Aalto University
School of Science

Nanoplasmonics within time-dependent density-functional theory

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GPAW 2016: Users and developers meeting
Jyväskylä

Wednesday 8th June 2016

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Outline

Nanoplasmonics

Methods and computations

Analyzing the plasmonic response

Case studies

Outline

In this talk: Finite systems

For extended systems, see
K. Andersen, *Quantum theory of plasmons in nanostructures*, PhD thesis (2015).

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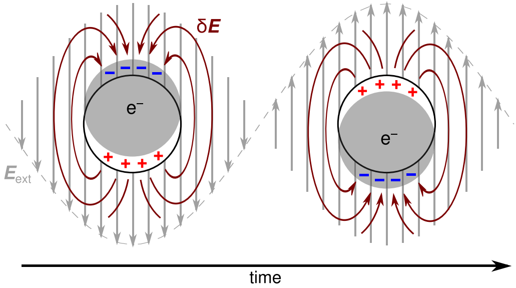
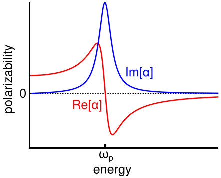
Localized surface plasmon

Collective oscillation of valence electrons





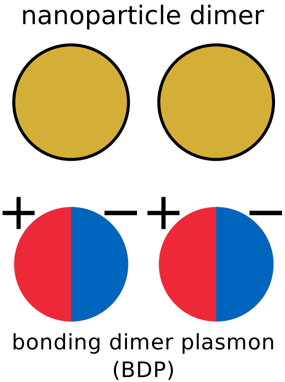
Plasmon resonance

- strong
- enhanced field
- tunable by
  - shape
  - composition
  - environment

- Plenty of applications
  - Light confinement
  - Spectroscopy
  - Biomedicine
  - ...

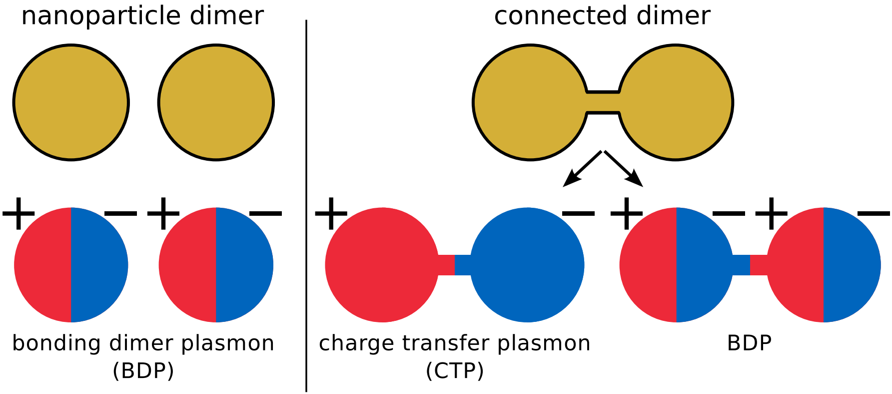
Plasmon coupling

Coupled plasmon modes (dipole-active):



Plasmon coupling

Coupled plasmon modes (dipole-active):

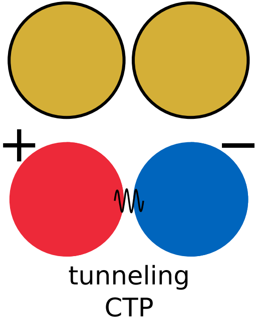


Nanoplasmonics

Nanoplasmonics

Small-size/quantum effects

- Tunneling



J. Zuloaga *et al.*, Nano Lett. **9**, 887 (2009)

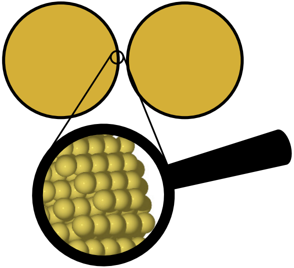
K. J. Savage *et al.*, Nature **491**, 574 (2012)

J. A. Scholl *et al.*, Nano Lett. **13**, 564 (2013)

Nanoplasmonics

Small-size/quantum effects

- Tunneling
- Atomistic details



P. Zhang *et al.*, Phys. Rev. B **90**, 161407(R) (2014)

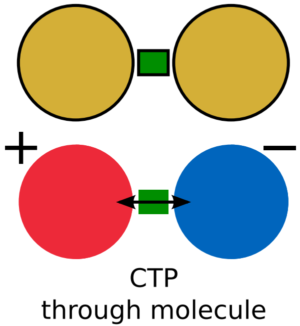
M. Barbry *et al.*, Nano Lett. **15**, 3410 (2015)

A. Varas *et al.*, J. Phys. Chem. Lett. **6**, 1891 (2015)

Nanoplasmonics

Small-size/quantum effects

- Tunneling
- Atomistic details
- Molecular junctions



P. Song *et al.*, J. Chem. Phys. **134**, 074701 (2011)

P. Song *et al.*, Phys. Rev. B **86**, 121410 (2012)

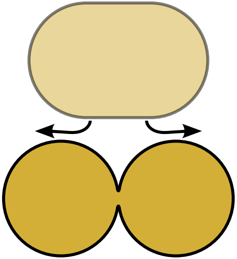
S. F. Tan *et al.*, Science **343**, 1496 (2014)

