COMSOL CONFERENCE
2017 ROTTERDAM

COMSOL Simulations to Study Nonlocal Properties of an Au Nanoshell using Quantum Hydrodynamic Theory

ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR BIOMOLECULAR NANOTECHNOLOGIES

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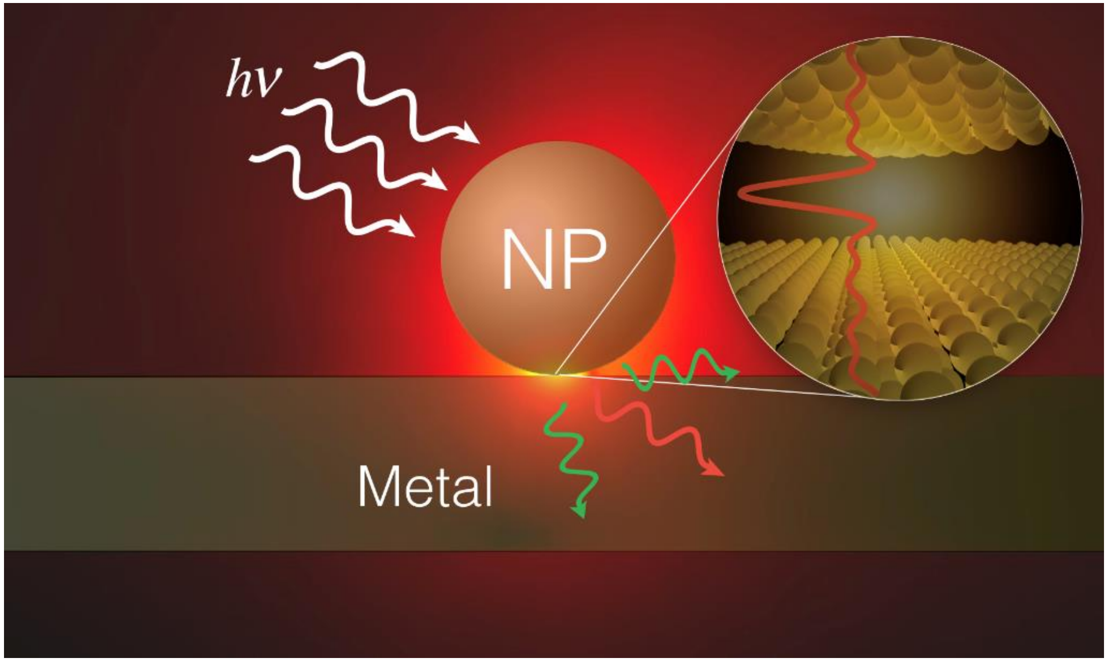
Quantum Hydrodynamic Theory (QHT)

- Purely classical theories fail to describe optical response of very small plasmonic nano-particles or nearly touching plasmonic components.

- QHT provides an excellent method to study both near-field and far-field properties of multiscale plasmonic systems.

- QHT can accurately and efficiently describe:



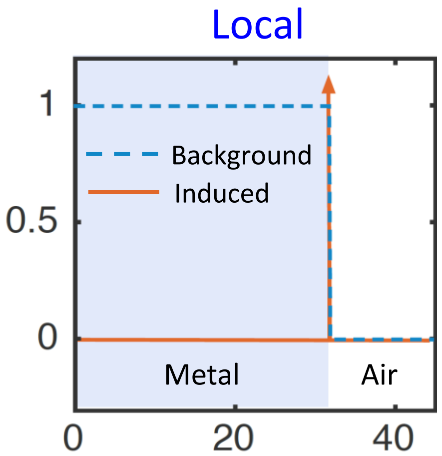
  - Plasmon resonances
  - Electron spill-out
  - Retardation effects

Quantum Hydrodynamic Theory (QHT)

$$\nabla \times \nabla \times \mathbf{E} - \frac{\omega}{c^2}\mathbf{E} = \omega^2 \mu_o \mathbf{P}$$

$$(\omega^2 + i\gamma\omega)\mathbf{P} = -\varepsilon_o \omega_p^2 \mathbf{E}$$

$$n = \frac{1}{e}\nabla \cdot \mathbf{P}$$



C. Ciracì and F. D. Sala, Phys. Rev. B **93**, 205405 (2016).

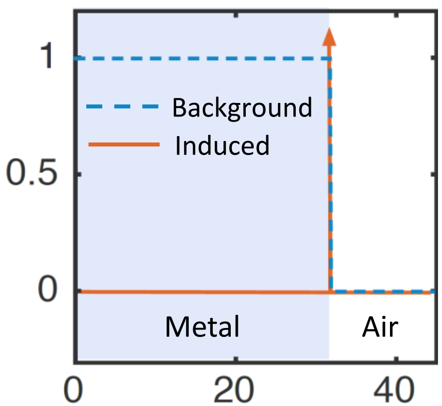
Quantum Hydrodynamic Theory (QHT)

$$\nabla \times \nabla \times \mathbf{E} - \frac{\omega}{c^2}\mathbf{E} = \omega^2 \mu_o \mathbf{P}$$

$$\frac{e n_o}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_1 + (\omega^2 + i\gamma\omega)\mathbf{P} = -\varepsilon_o \omega_p^2 \mathbf{E}$$

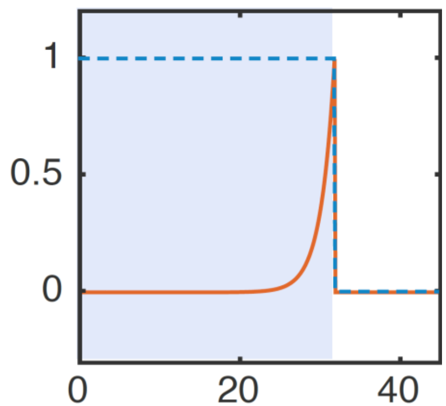
$$n = \frac{1}{e}\nabla \cdot \mathbf{P}$$

