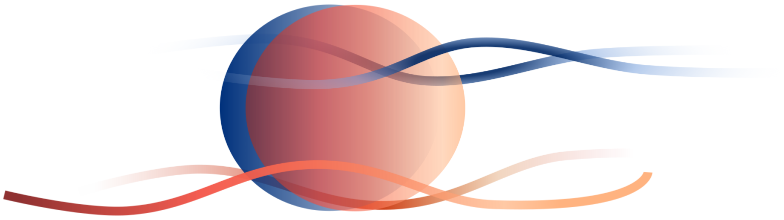
CECAM: Flagship Workshop

Light-matter interaction and ultrafast nonequilibrium dynamics in plasmonic material

University of Warwick, United Kingdom

18th to 21st July, 2022



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Invited Speakers

1.	Johannes Lischner	*Imperial College London*	UK
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3.	Franco P. Bonafé	*Max Planck Institute*	Germany
4.	Paul Erhart	*Chalmers University of Technology*	Sweden
5.	Hua Guo	*University of New Mexico*	USA
6.	Andrea Konečná	*CEITEC-Brno University of Technology*	Czech Republic
7.	Daniel Sánchez Portal	*Materials Physics Center*	Spain
8.	Ivor Lončarić	*Ruđer Bošković Institute*	Croatia
9.	Malte Rösner	*Radboud University*	Netherlands
10.	Sheng Meng	*Chinese Academy of Science*	China
11.	Javier Aizpurua	*Materials Physics Center*	Spain
12.	Oleg V. Prezhdo	*University of Southern California*	USA
13.	Vito Despoja	*Institute of Physics, Zagreb*	Croatia
14.	Anton Bykov	*King's College London*	UK
15.	Stefano Corni	*University of Padova*	Italy
16.	Lucas V. Besteiro	*Universidad de Vigo*	Spain
17.	Prashant K. Jain	*University of Illinois Urbana-Champaign*	USA
18.	Thibault Derrien	*Institute of Physics*	Czech Republic
19.	Frank Neubrech	*University of Stuttgart*	Germany
20.	Hrvoje Petek	*University of Pittsburgh*	USA
21.	Emilie Ringe	*University of Cambridge*	UK
22.	Martin Aeschlimann	*University of Kaiserslautern*	Germany
23.	Tomáš Neuman	*CNRP, University of Strasbourg*	France
24.	Laura Kim	*Massachusetts Institute of Technology*	USA
25.	John Mark P. Martirez	*University of California*	USA
26.	Vyacheslav Silkin	*University of the Basque Country*	Spain
27.	Peter Saalfrank	*University of Postdam*	Germany
28.	Rebecca L. M. Gieseking	*Brandeis University*	USA

Contributed Posters

1.	Pavel Terekhin	*Technical University of Kaiserslautern*	Germany
2.	Mirko Vanzan	*University of Padova*	Italy
3.	Eva Prinz	*Technical University of Kaiserslautern*	Germany
4.	Ieng-Wai Un	*Ben-Gurion University of the Negev*	Israel

5.	Sofia Canola	*Institute of Physics*	Czech Republic
6.	Juliana Morbec	*Keele University*	UK
7.	Neven Golenić	*SISSA*	Italy
8.	Julia Westermayr	*University of Warwick*	UK
9.	Connor L. Box	*University of Warwick*	UK
10.	James Gardner	*University of Warwick*	UK
11.	Wojciech G. Stark	*University of Warwick*	UK

Scientific Program

Monday July 18th 2022 - Day 1

- 12:00 to 13:50 - *Arrival*
- 13:50 to 14:00 - *Welcome Announcement*
- 14:00 to 16:00 - *Scientific Session 1*
- 16:00 to 16:30 - *Tea Time*
- 16:30 to 17:50 - *Scientific Session 2*
- 17:50 to 18:10 - *Moderated Discussion Session I*
- 18:10 to 18:30 - *Break*
- 18:30 to 20:00 - *Dinner*
- 20:00 to 21:00 - *Poster Session & Reception I*

