CECAM - Psi-K Workshop
Computational plasmonics: an ab initio and multiscale perspective
November 02, 2015 - November 04, 2015
CECAM-HQ-EPFL, Lausanne, Switzerland

Organizers: **Stefano Corni, Arrigo Calzolari**
CNR-NANO, Institute of nanoscience, Modena, Italy

Final Report for Psi-K

Summary

The workshop spanned three days and involved 38 attendees. The programme (see below) included invited talks, contributed talks and a poster session, as well as a general discussion section at the end of each morning and afternoon, led by the chairperson of that section.

The goal of the workshop was to address a list of issues in computational plasmonics that were summarized by the following questions:

- What is a plasmon from a microscopic point of view?
    - Molecular-like vs plasmon-like excitation
    - First-principles description: just a matter of size or other technical/conceptual issues?
- Multiscale approaches to molecular plasmonics: where are we? Is anything missing in the description? Chemical effects?
- Computations vs experiments:
    - Are experimental results calling for atomistic simulations to be understood?
    - Are new computational predictions still in need of experimental verification?
- Non-conventional plasmonics materials (e.g., graphene, metal oxides, nitrides):
    - New challenges to theory from them with respect to metals?
    - Classical electrodyanmics treatment good enough?
    - Effect of nanostructuring?

All these issues have been addressed during the workshop, both in talks/posters and in the general discussion sections. The latter have been very lively, with many participants taking part to the discussion (including some of the youngest). Different possible interpretation/solutions of the several discussed problems have been proposed and debated on both theoretical and experimental side. The conclusions of the workshop are summarized here below, following the wrap-up slot at the end of the workshop:

- Plasmons from microscopic point of view:
    - First-principle works for plasmons in metal clusters, scaling up to larger nanoparticles (NP) is a matter of **faster/better performing algorithms**.
    - How to **quantify** the plasmonic vs excitonic vs single-particle character of excitations? This is also needed to **extended** the concept of plasmon to molecules. The problem of quantify/discriminate excitations at the molecular scale is still open, and no general consensus has been reached on the way to solve it. **Coulomb potential** has been proposed as the key quantity, and it is related to the near-field enhancement. Separation of short-range vs long-range Coulomb interactions is a promising route to explore.

- Challenges in multiscale modeling of plasmonics

1. **Quantum effects** in NP plasmons. OI: Linking atomistic, jellium-based and quantum hydrodynamics models upon changing size
2. Molecule(s)+solvent+plasmonic system.
    a. SERS, SEIRA etc.. coupling **first-principles** molecules with **focused EM** fields description is needed
    b. Develop an embedding scheme to include a metal region atomistically (important for near-field, e.g atomic lighting rod, chemical interaction&conductivity, hot-electron photochemistry, including phonons)
3. Optical forces (e.g. metal atom rearrangements under plasmon excitation): models able to describe them are required. Computational challenge: no straightforward way to solve it has emerged.
4. Out of equilibrium is a common feature of plasmonics phenomena (photochemistry, heat production, dynamics of molecules close to plasmonic systems....)
5. Non-linear response of plasmonic systems are still modeled empirically, first-principles treatments are behind.

- Non-conventional plasmonic materials (doping&nanostructuring)
    - First-principles modeling needed to **predict** their optical properties (controlling tunability). Defects & doping are the important parameters to be included in the models
    - Need for computational material discovering to guide experimental choices. Define proper Figure of Merits
    - Modeling of **non-linear** optical properties are still missing
    - Simultaneous modeling of different properties (e.g., magnetic, optical and thermal) is important, as this is often the motivation of using these materials

- Quantized plasmons
    - Theoretically (almost) unexplored (e.g., extension of TDDFT to QED still lacking in practice).
        - Quantized plasmons with an atomistic description of the NP is still missing
        - Description of the **strong coupling** of atomically-described molecules and quantum plasmons are to be developed

The variety of open problems and different proposed attempts to solve them arisen during the workshop confirmed that (i) the field of computational plasmonics is a lively research field in quick development and (ii) the gathering of an interdisciplinary community tightly connected with the experimental counterpart is a necessary step to tackle this complex physical problem.

List of speakers (* marks invited speakers)

*Aizpurua, Javier - Materials Physics Center (UPV-EHU), Donostia-San Sebastián, Spain
Amendola, Vincenzo - University of Padova, Italy
***Andreussi, Oliviero** - University of Pisa, Italy
Barbry, Marc - Materials Physics Center (UPV-EHU), Donostia-San Sebastián, Spain
*Baumberg, Jeremy - University of Cambridge, United Kingdom
Biagioni, Paolo - Politecnico di Milano, Italy
Calderón, Jonathan - University of Valencia, Spain
Chikkaraddy, Rohit - University of Cambridge, United Kingdom
*Cirací, Cristian - Istituto Italiano di Tecnologia, Lecce, Italy
Clarke, Daniel - Queen's University Belfast, United Kingdom
De Angelis, Francesco - Italian Institute of Technology, Italy
Foerstner, Jens - University of Paderborn, Germany
Fortunelli, Alessandro - National Research Council (CNR), Pisa, Italy
Grynko, Yevgen - University of Paderborn, Germany
Hourahine, Benjamin - University of Strathclyde, United Kingdom
*Häkkinen, Hannu - University of Jyväskylä, Finland
*Jacob, Christoph - University of Braunschweig, Germany
*Jensen, Lasse - Pennsylvania State University, USA
*Kinsey, Nathaniel - Purdue University, USA
***Luo, Yi** - Royal Institute of Technology, Stockholm, Sweden
*Manjavacas, Alejandro - University of New Mexico, Albuquerque, USA
*Muskens, Otto - University of Southampton, United Kingdom
Pipolo, Silvio - École normale supérieure, France
Rossi, Tuomas - Aalto University, Finland
Ruini, Alice - University of Modena, Italy
Stener, Mauro - University of Trieste, Italy
Stenger, Nicolas - Technical University of Denmark, Denmark
*Thygesen, Kristian - Technical University of Denmark, Lyngby, Denmark
Timrov, Iurii - International School for Advanced Studies (SISSA), Italy
Varas, Alejandro - University of the Basque Country (UPV-EHU), Bilbao, Spain

Programme

Day 1 - Monday November 2, 2015

Day 1 - morning session. Chairs: Arrigo Calzolari; Cristian Ciraci
- 8:45 to 9:00 - Welcome and Introduction (S. Corni & A. Calzolari)

- 9:00 to 9:40 - **Javier Aizpurua**
  Quantum effects in the optical response of plasmonic nanoantennas

- 9:40 to 10:05 - **Daniel Clarke**
  Extending the scope of the jellium model for nanoplasmonics using deformable potentials

- 10:05 to 10:45 - **Oliviero Andreussi**
  Multiscale modeling of biohybrid devices for plasmon-enhanced light-harvesting

- 10:45 to 11:15 - Coffee Break

- 11:15 to 11:55 - **Hannu Häkkinen**
  Birth of the localized surface plasmon resonance in thiolate protected gold-silver nanoclusters

- 11:55 to 12:20 - **Alessandro Fortunelli**
  Designing ligand-enhanced optical absorption of thiolated gold nanoclusters and plasmonic effects in gold nanostructures

- 12:20 to 13:00 - Discussion

- 13:00 to 14:00 - Lunch

Day 1 - afternoon session. Chairs: Alessandro Fortunelli; Javier Aizpurua
- 14:00 to 14:40 - **Jeremy Baumberg**
  Squeezing light into nanogaps: plasmonics in the sub-nm and quantum domains, with graphene, mos2, and molecules

- 14:40 to 15:05 - **Silvio Pipolo**
  Real-time cis for molecules close to nanoparticles

- 15:05 to 15:30 - **Benjamin Hourahine**
  Semi-empirical time-dependent dft for plasmonic systems

- 15:30 to 16:00 - Coffee Break

- 16:00 to 16:40 - **Cristian Cirací**
  Quantum hydrodynamic model for multi-scale plasmonics

- 16:40 to 17:05 - **Yevgen Grynko**
  Modeling the second harmonic generation from plasmonic nanostructures with a hydrodynamic approach

- 17:05 to 17:30 - **Jens Foerstner**
Quantum theories for the ultrafast nonlinear optical response of metal slabs

- 17:30 to 18:00 - Discussion

- 18:00 to 19:00 - Poster Session

Day 2 - Tuesday November 3, 2015

Day 2 - morning session. Chairs: Yi Luo; Lasse Jensen
- 9:00 to 9:40 - **Alejandro Manjavacas**
Tunable molecular plasmons

- 9:40 to 10:05 - **Alejandro Varas**
First-principles nanoplasmonics on metal-clusters dimers

- 10:05 to 10:45 - **Kristian Thygesen**
Plasmon eigenmodes in metallic nano-structures and 2d materials from first principles response functions

- 10:45 to 11:15 - Coffee Break

- 11:15 to 11:55 - **Christoph Jacob**
Identifying plasmons in molecular quantum-chemical calculations

- 11:55 to 12:20 - **Mauro Stener**
A new time dependent density functional algorithm for plasmons in metal clusters

- 12:20 to 13:00 - Discussion

- 13:00 to 14:00 - Lunch

Day 2 - afternoon session. Chairs: Jeremy Baumberg, Francesco De Angelis
- 14:00 to 14:40 - **Nathaniel Kinsey**
Practical nanophotonics with plasmonic ceramics

- 14:40 to 15:05 - **Paolo Biagioni**
Characterization and modelling of the steady-state and transient  plasmonic properties of heavily-doped ge

- 15:05 to 15:30 - **Alice Ruini**
Transparent conductive oxides as near-ir plasmonic materials: the case of al-doped zno derivatives

