New Trends in Computational Plasmonics

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... the Romans Were Nanotechnology Pioneers

Lycurgus Cup, 4th century A. D.
(British Museum)
Nowadays Applications of Metal Nanoparticles (MNPs)
Outline

- **Introduction to Plasmonics**
  - Metal nanoparticles as optical antennas
  - Experimental challenges and future directions

- **LSPs within the Classical Description**
  - Strong coupling analysis example (DDA)
  - Plasmon blockade in the classical picture (BEM)

- **LSPs in the Semi-Classical framework**
  - TF-Hydrodynamic Models
  - Towards a Quantum Hydrodynamic Theory

- **LSPs within the Quantum-Mechanical Scheme**
  - Potentialities and limits of the Spherical Jellium Model
  - Advantages of Density Functional Tight Binding Method
Introduction to Plasmonics

Metal nanoparticles as optical antennas
Experimental challenges and future directions

A. E. Koenderink,
Single-Photon Nanoantennas, ACS Photonics, 4, 710 (2017)
MNPs vs Optical Antennas: the Physics Behind ..

\[ \vec{E}(\vec{r}, \omega) = \vec{E}_0 e^{i(k \cdot \vec{r} - \omega t)} \]

A. F. Koenderink,
Single-Photon Nanoantennas
ACS Photonics, 4, 710 (2017)

P. Bharadwaj et al., Optical Antennas, Advances in Optics and Photonics 1, 438–483 (2009)
Optical Antennas Engineering and their FOM

\[ l(\vec{r}, \omega_{\text{pump}}, \omega_{\text{em}}) \propto P_{\text{pump}}(\vec{r}, \omega_{\text{pump}}) \cdot \varphi(\vec{r}, \omega_{\text{em}}) \cdot C_{\text{NA}}(\vec{r}, \omega_{\text{em}}) \]

1. Dipole resonator
2. Phased array
3. Patch/MIM-based
4. Nano-patch antenna


Optical Antennas Plethora: Current Challenges

I-K. Ding et al.,
Plasmonic back reflectors: plasmonic dye-sensitized solar cells,

C. Fumeaux et al.,
Polarization Response of Asymmetric-Spiral Infrared Antennas,

L. Novotny,
From near-field optics to optical antennas,

P. Gerardo,
BioNem Laboratory

D. O. Sigle et al.,
Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic,
LSPs within the Classical Description

- Strong coupling analysis example (DDA)
- Plasmon blockade in the classical picture (BEM)

I.-K. Ding et al.,
Plasmonic back reflectors: plasmonic dye-sensitized solar cells,
TDBC-LSPs Coupling: Effects of Oxide (DDA)

J-Aggregated cyanine dyes layer

Ag Disks on Ag+Ag$_2$O Disks

SEM image (0 h) SEM image (72 h)

TDBC-LSPs Coupling: Effects of Oxide (DDA)

Aging Time $= 0\ h$
$g = 0.17\ eV$

Aging Time $= 24\ h$
$g = 0.20\ eV$

TDBC-LSPs Coupling: Effects of Oxide (DDA)

TDBC-LSPs Coupling: Effects of Oxide (DDA)

(a) Metal-oxide effective dielectric function

\[ \varepsilon_{\text{eff}} = \varepsilon_{\text{Ag}} \frac{2F(\varepsilon_{\text{Ag}_2\text{O}} - \varepsilon_{\text{Ag}}) + \varepsilon_{\text{Ag}_2\text{O}} + 2\varepsilon_{\text{Ag}}}{2\varepsilon_{\text{Ag}} + \varepsilon_{\text{Ag}_2\text{O}} + F(\varepsilon_{\text{Ag}} - \varepsilon_{\text{Ag}_2\text{O}})} \]

