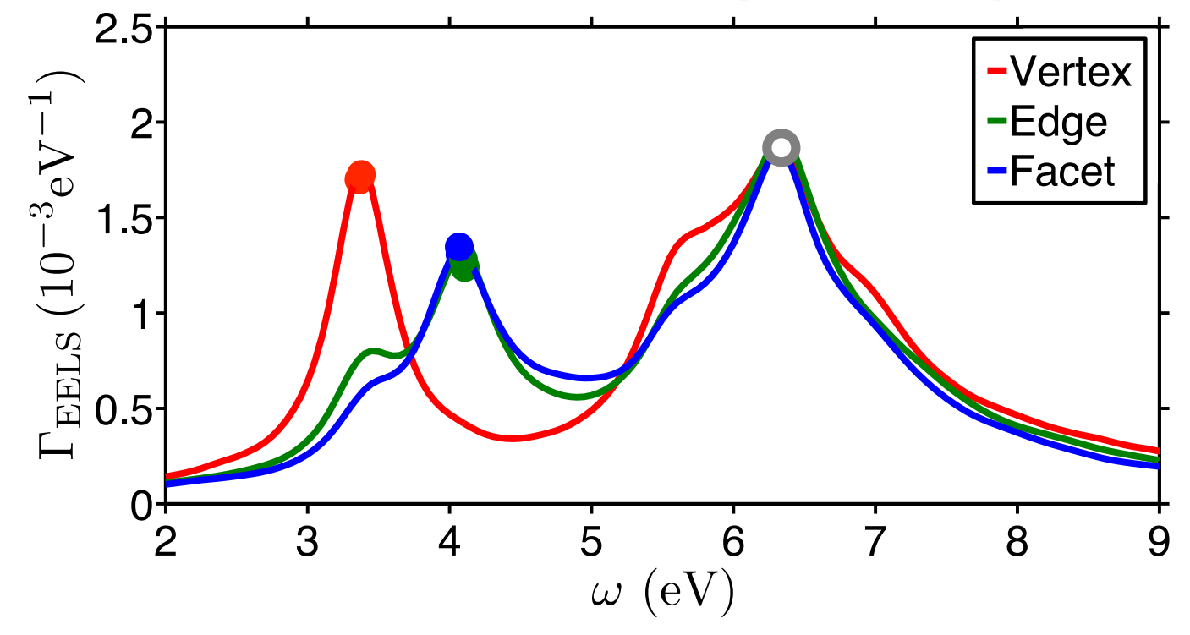
Electron energy loss spectroscopy (EELS)