Tuesday July 19th 2022 - Day 2

- 09:00 to 10:20 - *Scientific Session 3*
- 10:20 to 10:40 - *Coffee Break*
- 10:40 to 12:40 - *Scientific Session 4*
- 12:40 to 14:00 - *Lunch Break*
- 14:00 to 16:00 - *Scientific Session 5*
- 16:00 to 16:30 - *Tea Time*
- 16:30 to 17:50 - *Scientific Session 6*
- 17:50 to 18:10 - *Moderated Discussion Session II*
- 18:10 to 18:30 - *Break*
- 18:30 to 20:00 - *Dinner*
- 20:00 to 21:00 - *Poster Session & Reception II*

Wednesday July 20th 2022 - Day 3

- 09:00 to 10:20 - *Scientific Session 7*
- 10:20 to 10:40 - *Coffee Break*
- 10:40 to 12:40 - *Scientific Session 8*
- 12:40 to 14:00 - *Lunch Break*
- 14:00 to 16:00 - *Scientific Session 9*
- 16:00 to 16:30 - *Tea Time*
- 16:30 to 17:50 - *Scientific Session 10*
- 17:50 to 18:10 - *Moderated Discussion Session III*
- 18:10 to 18:30 - *Break*
- 18:30 to 20:00 - *Dinner*
- 20:00 to 21:00 - *Poster Session & Reception III*

Thursday July 21st 2022 - Day 4

- 09:00 to 10:20 - *Scientific Session 11*
- 10:20 to 10:40 - *Coffee Break*
- 10:40 to 11:20 - *Scientific Session 12*
- 11:20 to 11:40 - *Moderated Discussion Session IV*
- 11:40 to 11:50 - *Closing Remarks*
- 11:50 to 13:00 - *Lunch break*
- 13:00 to 14:00 - *Departure*

About the conference

The CECAM & Psi-k workshop **Light-matter interaction and ultrafast nonequilibrium dynamics in plasmonic materials** will be held at the University of Warwick in Coventry, UK. It will start on Monday July 18^{th} at 14:00 and it will be finalized on Thursday July 21^{st} at 14:00.

The main aim of this workshop is to bring together participants from different communities that represent the main computational techniques currently used to explore the optical, electronic, and catalytic properties associated with plasmonic materials ranging from metallic nanostructures to two-dimensional materials. This includes non-atomistic theories, field-theoretical approaches, and atomistic first-principles methods. The fundamental study of emergent ultrafast plasmonic dynamics at the nanoscale also requires a close interaction between theory and experiment. The workshop is organized into several scientific sessions with invited talks (28 talks). Each talk will last 30 minutes + 10 minutes questions. At the end of each day, we will have *Moderated discussion sessions* to recap the main points raised in each scientific session (20 minutes).

The workshop will be held at **Warwick Conference-Scarman hotel** located in the University of Warwick. The talks will be held in meeting space 41 on the upper level and the poster session will take place in the dinner room at ground floor. The conference organization will cover Lunch on Tuesday, Wednesday, and Thursday and also dinner on Monday, Tuesday and Wednesday..

We hope you enjoy this exciting meeting!

The organisers.

Invited Talks

Energetic Charge States in Plasmonic Chemistry

Prashant K. Jain[†]

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Abstract: Plasmon-driven chemistry is now a well-known albeit poorly understood phenomenon. In my talk, I will discuss experimentally deduced mechanisms behind this new paradigm of photochemistry. While hot carriers are at the forefront, I will argue that long-lived energetic charge states are important drivers of many of these effects. This mechanistic insight has allowed us to employ plasmonic excitations as redox equivalents in chemical reactions, for modifying the intrinsic catalytic activity and selectivity of transition metals, for the photosynthesis of fuels, and for boosting electrochemical conversions.

