Combining TDDFT and classical electrodynamics simulations for plasmonics

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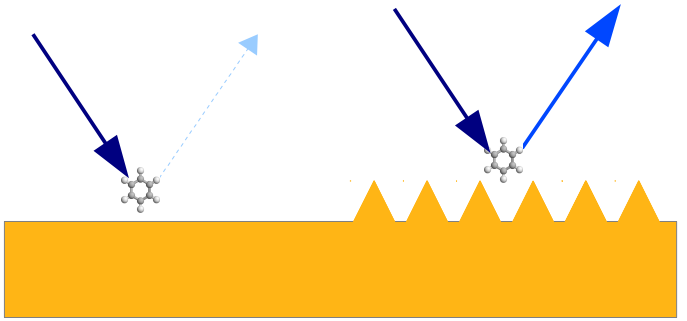
Electronic Properties of Materials
COMP - Centre of Excellence
Aalto University

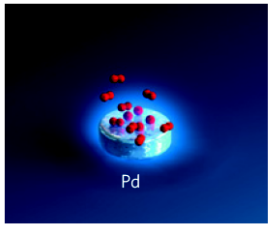
Outlook

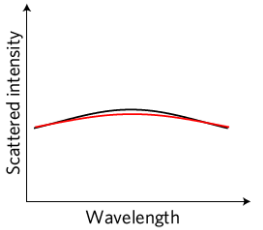
- Review of plasmons:
  - Plasmonics and applications
  - Classical and quantum plasmons
- Computational approaches
  - Classical methods: FDTD
  - Electronic structure calculations: TDDFT
  - Hybrid methods
- New developments:
  - Analysis of plasmonic near fields
  - Classical ED implementation in GPAW
  - Hybrid quantum/classical calculations

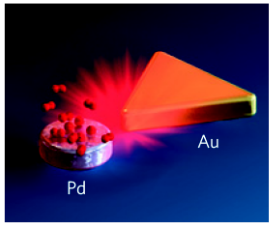
Review: plasmonics

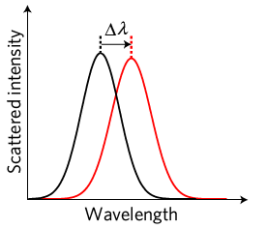
- Surface enhanced spectroscopies
  - Raman, Infrared, Fluorescence
- Sensors
- Waveguides, photovoltaics, nanoantennas
- Hot spots
  - Cancer therapy, water purification

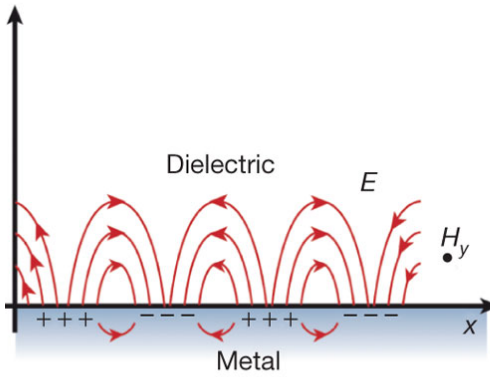


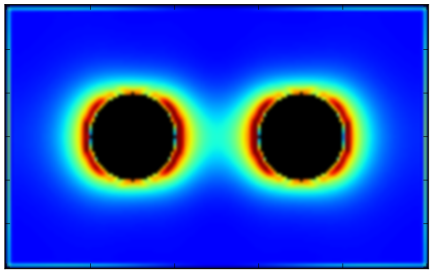


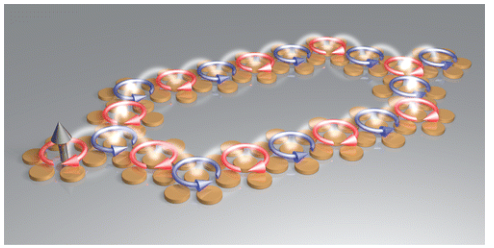








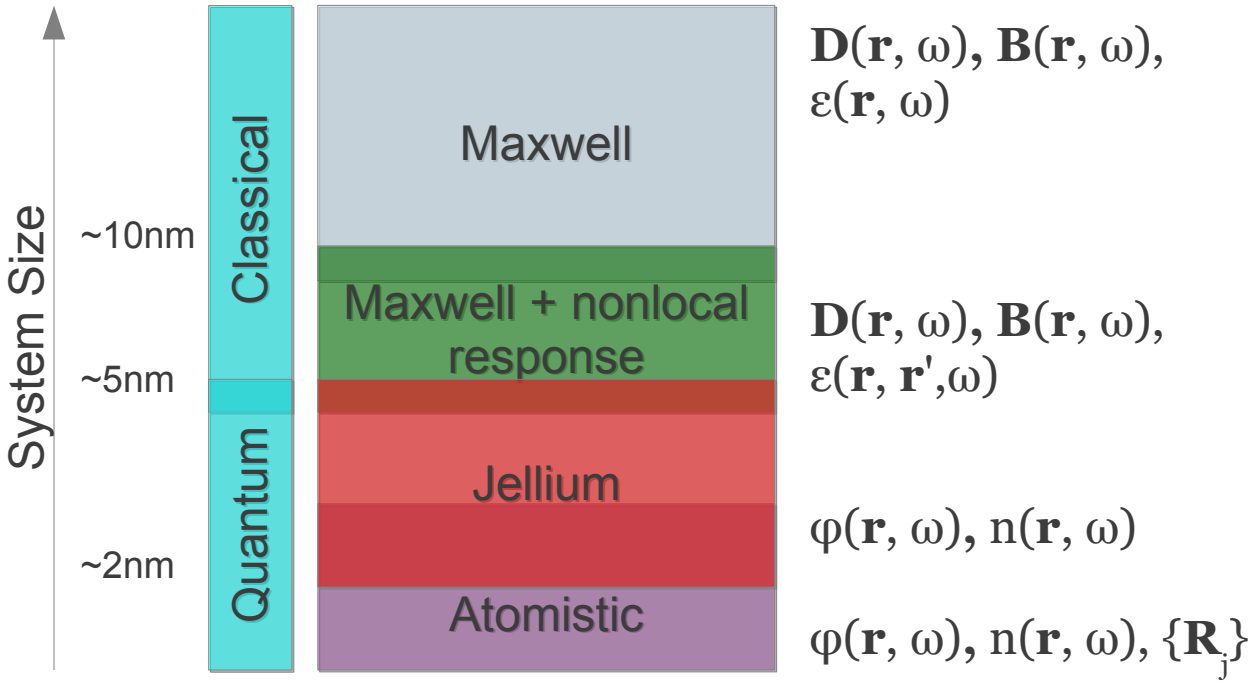




Liu et al., ACS Nano (2012)

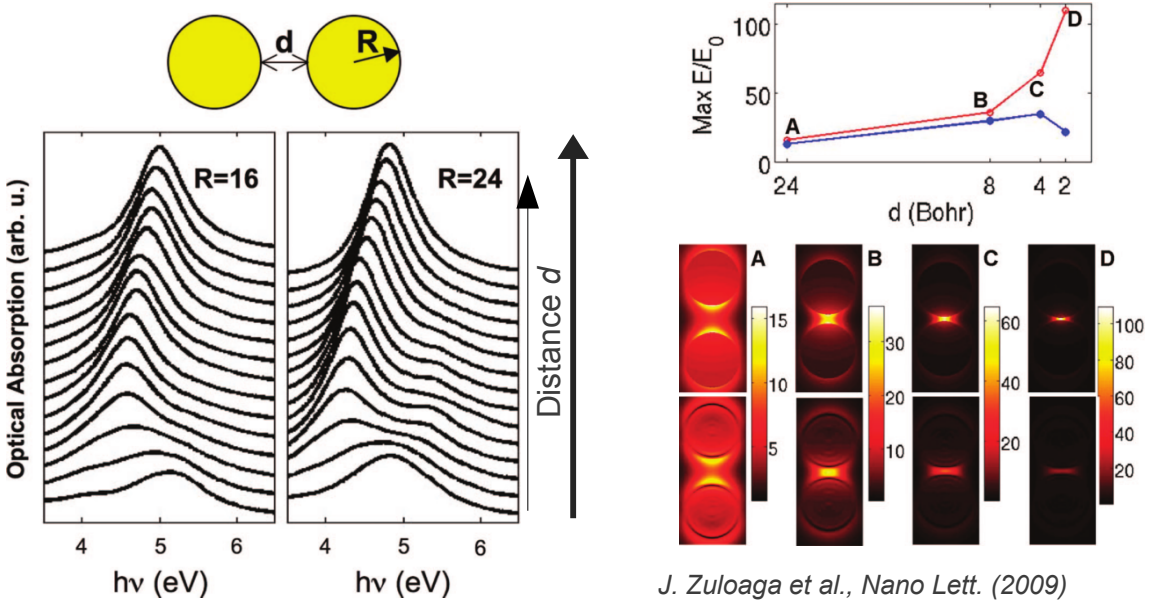
Review: plasmonics

- Classical charge oscillations
- Quantum effects
  - Tunneling
  - Spill-out of surface charge
  - Nonlocal response

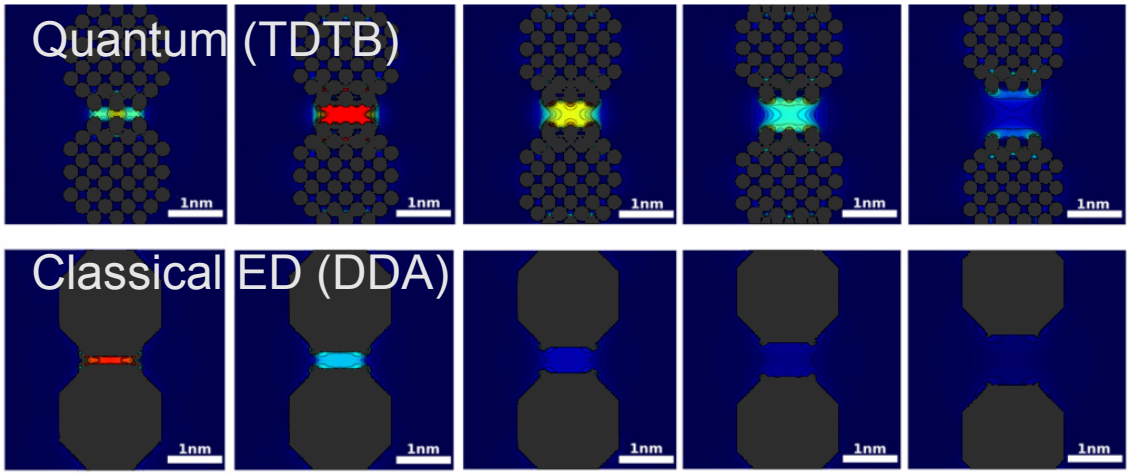


Review: plasmonics

- Plasmon coupling
  - Classical ED
  - Jellium nanosphere
  - Atomistic nanoparticle



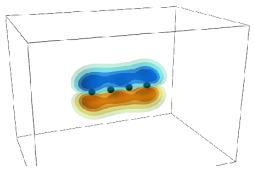
J. Zuloaga et al., Nano Lett. (2009)



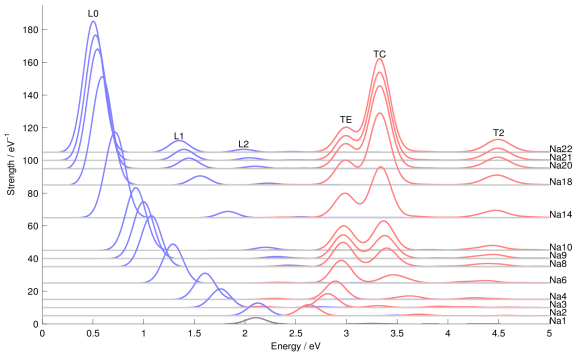
Negre et al., J. Phys.: Cond. Matt. (2013)