- 15:30 to 16:00 - Coffee Break

- 16:00 to 16:40 - **Otto Muskens**
Experiments and modelling of hotspot-mediated switching in plasmonic antennas

- 16:40 to 17:05 - **Vincenzo Amendola**
  Superior plasmon absorption in iron-doped gold nanoparticles

- 17:05 to 17:45 - Discussion

- 19:30 to 0:00 - Social Dinner

Day 3 - Wednesday November 4, 2015

Day 3 - morning session. Chairs: Mauro Stener, Stefano Corni
- 9:00 to 9:40 - **Lasse Jensen**
  Atomistic simulations of surface-enhanced spectroscopies

- 9:40 to 10:05 - **Rohit Chikkaraddy**
  Single-molecule strong coupling in plasmonic nanocavities to modify ground state vibrational states

- 10:05 to 10:30 - **Jonathan Calderón**
  Optimization of embedded gold nanorod arrays for sers analysis of ctcs

- 10:30 to 11:00 - Coffee Break

- 11:00 to 11:40 - **Yi Luo**
  Molecular response under the nanocavity plasmon

- 11:40 to 12:05 - **Tuomas Rossi**
  Quantum plasmonics of stretched nanorods

- 12:05 to 12:30 - **Marc Barbry**
  First-principles calculations of plasmonic resonances and electric field enhancement in metal-cluster dimers

- 12:30 to 13:00 - Discussion

- 13:00 to 14:00 - Lunch

Day 3 - afternoon session. Chairs: Arrigo Calzolari, Stefano Corni
- 14:00 to 14:25 - **Iurii Timrov**
  Simulating electron energy loss spectroscopy for complex surfaces

- 14:25 to 14:50 - **Nicolas Stenger**
  Higher-order surface plasmons and their disappearance in few-nanometer silver nanoparticles

- 14:50 to 15:30 - Discussion-Conclusions

Quantum effects in the optical response of plasmonic nanoantennas

Javier Aizpurua[1]
Centro de Física de Materiales (CSIC-UPV/EHU) and Donostia International Physics Center (DIPC) Donostia-San Sebastián, Spain

The optical response of nanometric-sized metallic particles is well described within the framework of Electrodynamics. Linear local dielectric theory within Maxwell's equations provides a very adequate description of the evolution of electric and magnetic fields that adapt to the boundaries of a particular structure, providing information about the absorption and scattering of light by it. In metallic nanoparticles, the optical response is mainly governed by the excitation of localized surface plasmons, the collective oscillation of the surface charge density at the particle following the electromagnetic modes imposed by the geometrical boundary conditions.   As the dimensions of nanoparticles reach a few nanometers or even Ångstroms, the quantum nature of the electrons building up the optical response becomes noticeable, and important departures of the standard local response can be identified. The description of a full quantum model to describe the optical response will be introduced within Time-Depedent Density Functional Theory (TDDFT). This fully quantum mechanical approach allows to consider (i) quantum size effects, (ii) nonlocal dynamical screening, and (iii) spill-out of the electron cloud at the boundaries.   Beyond the case of single nanoparticles, gap-nanoantennas formed by strongly-coupled metallic nanoparticles also provide the capability to tune the optical response on demand. A switch between a capacitive and conductive situation within the gap modifies the plasmonic modes allowing for a variety of applications such as all-optical switching, near-field coherent control of single emitters, or probing of transport properties at optical frequencies. As metallic nanoparticles come close together at subnanometric distances, the plasmonic nanogap enters a strong nonlocal regime. For the smallest separations, electron quantum tunnelling across the gap is possible at optical frequencies modifying dramatically the optical response of the system. To account for the effect of the spill-out of the electrons at the surface of the metal as well as the coherent tunnelling that can be established across the gap, full quantum mechanical calculations of the optical response are necessary [1,2]. Considering the limitations of quantum calculations to relatively small systems, I will present a method particularly suitable to include quantum effects in large realistic plasmonic systems, the quantum-corrected model (QCM) [3]. Recent experimental situations where the quantum regime in subnanometric gaps has been revealed will be described [4], as well as general concepts of nonlocality [5] and nonlinearities [2] within the quantum plasmonic response. Finally, I will present some results regarding the importance of an atomistic description of metallic nanoparticles to correctly address the near-field distribution around the particles, where we identify subnanometric localization of light thanks to the effect of crystallographic facets, edges and vertices [6].

[1] Zuloaga J., Prodan E., and Nordlander P., "Quantum description of the plasmon resonances of a particle dimer", Nano Lett., Vol. 9, 887 (2009).
[2] Marinica, C., Kazansky A., Nordlander, P. Aizpurua, J. and Borisov, A.G., "Quantum plasmonics: nonlinear effects in the field enhancement of a plasmonic nanodimer", Nano Lett., Vol. 12, 1333, 2012.
[3] Esteban R., Borisov A.G., Nordlander, P., and Aizpurua J., "Bridging quantum and classical plasmonics with a quantum-corrected model", Nat. Commun., Vol. 3, 825, 2012.
[4] Savage K.J., Hawkeye M.M., Esteban R., Borisov, Aizpurua J., and Baumberg J.J., "Revealing the quantum regime in tunneling plasmonics", Nature, Vol. 491, 574, 2012.
[5] T. Teperik, P. Nordlander, J. Aizpurua, A. Borissov, Phys. Rev. Lett. 110, 263901 (2013).
[6] M. Barbry, P. Koval, F. Marchesin, R. Esteban, A. G. Borisov, J. Aizpurua, and D. Sánchez-Portal, "Atomistic Near-Field Nanoplasmonics: Reaching Atomic-Scale Resolution in Nanooptics", Nano Lett. 15, 3410 (2015).

Extending the scope of the jellium model for nanoplasmonics using deformable potentials

Daniel Clarke[1], Lorenzo Stella

Atomistic Simulation Centre (ASC), School of Mathematics and Physics, Queen's University Belfast, University Road, Belfast BT7 1NN, United Kingdom

Experimental advances in the fabrication and control of plasmonic architectures, achieving nanometric and even sub-nanometric precision, have enabled the synthetic viability of metallic nanoparticles (MNPs) with a broad range of shapes and sizes. In parallel to fully ab initio calculations, the simple and robust jellium approximation has been employed extensively to model the response of MNPs to external electromagnetic fields. The predictive capacity of the jellium description has been successfully demonstrated for a range of simple geometries, e.g., spheres [1] and wires [2]. However, little is known regarding its reliability for more complicated background geometries, including MNPs with lower symmetries (e.g., icosahedra), as well as structures that are highly branched (e.g., nanostars) or internally porous (e.g. nanocages). In this contribution, we present a flexible jellium pseudopotential generator, which has been interfaced with the real-time, real-space, time-dependent density functional theory (TDDFT) code OCTOPUS [3]. Such a quantum mechanical framework permits a complete account of electronic delocalisation effects, along with the deformation of the background potential (the so called deformable, or ultimate, jellium model [4]), in a fully self-consistent manner. We demonstrate this computational approach for a selection of complex MNP morphologies that have played a prominent role in recent experimental and theoretical nanoplasmonic studies. Possible applications to modelling the photothermal behaviour of single MNPs, and aggregates thereof, are finally discussed.

[1] E. Townsend and G. W. Bryant, Nano Lett. 12, 429 (2012).
[2] L. Stella et al., J. Phys. Chem. C 117, 8941 (2013).
[3] X. Andrade et al., Phys. Chem. Chem. Phys., accepted, (2015).
[4] M. Koskinen, P.O. Lipas and M. Manninen, Z. Phys. D: At., Mol. Clusters 35, 285 (1995).

Multiscale modeling of biohybrid devices for plasmon-enhanced light-harvesting

Oliviero Andreussi[1], Stefano Corni3, Benedetta Mennucci4
Università della Svizzera Italiana, Lugano, Switzerland; and Institute of Materials Science and Engineering, École Polytechnique Fédérale de Lausanne, Switzerland; 3Center S3, CNR-Institute of Nanoscience, Modena, Italy; 4Dept.Chemistry, University of Pisa, Italy

Photosynthesis is triggered by the absorption of light by light-harvesting (LH) pigment-protein complexes followed by excitation energy transfer to the reaction center(s). A promising strategy to achieve control on and to improve light harvesting is to complement the LH complexes with plasmonic particles. In particular, it was shown both theoretically [1-2] and experimentally [3-4] that combining nano-plasmonic devices with natural LH proteins substantially increases the fluorescence and absorption properties of the system. This kind of biohybrid devices can have important applications in the characterization and design of efficient light-harvesting systems. In order to study these systems, a multi scale approach was recently developed [1], combining a quantum-mechanical description of the pigments, a classical atomistic polarizable model for the protein embedding, and a continuum dielectric approach for the plasmonic particles. Being able to treat each component of the system with the right degree of accuracy, the resulting QM/MMPol/PCM approach allows us to model in a computationally inexpensive way the effects of the environment on all the fundamental photo-physical processes of LH systems, namely light absorption, excitation energy transfer among the different pigments and towards the plasmonic device, and, eventually, light emission. Results on different biohybrid devices, comprising different LH complexes and metal nanoparticles, are able to confirm and explain available experimental trends. Moreover, the possibility to selectively analyze the effects of nanoparticles shape and configuration (number of particles, orientation, distance) on each photo-physical step of light harvesting

allows us to provide important design rules for optimally enhanced devices. In particular, enhancements of up to three orders of magnitude in the fluorescence decay rates were found for the peridinin-chlorophyll-protein (PCP) complex adsorbed on silver nanoparticles [1], with the hot-spot configuration, in which the protein complex is sandwiched between two metal aggregates, showing the largest enhancements. On the contrary, results on the FMO protein coupled with gold nanoparticles [2] showed smaller effects, with enhancements of up to two orders of magnitude limited by the poor alignment of the emitting excitonic state of the complex with the plasmonic environment.