Plasmonic heterogeneous catalysis: excited-state surface chemistry understood via embedded correlated wavefunction theory

John Mark P. Martirez[1,†] and Emily A. Carter[1,2]

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Abstract: The nearly-free-electron-like valence electrons in some metallic nanoparticles (MNPs) facilitate their enhanced ability to scatter/absorb light by means of local surface plasmon resonances (LSPRs). When the incident light has a frequency resonant with the MNP's LSPR, amplified electric fields are generated within and surrounding the MNPs that can lead to hot charge-carrier generation, induce local heating, or cause excitations of molecules or other materials nearby. Photocatalysis mediated by MNPs exploits this unique optical phenomenon. First-principles quantum mechanics can aid in understanding such light-driven chemistry, but the methods used must properly account for both electronic excitations and surface reactions. Multiconfigurational correlated wavefunction (CW) theories explicitly and rigorously describe electronically excited states but are computationally costly. To enable use of these powerfully predictive methods in the context of surface catalysis, we use a divide-and-conquer approach, wherein we partition the extended metal surface into a cluster (active site) and its environment. We then derive a fragment interaction potential (embedding potential) using density functional embedding theory. In the presence of the optimized embedding potential, we performed so-called embedded CW (ECW) theory simulations on the active site to describe the ground- and excited-state energy curves of a surface-catalyzed reaction. ECW calculations of a variety of endoergic reactions on pure and doped surface-plasmon-active metals reveal that enhanced kinetics can occur on excited-state reactive potential energy surfaces accessed via plasmon-enhanced light absorption or resonance energy transfer between the MNP and the surface-active site. Our calculations explain experimentally observed plasmon-driven enhanced rates and suggest candidate MNPs for photocatalytic nanoplasmonics.

Spatially Tailored Plasmonic Excitations in Twisted-Bilayer Graphene Supercells and Coulomb-Engineered Layered Materials

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Abstract: Weakly screened long-range Coulomb interactions in metallic layered materials yield gap-less $\sqrt{q}$-dispersive plasmonic excitations, which can be precisely controlled by dielectric screening from the environment. Here,we will focus on the real-space characteristics of these low-energetic excitations and how they can be spatially tailored by means of non-local external screening.Utilizing a highly performance real-space random phase approximation implementation together with most accurate ab initio down-folded generalized Hubbard models, we will show how quantum-dot like plasmonic excitations emerge in bilayer graphene super cells and how they can be controlled by the twist angle between the layers[1]. Afterwards, we show how spatially structured dielectric substrates can be utilized to non-invasively confine plasmonic excitations in a homogeneous metallic two-dimensional system by modifications of its many-body interactions[2]. We define optimal energy ranges for this mechanism and demonstrate plasmonic confinement within several nanometers allowing for novel plasmonic wave guide implementations.As an outlook we will discuss how real-space plasmonics forms a promising framework to control and enhance light-matter interactions.

Reference: *[1] T. Westerhout, M.I. Katsnelson,and M. Rösner, 2D Materials9,014004(2021). [2]Z. Jiang, S. Haas, and M.Rösner, 2D Materials8,035037(2021)*

Hot-carrier generation rates in noble metal nanoparticles containing more than one million atoms

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Abstract: State-of-the-art atomistic electronic structure methods for modelling plasmon-induced hot-carrier generations in metallic nanoparticles, such as ab initio time-dependent density-functional theory, are highly accurate, but can only be applied to relatively small nanoparticles containing up to a few hundred atoms. On the other hand, continuum electronic structure techniques, such as jellium or spherical well models, can be used to model large nanoparticles, but fail to capture d-band electrons or atomic structure of the exposed surfaces. To bridge this gap, we have recently developed a new atomistic approach that is capable of predicting hot-carrier generation rates of nanoparticles containing more than one million atoms (corresponding to diameters larger than 30 nanometers). In this approach, we combine the tight-binding approach for the electrons with a classical electrodynamics treatment of the perturbing light field. Costly diagonalization of the Hamiltonian is avoided by using spectral methods giving rise to a highly efficient linear-scaling technique. This is applied to nanoparticles of Ag, Au and Cu. For these systems, we study the dependence on the nanoparticle size, illumination frequency and dielectric environment and reveal an complex interplay of hot carrier generation from interband and intraband transitions.