Local



$$G[n] = 0$$

Thomas-Fermi



$$G[n] = T_{\mathrm{TF}}[n] = \beta^2 \nabla(\nabla \cdot \mathbf{P})$$

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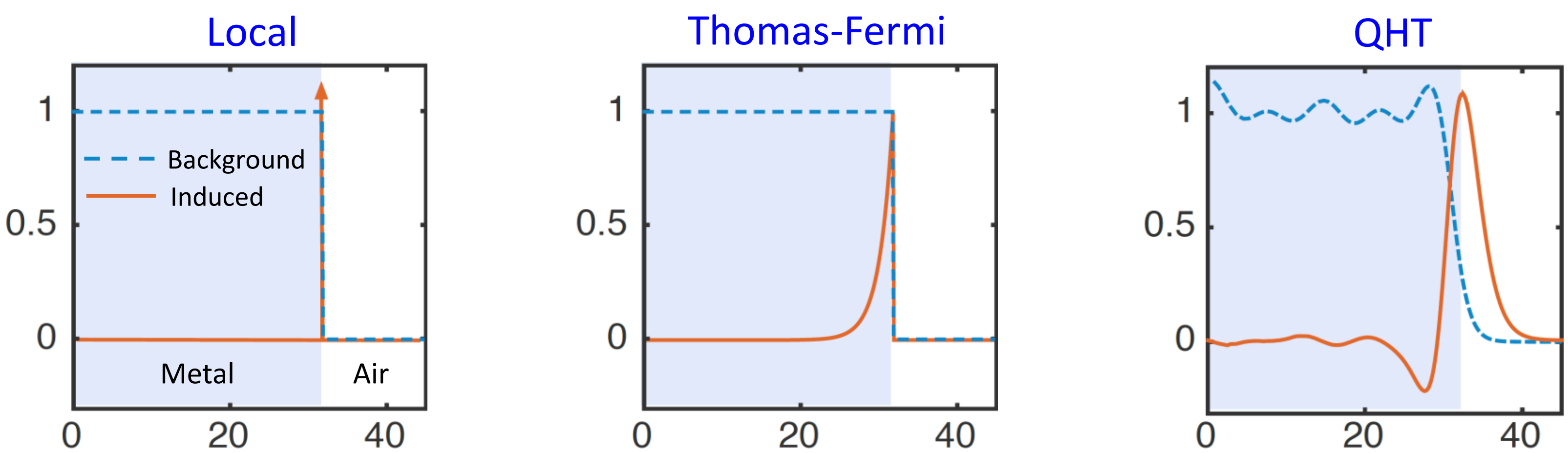

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$G[n] = T_{\mathrm{TF}}[n] = \beta^2 \nabla(\nabla \cdot \mathbf{P})$

$G[n] = T_{\mathrm{TF}}[n] + T_{\mathrm{vW}}[n, \nabla n] + v_{xc}[n]$

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Weak Form

$$\frac{en_o}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_1 + (\omega^2 + i\gamma\omega)\mathbf{P} = -\varepsilon_o\omega_p^2\mathbf{E}$$

- By multiplying the above equation with the test function $\widetilde{\mathbf{P}}$ and integrating by parts gives the following weak form:

$$\int -\frac{n_o e}{m_e}\left(\frac{\delta G}{\delta n}\right)_1 (\nabla\cdot\widetilde{\mathbf{P}}) + [(\omega^2 + i\gamma\omega)\mathbf{P} + \varepsilon_o\omega_p^2\mathbf{E}]\cdot\widetilde{\mathbf{P}}dV = 0$$

- It allows us to avoid calculating the gradient of the energy functional and the derivatives are distributed over the test function.
- $G[n] = T_{\mathrm{TF}}[n] + T_{\mathrm{vW}}[n,\nabla n] + v_{XC}[n].$

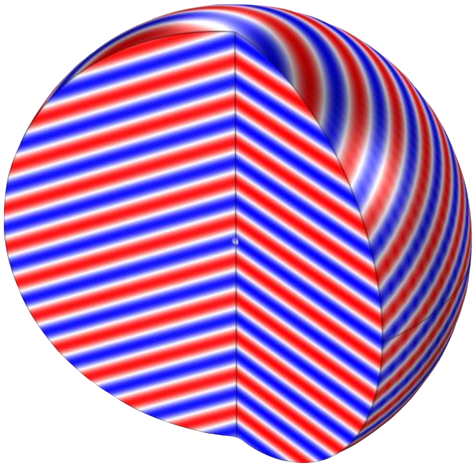
$$\left(\frac{\delta T_{\mathrm{vW}}}{\delta n}\right)_1 = (E_h a_0^2)\frac{1}{4}\left[\frac{\nabla n_0\cdot\nabla n_1}{n_0^2} + \frac{\nabla^2 n_0}{n_0^2}n_1 - \frac{|\nabla n_0|^2}{n_0^3}n_1 - \frac{\nabla^2 n_1}{n_0}\right]$$

- T_{vW} contains second order derivatives. We introduce a working variable $\mathbf{F}$, as:

$$\mathbf{F} = \nabla n \quad \Rightarrow \quad \nabla\cdot\mathbf{F} = \nabla^2 n$$

Axisymmetry

- Macroscopic plasmonic systems with subnanometer gaps: a multiscale problem.
- Full 3D implementation of such systems is computationally extremely demanding.
- Exploiting symmetry of the structures makes the task much easier.
- All fields can be decomposed in terms of azimuthal mode number, $m \in \mathbb{Z}$. For a vector field $\mathbf{v}$:



$$\mathbf{v}(\rho, \phi, z) = \sum_{m \in \mathbb{Z}} \mathbf{v}^{(m)}(\rho, z)\, e^{-im\phi}$$

- This method is termed as 2.5D formulation and its advantage is that an $N_\rho \times N_z \times N_\phi$ sized problem reduces to a problem of size $N_\rho \times N_z$.