Trajectories along the symmetry axes

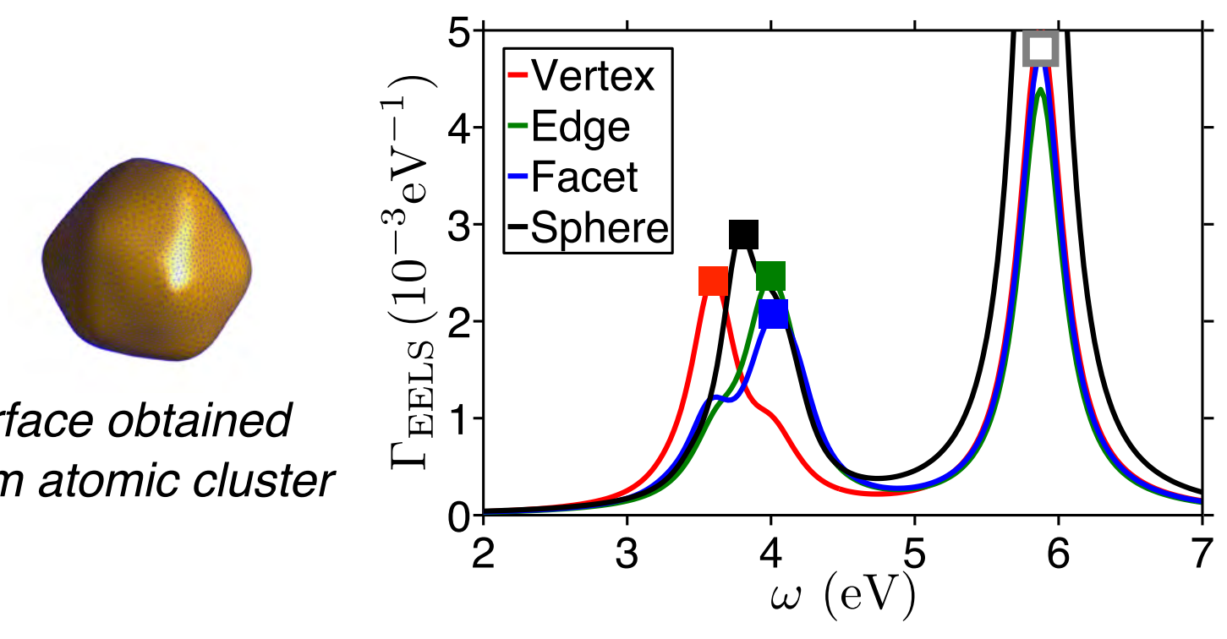



Atomic cluster 380 Na atoms

Quantum atomistic (TDDFT)

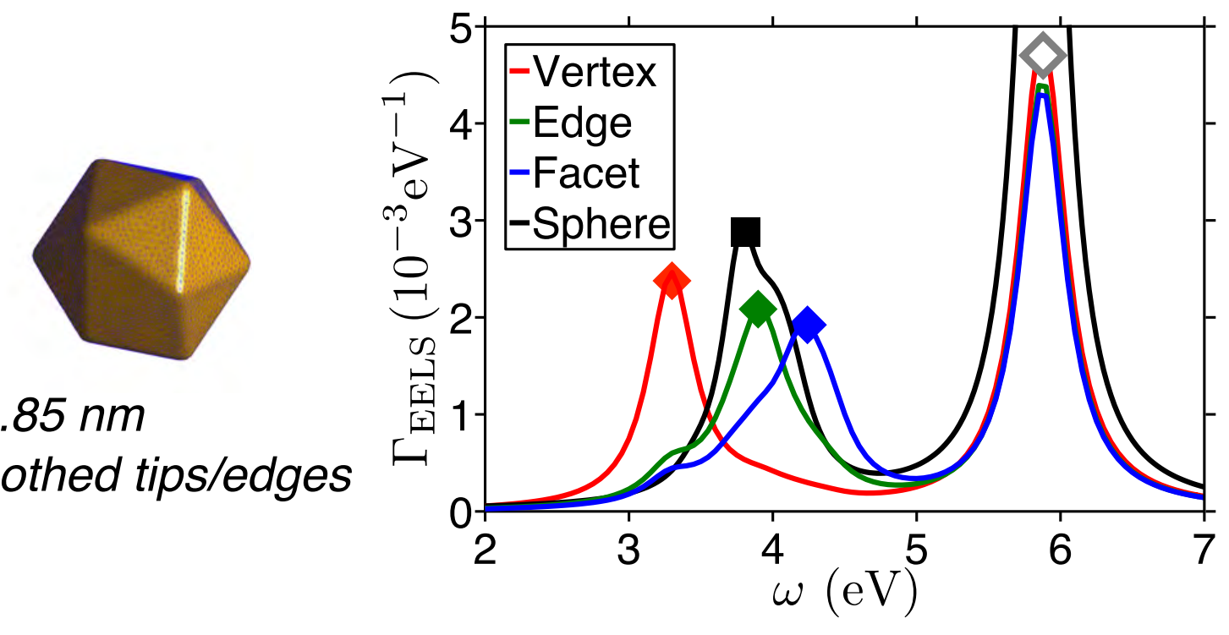


Smooth icosahedron (BEM)