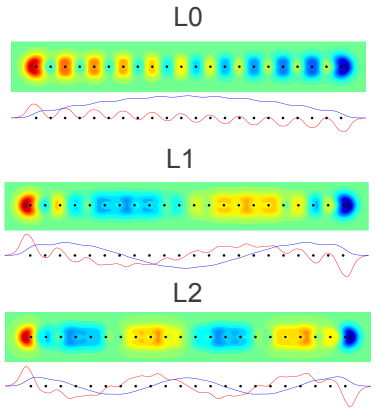
Review: plasmonics

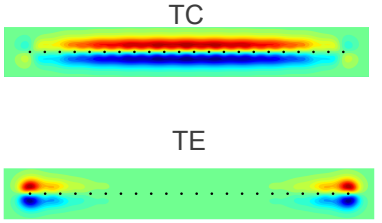
- Visual approach



Na chains

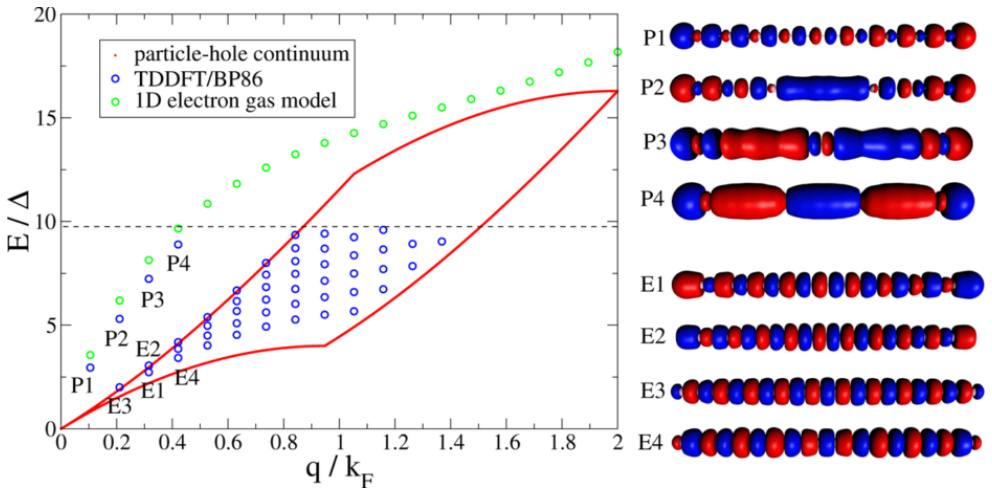


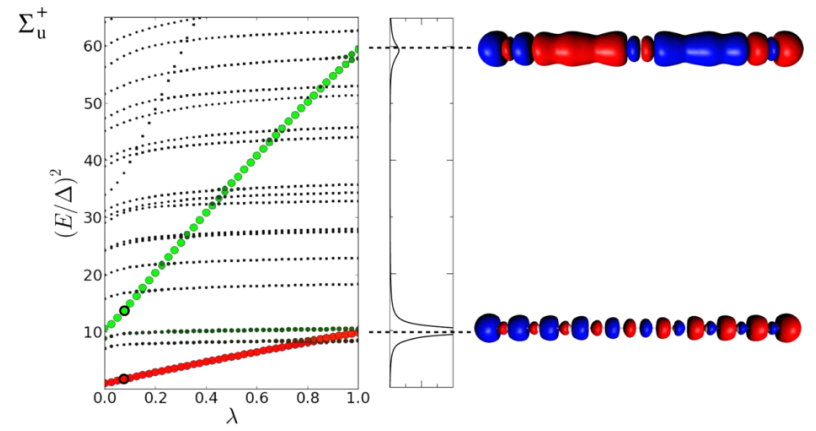




J . Yan et al., Phys. Rev. Lett. (2007)
T. Rossi, Special assignment work (2012)

- Dynamic interaction scaling approach





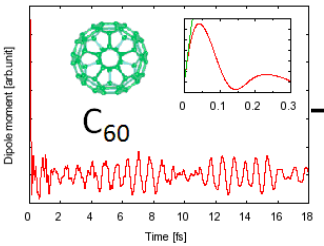
S. Bernadotte et al., J. Phys. Chem. C (2013)

Computational approaches

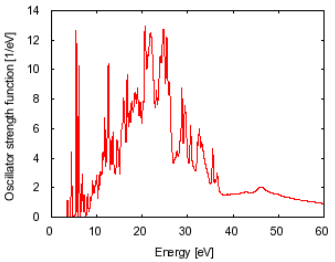
Quantum mechanics: TDDFT framework

$$V_{\text{ext}}(\mathbf{r},t) = \mathbf{E}_0 \cdot \mathbf{r}\ \delta(t)$$

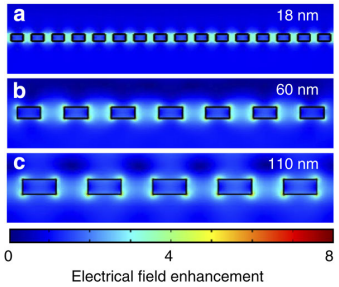
$U[t',t]\phi_j(\mathbf{r},t)$

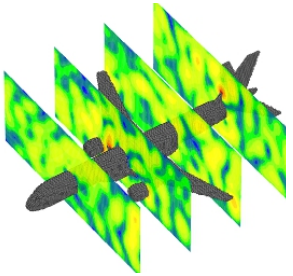


F[Δμ(**r**,t)](ω)



Classical Electrodynamics: FDTD





Li et al., Nature Communications (2011)
http://www.electromagneticapplications.com

$$\frac{\partial \mathbf{H}}{\partial t} = -\frac{1}{\mu}\nabla \times \mathbf{E} - \frac{1}{\mu}\mathbf{M}$$

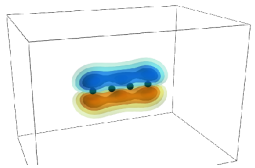
$$\frac{\partial \mathbf{E}}{\partial t} = -\frac{1}{\epsilon}\nabla \times \mathbf{H} - \frac{1}{\epsilon}\mathbf{J}$$

$$\nabla \cdot \mathbf{H} = 0$$

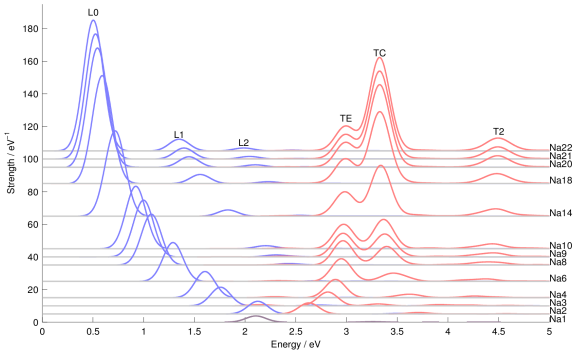
$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0}\rho$$

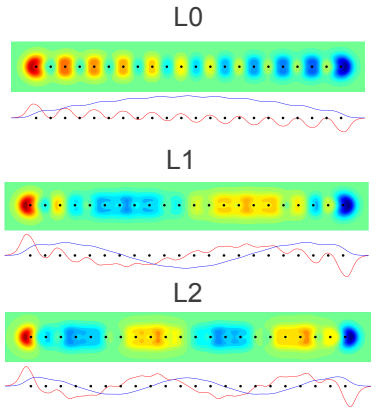
- Propagated quantities: $\rho(\mathbf{r},t)$ and $\varphi_j(\mathbf{r},t)$ vs $\boldsymbol{E}(\mathbf{r},t)$ and $\boldsymbol{H}(\mathbf{r},t)$
- Real space grid: Uniform spacing
- Derivative operators: Finite differences
- Grid spacing: Δx ~ 0.2Å vs ~λ/10
- Time step Δt ~ 10as vs ~$\Delta x/c$

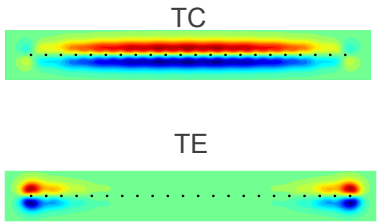
Near field distributions



Na chains





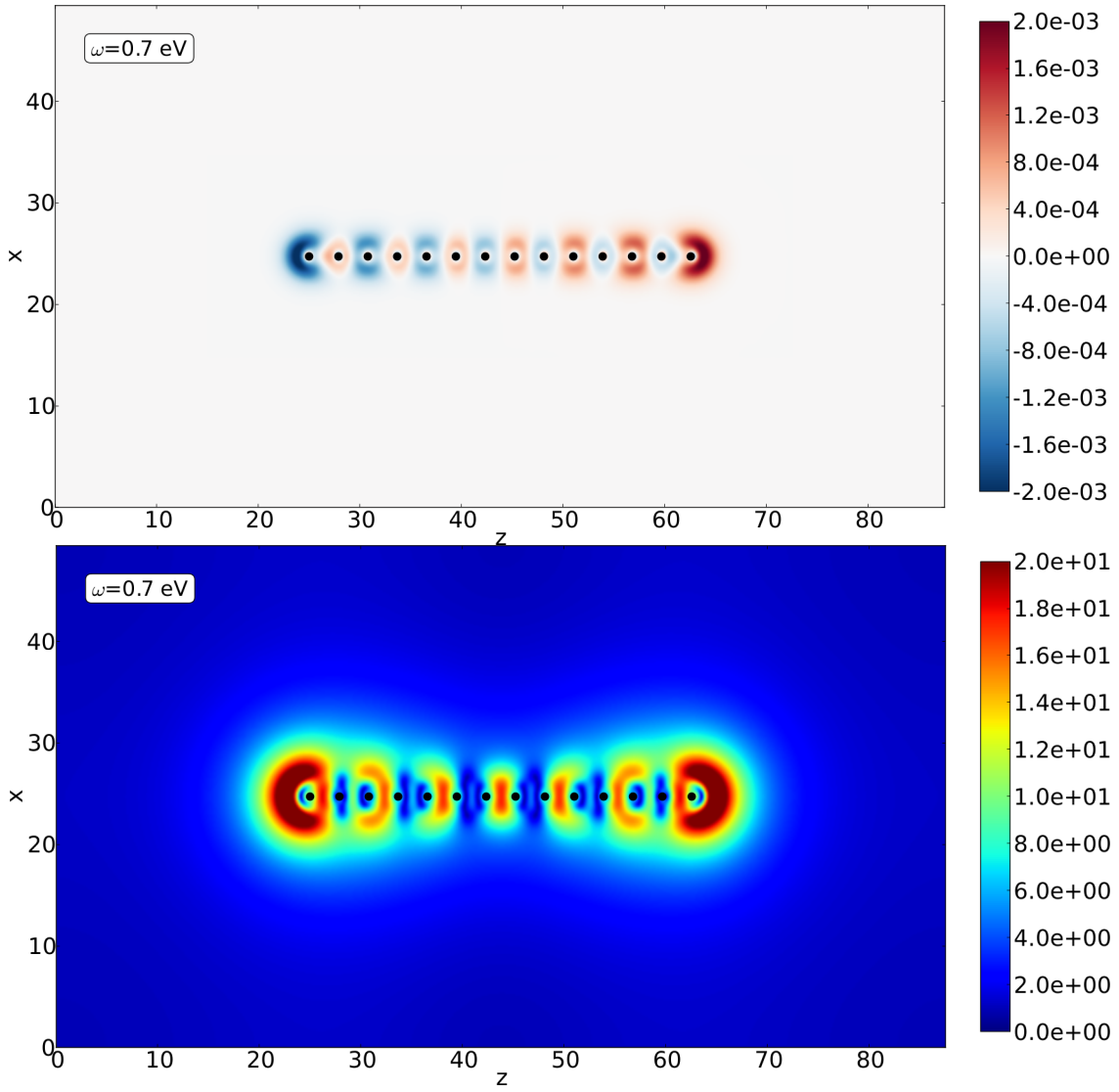


T. Rossi, Special assignment work (2012)

→ δV(**r**, ω) and δ**E**(**r**,ω) generated by the induced density δρ(**r**, ω)

$$\mathrm{FE}(\mathbf{r},\omega) = \frac{\left|\mathbf{E}_{\mathrm{EXT}}(\mathbf{r},\omega) + \delta\mathbf{E}(\mathbf{r},\omega)\right|}{\left|\mathbf{E}_{\mathrm{EXT}}(\mathbf{r},\omega)\right|}$$