V. Kulkarni and A. Manjavacas, ACS Photonics **2**, 987 (2015)

Nanoplasmonics

Small-size/quantum effects

- Tunneling
- Atomistic details
- Molecular junctions
- Case study:
  quantum transport
  through nanocontact



realize dimer by
stretching a nanorod

Outline

Nanoplasmonics

Methods and computations

- Time-dependent density-functional theory (TDDFT)
- Time-propagation TDDFT with localized basis
- Hybrid quantum–classical scheme
- Practical aspects

Analyzing the plasmonic response

Case studies

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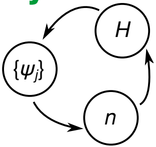
Time-dependent density-functional theory

DFT: The ground-state electronic structure



$$H[n]\psi_j(\boldsymbol{r}) = \epsilon_j\psi_j(\boldsymbol{r}), \quad j = 1, \ldots, N$$

TDDFT: The time-evolution/response of the system at the initial state $\{\psi_j(\boldsymbol{r}, t=0) = \psi_j^0(\boldsymbol{r})\}$

$$H[n](t)\psi_j(\boldsymbol{r}, t) = i\frac{\partial}{\partial t}\psi_j(\boldsymbol{r}, t)$$

Kohn-Sham Hamiltonian

$$H[n](t) = -\frac{1}{2}\nabla^2 + \int \frac{n(\boldsymbol{r}', t)}{|\boldsymbol{r} - \boldsymbol{r}'|}\mathrm{d}\boldsymbol{r} + v_{\mathrm{ext}}(\boldsymbol{r}, t) + v_{\mathrm{xc}}[n](\boldsymbol{r}, t)$$

Adiabatic approximation: $v_{\mathrm{xc}}[n](\boldsymbol{r}, t) = v_{\mathrm{xc}}[n(t)](\boldsymbol{r})$ (no memory)

E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
doi:10.1103/PhysRevLett.52.997

TDDFT in GPAW

Solve time-dependent equations by

- Real-time propagation (full non-linear response) or
  - `from gpaw.tddft import TDDFT`
  - `from gpaw.lcaotddft import LCAOTDDFT`
- Linear response in frequency space (sum over states)
  - `from gpaw.lrtddft import LrTDDFT`
  - `from gpaw.lrtddft2 import LrTDDFT2`

Note: also extended systems!

- `from gpaw.response.df import DielectricFunction`

(But in this talk the focus on finite systems!)

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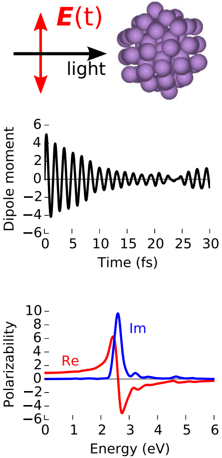
Recipe for time-propagation TDDFT

1. Calculate the ground state
   - ground state wave functions
2. "Kick" with a delta-pulse of light (linear regime)
   - dipole approximation: $\delta v_{\text{ext}}(\boldsymbol{r}, t) = \boldsymbol{r} \cdot \boldsymbol{E}_{\text{ext}} \delta(t)$
3. Propagate the wave functions in time
   - record the quantities of interest (density, dipole moment)
4. Analyze
   - Fourier transform

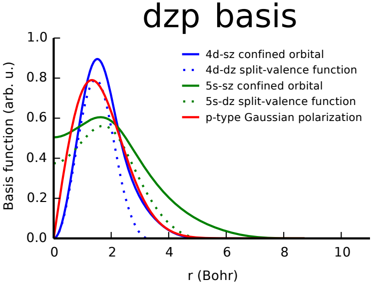


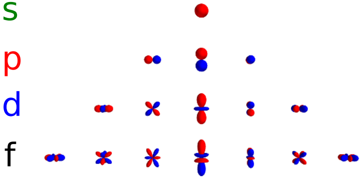
K. Yabana and G. F. Bertsch, Phys. Rev. B **54**, 4484 (1996).
doi:10.1103/PhysRevB.54.4484

Localized basis sets (LCAO)

Represent the wave functions as linear combinations of atomic orbitals/atom-localized functions (LCAO)

$\chi_i^a(\boldsymbol{r}) = \phi_{n,l}^a(r)\, Y_l^m(\theta, \varphi)$

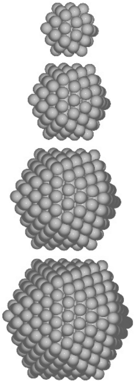


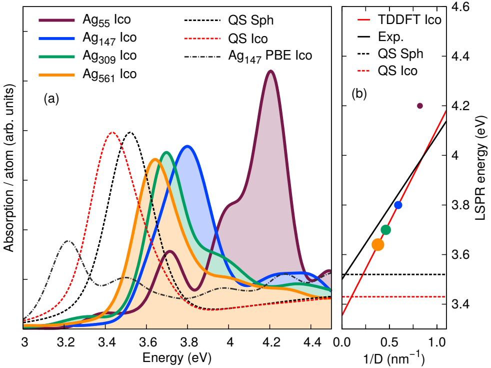


LCAO – Highly efficient calculations

Recent LCAO-TDDFT implementation in GPAW

- `from gpaw.lcaotddft import LCAOTDDFT`





M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, Phys. Rev. B **91**, 115431 (2015). `doi:10.1103/PhysRevB.91.115431`