[1] O. Andreussi, A. Biancardi, S. Corni and B. Mennucci, Nano Lett. 13, 4475 (2013)
[2] O. Andreussi et al., J. Phys. Chem. A 119, 5197 (2015)
[3] S. Mackowski et al., Nano Lett. 8, 558 (2008)
[4] E. Wientjes et al., Nature Comm. 5, 4236 (2014)

Birth of the localized surface plasmon resonance in thiolate protected gold-silver nanoclusters

Hannu Häkkinen[1]
 Physics and Chemistry, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland

Noble metal nanoclusters protected by a thiolate monolayer are widely studied for their potential applications in site-specific bioconjugate labeling, sensing, drug delivery, and molecular electronics.[1] Several monometallic and intermetallic clusters with 1_-2 nm metal cores are currently known to have a well-defined molecular structure, and they serve as an important link between molecularly dispersed and colloidal metal particles to understand the size-dependent electronic and optical properties. Here, we show by using an ab initio method together with atomistic models for experimentally observed thiolate-stabilized gold/silver clusters how collective electronic excitations change when the gold core of the cluster grows from 1.5 to 2.0 nm. A strong localized surface plasmon resonance (LSPR) develops at 540 nm (2.3 eV) in a cluster with a 2.0 nm metal core. The protecting molecular layer enhances the LSPR, while in a smaller cluster with 1.5 nm gold core, the plasmon-like resonance at 540 nm is confined in the metal core by the molecular layer. The plasmonic absorption can be sensitively changed by doping with silver or copper.[2-5] Very recently, plasmonic thiolate-stabilized silver clusters with atomistically resolved structures have been reported.[6] Our results demonstrate a threshold size for the emergence of LSPR in these systems and help to develop understanding of the effect of the molecular overlayer on plasmonic properties of noble metal nanoclusters enabling engineering of their properties for plasmonic applications.

[1] H. Häkkinen, Nature Chem. 4, 443 (2012).
[2] S. Malola and H. Häkkinen, J. Phys. Chem. Lett. 2, 2316 (2011).
[3] S. Malola, L. Lehtovaara, J. Enkovaara and H. Häkkinen, ACS Nano 7, 10263 (2013).
[4] S. Malola, L. Lehtovaara and H. Häkkinen, J. Phys. Chem. C 118, 20002 (2014).
[5] S. Malola, M.Hartman and H. Häkkinen, J. Phys. Chem. Lett. 6, 515 (2015).
[6] H. Yang et al., submitted (2015).

Designing ligand-enhanced optical absorption of thiolated gold nanoclusters and plasmonic effects in gold nanostructures

Alessandro Fortunelli[1], L. Sementa1, G. Barcaro1, A. Dass2, E. Aprà3, M. De Vetta4, O. Baseggio4, A. Marini5, M. Stener4
 CNR-ICCOM & IPCF, via G. Moruzzi 1, Pisa, 56124, Italy;
alessandro.fortunelli@cnr.it
1 CNR-ICCOM & IPCF, via G. Moruzzi 1, Pisa, 56124, Italy;
alessandro.fortunelli@cnr.it
2 Department of Chemistry and Biochemistry, University of Mississippi, 38677, Oxford (MS), USA

3 Pacific Northwest National Laboratory, Richland, Washington 99352, USA
4 Dip. di Scienze Chimiche e Farmaceutiche, Università di Trieste, via L. Giorgieri 1, 34127, Italy
5 CNR-ISM, v. Salaria Km 29.5, I-00016 Monterotondo, Italy

The absorption spectra of metal nanostructures are characterized by strong bands in the optical-UV region referred to as Surface Plasmon Resonances (SPR) [1]. This feature is very sensitive to the nanostructure environment: a first issue then arises because the environment (such as the shell of protecting ligands in thiolated clusters) can damp the absorption intensity in the visible region, thus e.g. requiring much larger particles observe the "birth" of SPR. This limits applications in molecule detection via Raman spectroscopy, enhanced plasmonic phenomena in metal nanogaps, biosensing, etc. Two different strategies are here investigated to overcome the issue of SPR damping and achieve intense SPR peaks in the whole near-IR/vis region.The first strategy is based on fine tuning the chemical features of ligands in monolayer-protected clusters [2]. Focusing on thiolated Au nanoclusters with formulae Au25(SR)18, Au23(SR)16 and Au30(SR)18, whose atomistic structure has been determined in selected cases, and predicting their spectra via time-dependent densityfunctional- theory (TDDFT) simulations, we show how large enhancements in absorption spectra in the whole optical region can be achieved by tuning the steric and electronic properties of the SR ligands. Charge decompression via steric hindrance and delocalization via π-conjugation to achieve optimal band alignment are used as guiding principles to design candidate species whose integrated optical spectral intensity exceeds that of much larger clusters. This occurs via a resonance phenomenon in which many excitations, of composite Au/S/R character and involving the nanocluster as a whole, crowd in a narrow energy interval. This strategy allows one to circumvent the issue of SPR damping by the environment (SPR "re-birth"), and represents a step forward toward the goal of an in silico design of nanoclusters with desired optical properties.The second strategy is based on molecule/nanostructure resonance coupled with plamon/plamon interactions due to proximity effects [3]. Attention is focused on Au nanowires, which allow a computationally economical study of sizeable systems due to exploitation of translational symmetry. The coupling between the plasmonic modes of the metal nanoparticle and those involving Au-ligand bonds is explored as a prototypical example of metal/ligand interface, and the search for synergic interactions in the optical response will be discussed. The dependence of plasmonic peaks upon stoichiometry and chemical ordering will be analyzed, together with its dependence upon inter-particle distance to explore coupled plasmonics effects and 'hot-spot' enhancement of response fields in the presence of ligated species. The role of the coating ligand shell in terms of both structural and optical properties will be underlined.

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2.	L. Sementa, G. Barcaro, A. Dass, M. Stener, A. Fortunelli, Chem. Comm. 51, 7935–7938 (2015); (article in preparation).
3.	A. Marini, G. Barcaro, F. R. Negreiros, A. Fortunelli, ACS Photon. 1, 315–322 (2014).

Squeezing light into nanogaps: plasmonics in the sub-nm and quantum domains, with graphene, mos2, and molecules

Jeremy Baumberg[1], Bart De Nijs1, Felix Benz1, Jan Mertens1, Daniel Sigle1, Oren A. Scherman2, Rohit Chikkaraddy1, Alan Sanders1, Christos Tserkezis3, Javier Aizpurua3
 NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK
1 NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK
 ‎2 Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

‎3 Donostia International Physics Center (DIPC) and Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, Paseo Manuel Lardizabal 4, 20018 Donostia-San Sebastian, Spain

Coupling between plasmonic nano-components generates strongly red-shifted resonances combined with intense local field amplification on the nanoscale. This allows directly seeing molecules as well as excitations in semiconductors. We have recently explored plasmonic coupling which can be tuned dynamically, through reliable bottom-up self-assembly. The crucial aspect of these systems is the extreme sensitivity to separation, and how quantum tunneling starts to be directly seen at room temperature in ambient conditions. We recently demonstrated how quantum plasmonics controls the very smallest space that light can be squeezed into.[1-3] We also demonstrate the possibility to track few molecules using the extreme enhancements. We show how the new generation of 2D semiconductors can couple to such nano-scale gaps utilizes our nanoparticle on mirror geometry. We find that changing just a single atom on each molecule of a self-assembled monolayer can shift the plasmon by over 50nm, and produce surprising vibrational signatures.[4-8] These have encouraging prospective applications in (bio)molecular sensing as well as fundamental science.[9-11]

(1) Nature 491, 574 (2012); Revealing the quantum regime in tunnelling plasmonics
(2) ACS Nano 5, 3878 (2011); Precise sub-nm plasmonic junctions within Au NP assemblies
(3) Nano Lett 13, 5033 (2013); Controlling sub-nm plasmonic gaps using graphene
(4) ACS Nano 9, 825 (2015); Monitoring Morphological Changes in 2D Monolayer Semiconductors ..
(5) Nano Letters 15, 669 (2015); Nano-optics of molecular-shunted plasmonic nanojunctions
(6) Science Reports 4, 5490 (2014); Watching individual molecules flex within lipid membranes …
(7) Nature Comm. 5, 4568 (2014); Threading plasmonic nanoparticle strings with light
(8) Nature Comm. 5, 3448 (2014); DNA origami based assembly of Au nanoparticle dimers for SERS ..
(9) Scientific Reports 4, 6785 (2014); Quantitative multiplexing with nano-self-assemblies in SERS
(10) Nano Lett 13, 5985 (2013); In-situ SERS … of photochemistry within a nano-junction reactor
(11) Nano Letters (2015); Demonstrating PL from Au is Electronic Inelastic Light Scattering of a Plasmonic Metal: The Origin of SERS Backgrounds

Real-time cis for molecules close to nanoparticles

Silvio Pipolo[1], Stefano Corni,2Roberto Cammi3
 IMPMC, Université Pierre et Marie Curie, Paris, France
2Center S3,CNR-Institute of Nanoscience,Modena,Italy; 2Dept. of Chemistry,University ofParma,Parma,Italy

We have recently proposed a general approach to couple the real-time TDDFT and TDHF dynamics of a molecule with the time-dependent response of a dielectric medium, employing a reformulation of the Polarizable Continuum Model (PCM) equations [1]. Here we extend such method to Configuration Interaction description of the electronic dynamics of molecular systems close to nanoparticles, addressing the non-trivial problem of formulating the time-dependent interaction between the two species. In fact, as for the dielectric case, the potential term that includes the nanoparticle polarization effects in the molecular Hamiltonian (the nanoparticle reaction potential - NRP), depends on the charge density of the molecule, and when the density is evolving in time, e.g., due to an external perturbation, such potential term also becomes time-dependent, in a non-trivial way, due to the delayed response of the nanoparticle rooted in its frequency-dependent dielectric constant. Furthermore, we show that our reformulation of the PCM-like equations for the nanoparticle case [1,2] not only is the key step for deriving a general expression for the time-dependent NRP but it also discloses a direct connection with multipolar plasmon resonances, and provides a useful tool for calculating the resonance frequencies of arbitrarily shaped nanoparticles. Finally we present a computationally efficient method for coupling the dynamics of the molecular system and the nanoparticle polarization based on an equation of motion for the NRP using a model dielectric constant.