Near field distributions



Classical ED

- Module for doing classical electrodynamics

THE JOURNAL OF CHEMICAL PHYSICS **135**, 084121 (2011)

Near-field: A finite-difference time-dependent method for simulation of electrodynamics on small scales

Arunima Coomar, Christopher Arntsen, Kenneth A. Lopata, Shlomi Pistinner, and Daniel Neuhauser[a)]
Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095-1569, USA

(Received 6 April 2011; accepted 1 August 2011; published online 29 August 2011)

We develop near-field (NF), a very efficient finite-difference time-dependent (FDTD) approach for simulating electromagnetic systems in the near-field regime. NF is essentially a time-dependent version of the quasistatic frequency-dependent Poisson algorithm. We assume that the electric field is longitudinal, and hence propagates only a set of time-dependent polarizations and currents. For near-field scales, the time step (dt) is much larger than in the usual Maxwell FDTD approach, as it is not related to the velocity of light; rather, it is determined by the rate of damping and plasma oscillations in the material, so $dt = 2.5$ a.u. was well converged in our simulations. The propagation in time is done via a leapfrog algorithm much like Yee's method, and only a single spatial convolution is needed per time step. In conjunction, we also develop a new and very accurate 8 and 9 Drude-oscillators fit to the permittivity of gold and silver, desired here because we use a large time step. We show that NF agrees with Mie-theory in the limit of small spheres and that it also accurately describes the evolution of the spectral shape as a function of the separation between two gold or silver spheres. The NF algorithm is especially efficient for systems with small scale dynamics and makes it very simple to introduce additional effects such as embedding. © *2011 American Institute of Physics*. [doi:10.1063/1.3626549]

$$\varepsilon(\omega) = \varepsilon_\infty + \varepsilon_0 \sum_{j=1}^{N_j} \frac{\beta_j}{\bar{\omega}_j^2 - i\alpha_j\omega - \omega^2}$$

$$\mathbf{E}_{\text{near field}}(\mathbf{r}, t) = -\frac{\nabla}{4\pi\varepsilon_0} \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J}$$

$$\rho = -\nabla \cdot \mathbf{P}$$

$$\frac{\partial \mathbf{J}_j(\mathbf{r}, t)}{\partial t} = -\alpha_j(\mathbf{r})\mathbf{J}_j(\mathbf{r}, t) - \bar{\omega}^2(\mathbf{r})\mathbf{P}_j(\mathbf{r}, t) + \varepsilon_0\beta_j(\mathbf{r})\mathbf{E}(\mathbf{r}, t)$$

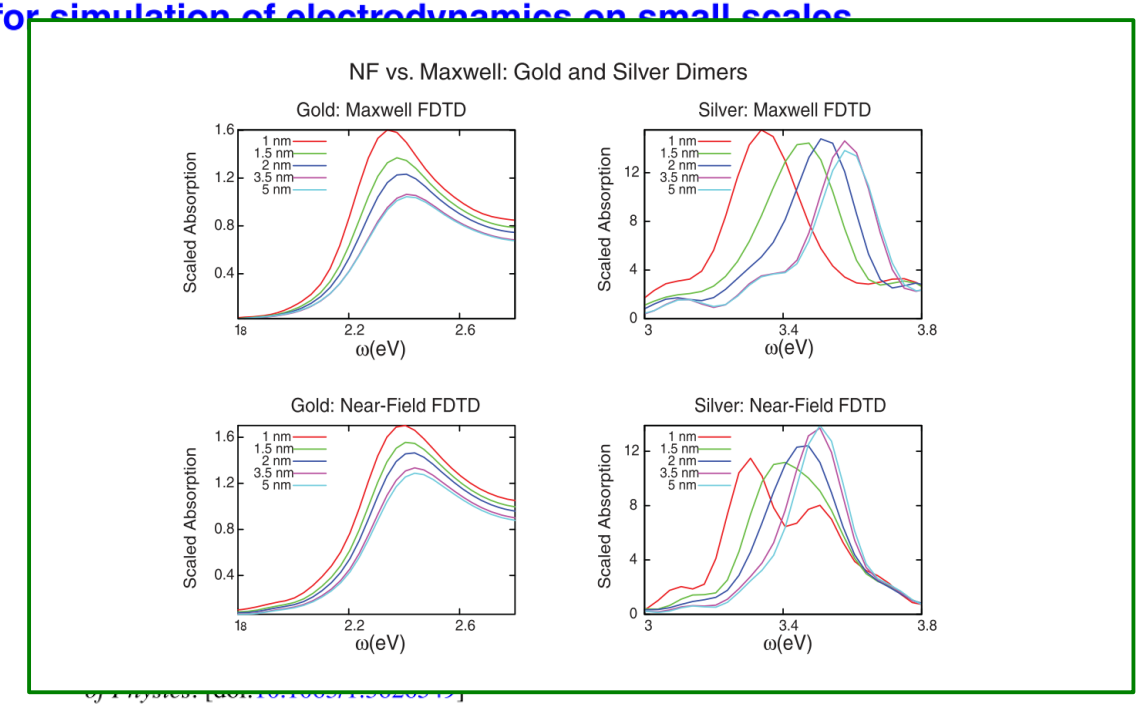
$$\frac{\partial \mathbf{P}_j(\mathbf{r}, t)}{\partial t} = \mathbf{J}_j(\mathbf{r}, t)$$

Classical ED

- Module for doing classical electrodynamics

THE JOURNAL OF CHEMICAL PHYSICS **135**, 084121 (2011)

Near-field: A finite-difference time-dependent method for simulation of electrodynamics on small scales



$$\varepsilon(\omega) = \varepsilon_\infty + \varepsilon_0 \sum_{j=1}^{N_j} \frac{\beta_j}{\bar{\omega}_j^2 - i\alpha_j\omega - \omega^2}$$

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$$\frac{\partial \mathbf{P}_j(\mathbf{r}, t)}{\partial t} = \mathbf{J}_j(\mathbf{r}, t)$$

Classical ED

- Module for doing classical electrodynamics

THE JOURNAL OF CHEMICAL PHYSICS **135**, 084121 (2011)

Near-field: A finite-difference time-dependent method

$$\varepsilon(\omega) = \varepsilon_\infty + \varepsilon_0 \sum_{j=1}^{N_j} \frac{\beta_j}{\bar{\omega}_j^2 - i\alpha_j\omega - \omega^2}$$

THE JOURNAL OF CHEMICAL PHYSICS **137**, 074113 (2012)

Dynamical quantum-electrodynamics embedding: Combining time-dependent density functional theory and the near-field method

Yi Gao and Daniel Neuhauser[a)]
Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569, USA

(Received 11 June 2012; accepted 31 July 2012; published online 21 August 2012)

We develop an approach for dynamical ($\omega > 0$) embedding of mixed quantum mechanical (QM)/classical (or more precisely QM/electrodynamics) systems with a quantum sub-region, described by time-dependent density functional theory (TDDFT), within a classical sub-region, modeled here by the recently proposed near-field (NF) method. Both sub-systems are propagated simultaneously and are coupled through a common Coulomb potential. As a first step we implement the method to study the plasmonic response of a metal film which is half jellium-like QM and half classical. The resulting response is in good agreement with both full-scale TDDFT and the purely classical NF method. The embedding method is able to describe the optical response of the whole system while capturing quantum mechanical effects, so it is a promising approach for studying electrodynamics in hybrid molecules-metals nanostructures. © *2012 American Institute of Physics*.
[http://dx.doi.org/10.1063/1.4745847]

$$) = -\frac{\nabla}{4\pi\varepsilon_0} \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

$$7 \cdot \mathbf{J}$$

$$\cdot \mathbf{P}$$

$$-\alpha_j(\mathbf{r})\mathbf{J}_j(\mathbf{r}, t)$$

$$(\mathbf{r})\mathbf{P}_j(\mathbf{r}, t) + \varepsilon_0\beta_j(\mathbf{r})\mathbf{E}(\mathbf{r}, t)$$

$$= \mathbf{J}_j(\mathbf{r}, t)$$

Classical ED

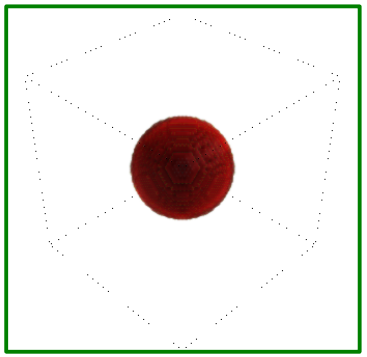
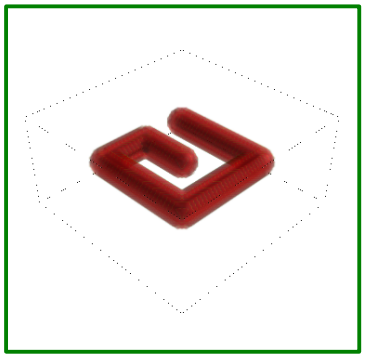
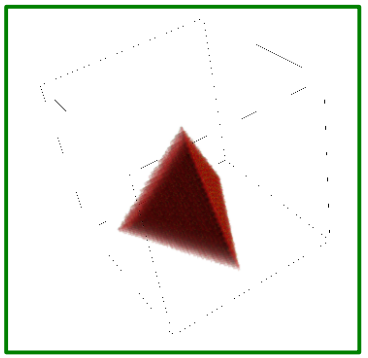
- What it does (FDTDPoissonSolver)
  1. Propagate $\mathbf{P}_j(\mathbf{r},t)$
  2. Solve $\rho(\mathbf{r},t) = -\nabla \cdot \mathbf{P}(\mathbf{r},t)$
  3. Solve $\nabla^2 V(\mathbf{r},t) = -4\pi\rho(\mathbf{r},t)$
  4. Solve $\mathbf{E}(\mathbf{r},t) = -\nabla \cdot V(\mathbf{r},t)$
  5. Propagate $\mathbf{J}_j(\mathbf{r},t)$

$$\frac{\partial \mathbf{P}_j(\mathbf{r},t)}{\partial t} = \mathbf{J}_j(\mathbf{r},t)$$

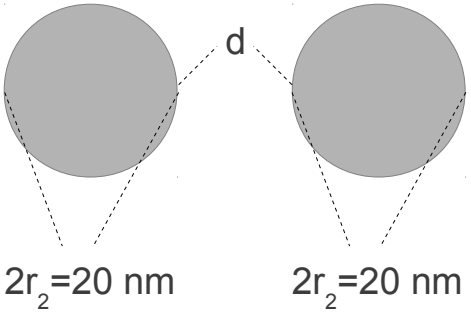
$$\mathbf{P}(\mathbf{r},t) = \sum_j \mathbf{P}_j(\mathbf{r},t)$$

$$\frac{\partial \mathbf{J}_j(\mathbf{r},t)}{\partial t} = -\alpha_j(\mathbf{r})\mathbf{J}_j(\mathbf{r},t) - \bar{\omega}^2(\mathbf{r})\mathbf{P}_j(\mathbf{r},t) + \varepsilon_0\beta_j(\mathbf{r})\mathbf{E}(\mathbf{r},t)$$

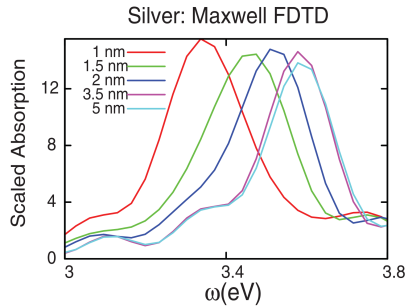
- What is implemented?
  - New FDTDPoissonSolver class
  - Lorentzian parametrization for permittivity (Na, Ag, Au)
  - Geometry of classical material