Atomic-scale electrodynamics of molecular emitters in a plasmonic picocavity formed in a scanning tunneling microscope

Tomas Neuman[1,2,†], Anna Roslawska[1], Benjamin Doppaggne[1] , Andrei G. Borissov[2], Michelangelo Romeo[1], Fabrice Scheurer[1], Javier Aizpurua[3] and Guillaume Schull[1]
[1]*Universite de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France.* [2]*Institut des Sciences Moleculaires d'Orsay (ISMO), UMR 8214, CNRS, Universite Paris-Saclay, 91405 Orsay Cedex, France.* [3]*Center for Materials Physics (CSIC-UPV/EHU) and DIPC,Paseo Manuel de Lardizabal 5, Donostia-San Sebastian 20018, Spain.*
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Abstract: Fundamental studies of the optical properties of single molecular emitters have led to the development of super-resolution optical microscopy techniques which go beyond the fundamental diffraction limit of optical resolution. Despite their success, the resolution of these microscopy techniques is still limited to scales larger than the size of individual organic molecules. This limitation has been lifted using the atomically sharp tip of a scanning tunnelling microscope (STM) covered by noble metal [1,2,3], which can squeeze optical electromagnetic fields into plasmons localized on the atomic scale, and, conversely, collect photons from within individual molecules with atomic-scale lateral resolution. In this presentation I will focus on the theoretical description of light-matter interaction in these plasmonic picocavities [4] and introduce the working principles of atomic-scale optical imaging of molecules in a STM. I will describe the fundamental principles leading to the excitation of molecular electronic states in organic molecules, and their subsequent plasmon-assisted photon emission. Importantly, the dynamics of these states is modified by the electromagnetic environment of the cavity via the plasmonic Purcell and Lamb effects, and the DC Stark effect induced by the static voltage applied across the tip-substrate gap. All these effects can then be exploited for atomically resolved imaging and hyperspectral analysis of the excited-state properties of nanoscale samples [3]

Reference: *[1] Chen, C., et al., 2010. Phys. Rev. Lett., 105(21), 217402. [2] Doppagne, B., et al., 2020, Nat. Nanotechnol., 15, 207-211. [3] Roslawska, A., et al., 2022, Phys. Rev. X, 12(1), 011012. [4] Benz, F., et al., 2016, Science, 354(6313), 726-729.*

Modeling ultrafast photoinduced dynamics of adsorbates on metals

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Abstract: I will present theoretical approaches for modeling the dynamics of molecules on metal surfaces induced by short laser pulses. Modeling is based on a density functional theory derived potential energy surface and the two-temperature model. Coupling of the adsorbates to the electronic system is modeled in terms of electronic friction and associated stochastic forces that depend on electronic temperature obtained from the two-temperature model. Using this methodology we have simulated systems such as O2/Ag(110) [1,2], CO/Ru(0001) [3], and CO/Pd(111) [4,5].

Reference: *[1] Phys. Rev. B 93, 014301 (2016) 10.1103/PhysRevB.93.014301. [2] NIM-B 382, 114 (2016) 10.1016/j.nimb.2016.02.051. [3] Phys. Rev. B 94, 165447 (2016) 10.1103/PhysRevB.94.165447 [4] J. Chem. Theory Comput 17, 8, 4648–4659 (2021) 10.1021/acs.jctc.1c00347. [5] Chemical Physics 558, 111518 (2022) 10.1016/j.chemphys.2022.111518.*

Fully-atomistic light-driven dynamics in plasmonic cavities and interfaces

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Abstract: The study of confined fields in plasmonic nanocavities and their interaction with molecules is an area of research with vast applications, including enhanced spectroscopies as well as photoinduced/photocatalytic non-equilibrium phenomena. From the theoretical perspective, either classical electromagnetic models or atomistic/quantum descriptions are usually considered. However, in many cases these models ignore the electronic and nuclear quantum effects arising from the chemical nature and dynamics of a junction, such as tunneling, adsorption geometry, structure of the interface, vibrations, etc., or include them only approximately. Hence, a full quantum dynamical description is sometimes inescapable.