LCAO – . . . but no simple convergence parameters

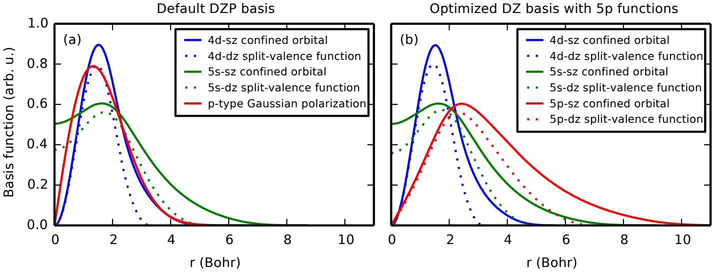
Default basis sets (designed for DFT ground-state-energy calculations) may not be suitable for response calculations

How to extend the basis sets?

- Generate functions based on atomic orbitals (*e.g.*, split-valence)
- Use some general function form (*e.g.*, Gaussian)

LCAO – *pvalence* basis sets

Replace the default p-type polarization function with diffuse 5p unoccupied orbital (and its split-valence function)



M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, Phys. Rev. B **91**, 115431 (2015). doi:10.1103/PhysRevB.91.115431

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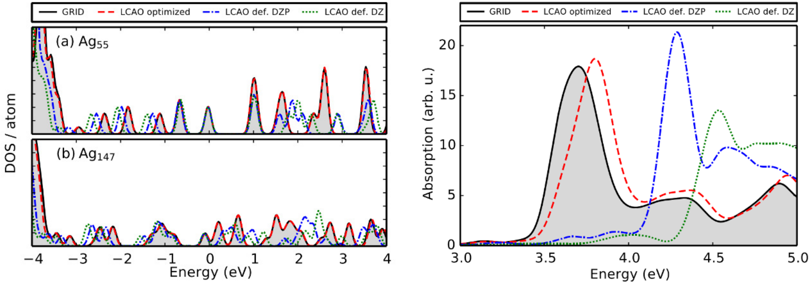


Generated for all suitable elements, available in GPAW:

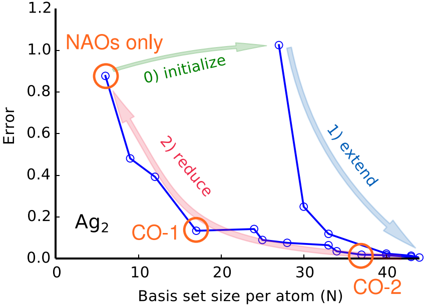
```
gpaw install-data <dir> --basis --version=pvalence
```

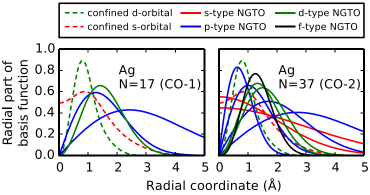
M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, Phys. Rev. B **91**, 115431 (2015). `doi:10.1103/PhysRevB.91.115431`

Completeness-optimization: NAO+NGTO basis sets

Augment atomic-orbital (NAO) basis set with numerical Gaussian-type orbitals (NGTOs)

- NGTOs selected by systematic completeness-optimization of the spectrum of the atomic dimer (*e.g.*, Ag_2)

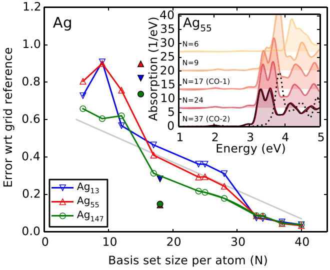


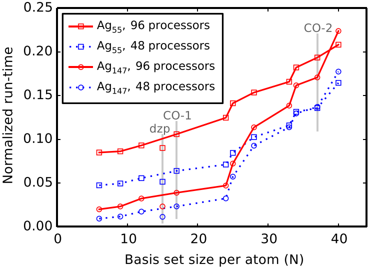


T. P. Rossi, S. Lehtola, A. Sakko, M. J. Puska, and R. M. Nieminen, J. Chem. Phys. **142**, 094114 (2015). `doi:10.1063/1.4913739`

Co-optimized NAO+NGTO – *coopt* basis sets

The obtained basis sets are transferable to larger systems





Generated for Cu, Ag, and Au, available in GPAW:

```
gpaw install-data <dir> --basis --version=coopt
```


T. P. Rossi, S. Lehtola, A. Sakko, M. J. Puska, and R. M. Nieminen,
J. Chem. Phys. **142**, 094114 (2015). doi:10.1063/1.4913739

Outline

Hybrid quantum–classical scheme

Idea: separate the system to quantum and classical parts

Quantum part (*e.g.*, a molecule):

- Time-propagation TDDFT

Classical part (*e.g.*, a large nanoparticle):

- Describe material with (experimentally measured) permittivity $\epsilon(\omega)$
- Solve Maxwell's equations at the quasistatic description by time-propagation