[1] S. Corni, S. Pipolo and R. Cammi, J. Phys. Chem. A 119, 5405 (2015).
[2] S. Corni and J. Tomasi J. Chem. Phys. 114, 3739 (2001).

Semi-empirical time-dependent dft for plasmonic systems

Benjamin Hourahine[1], Thomas Niehaus,2 Bálint Aradi,3   Adriel Domínguez,3
Thomas Frauenheim3
 SUPA, Department of Physics, University of Strathclyde, United Kingdom
2Theoretical Physics, University of Regensburg, Germany 3BCCMS, University of
Bremen, Germany

Ground, and increasingly excited state, properties of nanosystems are now commonly calculated via linear-response density functional theory. There are a variety of formulations of this approach for DFT methods (coupled-perturbed equations, Casida equations, Sternheimer equations, ...), where the static or time dependent response of the system is calculated for chosen perturbations. In turn, the faster density-functional based tight binding method (DFTB [1]) has similarly successfully applied many of these approaches [2,3] with good accuracy and substantially lower computational costs. There are also continuing efforts to improve the accuracy of the underlying model [4,5]. For example in the case of charge transfer excitations, such as plasmons in graphene, either including (at least approximately) Hartree-Fock exchange [5] or more novel approaches such as electronic constraints [6] are required.In this contribution, the possibilities of using DFTB to rapidly evaluate plasmonic properties of large system will be explored, discussing several of the approaches implemented within the framework of the DFTB+ code. In particular, response calculations for systems containing ~1000 atoms on desktop class computers and larger structures on parallel computing platforms will be demonstrated.

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Quantum hydrodynamic model for multi-scale plasmonics

Cristian Ciraci[1], Fabio Della Sala
 Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia (IIT), via Barsanti,
Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia (IIT), via Barsanti, I-73010, Arnesano, Italy; Istituto Nanoscienze-CNR, via per Arnesano 16, 73100 Lecce, Italy

Plasmonic nanostructures supporting gap-plasmon modes have received a great deal of attention for their unique ability to localize electromagnetic radiation well below the diffraction limit and strongly enhance the local electric fields [1,2]. Advances in nano-fabrication techniques [3] have made possible to achieve separation between metallic elements of only few nanometers. At such distances nonlocal or quantum effects become non-negligible, producing enormous variations in the macroscopic optical response [1]. Form the theory stand point, it is really challenging to fully take into account the multi-scale nature of such systems. A density functional approach allows a full description of the quantum nature of the free electrons however, it becomes prohibitive for clusters that exceed only few thousands atoms. An alternative approach is to use the hydrodynamic model that takes into account the

nonlocal behavior of the electron response by including the electron pressure [4]. The Hydrodynamic model can be generalized in order to describe nonlocal and spill-out effects near metal surfaces by using orbital-free energy functionals [5,6]. We explore the impact of the equilibrium charge density in such model for the case of spherical nanoparticles and compare our results to time-dependent density functional theory based calculations up to 5000 electrons, using an in-house developed numerical code (see Fig. 1a). Our implementation [7] allows to compute extinction spectra for spheres or more in general axis symmetric structures of order of many tens of nanometer in size, describing the full range of effects going from the nonlocal/spill-out effects up to retardation effects (Fig. 1b). The quantum hydrodynamic theory (QHT) is a suitable tool for studying plasmonic systems in which nonlocal and spill-out properties cannot be neglected. Our approach can be employed to investigate the influence of electron density profile on linear response of mesoscopic axis-symmetric three-dimensional geometries.

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Modeling the second harmonic generation from plasmonic nanostructures with a hydrodynamic approach

Yevgen Grynko[1], Heiko Linnenbank2, and Stefan Linden2, Jens Förstner1
 University of Paderborn, Paderborn, Germany
1University of Paderborn, Paderborn, Germany; 2University of Bonn, Bonn, Germany

Experimental and numerical studies of the nonlinear optical response from plasmonic nanostructures give evidence that different microscopic nonlinear mechanisms at the surface and in the metal volume are responsible for the second harmonic generation, its spectral response and dependence on the geometry of the structure [1-3]. It is, however, not obvious which effect is dominating in each special case. The hydrodynamic Maxwell-Vlasov model has been shown to provide qualitative agreement of the SHG conversion efficiencies to various experimental setups [1, 3]. We use the Nodal Discontinuous Galerkin Time domain (DGTD) method [4] to solve the full hydrodynamic equation including a semi-classical Fermi pressure contribution for the free electron gas confined in the volume of the plasmonic nanostructure. The DGTD numerical scheme is explicit in time and allows unstructured meshing and local mesh refinement. These features simplify the solution of the nonlinear problem that requires high spatial resolution. We performed simulations for pure and hybrid plasmonic/dielectric antennas with random small-scale surface roughness and compare the results with experimental measurements [5]. The property of surface roughness is a necessary condition for making the SHG mode radiate into the far zone for a generally symmetric geometry. As expected, we observe correlation between the linear optical extinction and the SHG signal for hybrid and pure antennas (see Fig.). Our simulations qualitatively reproduce the increase of the SHG and its polarization for hybrid structures and indicate that it is caused by the change of the dielectric environment near the gap, in particular, by the increased dipole moment of the entire system.

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Quantum theories for the ultrafast nonlinear optical response of metal slabs

Jens Foerstner[1], Arno Schindlmayr, Torsten Meier, Jens Förstner
 University of Paderborn, Paderborn, Germany
University of Paderborn, Paderborn, Germany

We present a numerical method for calculating the nonlinear dynamics of surface electrons in metals. This allows the simulation of the nonlinear response of small plasmonic nanostructures as used for meta materials and in nanoplasmonics. As shown by Rudnick and Stern [1], the motion of electrons perpendicular to the surface requires a quantum mechanical treatment due to nonlocal effects. As we want aim to incorporate the ultrafast non-equilibrium material response into a Maxwell solver, it is highly desirable to have a time-domain description of the surface electron dynamics. We achieve this using the dynamical time-dependent density functional theory (TDDFT) consisting of two parts: First, a static DFT calculation is performed in order to obtain the ground state density which is the starting point of a time-domain simulation. For the Jellium model, our results are in good agreement with those of Ref. [2]. The second part of the simulation consists of propagating the Kohn-Sham orbitals by one of the methods described in Ref. [3]. We investigated several methods to include damping effects.Using this approach, we were able to simulate the SHG signal of a metal slab, see the Figure, which shows how the current at the second harmonic is localized at the surface [4]. We also report on our effort to simulate the nonlinear dynamics using a quantum Wigner-Maxwell approach based on the Density Matrix method [5].

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Tunable molecular plasmons

Alejandro Manjavacas[1]
 Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131, USA

Polycyclic aromatic hydrocarbons (PAHs) have been recently proposed [1] as a very promising platform for controlling light-matter interaction at the nanoscale. These molecules exhibit strong visible-light resonances that can be switched on/off by the addition or removal of a single electron. PAHs are easily accessible via chemical synthesis free from structural imperfections, and can be regarded as the nanometer-sized forms of graphene, from which they inherit their high electrical tunability. Here [2], we present an experimental verification of these predictions using a spectro-electrochemical experimental setup, which allows us to measure the absorption spectrum of PAHs in different dielectric environments while controlling simultaneously the charge state of the molecules. The experimental results are well supported by first-principles calculations of the vibrationally-resolved absorption spectrum using state-of-the-art time-dependent density-functional theory (TDDFT) combined with the Franck-Condon principle. Furthermore, we use the switchable molecular plasmon of anthracene to demonstrate a proof-of-concept low-voltage electrochromic device. This work opens a new avenue for the development of novel plasmonic devices based upon chemically available molecules.