3D problem reduces to $(2m_{\max} + 1)$ 2D problems.

C. Ciracì *et. al.*, Opt. Express, **21**, 9397 (2013).

Numerical Implementation

Thus, the final system of equations to solve for the unknown variables $\mathbf{E}$, $\mathbf{P}$ and $\mathbf{F}$ takes the expressions:

$$2\pi \int (\nabla \times \mathbf{E}^{(m)}) \cdot (\nabla \times \tilde{\mathbf{E}}^{(m)}) - (k_o^2 \mathbf{E}^{(m)} + \mu_o \omega^2 \mathbf{P}^{(m)}) \cdot \tilde{\mathbf{E}}^{(m)} \rho d\rho dz = 0$$

$$2\pi \int -\frac{n_o e}{m_e} \left(\frac{\delta G}{\delta n}\right)_1^{(m)} (\nabla \cdot \tilde{\mathbf{P}}^{(m)}) + [(\omega^2 + i\gamma\omega)\mathbf{P}^{(m)} + \varepsilon_o \omega_p^2 \mathbf{E}^{(m)}] \cdot \tilde{\mathbf{P}}^{(m)} \rho d\rho dz = 0$$

$$2\pi \int -(\nabla \cdot \mathbf{P}^{(m)})(\nabla \cdot \tilde{\mathbf{F}}^{(m)}) - e\mathbf{F}^{(m)} \cdot \tilde{\mathbf{F}}^{(m)} \rho d\rho dz = 0$$

Maxwell Equations and the polarization equations are written according to the following definitions:

$$\nabla \cdot \mathbf{v}^{(m)} := \left(\frac{1}{\rho} + \frac{\partial}{\partial \rho}\right) v_\rho^{(m)} - \frac{im}{\rho} v_\phi^{(m)} + \frac{\partial}{\partial \rho} v_z^{(m)}$$

$$\nabla \times \mathbf{v}^{(m)} := \hat{\rho}\left(-\frac{\partial v_\phi^{(m)}}{\partial z} - \frac{im}{\rho} v_z^{(m)}\right) + \hat{\phi}\left(\frac{\partial v_\rho^{(m)}}{\partial z} - \frac{\partial v_z^{(m)}}{\partial \rho}\right) + \hat{z}\left(\frac{v_\phi^{(m)}}{\rho} - \frac{\partial v_\phi^{(m)}}{\partial \rho} + \frac{im}{\rho} v_z^{(m)}\right)$$

Numerical Implementation

Thus, the final system of equations to solve for the unknown variables $\mathbf{E}$, $\mathbf{P}$ and $\mathbf{F}$ takes the expressions:

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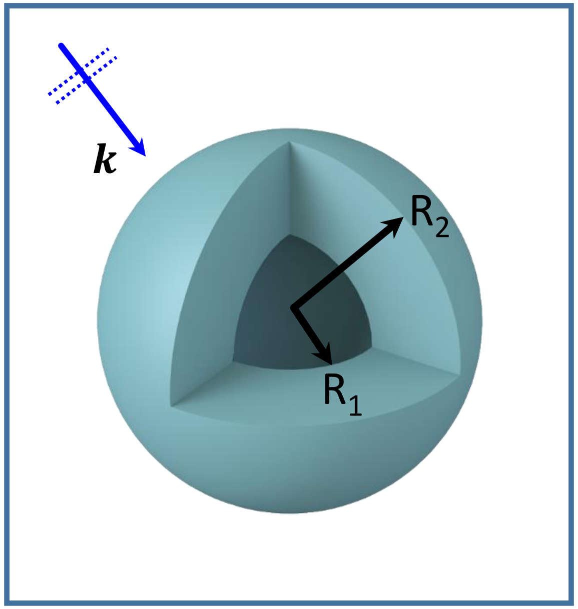
$$2\pi \int -(\nabla \cdot \mathbf{P}^{(m)})(\nabla \cdot \tilde{\mathbf{F}}^{(m)}) - e\mathbf{F}^{(m)} \cdot \tilde{\mathbf{F}}^{(m)} \rho d\rho dz = 0$$