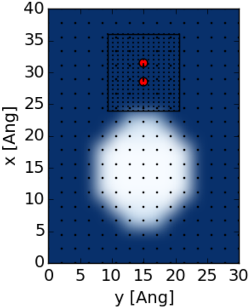
Coupling

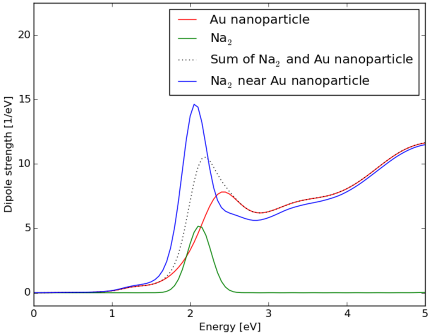
- The potential $\nabla^2 V^{\text{tot}}(\boldsymbol{r}, t) = -4\pi[\rho^{\text{cl}}(\boldsymbol{r}, t) + \rho^{\text{qm}}(\boldsymbol{r}, t)]$

```
from gpaw.fdtd.poisson_fdtd import QSFDTD
```

A. Sakko, T. P. Rossi, and R. M. Nieminen, J. Phys.: Condens. Matter **26**, 315013 (2014).
doi:10.1088/0953-8984/26/28/315013

Hybrid quantum–classical scheme: Example





A. Sakko, T. P. Rossi, and R. M. Nieminen, J. Phys.: Condens. Matter **26**, 315013 (2014).
doi:10.1088/0953-8984/26/28/315013

Outline

Poisson equation

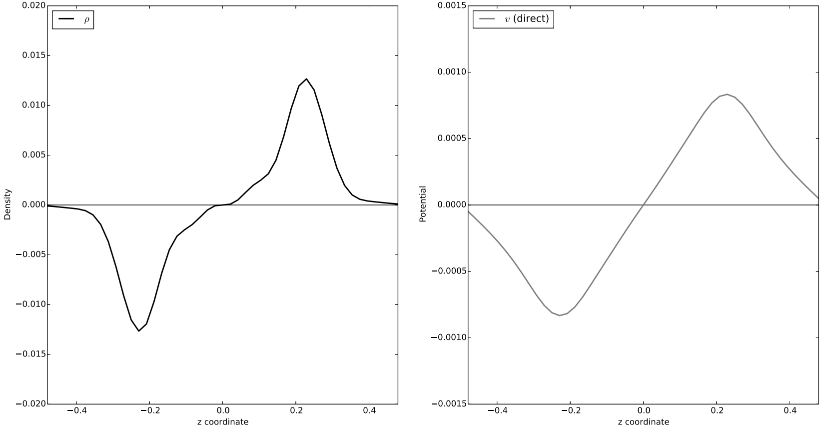
Problem

- Charge oscillation at plasmonic resonance induces strong global dipole
  $\rightarrow$ Small cell with zero boundary conditions for potential is not ok!

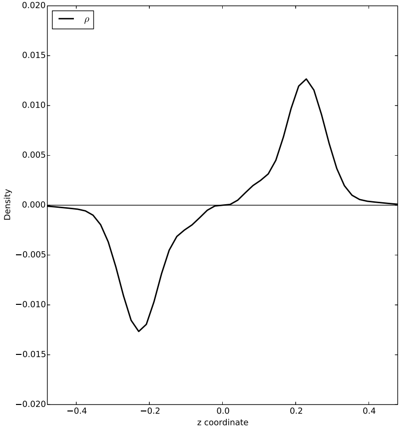
Solution

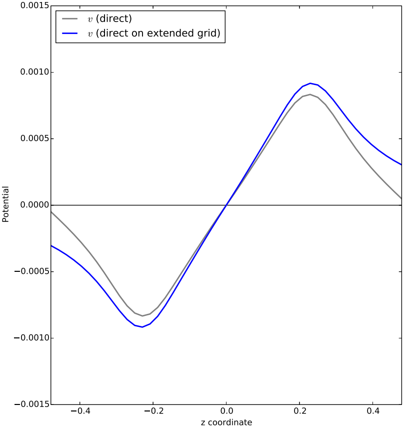
- Use multipole moment corrections
- Calculate potential on an extended grid

Poisson equation: illustration

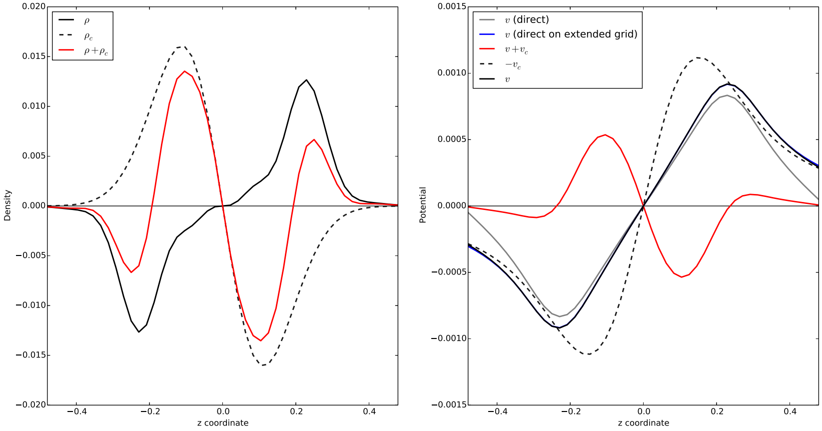


Poisson equation: illustration





Poisson equation: illustration



PoissonSolver zoo

Multipole moment corrections

```
from gpaw.poisson import PoissonSolver

PoissonSolver(eps=1e-20, remove_moment=1+3+5)
```

- For $\sim$ spherical systems (or spherical unit cells)