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First-principles nanoplasmonics on metal-clusters dimers

Alejandro Varas[1], Pablo García-González 2; F. J. García-Vidal,2; Angel Rubio,1,3
Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre,
Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, Av.
Tolosa 72, E-20018 San Sebastián, Spain
1 Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre,
Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, Av.
Tolosa 72, E-20018 San Sebastián, Spain; 2Departamento de Física Teórica de la
Materia Condensada and Condensed Matter Physics Center (IFIMAC), Universidad
Autónoma de Madrid, E-28049 Cantoblanco, Madrid, Spain; 3 Max Planck Institute
for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science
and Department of Physics, Luruper Chaussee 149, 22761 Hamburg, Germany

Plasmonic nanostructures are able to confine and enhance light in sub-wavelength regions in a unique tunable manner. This is the basis of a number of applications including surface-enhanced spectroscopies, designing of light-harvesting devices, molecular sensors, and hybrid optoelectronic devices. A prototypical system is made up by two metallic nanoparticles separated by a narrow spacial gap, that is, a nanoparticle dimer. These systems has been extensively studied using classical-optics prescriptions as well as under a quantum description of the electron light-induced dynamics. However, only recently fully ab-initio simulations of the optical response of nanoparticle dimers have been carried out [1-2]. In this work, we present ab initio time-dependent density functional theory (TDDFT) studies of the anisotropy and atomic relaxation effects on the optical properties of nanoparticle dimers. Special emphasis is placed on the hybridization process of localized surface plasmons, plasmon-mediated photoinduced currents, and electric-field enhancement in the dimer junction. We show that there is a critical range of separations between the clusters in which the detailed atomic structure in the junction and the relative orientation of the nanoparticles have to be considered to obtain quantitative predictions for realistic nanoplasmonic deivices. It is worth noting that this regime is characterized by the emergence of electron tunneling as a response to the driven electromagnetic field. The orientation of the particles not only modifies the attainable electric field enhancement but can lead to qualitative changes in the optical absorption spectrum of the system [3]. In addition we study the effects of different atomic and molecular junctions on the optical properties of these nanoparticle dimers, as well as the corresponding plasmon-induced electric currents along the junctions.

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Plasmon eigenmodes in metallic nano-structures and 2d materials from first principles response functions

Kristian Thygesen[1]
Center for Atomic-scale Materials Design (CAMD), Department of Physics,
Technical University of Denmark

Electron energy loss spectroscopy (EELS) can be used to probe plasmon excitations in nanostructured materials with atomic-scale spatial resolution. For structures smaller than a few nanometers, quantum effects are expected to be important, limiting the validity of widely used semiclassical response models. Here we present a method to identify and compute spatially resolved plasmon modes from first-principles based on a spectral analysis of the

microscopic dielectric function. As illustrating examples we calculate the plasmon modes in metallic thin films[1], nano-wires and their dimers[2] as well as MoS2 nano-structures[3]. The examples show that the concept of plasmon eigenmodes provides an unambiguous classification of the plasmon excitations of a given structure and can be viewed as a collective analogue of the single-particle wave function. Moreover, the modes offer a clear interpretation of spatially resolved EELS spectra.Vertical stacking of two-dimensional (2D) crystals, such as graphene and hexagonal boron nitride, has recently lead to a new class of materials known as van der Waals heterostructures (vdWHs) with unique and highly tunable electronic properties. Ab initio calculations should in principle provide a powerful tool for modeling and guiding the design of vdWHs, but in their traditional form such calculations are only feasible for commensurable structures with a few layers. Here we show that the dielectric properties of realistic, incommensurable vdWHs comprising hundreds of layers can be efficiently calculated using a multiscale approach where the dielectric functions of the individual layers (the dielectric building blocks) are computed ab initio and coupled together via the long-range Coulomb interaction[4]. We use the method to illustrate the 2D-3D transition of the dielectric function of multilayer MoS2 crystals, the hybridization of quantum plasmons in thick graphene/hBN heterostructures, and the efficient evaluation of EELS spectra of multilayer stacks. The dielectric building blocks for a variety of 2D crystals are available in an open database together with the software for solving the coupled electrodynamic equations[5].

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Identifying plasmons in molecular quantum-chemical calculations

Christoph Jacob[1]
 TU Braunschweig, Institute of Physical and Theoretical Chemistry,
Hans-Sommer-Str. 10, 38106 Braunschweig, Germany

The classification of electronic excitations in molecules and molecular nanostructures as "plasmons" is at the heart of understanding the electric field enhancements in photochemistry. While in solid-state physics, Plasmons are characterized as density oscillations in an electron gas. However, in finite systems, such as molecules, clusters, and molecular nanostructures the distinction between plasmons and single-particle excitations is less clear, because they lack the basic properties (momentum conservation and uniform exchange interaction) responsible for the formation of plasmons in the solid-state case. Here, it is discussed how plasmons can be identified in quantum-chemical calculations for such finite molecular systems [2]. We show that this can be achieved by scaling the electron--electron interaction in quantum-chemical response calculations [1,3]. This approach is illustrated for molecular chains and clusters and we show how this can be employed for selectively calculating plasmonic excitations and for designing molecular plasmonic systems.

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A new time dependent density functional algorithm for plasmons in metal clusters

Mauro Stener[1], Oscar Baseggio,1 Giovanna Fronzoni1
 Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy.
Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L.

Giorgieri 1, 34127 Trieste, Italy.

A new algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented [1]. The method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization. The original idea which made the present scheme very efficient consists in the simplification of the double sum over occupied-virtual pairs in the definition of the dielectric susceptibility, which allows an easy calculation of such matrix as a linear combination of constant matrices with photon energy dependent coefficients. The method has been applied to very different systems in nature and size (from H2 to [Au147]-). In all cases, the maximum deviations found for the excitation energies with respect to the Amsterdam Density Functional code are below 0.2 eV. The new algorithm has the merit to calculate the spectrum at whichever photon energy but also to allow a deep analysis of the results, in terms of Transition Contribution Maps [2], plasmon scaling factor analysis [3] and induced density analysis, which have been all implemented.

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Practical nanophotonics with plasmonic ceramics

Nathaniel Kinsey[1], Alexandra Boltasseva
 School of Electrical and Computer Engineering and Birck Nanotechnology Center, Purdue University

In recent years, two avenues of nanophotonics, namely plasmonics and metamaterials, have seen an explosion of novel ideas and designs that could provide breakthrough devices and exotic functionalities. However, transforming these concepts into practical devices requires a significant amount of effort. The constituent materials in these structures play a crucial role in realizing efficient devices. Similar to the way silicon shaped the nanoelectronics field, efforts toward finding the best set of materials for plasmonic and metamaterial devices could revolutionize the field of nanophotonics. As a potential solution, alternative plasmonic materials have recently gained significant attention. Metals, despite being essential components of plasmonic and metamaterial structures, pose many technological challenges toward the realization of practical devices—primarily due to their high optical loss, integration and fabrication limitations. Hence, searching for an alternative to metals is vital to the success of future nanophotonic devices. In this course, recent developments in the pursuit of better plasmonic materials will be outlined, and several classes of materials including transparent conducting oxides and plasmonic ceramics as potential alternatives to metals will be discussed as material platforms that provide low intrinsic loss, tunability and compatibility with standard semiconductor fabrication processes.

Characterization and modelling of the steady-state and transient  plasmonic properties of heavily-doped ge

Paolo Biagioni[1], Leonetta Baldassarre2, Emilie Sakat1, Michele Virgilio3, Jacopo Frigerio1,  Valeria Giliberti4, Monica Bollani5, Enrico Napolitani6, Davide De Salvador6, Marco Fischer7,  Giovanni Isella1, Michele Ortolani4, Daniele Brida7
 Physics Department and L-NESS, Politecnico di Milano, IT
1Physics Department and L-NESS, Politecnico di Milano, IT
2Center for Life NanoScience@Sapienza, Istituto Italiano di Tecnologia, Roma, IT
3Dipartimento di Fisica "E. Fermi", Università di Pisa, Pisa IT
4Dipartimento di Fisica, Università di Roma "La Sapienza", Roma IT

5CNR – Istituto di Fotonica e Nanotecnologie, Como, IT
6Dipartimento di Fisica e Astronomia, Università di Padova and CNR - IMM Matis, Padova, IT
7Physics Department, Universität Konstanz, Konstanz, DE

In the last decade, heavily-doped semiconductors have been proposed as low-loss and tunable plasmonic materials for the mid-infrared spectral region. In this framework, we investigate heavily-doped germanium films epitaxially grown on silicon wafers by low-energy plasma-enhanced chemical vapor deposition. Germanium uniquely displays both high mobility (both electron and hole mobilities are higher than those of silicon by factors of 3 and 4) and a non-polar lattice. In terms of losses, there is a possibility that the combination of the impurity field screening by highly mobile charge carriers and the deformation scattering potential, which is less efficient than direct coupling to polar phonons in scattering electron fields, might lead to improved performances of plasmonic resonators. Moreover, advanced large-scale fabrication technologies developed in semiconductor foundries may be employed to obtain almost ideal geometries. In this work we present both a full infrared spectroscopy study of the dielectric constant of heavily-doped (both n-type and p-type) Ge and we employ it to describe the transient plasmonic behavior obtained in nominally intrinsic Ge antennas after all-optical carrier excitation with near-infrared pulses. Preliminary results demonstrate that both the electron and the hole populations need to be taken into account to properly describe the transient behavior. We also experimentally characterize the steady-state frequency-dependent scattering rate of electron-doped Ge. We derive the free carrier concentration (activated dopants) from the Hall coefficient and obtain the incorporated donor density from secondary ion mass spectroscopy. We then compare the data with first-principle scattering cross-sections for electrons possessing energies comparable with those associated with the plasmon field frequency. The research leading to these results has received funding from the European Union's Seventh Framework Programme under grant agreement n° 613055.

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Transparent conductive oxides as near-ir plasmonic materials: the case of al-doped zno derivatives

Alice Ruini[1], Arrigo Calzolari and Alessandra Catellani
 Universita' di Modena e Reggio Emilia and CNR-NANO Centro S3, Modena Italy
CNR-NANO Centro S3, Modena Italy

Noble metals such as gold and silver are conventionally used as the primary plasmonic building blocks in the fields of the telecommunications and energy conversion [1]. However, metals are plagued by large losses, especially in the UV–vis and IR spectral ranges, due to interband electronic transitions and dissipative scattering events. These losses seriously limit the feasibility of many plasmonic applications. As an alternative, transparent conductive oxides (TCOs) can exhibit a high conductivity and very small losses at the infrared and longer wavelengths. [2]Here we present a first principles investigation of plasmonic properties of metal-doped ZnO TCOs [3-5], based on density functional theory, within the Random-Phase-Approximation. We first show the formation of SPP resonances at Al:ZnO/ZnO interfaces, and their dependence on doping and defects. These systems present tunable plasmonic activity in the near-IR range and in particular at wavelength relevant for telecommunications (1,5 Î¼m) [4]. Then we characterize the plasmon properties of In-doped nanowires [6] that have been envisaged as plasmonic nanoparticles in energy conversion devices and telecommunications.