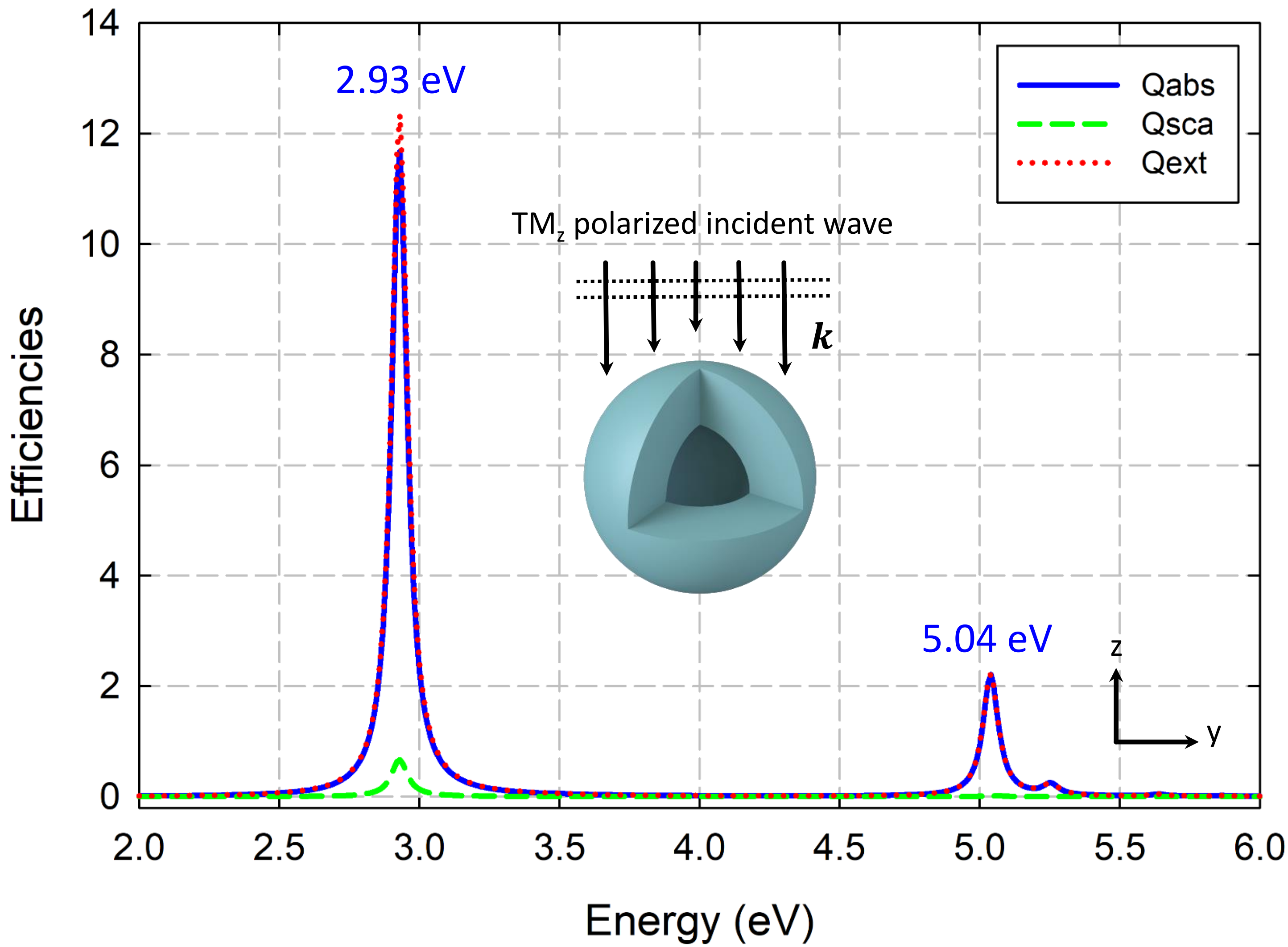
- For specific cases, the cylindrical harmonic expansion converges rapidly and therefore it can be truncated at a relatively small $m = m_{\max}$ (For subwavelength structures $m_{\max} < 3$).
- A parity condition relating positive and negative azimuthal number exists which further reduces the computational load by a factor of 2.
- Thus, reducing extremely large computational load in terms of memory and processing time.

Plasmonic Nanoshell: Example

- By using the Quantum Hydrodynamic Theory we study the optical properties of plasmonic nanoshells with vacuum core placed in vacuum.
- The nanoparticle with inner radius R_1=2nm and outer radius R_2=3.72nm is modeled with a Drude dielectric function.
- We investigate the nanoparticle under plane wave excitation by using the FEM implementation based on 2.5D technique.