Multiple multipole moment corrections

```
from gpaw.poisson_extended import ExtendedPoissonSolver
moment_corrections = [{'moms':  moments, 'center':  center1},
                      {'moms':  moments, 'center':  center2},
                       ...]

ExtendedPoissonSolver(eps=1e-20, moment_corrections=moment_corrections)
```

- For nanoparticle dimer, trimer, …

Calculate potential on an extended grid

```
ExtendedPoissonSolver(eps=1e-20, extended={'gpts':  (512, 256, 256)})
```

- For general cases

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- Spectra
- Real-space quantities
- Spatially resolved spectra
- Electron transitions

Case studies

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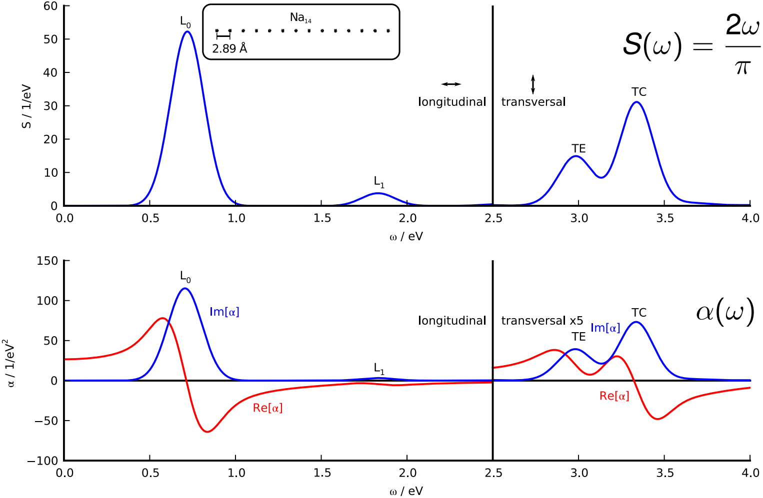
Photoabsoprtion and polarizability



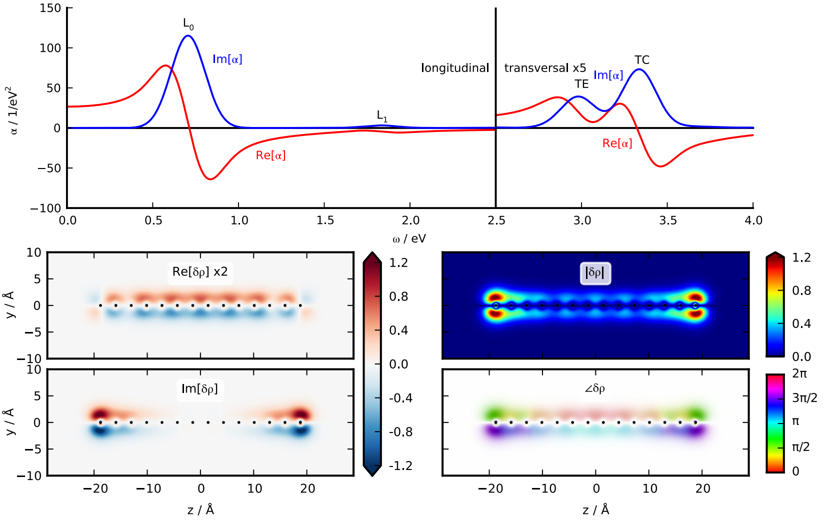
$$S(\omega) = \frac{2\omega}{\pi}\mathrm{Im}[\alpha(\omega)]$$