(b) Complex dielectric function of the J-aggregated dyes

\[ \varepsilon_{\text{TDBC}} = \varepsilon_{\infty} - f \frac{\omega_{\text{exc}}^2}{\omega^2 - \omega_{\text{exc}}^2 + i\gamma_{\text{exc}} \omega} \]

\[ F = \frac{V_{\text{Ag}_2\text{O}}}{V_{\text{Disk}}} \]

Oxide volume fraction

TDBC-LSPs Coupling: Effects of Oxide (DDA)

\[ \Gamma = \Gamma_0 + \frac{4g^2}{\gamma_{SP}} \]

\[ g = 0.168 \text{ eV} \]

Plasmon Blockade with Au Dimers (BEM)

Nonlinear shift

\[ U_{nl} = \frac{\hbar \omega_0}{\varepsilon_0} \int d^2 \vec{r} \chi^{(3)}(\vec{r})|\xi(\vec{r})|^4 \]

F. Alpeggiani, S. D’Agostino, D. Sanvitto and D. Gerace,
.. what about the classical field in the tunneling and contact regimes?

1/D divergence

R. Esteban et al.,
LSPs in the Semi-Classical Framework

- TF-Hydrodynamic Models
- Towards a Quantum Hydrodynamic Theory

*D. O. Sigle et al.,*
Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic,
*ACS Nano, 9 (1), 825 (2015)*
.. what about Multiscale Plasmonic Systems?


D. Yoo et al., High-Throughput Fabrication of Resonant Metamaterials With Ultrasmall Coaxial Apertures via Atomic Layer Lithography, Nano Lett. 16, 2040 (2016)

TF-Hydrodynamic Models


Generalized Nonlocal Optical Response model (GNOR)

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \]

\[ \varepsilon_L(\omega, k) = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega - \beta^2 k^2} \]

\[ \beta^2 \rightarrow \xi^2 = \beta^2 + D(\gamma - i \omega) \approx \beta^2 - i \omega D \]
Nonlocality in Strong-Coupling

\[ S(\omega) = \frac{\hbar \omega}{2\pi} q(\omega) \Gamma(\omega) S'(\omega) \]

\[ S'(\omega) = \left( \frac{1}{i[\omega_0 - \omega - \delta\omega(\omega)] + \frac{1}{2} \Gamma(\omega)} \right)^2 \]

\[ \delta\omega(\omega) = \frac{\omega^2}{\hbar \varepsilon_0 c^2} \tilde{p}_0 \text{Re} \left[ G_{sc}(\vec{r}, \vec{r}_0, \omega) \right] \tilde{p}_0 \]

Towards a Quantum Hydrodynamic Theory (QHT)

TF-HT

KSH/QHT1

\[ \nabla \times \nabla \times \mathbf{E} - \frac{\omega^2}{c^2} \mathbf{E} = \omega^2 \mu_0 \mathbf{P} \]

\[ \beta^2 \nabla (\nabla \cdot \mathbf{P}) + \left( \omega^2 + i \gamma \omega \right) \mathbf{P} = -\varepsilon_0 \omega_p^2 \mathbf{E} \]

\[ \beta^2 \rightarrow \xi^2 = \beta^2 + D(\gamma - i \omega) \approx \beta^2 - i \omega D \]

\[ \frac{e n_0}{m_e} \nabla \left( \frac{\delta G_n^\alpha}{\delta n} \right)_1 + \left( \omega^2 + i \gamma \omega \right) \mathbf{P} = -\varepsilon_0 \omega_p^2 \mathbf{E} \]

\[ G[n] \approx G_n[n] = \left( T_s^{TF}[n] + \frac{1}{\eta} T_s^w[n] \right) + E_{xc}^{LDA}[n] \]


C. Ciraci’ and F. Della Sala, Quantum hydrodynamic theory for plasmonics: Impact of the electron density tail, Phys. Rev. B 93, 205405 (2016)
what about hybrid “organic-plasmonic” systems?