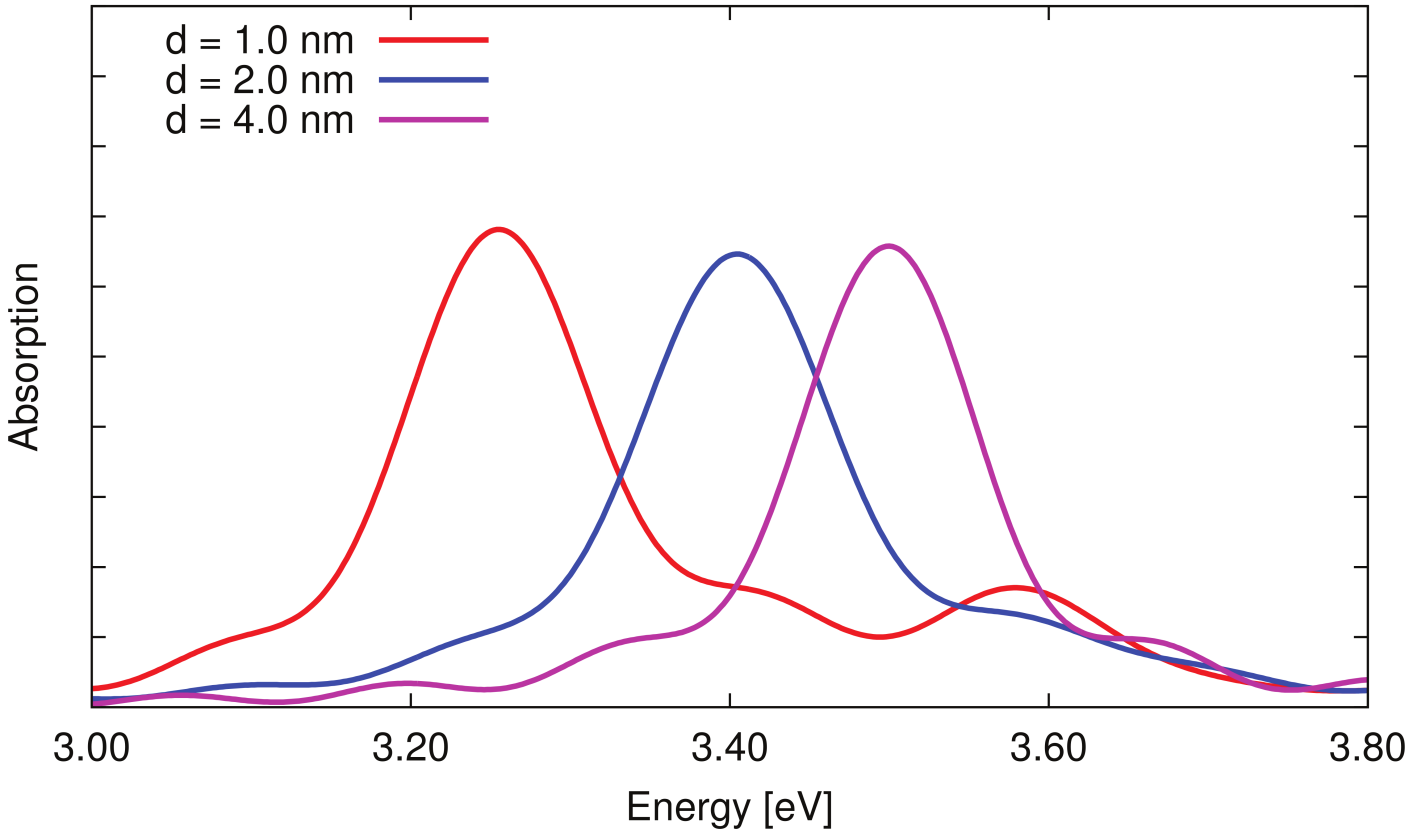
Classical ED



Extract from Fig. 4 of the original NF paper of Coomar et al., JCP 135, 084121 (2011):

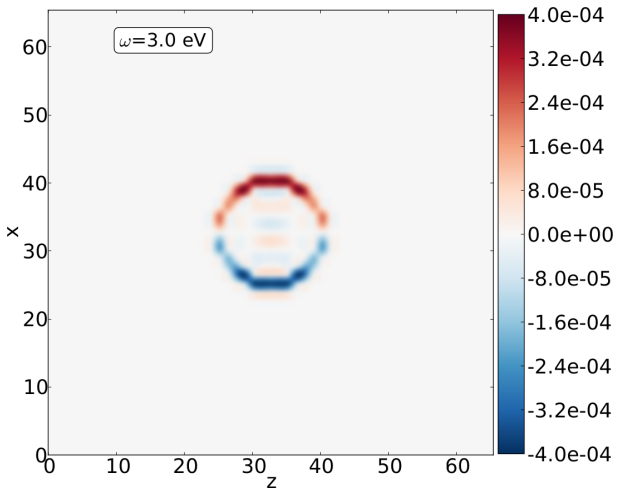


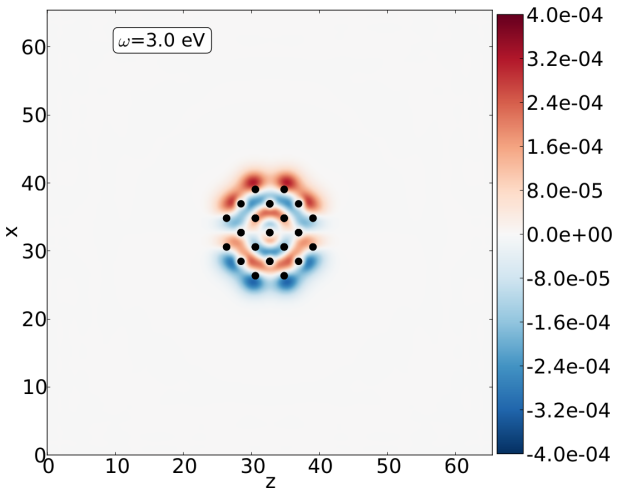
Ag dimer with classical ED (Maxwell equations, GPAW.FDTD)