Surface obtained from atomic cluster

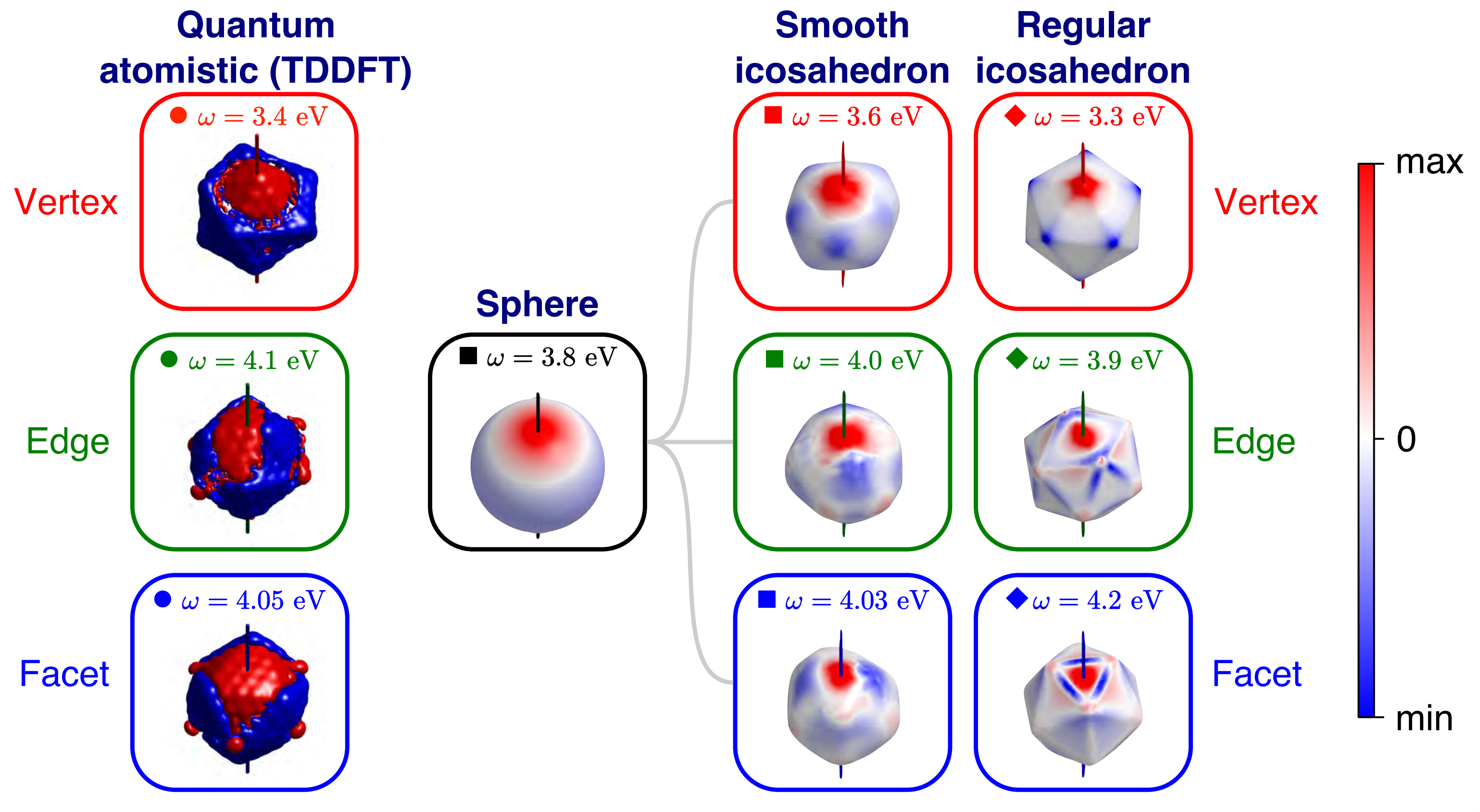
Regular icosahedron (BEM)