Plasmonic Nanoshell: Example



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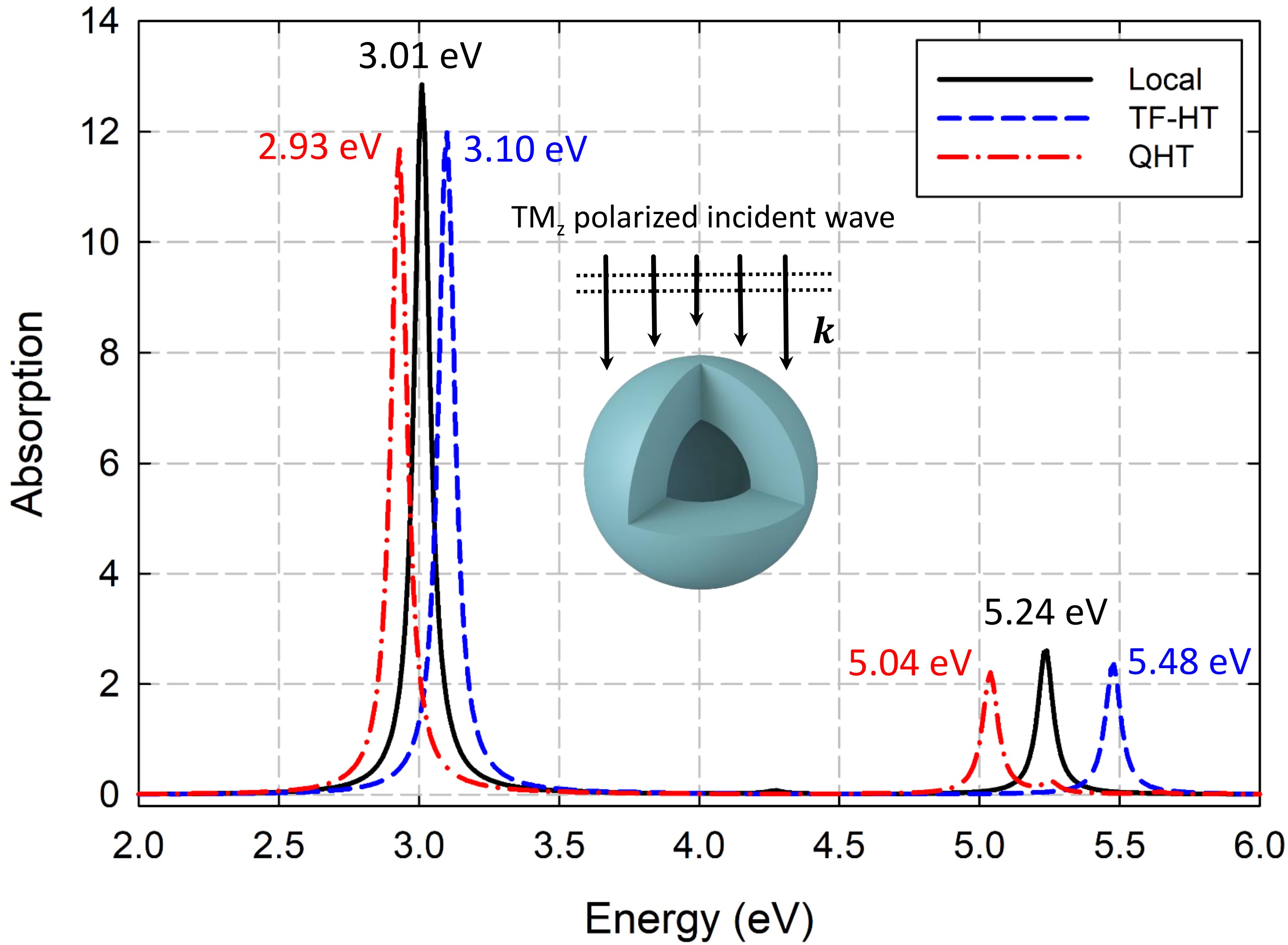
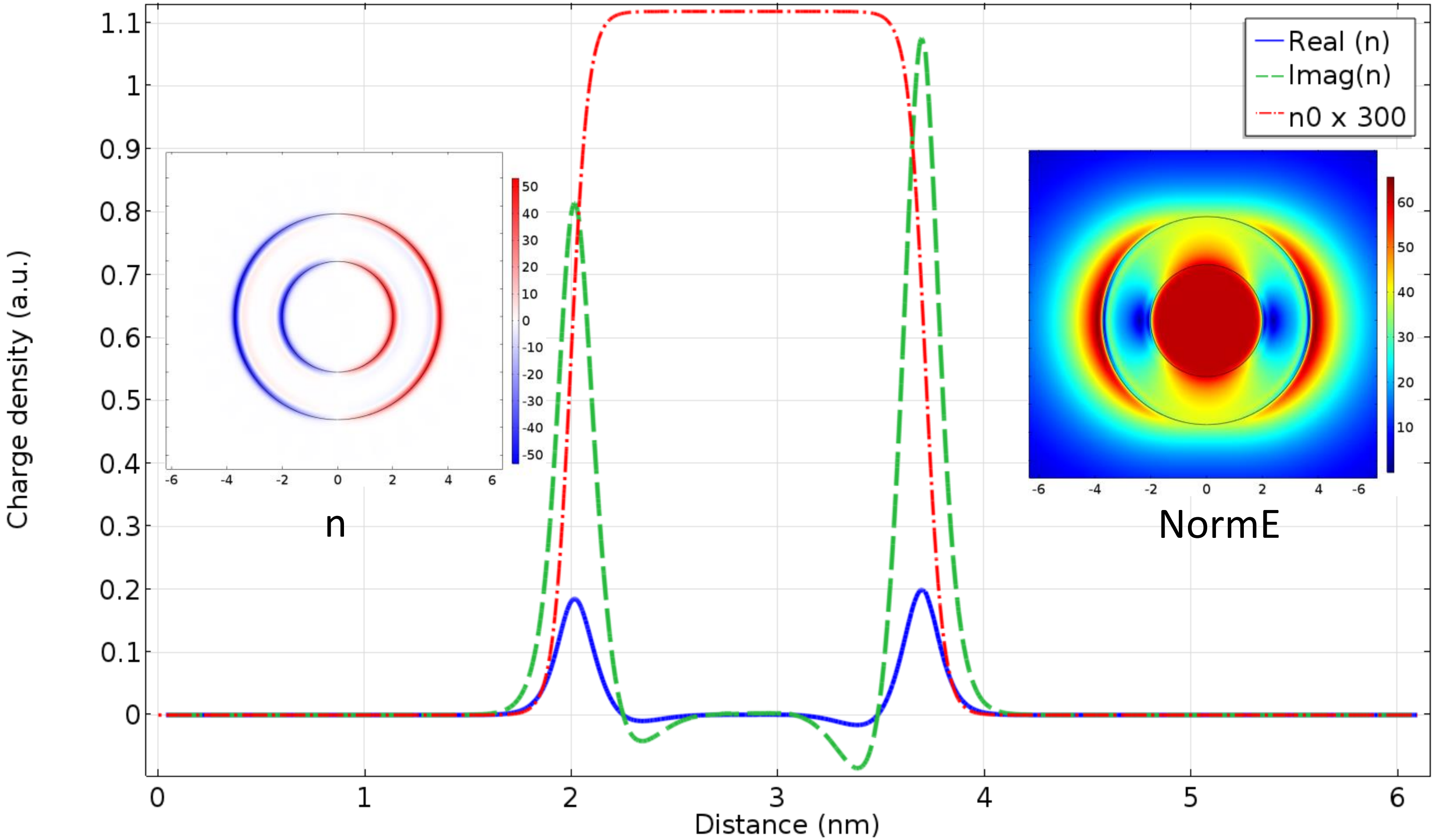