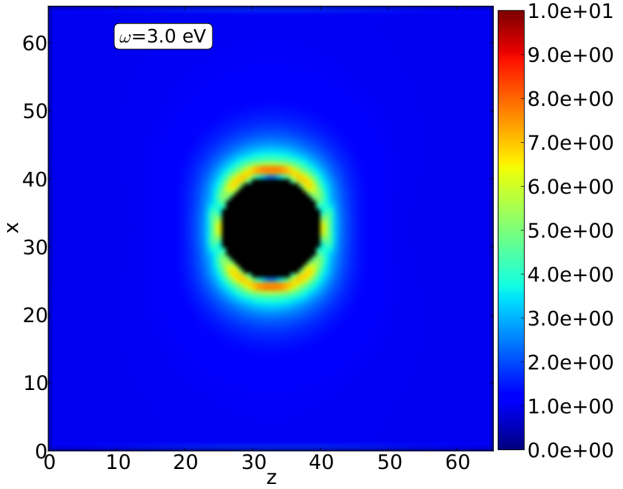


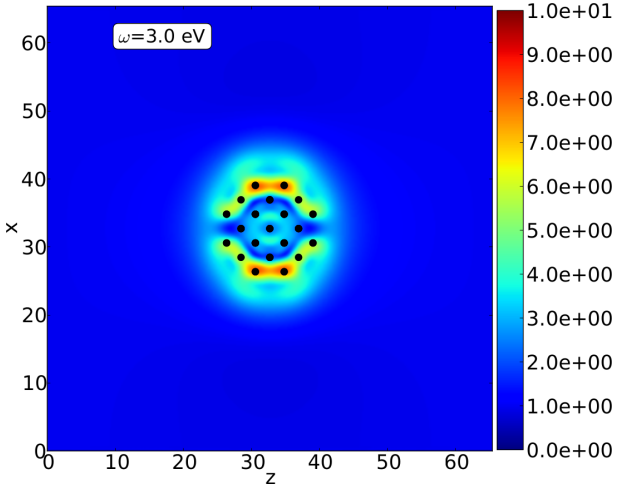
Classical ED

- Results: Sodium nanospheres



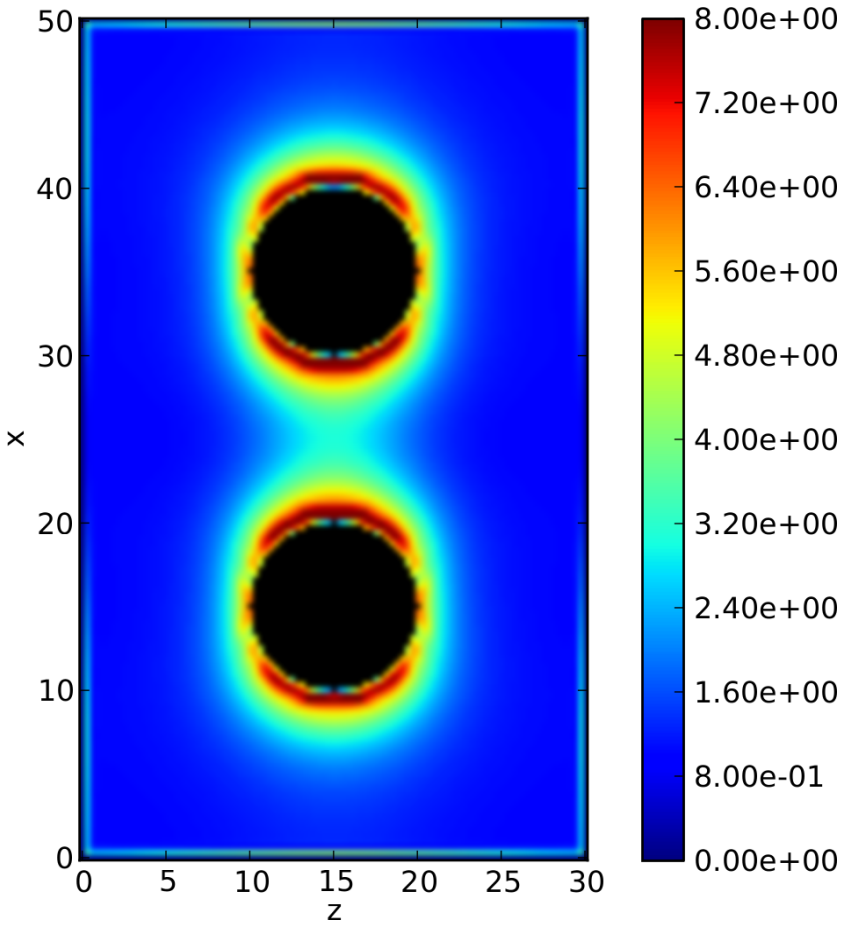




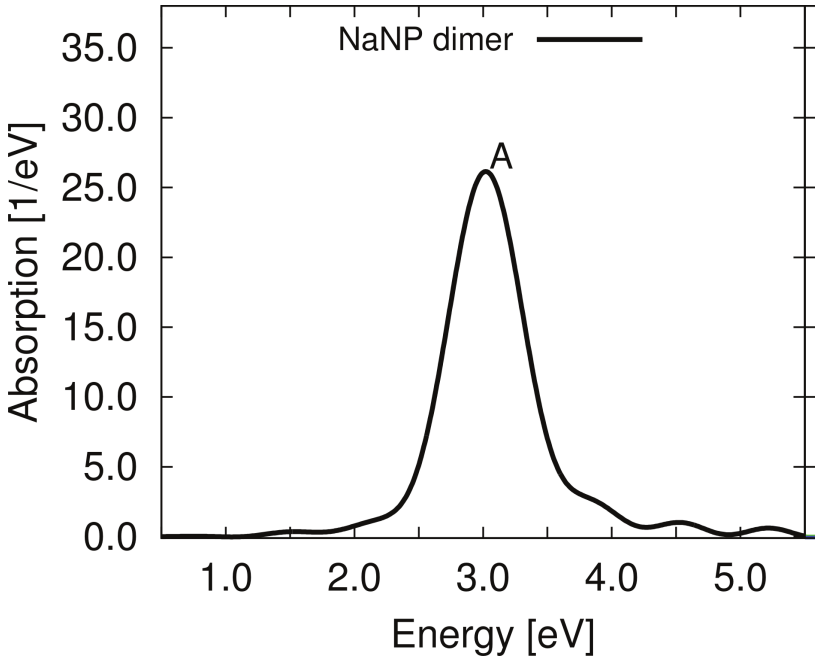


Classical ED

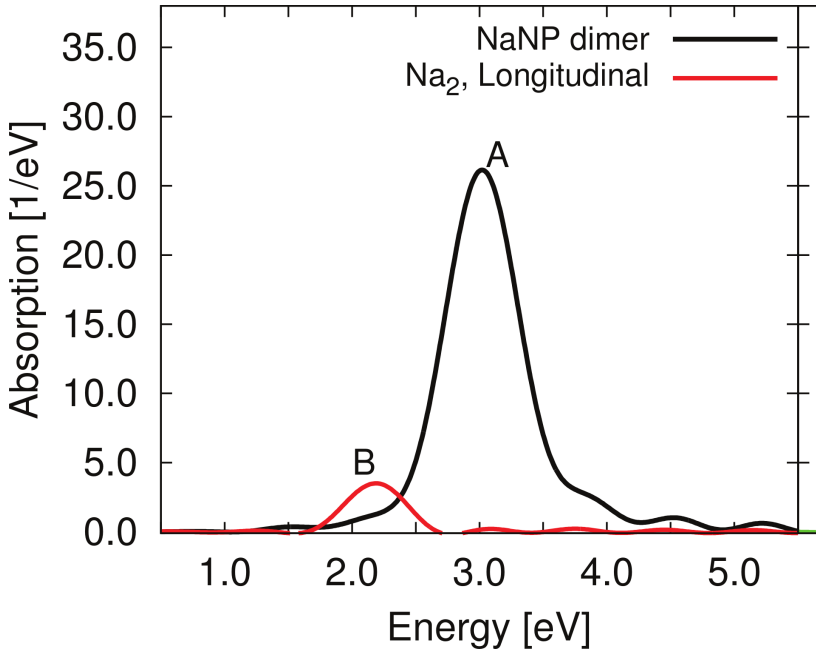
- Results: Sodium nanosphere dimer



Classical ED



Classical ED



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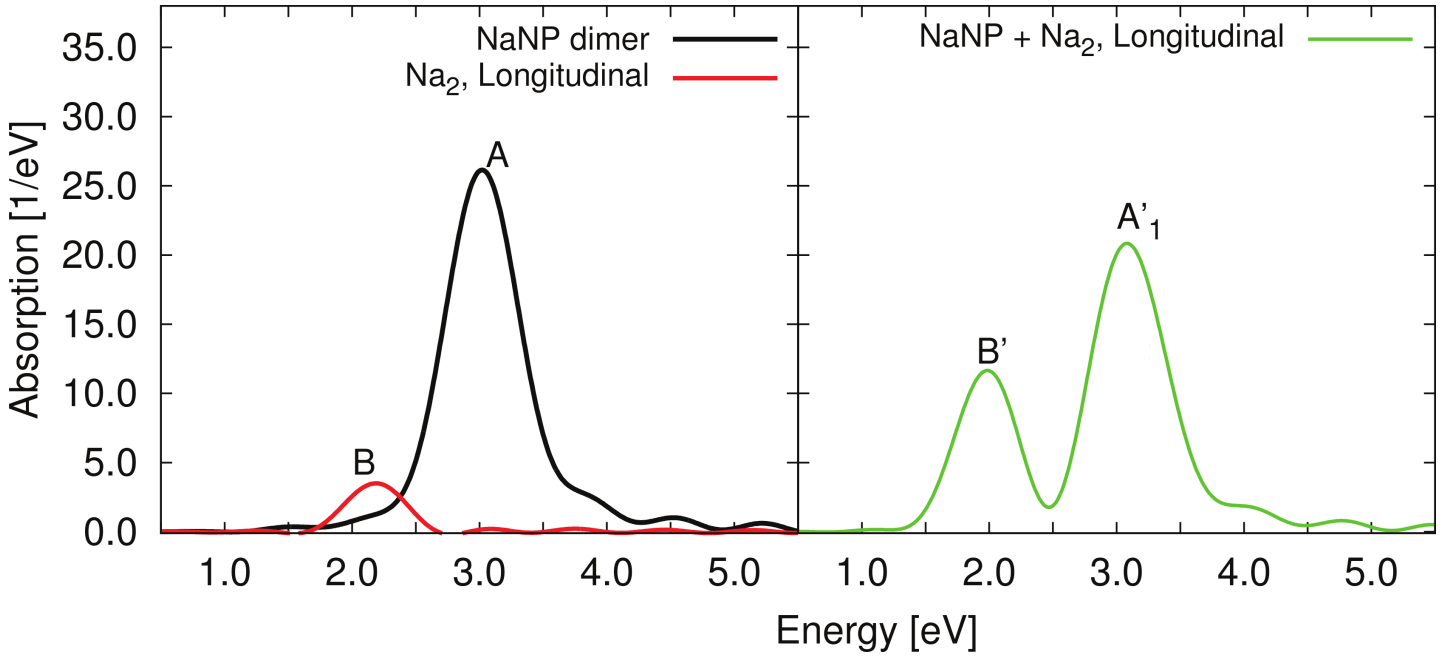

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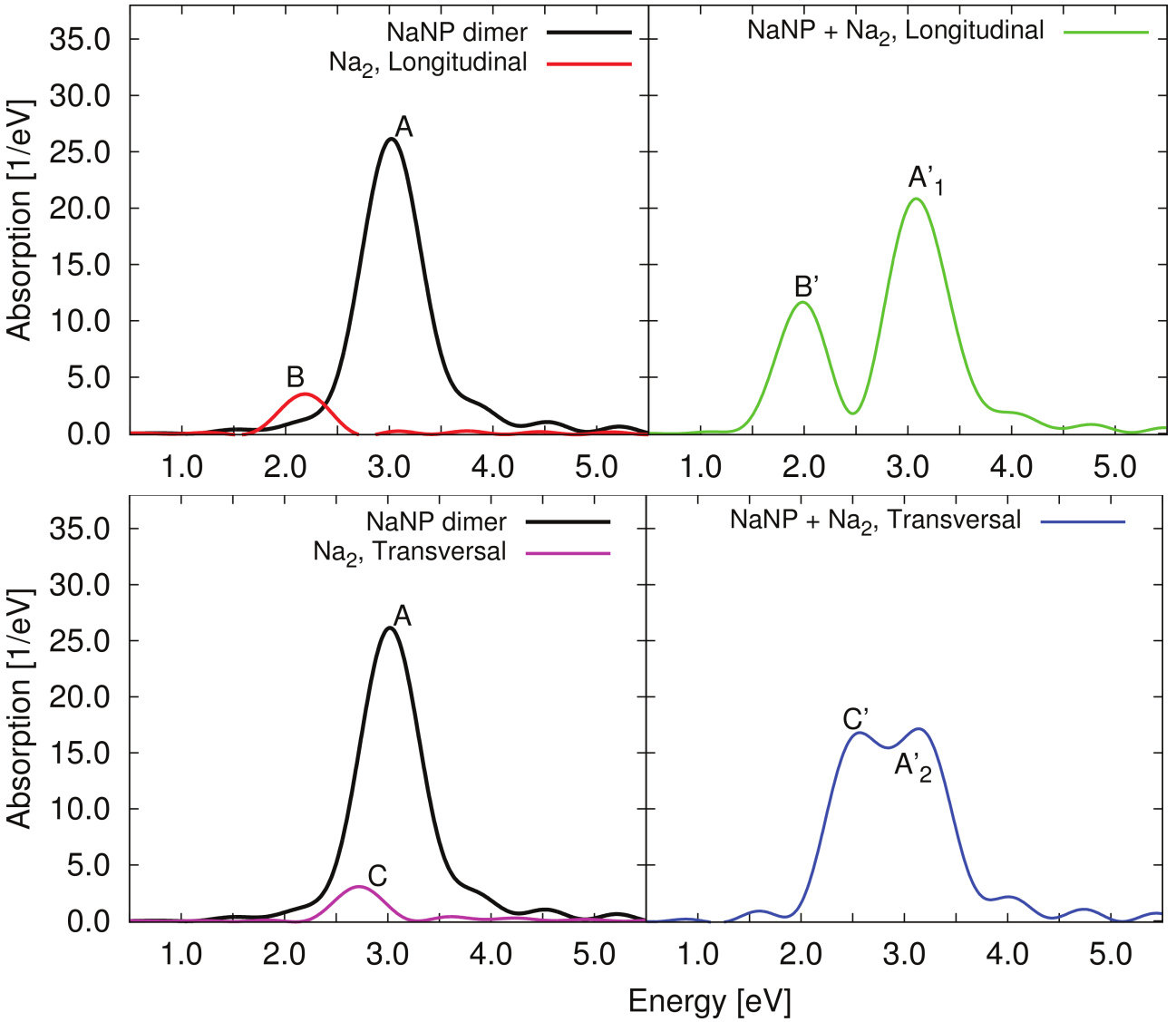

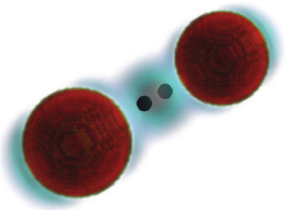

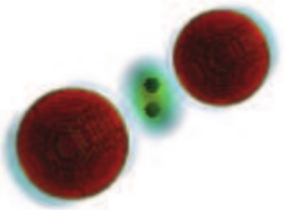

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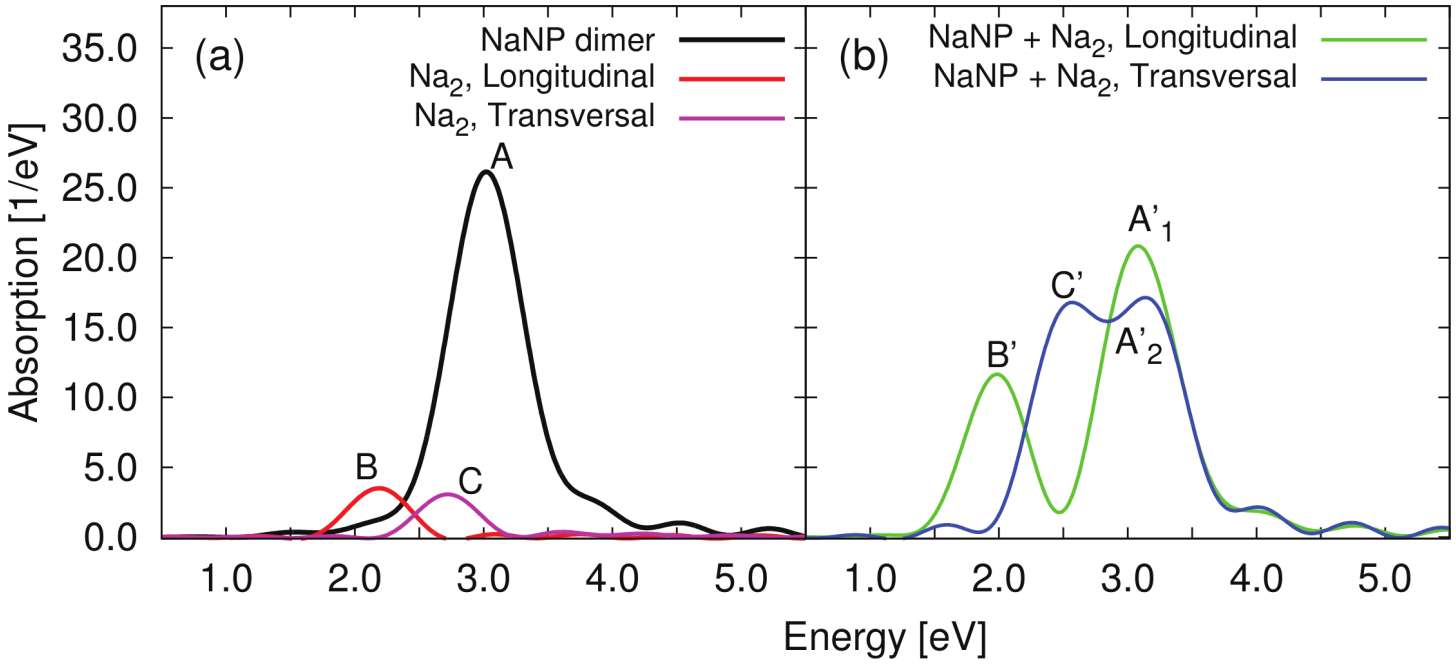