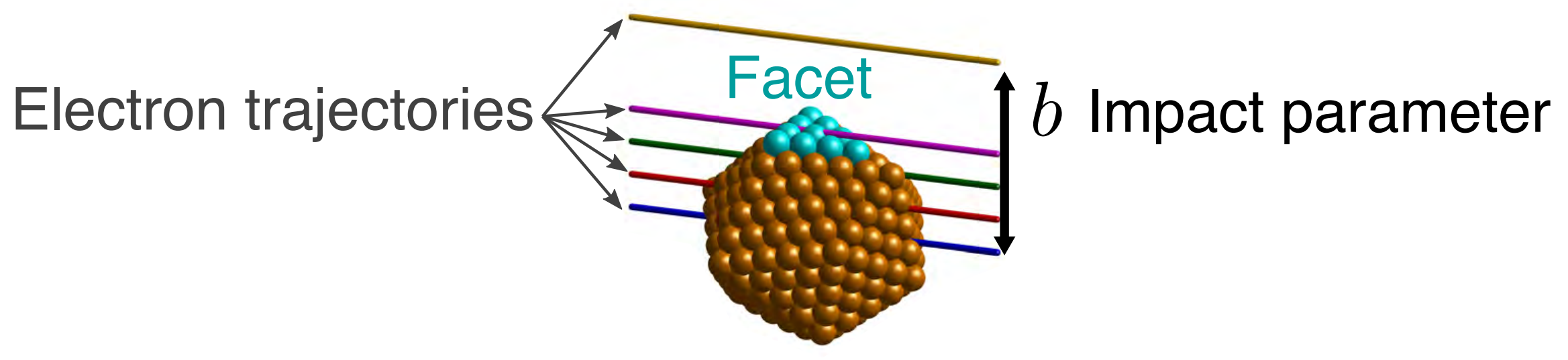
r = 1.85 nm Smoothed tips/edges

- **Atomic-scale features** break the spherical symmetry and mode degeneracy.
- EEL spectra are ruled by **relative symmetry** between NP and electron beam.
- **Classical models** address the influence of atomic-scale **shape** on EELS.