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Experiments and modelling of hotspot-mediated switching in plasmonic antennas

Otto Muskens[1], Luca Bergamini,2 Martina Abb,1 Nerea Zabala,2 Javier Aizpurua2
 Faculty of Physical Sciences & Engineering, University of Southampton, Southampton, UK
1 Faculty of Physical Sciences & Engineering, University of Southampton, Southampton, UK; 2Centro de Fisica de Materiales, DIPC and CSIC-UPV/EHU, San Sebastian, Spain

Plasmonic nanoantennas have been developed as a class of nanoscale devices capable of converting far-field radiation into near-field hotspots and vice versa. Their potential applications span a wide range from local field enhancement for sensing, Raman spectroscopy, and nonlinear frequency conversion, to control of local density of states, radiative efficiency, and directionality of emitters. Tuning of the resonance and near-field properties of antennas using external control signals is of tremendous interest as it enables new transistor-type devices where light-matter interaction can be switched and redirected on demand. The design of optical nonlinearity at the nanoscale requires detailed multiphysics modelling of antennas in an active environment which responds to electronic, thermal, magnetic and/or vibrational excitations in a dynamic way. Combined with precise shaping of linear antenna interactions [1], nonlinear simulations push the requirements of computational modelling.Here, I will present our recent progress on nonlinear plasmonic antennas exploiting the local field enhancement in plasmonic hotspots to drive an external, nonlinear medium. We explored the alternative plasmonic material indium-tin oxide as a medium with very strong, Kerr-type third-order nonlinearity on ultrafast time scale. Using a thin film of ITO as a Kerr nonlinear substrate, we demonstrate experimentally the transfer of ultrafast optical effects between two perpendicularly oriented, adjacent gold nanoantennas (see Figure) [2]. The substrate nonlinearity is driven by a plasmonic hot spot through resonant pumping of an antenna, and subsequently transfers this nonlinear modulation to another, perpendicular 'readout' antenna. In contrast to the hotspot-mediated modulation, heat effects are contained primarily in the excited antenna, opening up a route for nonlocal plasmonic modulation without excessive local heating of e.g. quantum emitters. In recent experiments the active substrate is replaced by a vanadium oxide (VO2) phase-change material. Here the plasmonic field enhancement drives a highly localized phase transition directly around the antennas. In this case, we demonstrate nonlinear control of individual antennas less than 100nm apart without any cross-interaction. The local phase change response was successfully modelled using a combination of nanometer-scale optical and plasmonic heating simulations in a multiphysics modelling environment.

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Superior plasmon absorption in iron-doped gold nanoparticles

Vincenzo Amendola[1]
 Department of Chemical Sciences, University of Padova, via Marzolo 1, I-35131 Padova, Italy

Although the excitation of localized surface plasmons is associated with enhanced scattering and absorption of incoming photons, only the latter is relevant for the efficient conversion of light into heat. We show that the absorption cross section of goldnanoparticles is sensibly increased when iron is included in the lattice as a substitutional dopant, i.e. in a gold-iron nanoalloy.[1] Such increase is size and shape dependent, with the best performances observed in nanoshells where a 90-190% improvementis found in a size range that is crucial

for practical applications. Our findings are unexpected according to the common believe and previous experimental observations that alloys of Au with transition metals show depressed plasmonic response. This showsthat Au-Fe nanoalloys are attractive nanostructures with plasmonic and magnetic properties, of special interest for nanomedicine applications.[2,3,4] Overall, these results are promising for the design of efficient plasmonic converters of light into heatand pave the way to more in-depth investigations of plasmonic properties in noble metal nanoalloys.

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Atomistic simulations of surface-enhanced spectroscopies

Lasse Jensen[1]
Department of Chemistry, The Pennsylvania State University 104 Chemistry Building University Park, PA 16803

Atomistic simulations of surface-enhanced spectroscopes remains a challenge due the necessity of bridging the different length scale of the molecule and the metal nanoparticle. Here we present our recent progress on developing a reliable and efficient hybrid computational method that bridges classical electrodynamics and electronic structure theory. Focus will be on understanding chemical, resonance, nonlinear effects, and inhomogeneous electric fields in surface-enhanced spectroscopies. We will discuss applications of this approach to describe surface-enhanced Raman scattering (SERS) and its nonlinear analogue surface-enhanced hyper-Raman scattering (SEHRS) as well as surface-enhanced Raman optical activity.

Single-molecule strong coupling in plasmonic nanocavities to modify ground state vibrational states

Rohit Chikkaraddy[1], Bart de Nijs1, Felix Benz1, Steven J. Barrow2, Oren A. Scherman2, Peter Fox3, Ortwin Hess3, Edina Rosta4 and Jeremy J. Baumberg1
NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK
1 NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK
‎2 Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
3 Blackett Laboratory, Department of Physics, Imperial College, London, SW7 2AZ, UK
4 Department of Chemistry, King's College London, London SE1 1DB, United Kingdom

Emitters placed in an optical cavity experience an environment that changes their coupling to light. Cavities made of metallic nanostructures have gained tremendous attention recently due to ultra-low mode volumes (103)1. Coupling of single-molecular emitters to such plasmonic cavities has been always hindered by unreliable fabrication, orientation and positioning of an emitter. This has also obscured the full understanding of chemical interactions between the electronic-vibrational states of the molecule and the plasmons.Here we use reliable self-assembled nanoparticle-on-mirror constructs to couple plasmons with a molecular emitter (Fig.

1)2–4. By scaling the cavity volume below 10 nm3 and using host-guest chemistry to align 1-10 protectively-isolated dye molecules, we reach the strong-coupling regime at room temperature and in ambient conditions5. Dispersion curves from >50 plasmonic nanocavities display characteristic anticrossings, with Rabi frequencies of 300 meV for 10 molecules decreasing to 90 meV for single molecules, matching quantitative models. Strong coupling of single molecules can lead to modification of photochemistry, opening up the exploration of complex natural processes such as photosynthesis and pathways towards manipulation of chemical bonds. We also find that specific vibrations now become coupled into the mixed light-matter states.

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Optimization of embedded gold nanorod arrays for sers analysis of ctcs

Jonathan Calderón[1], M. I. Gómez1, D. Hill
 Group of Solid Spectroscopy, Material Science Institute, University of Valencia, Spain
Group of Solid Spectroscopy, Material Science Institute, University of Valencia, Spain

We report on the modelling, using the Finite Element Method (FEM), of gold nanorod arrays embedded into an Indium Tin Oxide (ITO) layer for the Surface Enhanced Raman Spectroscopy (SERS) analysis of circulating tumor cells (CTCs).The enumeration of CTCs is a promising approach for early detection and frequent monitoring of cancer. Through the engineering of nanostructured substrates, targeted CTCs can be directly identified using SERS. When gold is conveniently nanostructured, field enhancements large enough to overcome the low molecular Raman cross-section of adsorbed molecules enable their detection, such as for CTC biomarkers and even single molecules. There is a refraction index mismatch present in arrays placed over substrates which results in different phase velocities and conditions for constructive interference, this can be avoided burying the array in a homogeneous background, improving the collective plasmonic characteristics [1]. Here, we report on the modelling of arrays of gold nanorods embedded into an ITO layer for SERS analysis. Using FEM, the Localized Surface Plasmon Resonance (LSPR) characteristics of the arrays [2] are calculated, in order to investigate their potential as SERS substrates. Averaging the electric field in a volume over each nanorod, provides an estimation of its suitability for SERS. Their geometrical parameters (size, aspect ratio, pitch distances and different depth of the nanohole) are then optimized for an excitation wavelength of 785 nm (a common line in Near IR Raman spectroscopy). This optimization corresponds to enhancement factors of more than 106, corresponding to electric fields ~35 times greater than the incident field, once the design parameters are moderated from the consideration of fabrication limitations. The tuning of the pitch distances for the arrays of nanorods provides a substantial increase of this factor (~103) over isolated nanorods.

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Molecular response under the nanocavity plasmon

Yi Luo[1]
 Royal Institute of Technology, Stockholm, Sweden; and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of

China, Hefei, China

A metallic nanocavity can act like an optical lens to generate highly confined intensive plasmon with broad energy distribution. Such a unique excitation source can lead to many exciting new applications. One of the representative applications is the well-established surface enhanced Raman spectroscopy (SERS) that takes advantage of the high intensity of the plasmon to achieve effective detection of a very small numbers of molecules. Our combined theoretical and experimental studies in recent years have revealed that the nanocavity plasmon (NCP) mimics a tunable, strong and ultra-fast electromagnetic field that can naturally alter the color of the emission of a molecule through nonlinear optical processes[1]. Moreover, the NCP can even produce a completely new physical process, namely the nonlinear inelastic electron scattering[2]. We have also found that the NCP can result in Raman spectral images with unprecedented spatial resolution, below one nanometer, allowing to resolve the inner structure and surface configuration of a single molecule with optical means for the first time[3]. A new theory that takes into account the interaction between the highly spatial confined field and a molecule is developed and its implications on the high resolution Raman images will be discussed in details[4].