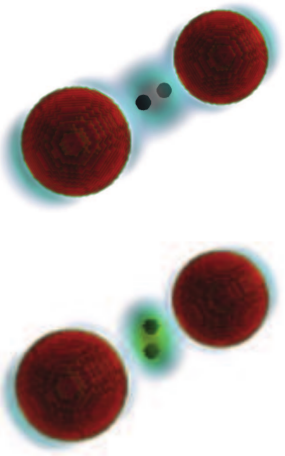

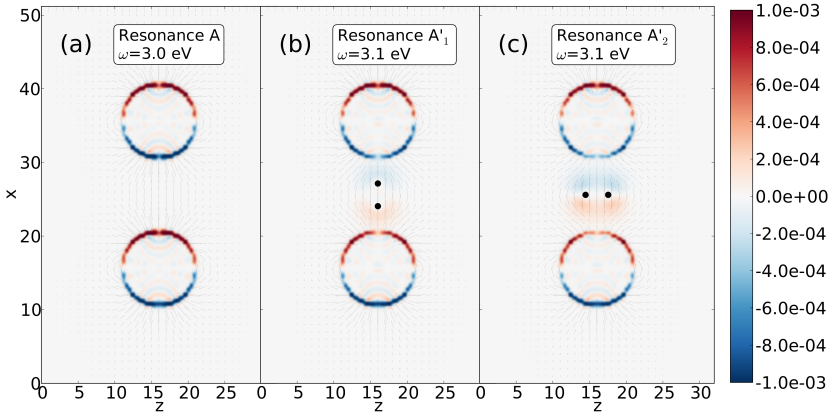

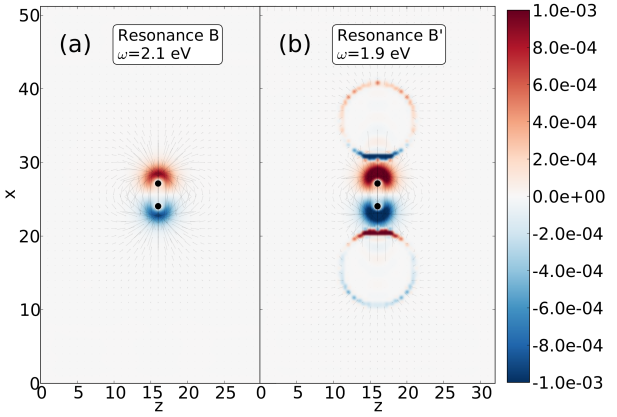

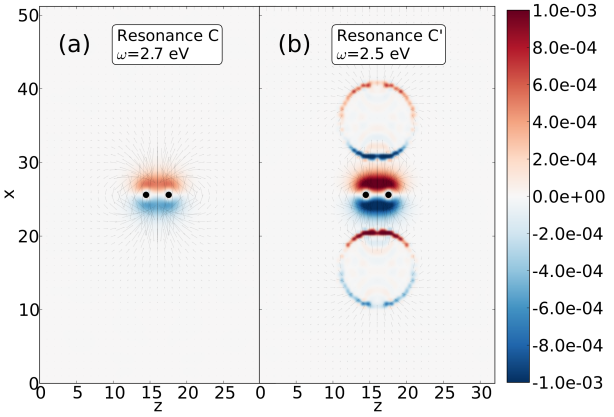

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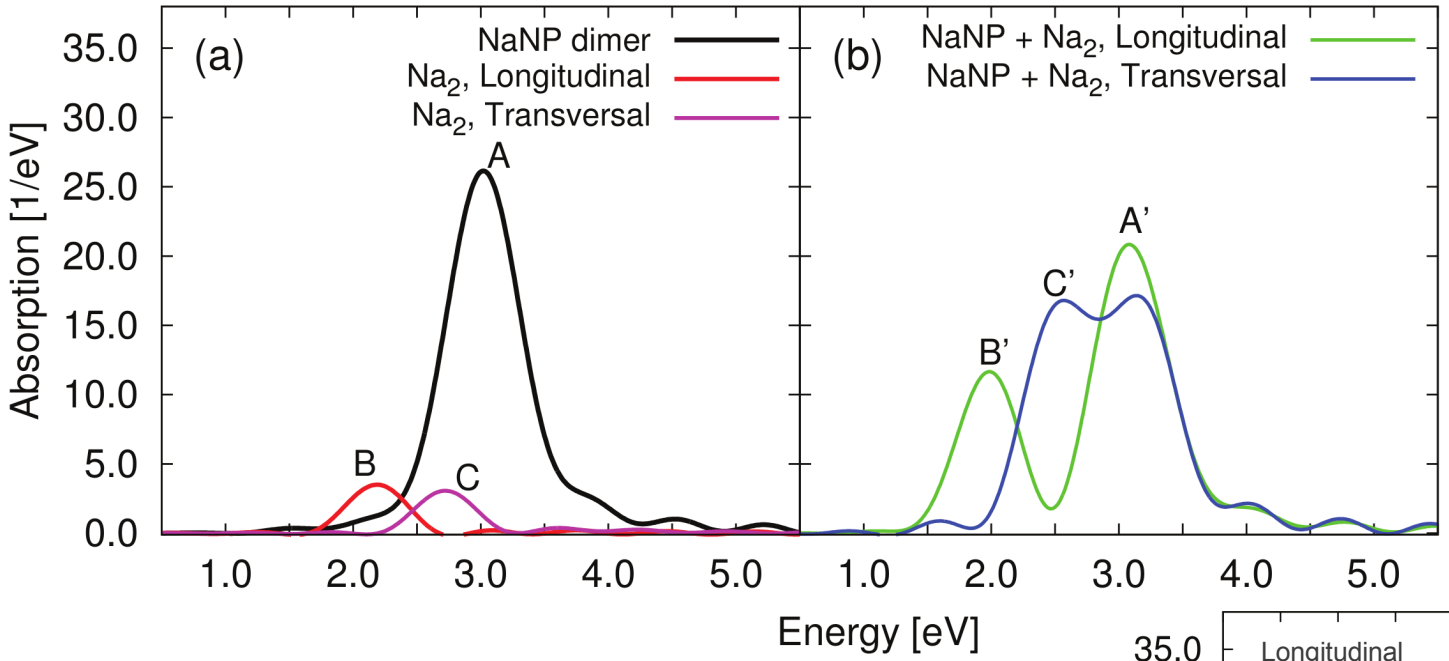
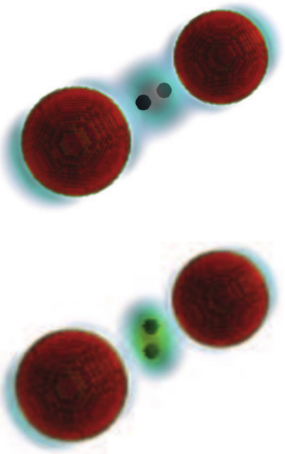
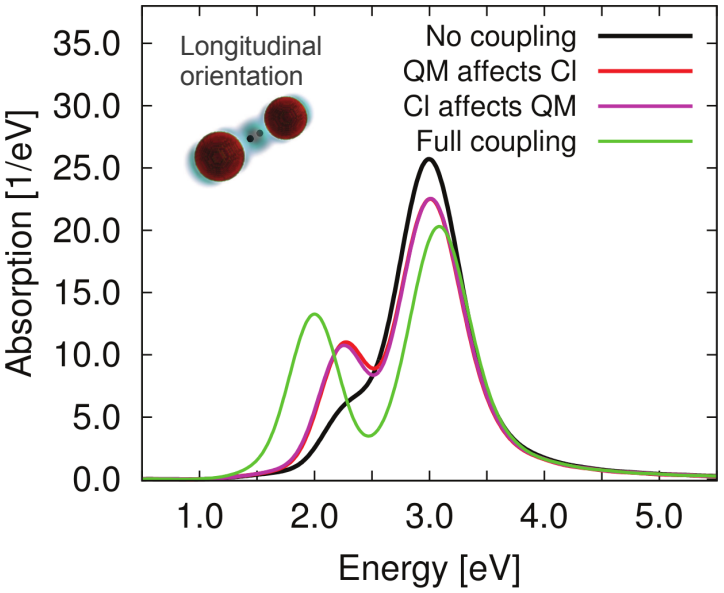




$$\nabla^2 V(\mathbf{r},t) = -4\pi\rho^{\mathrm{QM+CL}}(\mathbf{r},t)$$

$$\rightarrow \begin{cases} \nabla^2 V^{\mathrm{QM}}(\mathbf{r},t) = -4\pi\rho^{\mathrm{QM}}(\mathbf{r},t) \\ \nabla^2 V^{\mathrm{CL}}(\mathbf{r},t) = -4\pi\rho^{\mathrm{CL}}(\mathbf{r},t) \end{cases}$$

$$\mathbf{E}(\mathbf{r},t) = -\nabla\cdot V^{\mathrm{CL}}(\mathbf{r},t) - \nabla\cdot V^{\mathrm{QM}}(\mathbf{r},t)$$



Electric near field from TDDFT

Electric perturbation $\boldsymbol{r} \cdot \boldsymbol{E}_{\mathrm{ext}}(\omega)$ induces charge density oscillations

$$\delta\rho(\boldsymbol{r},\omega) = \int_0^\infty \mathrm{d}t \left(\rho(\boldsymbol{r},t) - \rho^0(\boldsymbol{r})\right) e^{i\omega t}$$

↓

Induced electric potential $\nabla^2 \delta\varphi(\boldsymbol{r},\omega) = -4\pi\delta\rho(\boldsymbol{r},\omega)$

↓

Induced electric field $\delta\boldsymbol{E}(\boldsymbol{r},\omega) = -\nabla\delta\varphi(\boldsymbol{r},\omega)$

↓

Field enhancement $\mathrm{FE}(\boldsymbol{r},\omega) = \dfrac{|\boldsymbol{E}_{\mathrm{ext}}(\omega) + \delta\boldsymbol{E}(\boldsymbol{r},\omega)|}{|\boldsymbol{E}_{\mathrm{ext}}(\omega)|}$

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TDDFT: time propagation or Casida method

↓

Induced electric potential $\nabla^2 \delta\varphi(\boldsymbol{r},\omega) = -4\pi\delta\rho(\boldsymbol{r},\omega)$

`gpaw.poisson.PoissonSolver`

↓

Induced electric field $\delta\boldsymbol{E}(\boldsymbol{r},\omega) = -\nabla\delta\varphi(\boldsymbol{r},\omega)$

`gpaw.fd_operators.Gradient`

↓

Field enhancement $\mathrm{FE}(\boldsymbol{r},\omega) = \dfrac{|\boldsymbol{E}_{\mathrm{ext}}(\omega) + \delta\boldsymbol{E}(\boldsymbol{r},\omega)|}{|\boldsymbol{E}_{\mathrm{ext}}(\omega)|}$

Induced density from time propagation

Time propagation TDDFT: explicit time evolution of density (`gpaw.tddft`)

Induced density

$$\delta\rho(\boldsymbol{r},\omega) = \int_0^\infty \mathrm{d}t \left(\rho(\boldsymbol{r},t) - \rho^0(\boldsymbol{r})\right) e^{i\omega t} g(t)$$

finite lifetime for excitations

$g(t) = e^{-\eta t}$ or $g(t) = e^{-\frac{1}{2}\sigma^2 t^2}$

In PAW formalism

$$\delta\rho(\boldsymbol{r},\omega) = -\sum_\sigma \delta\tilde{n}_\sigma(\boldsymbol{r},\omega) - \sum_a \sum_{ij} \delta D^a_{\sigma ij}(\omega) \left(\phi^{a*}_j(\boldsymbol{r})\phi^a_i(\boldsymbol{r}) - \tilde{\phi}^{a*}_j(\boldsymbol{r})\tilde{\phi}^a_i(\boldsymbol{r})\right)$$

all-electron corrections

or

$$\delta\tilde{\rho}(\boldsymbol{r},\omega) = -\sum_\sigma \delta\tilde{n}_\sigma(\boldsymbol{r},\omega) - \sum_a \sum_L \delta Q^a_L(\omega)\tilde{g}^a_L(\boldsymbol{r})$$

compensation charges →

$$\delta Q^a_L(\omega) = \sum_{\sigma ij} \Delta^a_{Lij} \delta D^a_{\sigma ij}(\omega)$$

correct electric potential and field outside augmentation spheres

Induced density from time propagation

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all-electron corrections

or

time-dependent time-independent

$$\delta\tilde{\rho}(\boldsymbol{r},\omega) = -\sum_\sigma \delta\tilde{n}_\sigma(\boldsymbol{r},\omega) - \sum_a \sum_L \delta Q^a_L(\omega)\tilde{g}^a_L(\boldsymbol{r})$$

compensation charges

$$\delta Q^a_L(\omega) = \sum_{\sigma ij} \Delta^a_{Lij} \delta D^a_{\sigma ij}(\omega)$$

correct electric potential and field outside augmentation spheres

Fourier transforms $\delta\tilde{n}_\sigma(\boldsymbol{r},\omega)$ and $\delta D^a_{\sigma ij}(\omega)$ are calculated during time propagation for fixed ω, $\delta\rho(\boldsymbol{r},\omega)$ can be constructed afterwards