$$\alpha(\omega) = \frac{\delta\mu(\omega)}{E_0}$$

Kramers-Kronig relations

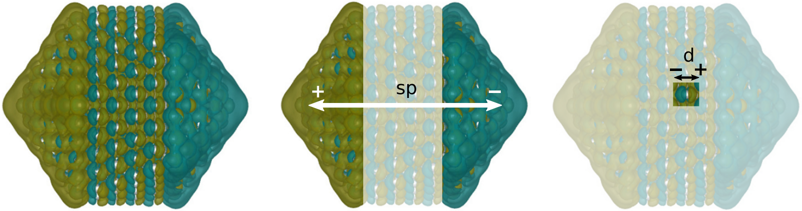
Outline

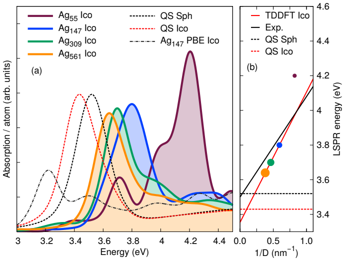
Induced density



Induced density

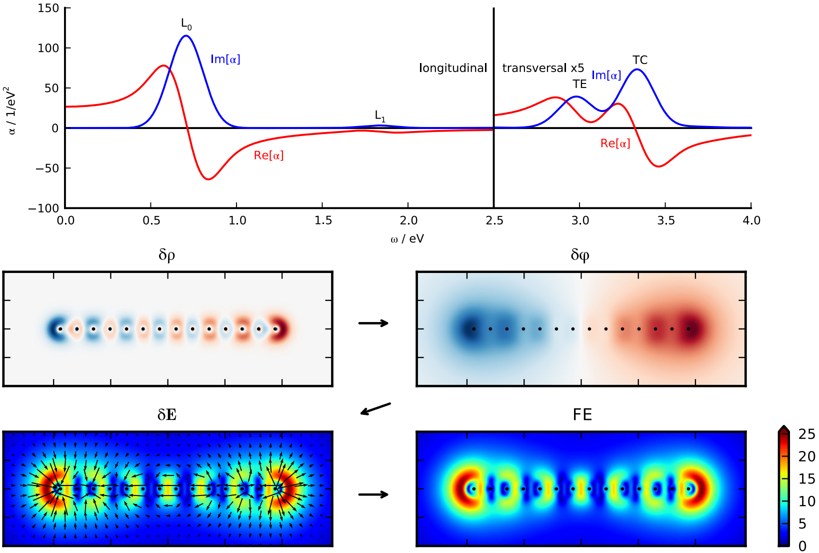
Ag_{561}





M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, Phys. Rev. B **91**, 115431 (2015). `doi:10.1103/PhysRevB.91.115431`

Induced density → potential → electric near field




```
from gpaw.inducedfield.inducedfield_tddft import TDDFTInducedField
```

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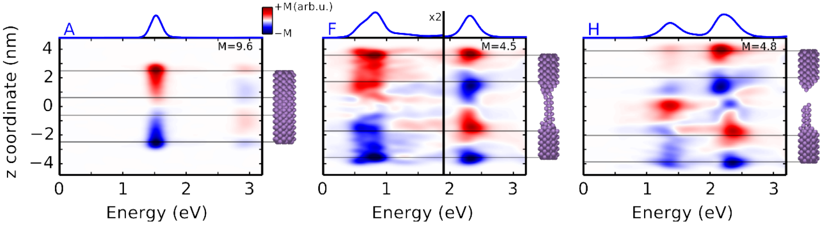
Integrated induced density map

$$\delta\tilde{\rho}(z,\omega) = \mathrm{Im}\left[\int \delta\rho(\boldsymbol{r},\omega)\,\mathrm{d}x\mathrm{d}y\right]$$

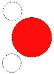


$$S(\omega) \propto \omega \int z\,\delta\tilde{\rho}(z,\omega)\,\mathrm{d}z$$

T. P. Rossi, A. Zugarramurdi, M. J. Puska, and R. M. Nieminen,
Phys. Rev. Lett. **115**, 236804 (2015). `doi:10.1103/PhysRevLett.115.236804`

Outline

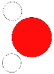
Kohn–Sham decomposition



Small systems:
List transitions

```
H2O
E=8.065 eV, f=0.031533
   3->4 u 0.99986
   0->8 u 0.00013
   rest=1.57e-16
```

Kohn–Sham decomposition



Small systems:
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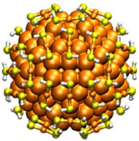

$Au_{314}(SH)_{96}$

Large systems:
Transition contribution map

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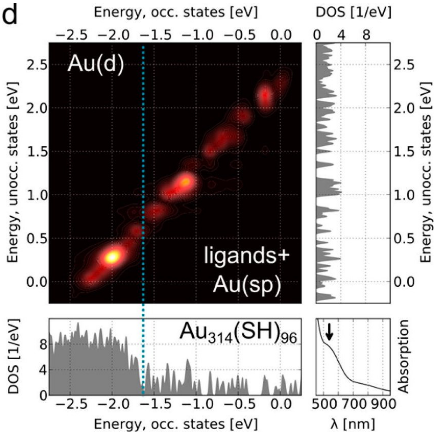
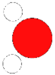
```



S. Malola, L. Lehtovaara, J. Enkovaara, and H. Häkkinen, ACS Nano **7**, 10263 (2013).
doi:10.1021/nn4046634

Kohn–Sham decomposition



Small systems:
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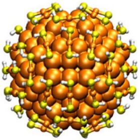

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```
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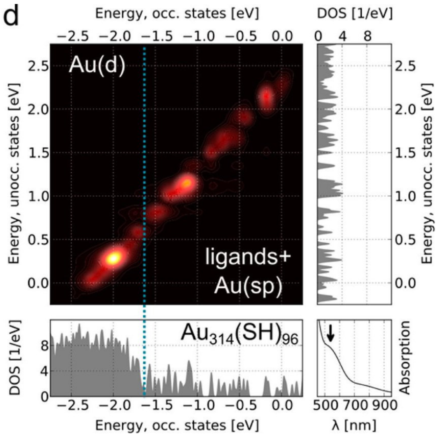
```

Also from time-propagation!

- Talk by M. Kuisma

Large systems:
Transition contribution map



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- Quantized evolution of the plasmonic response in a stretched nanorod
- ...

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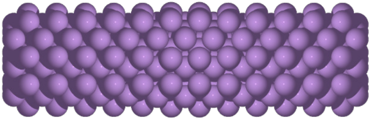
Stretched nanorod



The nanorod

- 261 sodium atoms
- length 5.0 nm
- diameter 1.3 nm

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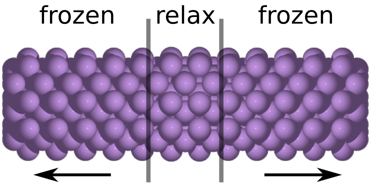
Stretched nanorod



The nanorod

- 261 sodium atoms
- length 5.0 nm
- diameter 1.3 nm

Computational details

- DFT and TDDFT
- APBE xc functional

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Stretched nanorod

(animation)