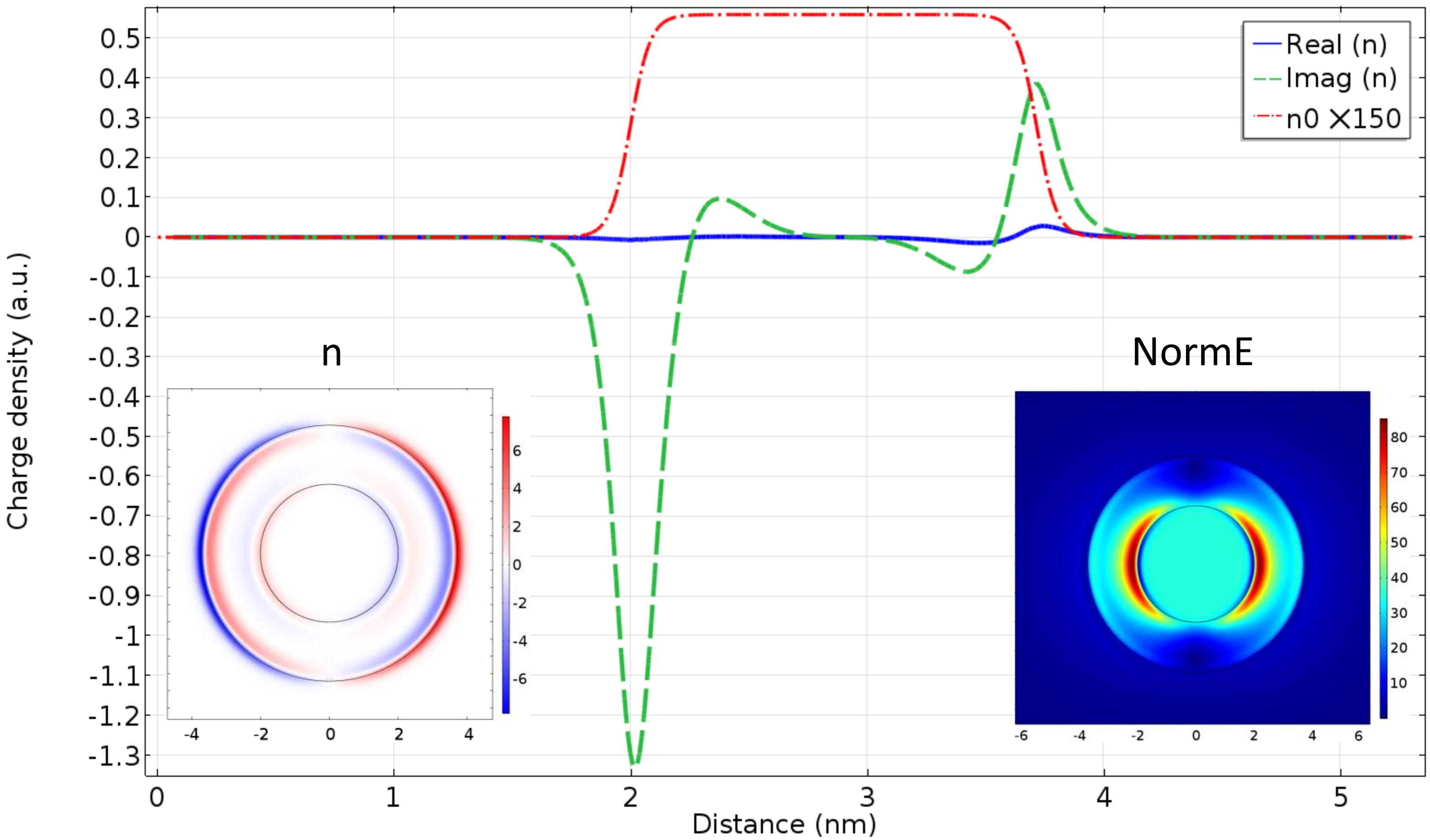
Plasmonic Nanoshell: Example

At lower energy mode (E=2.93 eV)