Induced density from Casida method

Casida method: linear response TDDFT formulation directly in frequency space (`gpaw.lrtddft`)

Induced density

$$\delta\rho(\boldsymbol{r},\omega) = \sum_I \frac{1}{\omega_I^2 - \omega^2} 2 \sum_{ij\sigma,kl\tau}^{\mathrm{ph}} \rho^*_{ij\sigma}(\boldsymbol{r}) \sqrt{f_{ij\sigma}\omega_{ij\sigma}} F_{I,ij\sigma} F^*_{I,kl\tau} \sqrt{f_{kl\tau}\omega_{kl\tau}} z_{kl\tau}$$

$\Omega F_I = \omega_I^2 F_I$

divergent at excitation frequencies
→ modify to recover finite lifetime

pair density $\rho_{ij\sigma}(\boldsymbol{r}) = \psi^*_{i\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r})$

$$\rho_{ij\sigma}(\boldsymbol{r}) = \tilde{\psi}^*_{i\sigma}(\boldsymbol{r})\tilde{\psi}_{j\sigma}(\boldsymbol{r}) + \sum_a \sum_{kl} D^a_{ij\sigma kl} \left(\phi^{a*}_l(\boldsymbol{r})\phi^a_k(\boldsymbol{r}) - \tilde{\phi}^{a*}_l(\boldsymbol{r})\tilde{\phi}^a_k(\boldsymbol{r}) \right)$$

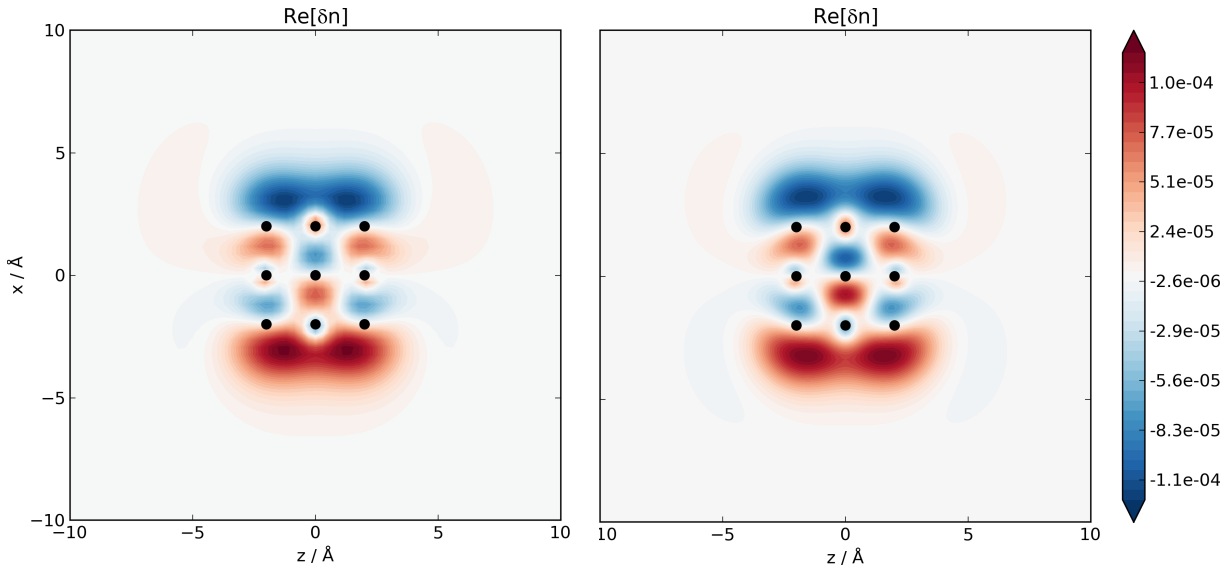
or

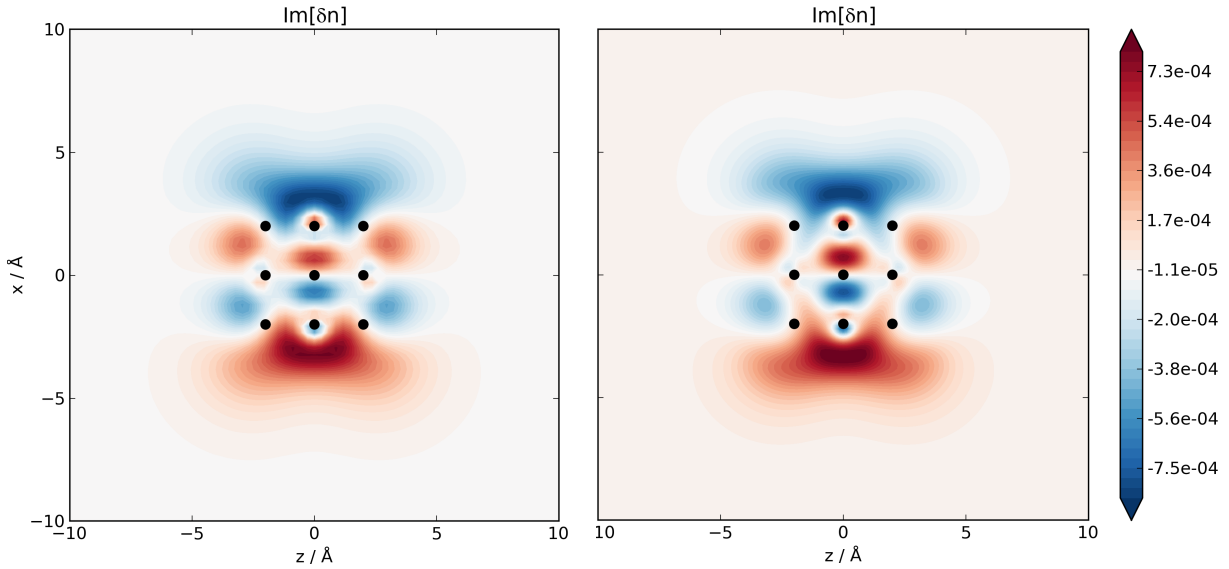
$$\tilde{\rho}_{ij\sigma}(\boldsymbol{r}) = \tilde{\psi}^*_{i\sigma}(\boldsymbol{r})\tilde{\psi}_{j\sigma}(\boldsymbol{r}) + \sum_a \sum_L Q^a_{ij\sigma L} \tilde{g}^a_L(\boldsymbol{r})$$

Implemented as a post-processing step (`LrTDDFT` and `GPAW` objects required)