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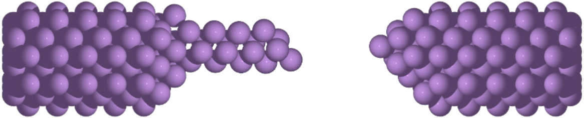

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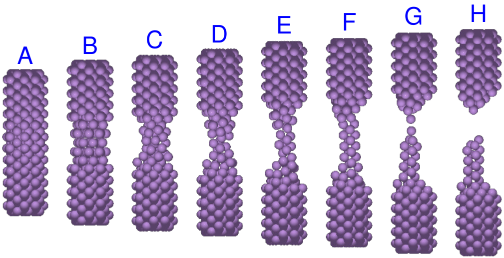

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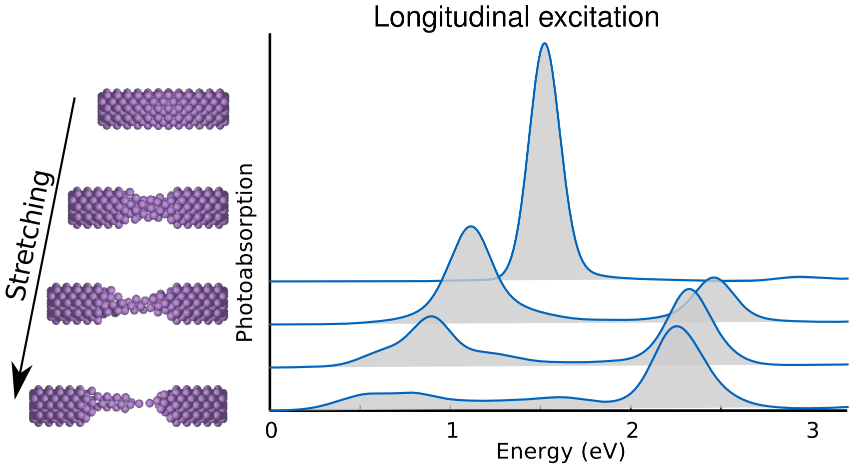
Plasmonic response during stretching



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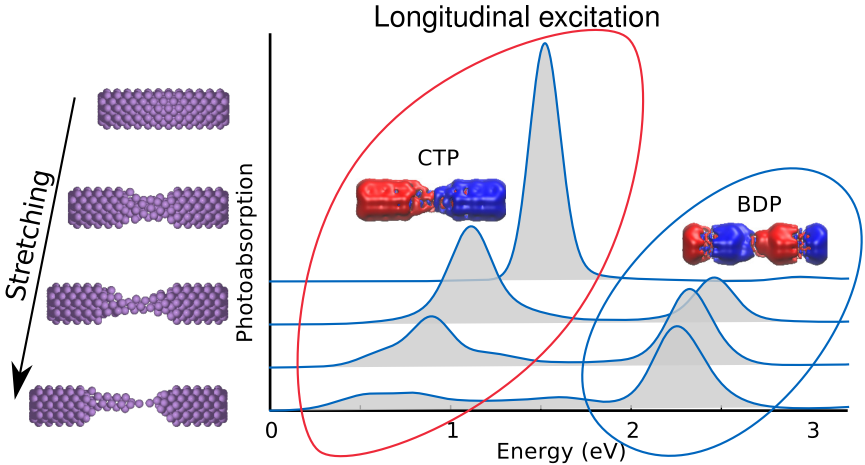

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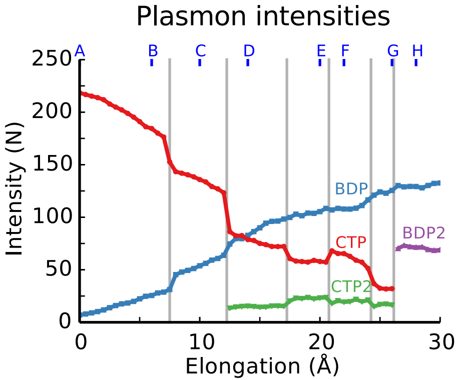
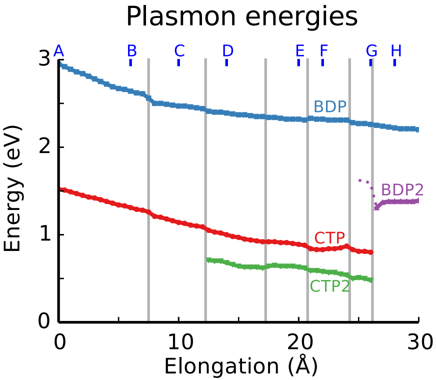
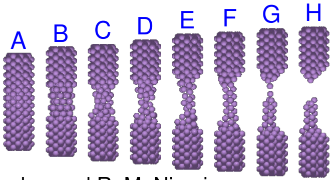
Quantized evolution of the plasmonic response