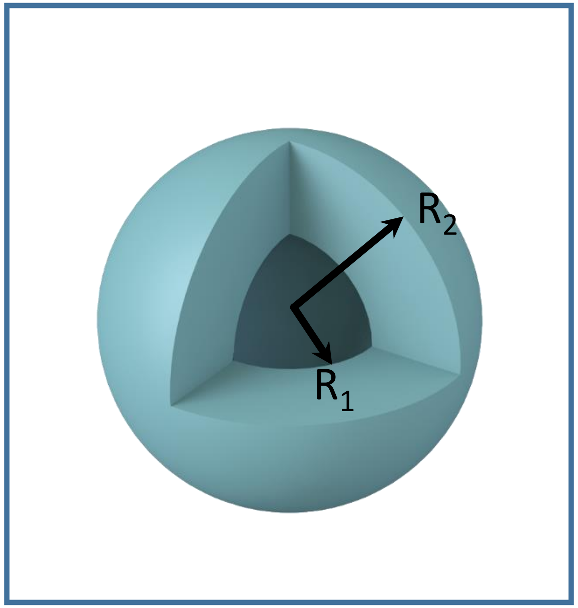


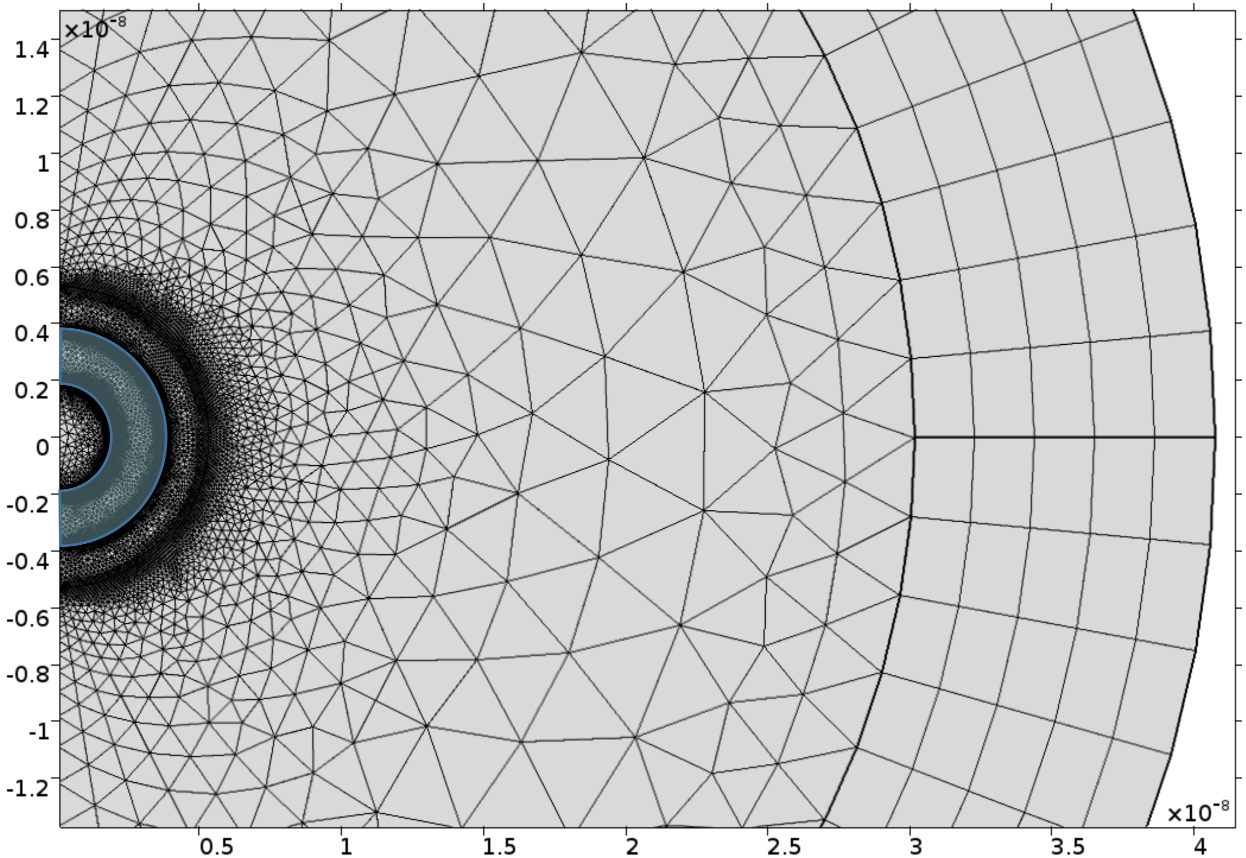
Plasmonic Nanoshell: Example

At higher energy mode (E=5.04 eV)



Plasmonic Nanoshell: Example





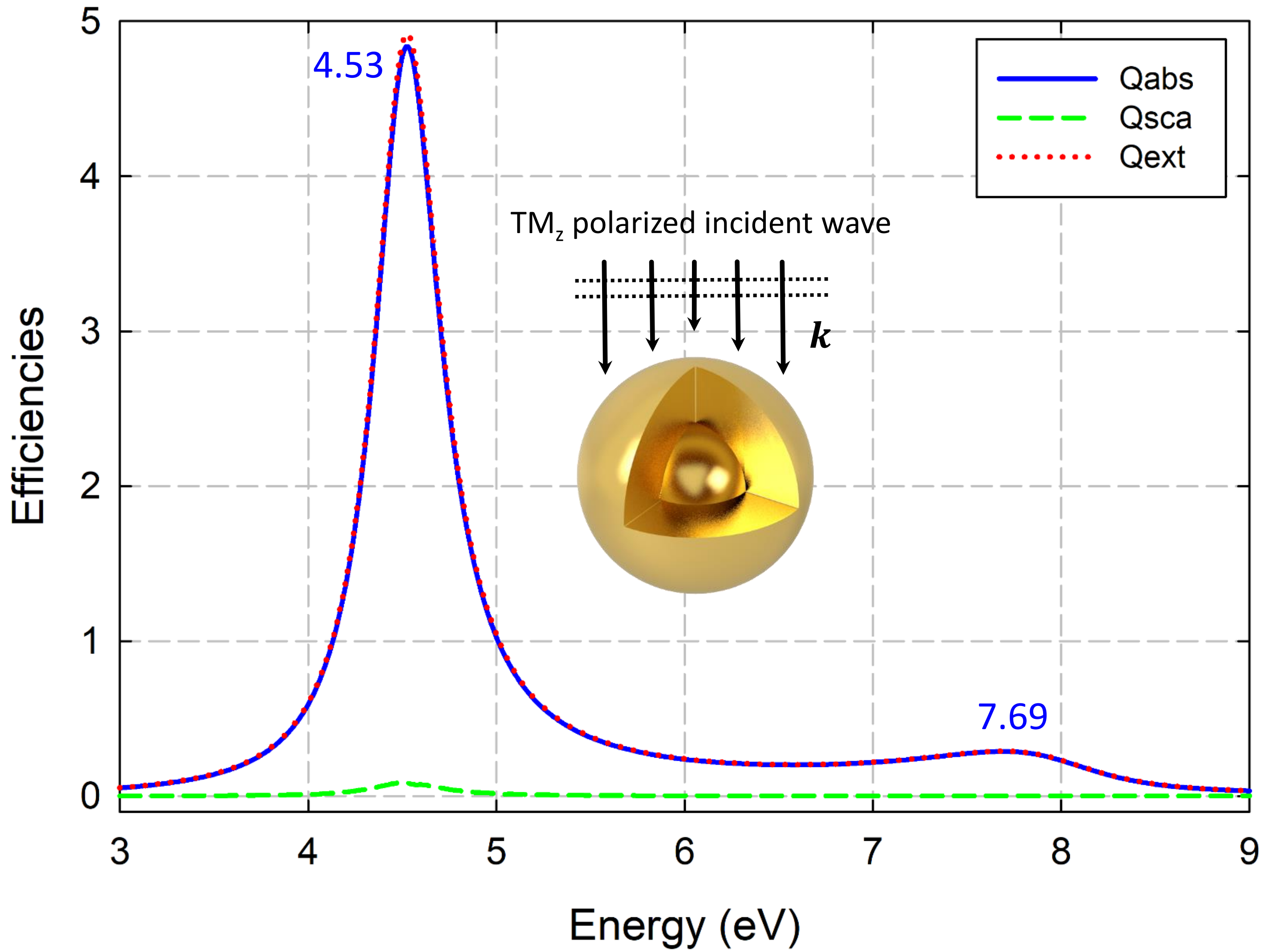
Far field properties:

14378 domain elements
675 boundary elements.
10 GB memory is required

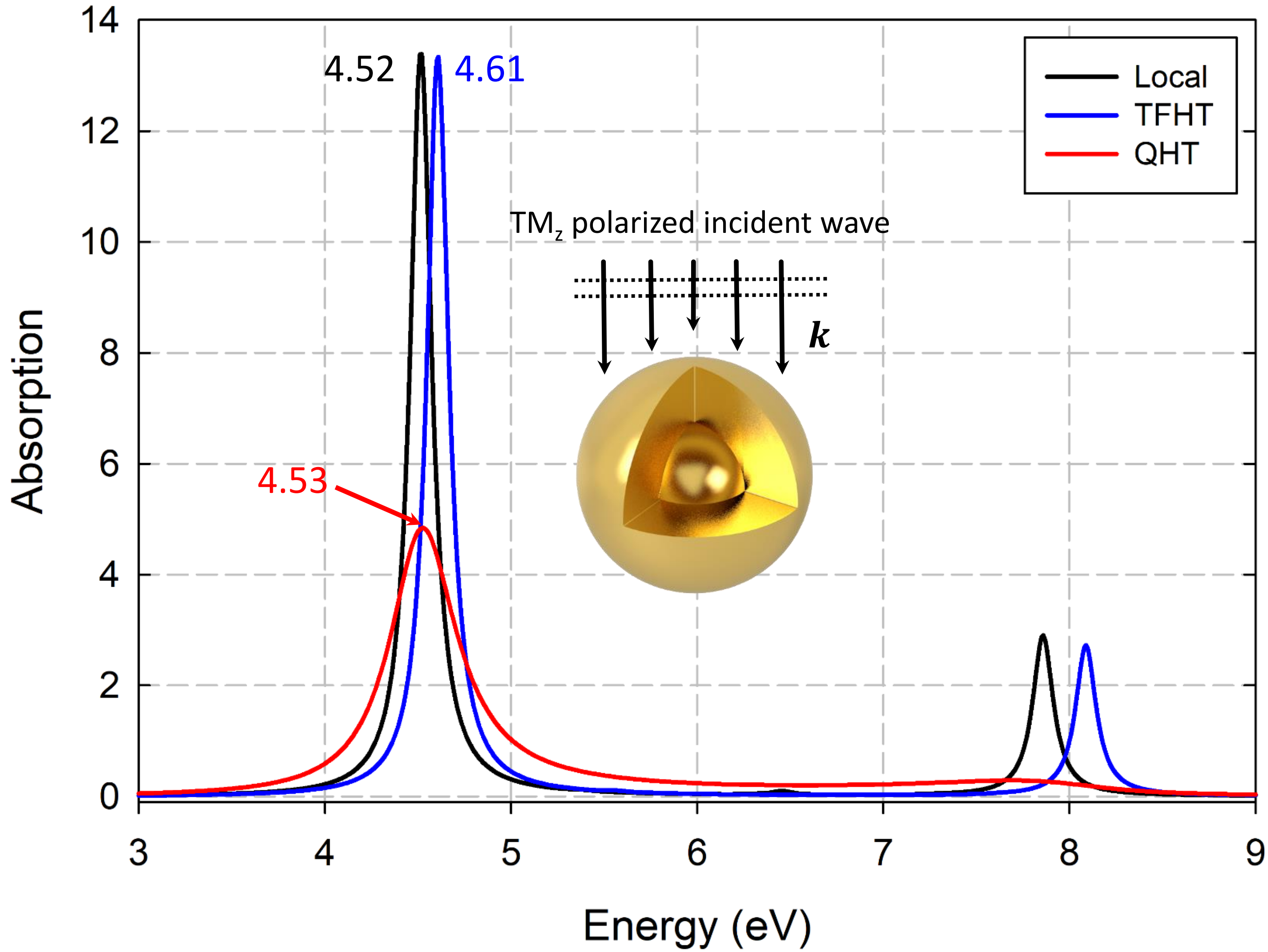
Near field properties:

44852 domain elements
1271 boundary elements.
32 GB memory is required

Plasmonic Nanoshell: Example



Plasmonic Nanoshell: Example



Conclusions

- QHT method can describe the full range of effects going from the nonlocal/spill-out effect up to retardation effects.
- We have implement the method using 2.5D technique which allows to efficiently compute the absorption spectra of the axisymmetric structures by remarkably reducing the computational load.
- FEM allows us to use different type of mesh for a geometry. We used a rough mesh in the continuous domain and a fine mesh at the metallic surface/boundaries.
- We found that Lagrange elements work pretty well in the domain where fields are continuous and they give much more "stable" solutions.


Thank you
for your kind attension!