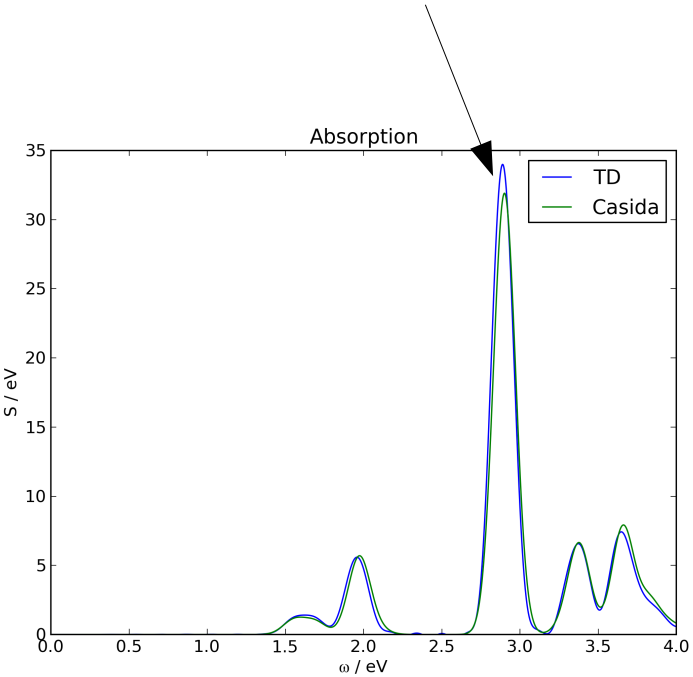
Examples

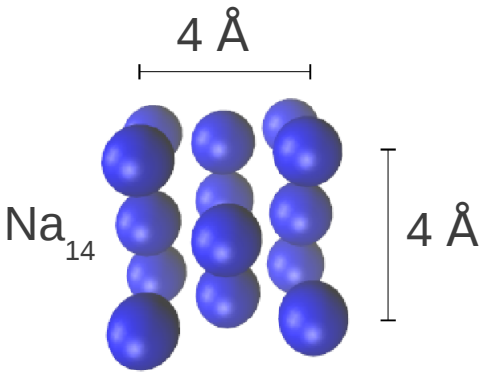
Casida



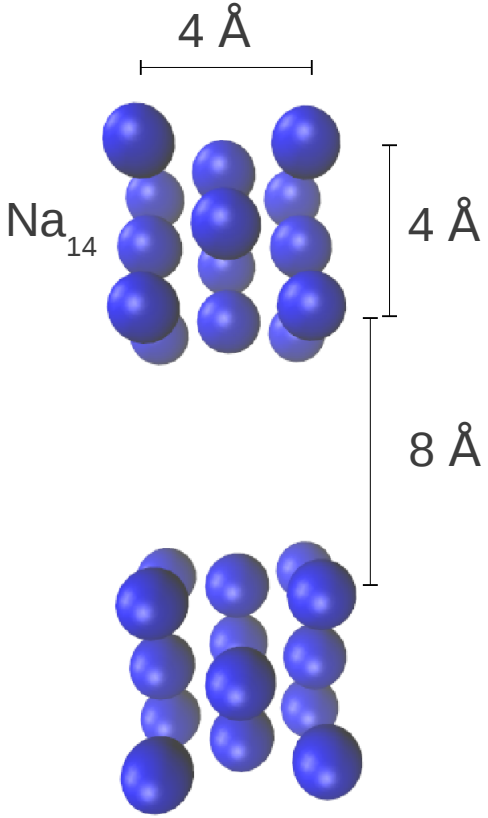


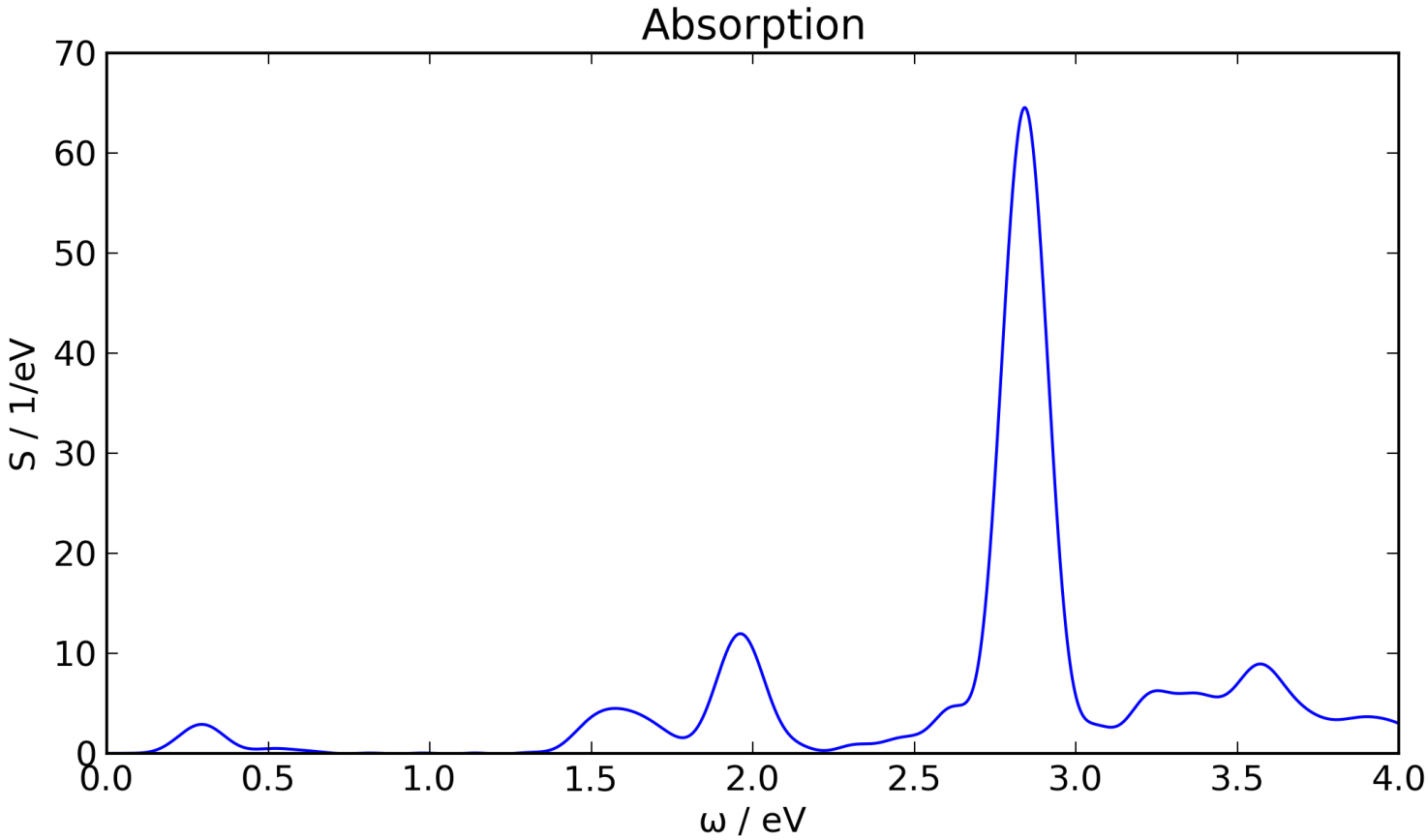
TD



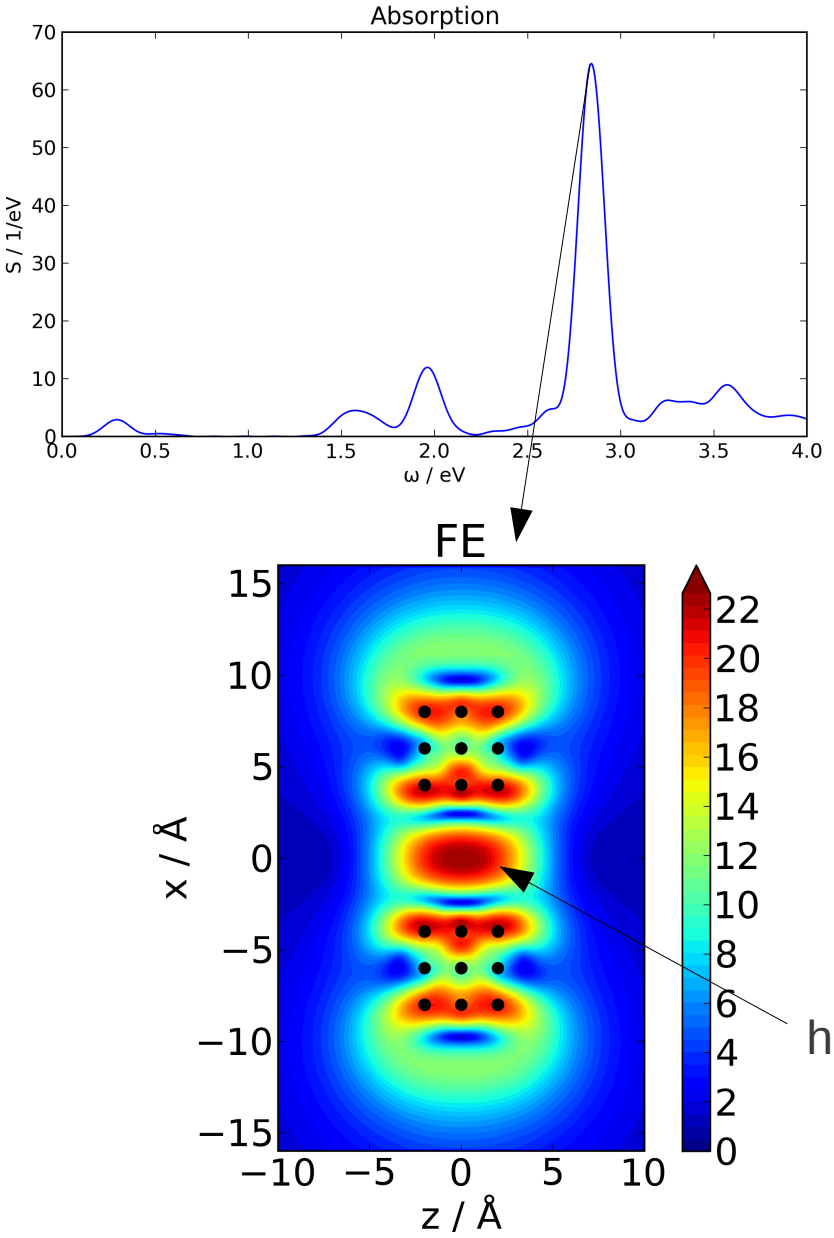


Examples

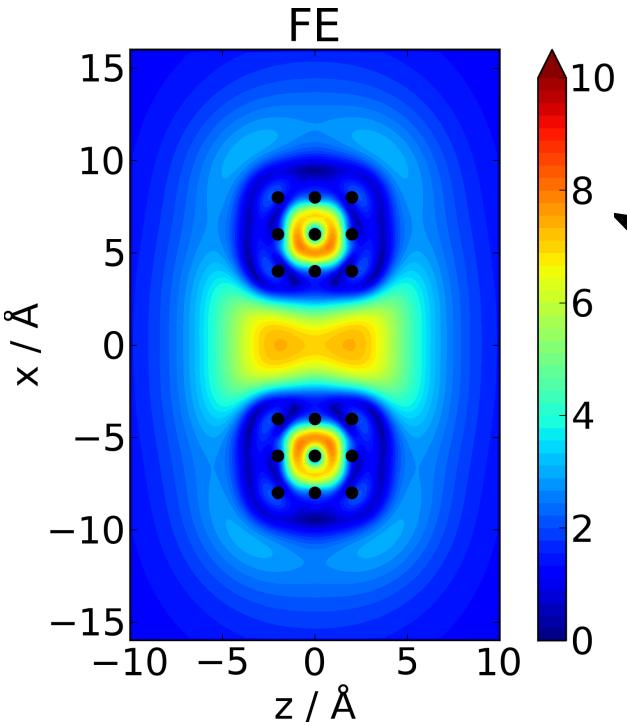

4 Å
Na14
4 Å
8 Å

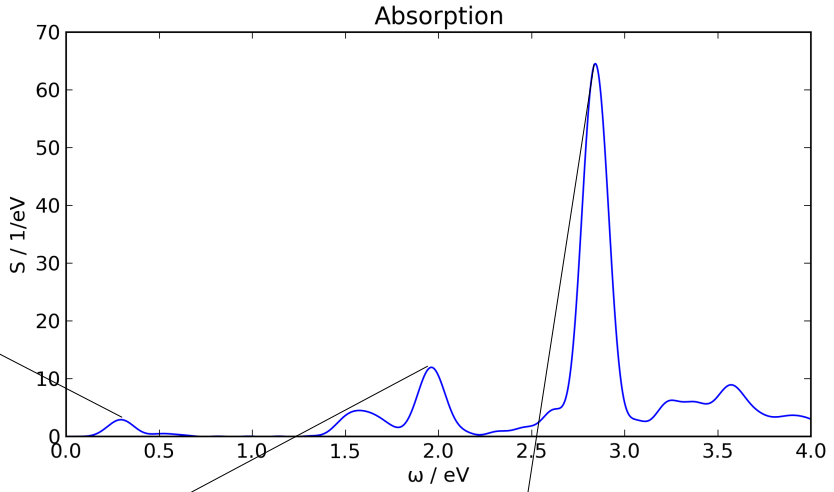

Absorption
S / 1/eV
ω / eV
0
10
20
30
40
50
60
70
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

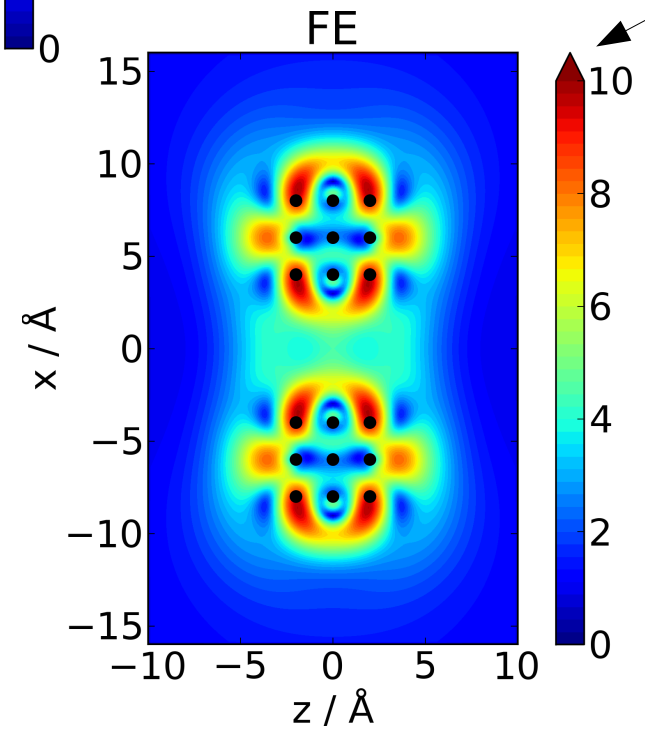
Examples

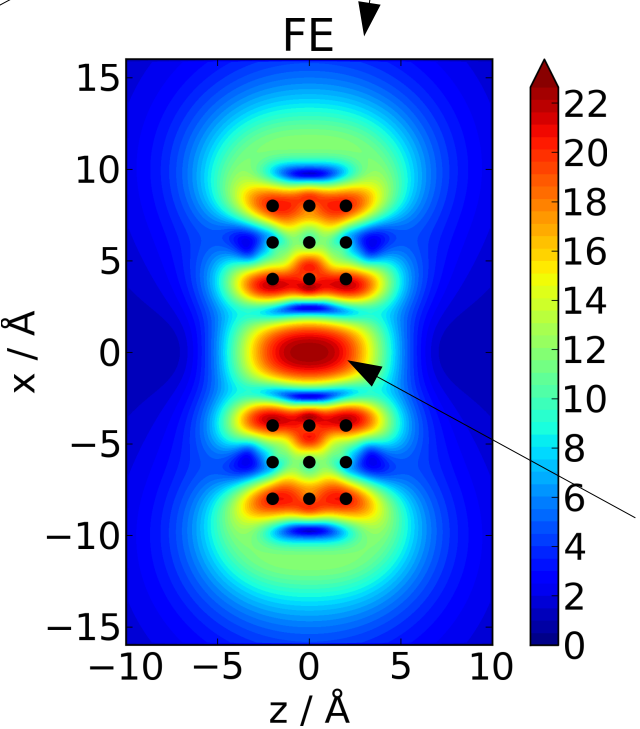


Examples









hot spot

Conclusions

- New methods:
  - Induced charge density
  - Near field distributions
  - Quasistatic classical electrodynamics
  - Hybrid quantum/classical simulations

Thank you for your attention!