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Quantum plasmonics of stretched nanorods

Tuomas Rossi[1], Asier Zugarramurdi, Martti Puska, Risto Nieminen
Aalto University, Department of Applied Physics, Espoo, Finland
Aalto University, Department of Applied Physics, Espoo, Finland

A metallic nanoparticle dimer is a prototypical system for studying plasmonic coupling and hybridization. At subnanometer particle separations the plasmonic response of the dimer is strongly affected by electron tunneling that creates an effective conductive bridge between the two particles. This quantum regime has been studied both theoretically and experimentally as the two nanoparticles are brought from a distance to a close proximity and eventually into contact [1–7]. In our theoretical work, we approach the dimer system from an opposite point of view. We start by considering a metallic nanorod, and then slowly split it into two smaller subnanorods by stretching it. The stretching leads to the formation of a narrowing atomic contact between the two nanorod ends, until the rod is eventually broken apart. During this process, we track the evolution of the plasmon modes by first-principles time-dependent density-functional theory calculations. In between the limiting cases of the initial single nanorod and the final split nanorod dimer, the plasmonic response of the system shows novel quantum features [8]. These features and their origin are discussed in detail in the presentation.

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First-principles calculations of plasmonic resonances and electric field enhancement in metal-cluster dimers

Marc Barbry[1], P. Koval1, F. Marchesin1 , R. Esteban1, A. G. Borisov2 , J. Aizpurua1 , D. Sanchez-Portal1
 Centro de Física de Materiales, Centro Mixto CSIC-UPV/EH_U, and Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastian, Spain
1 Centro de Física de Materiales, Centro Mixto CSIC-UPV/EH_U, and Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastian, Spain 2 Institut des Sciences Moléculaires d'Orsay ISMO, UMR 8214 CNRS-Université Paris-Sud, Bât. 351, Université Paris-Sud, 91405 Orsay Cedex, France

Recent progress in fabrication of nanodevices has made possible the production of nanoobjects of controlled composition and shape down to atomic precision. Metallic clusters of Ag, Cu, Au have been used to amplify Raman spectroscopy signal [1]. One of the mechanism that leads to amplification of Raman signal is the enhancement of the electromagnetic field in the vicinity of clusters . Namely, if a metal cluster locates in the vicinity of a molecule, then the electromagnetic field induced by the cluster response can be much larger than the driving laser field.In this work [2], we present an ab-initio study of the polarizability and electric field enhancement in the vicinity of metal cluster dimers. The approach is based on time-dependent density functional theory (TDDFT) because only TDDFT offers a feasible ab-initio description for finite systems of several hundred of atoms. TDDFT reproduces the basic features of experimental absorption spectra and it allows to examine the spatial- and frequency-dependence of the field enhancement in nano- cavities of different sizes and shapes [3].For our calculations, we employ an original implementation of TDDFT in the linear response regime [4]. This implementation is optimized for utilizing locality of operators in order to construct an algorithm of low computational complexity. Our TDDFT code is interfaced with SIESTA: an efficient density functional theory implementation [5]. The low complexity algorithms employed in SIESTA and in our TDDFT code made possible to address electric field enhancement between sodium cluster dimers composed of several hundreds of atoms. We perform a detailed analysis of the density change and the induced electric field distribution. From the calculations, we demonstrate that the atomic structure plays a crucial role for the absorption cross-section and the electric field enhancement, especially for small dimer separations. In the Figure 1, we show the electric field enhancement and the polarizability for a 2xNa380 dimer.

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Simulating electron energy loss spectroscopy for complex surfaces

Iurii Timrov[1], Nathalie Vast,2 Ralph Gebauer,3 Stefano Baroni1
 SISSA – Scuola Internazionale Superiore di Studi Avanzati, Trieste 34136, Italy
1SISSA – Scuola Internazionale Superiore di Studi Avanzati, Trieste 34136, Italy
2Ecole Polytechnique, Laboratoire des Solides Irradies, Palaiseau 91128, France
3ICTP – International Centre for Theoretical Physics, Trieste 34151, Italy

Electron Energy Loss Spectroscopy (EELS) and Inelastic X-ray Scattering Spectroscopy (IXSS) are the methods of choice to sample collective charge excitations (plasmons) in solids. The strong dependence of plasmon dynamics on the size and shape of nano-structured

devices holds the promise of an extraordinary control over their optical properties. When the distances between the nanoscale components in the device are themselves nanometric, quantum effects must be taken into account, and a fully quantum-mechanical description is called for. The EELS and IXSS cross sections are proportional to the imaginary part of the diagonal elements of the inverse dielectric matrix, which can be computed using Time-Dependent Density Functional Theory (TDDFT) [1]. Current TDDFT-based approaches to dynamical screening involve the computation of single-particle unoccupied states and the manipulation (multiplication, inversion) of large matrices [2], two tasks that make these approaches unfit to address systems larger than a handful of atoms. We present a new method, based on the iterative solution of the TDDFT equations within first-order perturbation theory, that avoids these difficulties by using a Lanczos recursion technique and adopting a representation of the response orbitals borrowed from density-functional perturbation theory [3]. The resulting algorithm allows to compute the EELS and IXSS cross sections for a same transferred momentum and over an entire, wide, frequency range with a numerical workload comparable to a single ground-state DFT calculation. Our method has been implemented [4,5,6] in the Quantum ESPRESSO distribution of computer codes [7,8], and successfully tested on prototypical examples, such as bulk silicon and aluminum, and applied to the bulk semimetal bismuth, where spin-orbit effects play a prominent role. The new method can be readily applied for calculations of surface plasmons, and a demonstration of the validity of the approach will be given for a test case of Al(111) surface [9]. Prospects for applying the newly developed methodology to such challenging cases as high-Miller index surfaces will be finally discussed.

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Higher-order surface plasmons and their disappearance in few-nanometer silver nanoparticles

Nicolas Stenger[1], Søren Raza
 Department of Photonics Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark ; Center for Nanostructured Graphene, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark.
Department of Photonics Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark ; Center for Nanostructured Graphene, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark.

The optical properties of silver metal nanoparticles are dominated by the excitation of localized surface plasmons. Light incident on silver particles with spherical shape and diameters below 100 nm excites primarily the dipolar mode. The higher-order modes, i.e., modes with larger angular momentum l, such as the quadrupole mode, are strongly damped as their larger resonance energy tend to be positioned in the range of interband transitions in silver. By encapsulating silver nanoparticles in a high permittivity dielectric medium, in this work silicon nitride, we redshift all of the plasmon modes and thereby get access to the higher-order modes of silver nanoparticles. We map the dipolar and higher-order modes of silver nanoparticles with electron energy-loss spectroscopy (EELS) in a state-of-the-art transmission electron microscope.We acquire EELS maps and line scans from isolated silver nanoparticles. For impact parameters outside the particle, we find that the EELS signal is dominated by the dipole mode, which shows a resonance energy around 2.8 eV for particle

radii 4 - 20 nm. For impact parameters close to the surface of the particle or inside the particle, an additional resonance at higher energy shows up due to the excitation of modes with larger angular momentum, i.e., $l > 1$. The resonance energy of the additional peak is around 3.2 eV for the same particle radius range. To our knowledge, this is the first experimental observation of higher-order modes in nanometer-sized silver nanoparticles. For impact parameters inside the nanoparticle, we also excite the bulk plasmon which has a resonance energy close to 3.8 eV and is clearly distinguished from the peak at 3.2 eV. We note that the measured EELS peak at 3.2 eV contains several modes with $l > 1$ as the energy spacing between these modes is lower than the resolution of our EELS setup. We also perform electron energy-loss simulations using the boundary element method (BEM) [1], which shows excellent agreement with our experimental observations.For particle radii lower than 4 nm, we observe a strong blueshift of the dipolar mode of 0.9 eV and the disappearance of the higher-order mode in qualitative agreement with a generalized nonlocal optical response theory [2].

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Abstracts (Poster)

Highly tunable optical and magneto-optical properties of arrays of anisotropic nanoantennas

Luca Bergamini[1], Nicolò Maccaferri4, , Matteo Pancaldi4, Mikko Kataja5, Mikolaj Schmidt2,3, Sebastiaan van Dijken5, Paolo Vavassori4, Nerea Zabala1,2,3, and Javier Aizpurua2,3

Department of Electricity and Electronics, Faculty of Science and Technology, UPV/EHU, Bilbao, Spain

1Department of Electricity and Electronics, Faculty of Science and Technology, UPV/EHU, Bilbao, Spain; 2Materials Physics Center and CSIC-UPV/EHU, Donostia-San Sebastian, Spain; 3Donostia International Physics Center, Donostia-San Sebastian, Spain; 1CIC nanoGUNE, Donostia-San Sebastian, Spain; 5NanoSpin, Department of Applied Physics, Aalto University School of Science, Aalto, Finland; 6Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Recently it has been demonstrated that random ferromagnetic nanoantennas (NAs) can jointly support Localized Surface Plasmons (LSPs) and Magneto-Optical Activity (MOA) when magnetized by an external static magnetic field [1]. In particular, nanosized nickel particles seem to combine in a single material effective plasmonic and magneto-optical (MO) properties. Moreover, the dependence of the optical and MO responses on the nanoantenna shape/size is further enriched when shape anisotropy of the NAs is exploited, which introduce resonance modes dependent on the incident light polarization.Furthermore, ordered arrays of metal nanoparticles have been found to exhibit Fano-like resonances (called Surface Lattice Resonances - SLRs), due to the interference between the inherent broad LSP resonances of the antennas and the narrow diffraction orders of the array [2]. In this work, we combine the NA-shape anisotropy and the array arrangement to obtain magnetoplasmonic nanosystems with highly tunable optical and magneto-optical responses. We theoretically investigate 2D square-arrays of ellipsoidal nickel nanodisks by simulating their optical and magneto-optical properties via Coupled Dipole Approximation [3] and Finite-Difference Time-Domain [4] techniques. The calculations reveal a notable difference in the SLR behaviour according to whether the incident electric field is applied along either the long- or short-axis of the NAs. We show not only that the SLR behaviour is light-selectable but also that, by playing with the NA size and lattice periodicity, the optical and MO response could be actively tuned at wish, for instance, to achieve either transparency or enhancement of the MOA. The calculations predictions are also fully confirmed by experiments. The results of our study show the advantages of combining anisotropic plasmonic/magneto-optical nanoantennas with lattice diffraction, paving the way for the realization of a new class of highly tunable magnetoplasmonic nanodevices.