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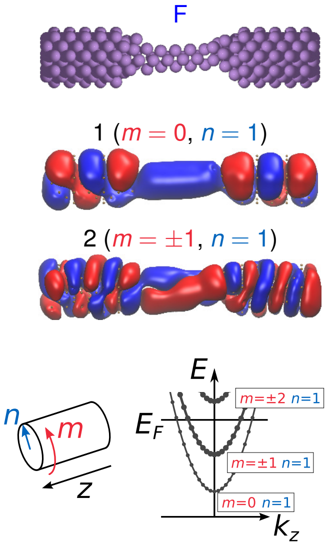
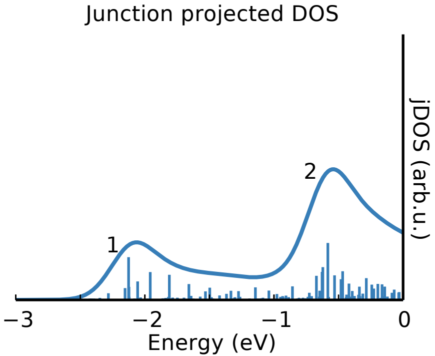
Junction electronic structure





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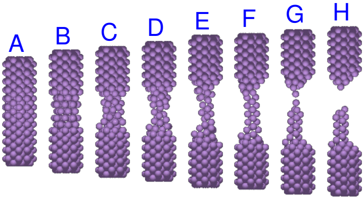
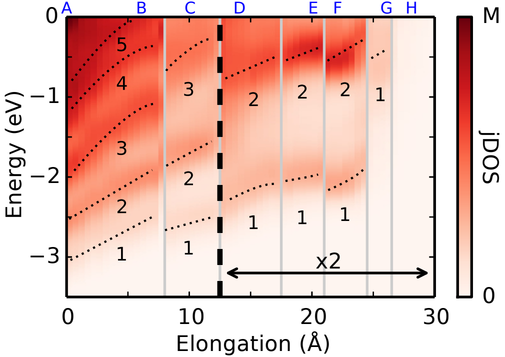
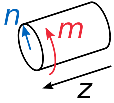
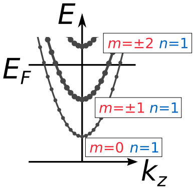
Junction electronic structure – Evolution









Associated (m, n) states:

1. $(0, 1)$
2. $(\pm1, 1)$
3. $(\pm2, 1)$ and $(0, 2)$
4. $(\pm3, 1)$
5. $(\pm1, 2)$

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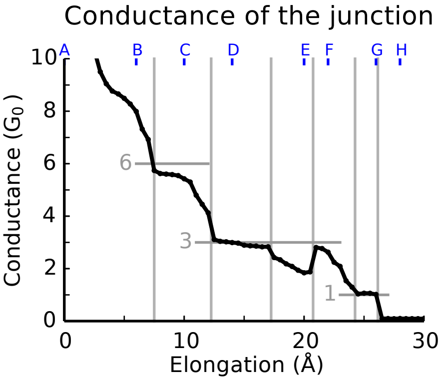
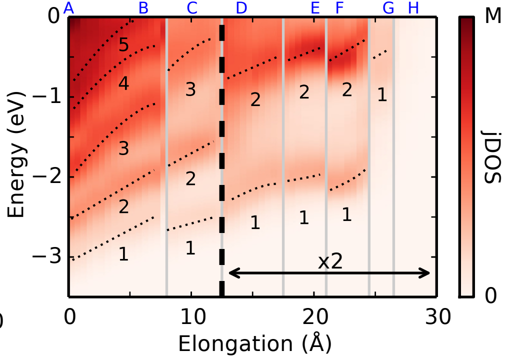
Electronic structure → Transport





- Quantized 1DEG "bands" serve as conduction channels

Associated (m, n) states:

1. (0, 1)
2. (±1, 1)
3. (±2, 1) and (0, 2)
4. (±3, 1)
5. (±1, 2)

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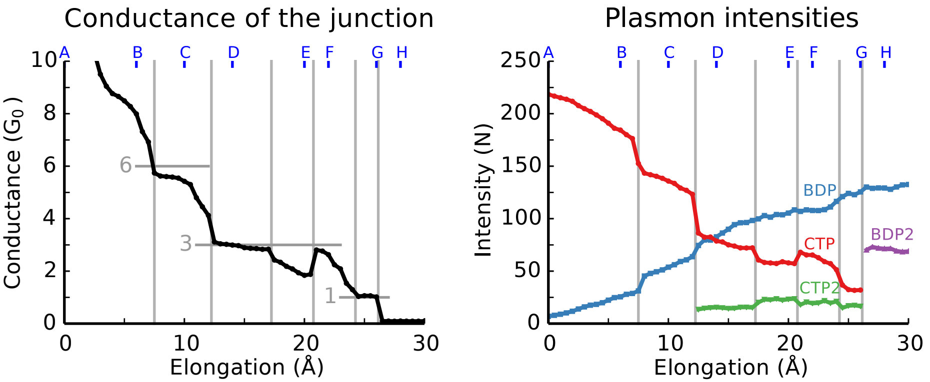
Origin of the quantized plasmonic evolution



- Quantized transport reflected in coupled plasmon modes (especially CTP)
- Plasmonic counterpart of conductance quantization

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Outline

Nanoplasmonics

Methods and computations

Analyzing the plasmonic response

Case studies

- Quantized evolution of the plasmonic response in a stretched nanorod
- ...

Summary

Nanoplasmonics

Methods and computations

- Time-dependent density-functional theory (TDDFT)
- Time-propagation TDDFT with localized basis
- Hybrid quantum–classical scheme
- Practical aspects

Analyzing the plasmonic response

- Spectra
- Real-space quantities
- Spatially resolved spectra
- Electron transitions

Case studies

- Quantized evolution of the plasmonic response in a stretched nanorod
- . . .