F. Benz et al.,
Nanooptics of Molecular-shunted Plasmonic Nanojunctions,
LSPs within the Quantum-Mechanical Scheme

- Potentialities and limits of the Spherical Jellium Model
- Advantages of Density Functional Tight Binding Method

The Electronic Structure Problem

A detailed comprehension of electronic phenomena in molecules and nanomaterials requires a detailed atomistic description of their electronic structure. This is primarily achieved via the solution of the Schrödinger equation

\[ H \Psi(r_1, \ldots, r_N) = E \Psi(r_1, \ldots, r_N) \]

With the electronic Hamiltonian being

\[ H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{\mathbf{R}_i}^2 + V_{\text{ext}} + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \]

However, except for few simple cases, this problem is too complex to be solved directly (even numerically).

A large number of methods have then been developed to deal with the electronic structure problem:

- **Wave function methods**
- **Density Functional Theory (DFT)**
- **Semiempirical methods**
Density Functional Theory (DFT) and Time-Dependent DFT within the Jellium Model (JM)

$\Delta \rho(\vec{r}, \omega)$

Dipole Surface Plasmon Density

$Ne = 18$

$D = 0.8 \text{ nm}$

TURBOMOLE CODE (6.3)
http://www.turbomole.com/
Potentialities of JM:
1. capability to capture the charge transfer plasmons;
2. possibility to describe multi-scale systems (QCM, DPM)


Limits of JM:
atomic structure is neglected (orientation and relaxation cannot be distinguished).

A. Varas et al., Quantum plasmonics: from jellium models to ab initio calculations, Nanophotonics, 5(3), 409 (2016).
Density-Functional based Tight-Binding (DFTB)

\[ \phi_i = \sum_v c_v^i \psi_v \]
\[ \sum_v c_v^i (H_{\mu v} - \varepsilon_i S_{\mu v}) = 0 \quad \forall \mu, i \]

\[ H_{\mu v} = H_{\mu v}^0 + \frac{1}{2} S_{\mu v} \sum_\xi (\gamma_{\xi \mu} + \gamma_{\xi v}) q_\xi \]

Two-center Approximation:

\[ H_{\mu v}^0 = \left\langle \psi_{\mu} \left| \hat{H}^0 \right| \psi_{v} \right\rangle = \begin{cases} \varepsilon_{\mu}^{\text{free}} & \mu = v \\ \left\langle \psi_{\mu} \left| \hat{T} + V_{\text{eff}}^{AB} \right| \psi_{v} \right\rangle & \mu \in A, v \in B, A \neq B \\ 0 & \text{otherwise} \end{cases} \]

Potential Superposition:

\[ V_{\text{eff}}^{AB} = V_0^A (r - R_A) + V_0^B (r - R_B) \]

M. Wahiduzzaman et al.,
Slater-Koster Parameters Optimization

\[ E_\sigma = \int |\sigma_{DFTB \, abs} - \sigma_{DFT \, abs}| \, d\omega \]

New Transferible Parametrization

\(-0.028;0.012\)

\(hyb-0-1/Ag-Ag.skf\)

\((0;0)\)
DFT/DFTB Comparison: Accuracy

\[ \text{Absorption Efficiency (arb. u.)} \]

\[ \begin{array}{c}
\text{Wavelength (nm)} \\
\text{Wavelength (nm)}
\end{array} \]

S. D'Agostino, R. Rinaldi, G. Cuniberti and F. Della Sala,
DFT/DFTB Comparison: Computational Cost

\[ T_{\text{DFTB}} < 0.1\% T_{\text{DFT}} \]

1 day 3 h

125 s

Number of Atoms

Total Wall Time (s) \( \log_{10} \)
DFTB Analysis for Tetrahedral Ag Dimers

[TNT2017-POSTER] G. Giannone, R. Rinaldi, G. Cuniberti and S. D’Agostino,
Density Functional Tight Binding Method for Plasmonics.
(Università del Salento, Italy)
Future Perspectives

i. Plasmonic Switches


ii. Molecular electronic plasmonic devices (MEPs)

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