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Comparison of theoretical and experimental band structures of noble metals

Moses Abraham BOKINALA[1]

Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad,

Prof. C. R. Rao Road, Gachibowli, Hyderabad 500 046, Andhra Pradesh, India

For the noble metals, Generalized-gradient approximations such as PBEsol predict the d band positions to be closer to the Fermi level than that of experiment because of the self-interaction error for localized electrons. The GLLB-sc orbital-dependent functional[1] partially

remedies this situation, as shown by a recent density functional study of Plasmon dispersions on noble metal surfaces[2] However, the band structure predicted by this functional still exhibits significant deviations from angle-resolved photoemission measurements[3][4][5]. These deviations are largest (~0.5â€°eV) near the L point in the Brillouin zone, and this region of the Brillouin zone is particularly active for interband transitions in these metals. Many-body perturbation theory methods, such as the quasiparticle self-consistent GW approximation, significantly improve the agreement with experiment. We find that the DFT+U method[6], which improves the description of localized electrons with a local semi-empirical correction on each atom, yields the best agreement (~0.1â€°eV) to the quasiparticle bandstructure of all three noble metals (indicated by PBEsol+U since we combine the U correction with the PBEsol density functional). We pick the value of U to reproduce the experimental energies at the Î“ point, which results in U=1.63, 2.45 and 2.04â€°eV for copper, silver and gold, respectively.The calculations presented here account for relativistic effects including spin-orbit coupling fully self-consistently. The spin-orbit splitting at the X point is particularly relevant, since it determines the inter-band threshold energy. The magnitude of the effect is ~0.5â€°eV in gold, ~0.2â€°eV in silver and ~0.1â€°eV in copper. Therefore, the inclusion of spin-orbit splitting is critical in calculations of optical transitions in â€‹gold, still quite significant for â€‹silver and negligible at the achievable accuracy for copper. Computational detailsWe perform density functional calculations for face-centred cubic â€‹aluminium, â€‹silver, â€‹copper and â€‹gold in the plane-wave electronic density functional software, JDFTx[7], using full-relativistic norm-conserving pseudopotentials at a kinetic energy cut-off of 30 hartrees (816â€°eV) and at the experimental lattice geometry. We use the PBEsol[8] exchange-correlation approximation along with a rotationally invariant DFT+U correction[6] or the d electrons, with U=1.63â€°eV for â€‹copper, 2.45â€°eV for â€‹silver and 2.04â€°eV for â€‹gold fit to reproduce experimental photoemission data.

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Technical issues in the calculation of the dielectric function of graphene-boron nitride heterostructures from first principles

Morten Gjerding[1], Kristian Sommer Thygesen
 Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark
Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark

It has been proposed that graphene-boron nitride heterostructures could function as hyperbolic metamaterials [1]. The emergence of hyperbolicity in the photonic isofrequency surface is closely related to the plasmonic properties of the material which in turn is described by its dielectric function. A central obstacle for calculating the optical response of graphene boron-nitride heterostructures from first principles is the dense k-point sampling needed to

converge calculations for optical and sub-optical frequencies. These difficulties arise from the large band dispersion of graphene near the Dirac point. The typical way to obtain converged results is to smear out the calculated optical response by including a small lifetime of carriers. This unfortunately limits the resolution of calculated optical response and does not reflect the actual experimental lifetimes. We explain how the number of k-points can be reduced by employing crystal symmetries with almost no expense on program clarity. In summary, it involves calculating an "unsymmetrized" response over only the irreducible Brillouin zone (IBZ) and employing a simple post-processing symmetrization procedure to obtain the true response. We explain an algorithm for generally determining the IBZ from a set symmetry operations. We show that the IBZ is easily determined by a Voronoi diagram of a particular set of points in reciprocal space just like the Wigner-Seitz cell definition of the Brillouin zone. To overcome the problem with the limited resolution due to the unphysical lifetimes we have implemented the tetrahedron integration method [2] for the optical response calculation which depends less critically on the smearing described above. We compare this method to the normal point sampling integration. The algorithms have been implemented in the electronic structure code GPAW [3] and are general in that they will work for any material of any crystal-structure.

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Plasmonic modes

Benjamin Hourahine[1], Duncan McArthur1 and Franceso Papoff
 SUPA, Department of Physics, University of Strathclyde, Glasgow G4 0NG, United Kingdom
SUPA, Department of Physics, University of Strathclyde, Glasgow G4 0NG, United Kingdom

Mie's 1908 theory provides an analytical description of the electromagnetic resonances of spherical particles in terms of paired sets of modes of the macroscopic Maxwell equations. This is a special case of a more general explanation for resonances in Maxwell's equations that applies to all smooth nano-structures [1]. In general, the interaction of light with wavelength and sub-wavelength structures can be understood as the coupling between the subspaces of the electromagnetic field that are inside and outside the structure boundary, allowing an almost analytical calculations of optical responses [1]. Pictorially, the interaction between the internal and scattered waves at the interface can be understood in terms of correlation between internal and scattered optical modes, where the induced amplitudes are the projection of incident light onto correlated internal and scattering principal mode pairs. Modes are bright or dark depending on the particular excitation source, but the resulting amplitudes depend also on their intrinsic correlation (the angle θ_n of the pair).In this contribution we will discuss the application of this concept of principal modes to study a variety of systems including understanding experimental scanning near-field microscopy (SNOM/NSOM) of plasmonic nano-discs [2], the optical forces on and resonances of metal nano-particle collections, and the control of linear and non-linear responses of gold particles [3] including cases where non-local responses matter.Sketch of the interaction of light with a general smooth nanostructure, a) The incident (F0), internal (I(r)) and scattered (S(r)) fields and their amplitudes, b) the geometry of the nth pair of modes at the surface of the structure showing the internal (in) and scattered (sn) modes and the resulting amplitudes (ani and ans) that are excited by the projected incident field (f0n). The intrinsic principal angle between the internal and scattered mode pair (θ_n) determines the amplitudes caused by a given incident field.

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Surface plasmon resonance – the role of dielectric function of the metal

Katarzyna Kluczyk[1], Witold A. Jacak
 Department of Quantum Technology, Wroclaw University of Technology,
Wrocław, Poland
Department of Quantum Technology, Wroclaw University of Technology,
Wrocław, Poland

The first theoretical study of bright colors of metallic particle colloids was conducted by Gustav Mie in 1908. Despite of its wide application, the Mie theory does not describe microscopic mechanism of resonance observed in metallic particle colloids extinction spectra, which is determined by the dielectric function of the metal in particular geometry. The dielectric function is therefore crucial for proper description of plasmon resonance behavior (for instance of dependence on particle size) within this model. The paper reports the semi-classical model of surface plasmon oscillation in metallic nano-sphere based on Random Phase Approximation (RPA) [1]. The two channels of plasmon damping are concerned, one connected to electron scattering and second to the electromagnetic field irradiation (described by the Lorentz friction [2]). Obtained damping is then implemented as damping constant in Drude dielectric function model, which is then used for extinction spectra calculation.   The extinction spectra are calculated within Finite Element Method (COMSOL) for different dielectric functions (based on experimental data grasped upon the Drude model with different damping constants). Obtained surface plasmon resonance shift with respect to particle radius for Au and Ag spheres is compared with the experimental data and the theoretical predictions of RPA model.

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Optical response of metallic nanoparticles in wet environments

Asier Zugarramurdi[1], Tuomas Rossi, Martti Puska
 Aalto University, Department of Applied Physics, Espoo, Finland
Aalto University, Department of Applied Physics, Espoo, Finland

The progress in synthetization of metallic nanoparticles of small dimensions in solutions is reaching the limit [1] where the atomic details of the nanoparticles can be important for the description of their optical properties [2,3]. For direct comparison to theoretical calculations one has in addition to take into account the much more important effect of the (wet) environment on the optical response of the nanoparticles. In classical electrodynamics this is easily taken into account through the use of a different dielectric constant (1.77 for water) for the surrounding material [4]. Here we approach the effect of wet environments on the optical response of metallic nanoparticles from a microscopic viewpoint. Using atomistic first-principles time-dependent density-functional theory (TDDFT) we calculate the absorption spectrum of metallic nanoparticles for different water coverages. The recently developed linear-combination of atomic-orbitals (LCAO) description within the TDDFT implementation [5] in the GPAW code [6] allowed us to efficiently tackle the large number of atoms required by the problem. This approach, however, requires a careful choice of the basis set for the description of water molecules. In Figure 1 we show a test example of our calculations for a small (unrealistic) sodium nanoparticle (55-atom icosahedral cluster) surrounded by randomly scattered water molecules. Our preliminary results show the classically expected redshift with increasing water coverage. The damping and broadening of the peak is observed as well. Ongoing work is focused on more realistic materials.

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