In this seminar I will present insights on ab-initio, light-driven, real-time dynamics at the atomistic level in scanning tunneling microscopes (STM) cavities and metal-semiconductor interfaces, by means of simulations within time-dependent density functional theory (TD-DFT) using the Octopus code [1] and time-dependent density functional tight-binding (TD-DFTB) using the DFTB+ code [2]. Results on the tip-enhanced Raman scattering from single-atom vibrations in a picocavity [3], as well as the role of dynamical interfatial potential barrier for electron-hole stabilization in a paradigmatic Au-TiO2 system [4], will be presented. These findings highlight the role of the electron dynamics (e.g. tunneling) and structural relaxation on the plasmon-induced phenomena. Finally, outlooks on how to include the back-reaction of the induced currents onto the fields by a full ab-initio treatment of electrons, nuclei and photons in the mean field, which leads to the coupled Ehrenfest-Maxwell-Pauli-Kohn-Sham equations [5], will be discussed.

Reference: *[1] N. Tancogne-Dejean, M. J. T. Oliveira, et al. J. Chem. Phys. 152 124119 (2020). [2] B. Hourahine, B. Aradi, et al, J. Chem. Phys., 152, 124101 (2020).[3] S. Liu, F. Bonafé, H. Appel, A. Rubio, M. Wolf, and T. Kumagai. Submitted (2022). [4] M. Berdakin, G. Soldano, F. Bonafé, V. Liubov, B. Aradi, T. Frauenheim, and C.G. Sánchez. Nanoscale, 14(7), 2816 (2022).[5] R. Jestädt, M. Ruggenthaler, M.J.T. Oliveira, A. Rubio, and H. Appel. Advances in Physics 68:4, 225-333 (2019)*

Probing optical excitations by fast-electron spectroscopies

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Abstract: High-resolution mapping of low-energy excitations such as plasmons, excitons, or phonons and their interaction is required for understanding and engineering the optical, electrical, or thermal properties of nanostructured materials. An unparalleled technique for analyzing the low-energy excitations down to the atomic scale is electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM), which enables the acquisition of spectra with a few-meV/Å spectral/spatial resolution. Further information on excitation dynamics down to fs time resolution can be accessed within the so-called photon-induced near-field electron microscopy (PINEM) utilizing pulsed laser excitation of a sample probed by a synchronized electron pulse [1].

I will review recent applications of STEM-EELS in probing plasmons in unconventional materials, such as highly-doped perovskites. The broad spectral range provided by EELS enables us to correlate information on plasmonic response with dopant percentage down to the atomic scale and thus understand the influence of doping inhomogeneities on the optical properties [2]. I will also discuss a possible application of PINEM in determining the nonlinear response of plasmonic nanoparticles emerging upon the strong laser pumping [3]

Reference: *[1] J García de Abajo and V Di Giulio, ACS Photonics 8 (2021), 945-974.[2] H Yang et al., Small 18 (2022), 2106897.[3] A Konečná et al, ACS Photonics 7 (2020), p. 1290-1296.*

Plasmonic hot carrier excitation: connecting quantum and semiclassical models

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Abstract: Modelling the excitation of hot carriers in plasmonic systems is a challenging prospect, due to the disparity between two relevant scales in the system. On one side, we are interested in the detailed simulation of electronic states in the material, which determine the physical properties of the excited carriers and their interaction with the environment, across material interfaces and with adsorbed molecules. This pulls us towards modelling smaller systems that can be simulated with ab initio methods. On the other side, we care about describing the collective charge dynamics in plasmonic systems of—comparably—large sizes, so that we account for practical regimes in which they function as tunable nanoantennas in the visible and IR spectral regions. Given the practical impossibility of modelling structures larger than a few nanometers through atomistic ab initio methods, we are faced with the need of finding methodologies that bridge these two regimes.