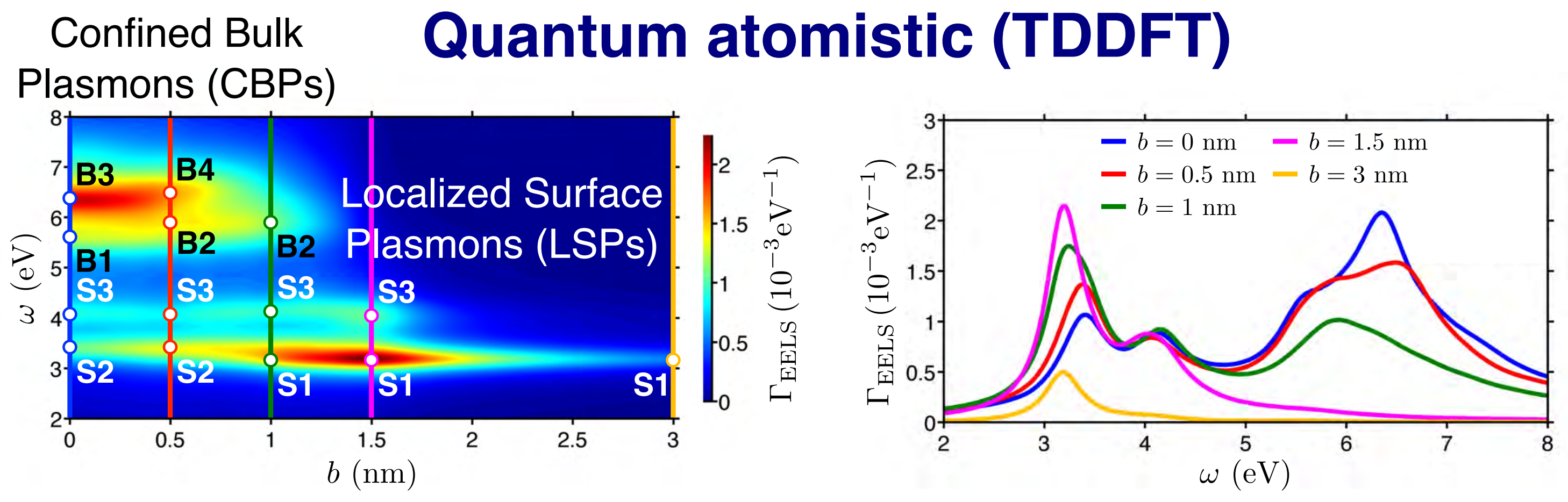
Charge density distribution



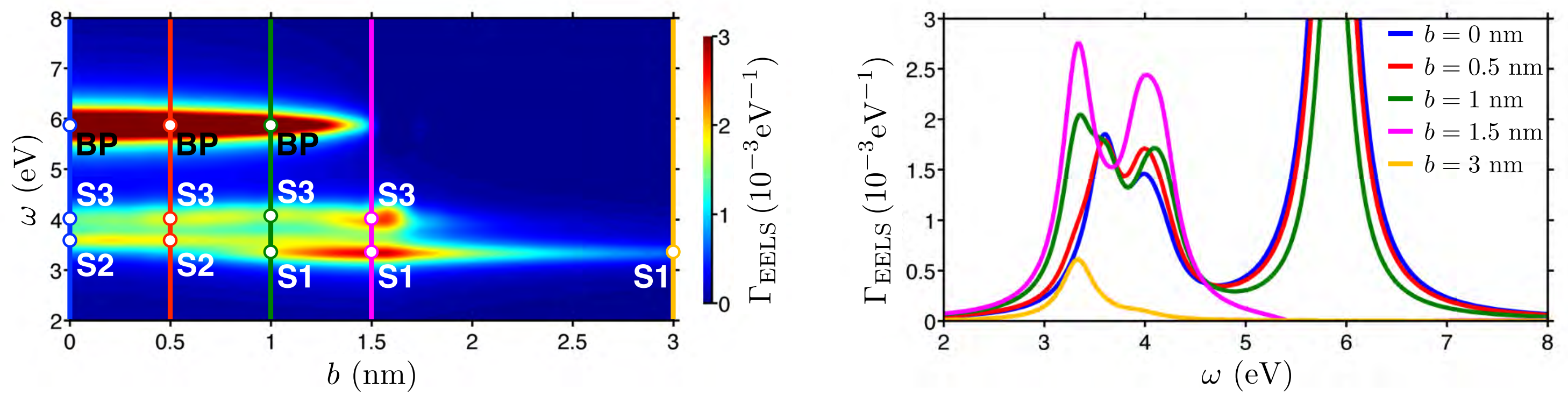
Impact parameter dependence



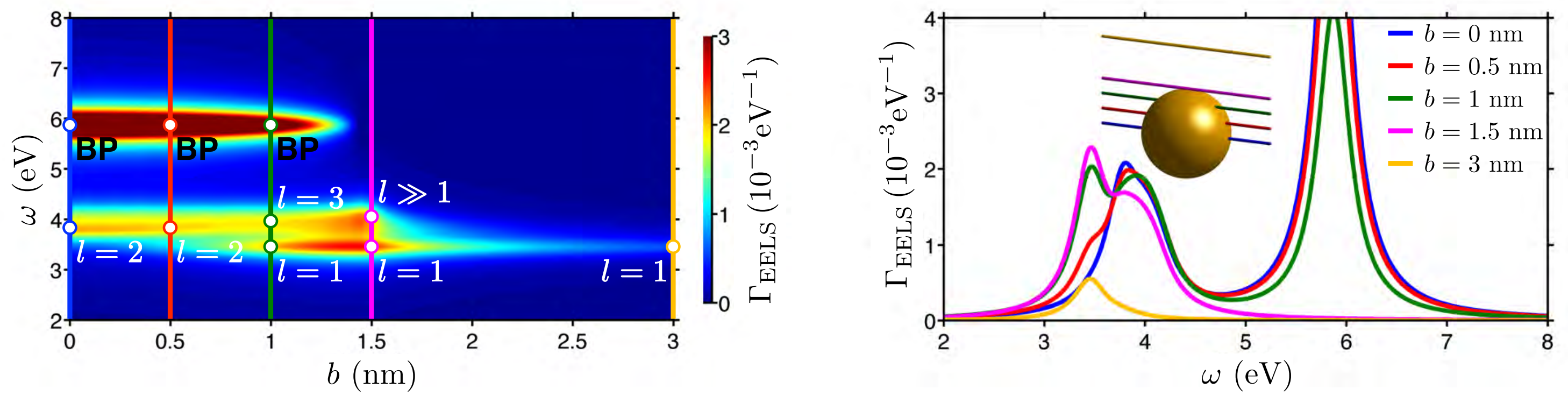
Quantum atomistic (TDDFT)



Smooth icosahedron (BEM)



Sphere (BEM)



- An appropriate **shape** within BEM can capture the fine details of the **atomistic** TDDFT spectra.
- Lower intensity of **higher-order LSP modes** within atomistic TDDFT (due to **non-local** effects).
- Local approaches fail to reproduce **Confined Bulk Plasmons (CBPs)**.
- CBPs can be reproduced within a **hydrodynamic model** [6] for a spherical NP.

Conclusions

- **Atomic-scale features** have to be addresed for small nanoparticles in EELS [7].
- **Classical** approaches **reproduce** qualitatively the TDDFT results at **LSP frequencies** when the **shape** of the NP is addresed properly.
- EEL spectra for penetrating trajectories show excitation of **confined bulk plasmons**, which strongly depend on the **impact parameter** due to symmetry.
- **Classical** models **fail** to describe the **confined bulk plasmons** - we used a **hydrodynamic model** [6] to characterize them.

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