In this talk we will discuss a semiclassical formalism that integrates general results from fully quantum models capturing the surface-mediated mechanism of plasmonic hot carrier excitation, into commonly-used classical electrodynamic models capable of solving the electromagnetic response of arbitrary plasmonic geometries.[1] From the perspective that it affords, we can contrast the differential contributions, in terms of hot carrier injection, between plasmonic nanocrystals of varied sizes and shapes in photocatalytic setups, as well as analyze the relative weight of the power dissipated across the different plasmon dephasing mechanisms in large nanoparticles.[2] We will also discuss how this formalism can be used to explore the role of hot carrier injection on the photocatalytic growth of plasmonic nanoparticles.[3]

Reference: *[1] L. Besteiro, X. Kong, Z. Wang, G. Hartland, A. Govorov, ACS Photonics, 4, 2759-2781 (2017)[2] E. Santiago, L. Besteiro, X. Kong, M. Correa-Duarte, Z. Wang, A. Govorov, ACS Photonics, 7, 2807-2824 (2020).[3] L. Besteiro, A. Movsesyan, O. Ávalos-Ovando, S. Lee, E. Cortés, M. Correa-Duarte, Z. Wang, A. Govorov, Nano Lett., 21, 10315-10324 (2021)*

Mechanistic Insights into Plasmon Catalysis: H_2 Dissociation on Au Cluster

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Abstract: Localized surface plasmon resonances (LSPRs) have attracted much recent attention for their potential in promoting chemical reactions with light. However, the mechanism of LSPR-induced chemical reactions is still not clear, even for H2 dissociation on metal nanoparticles. In this work, we investigate the mechanism for photoinduced H2 dissociation using a simple H2@Au6 model. Our time-dependent density functional theory calculations indicate that the initial excitation is largely restricted to the metal cluster, involving intraband excitation that produces hot electrons (HEs). However, diabatization via overlapping orbitals reveals two types of nested electronic states, one involving excitations of the metallic electrons, namely, the HE states, and the other concerned with charge transfer (CT) to the adsorbate antibonding * orbital. Dissociation of H2 thus takes place by transitions from the former to the latter. Quantum dynamics simulations on the diabatic CT states suggest rapid dissociation of H2, while no such dissociation occurs on diabatic HE states. Our research provides a clear physical picture of photoinduced H2 dissociation on Au clusters, which has important implications in plasmonic facilitated photocatalysis.

keywords: plasmon catalysis, charge transfer, hot electrons, potential energy surface.

Reference: *[1] Zhang, Y.; Nelson, T.; Tretiak, S.; Guo, H.; Schatz, G. C. ACS Nano 2018, 12, 8415-8422.)[2] Wu, Q.; Zhou, L.; Schatz, G. C.; Zhang, Y.; Guo, H. J. Am. Chem. Soc. 2020, 142, 13090-13101.*

The nonperturbative plasmon response at epsilon-near-zero

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Abstract: We investigate the nonlinear optical response of metals and semiconductors by nonlinear multiphoton photoemission spectroscopy at the threshold for nonperturbative light-matter interaction.1 The nonperturbative responses appear as suppression of low-order, with respect to high-order, responses, as well as in acquiring attosecond time structures in femtosecond pulse excitation. The difference between metal and semiconductor responses is intriguing, but even more telling is the frequency dependence of metallic response under epsilon near-zero excitation. One necessary condition of the metallic state is the existence of a partially occupied band that defines the Fermi energy. The existence of such a band causes the metallic dielectric function to transit from negative, through zero, to positive in the high frequency limit.2 The nonlocal in space and time epsilon near zero response enables optical fields to penetrate metals as transverse charge density waves, or bulk plasmons.3 At epsilon-near-zero the linear response vanishes, and nonlinear interaction dominates, causing the metallic response to become essentially nonperturbative. We examine such nonperturbative responses at PHz frequencies, with femtosecond pulse excitation

keywords: plasmon catalysis, charge transfer, hot electrons, potential energy surface.

Reference: *[1] M. Reutzel, A. Li, Z. Wang, and H. Petek. Nature Commun. 11, 2230 (2020).[2] M. Reutzel, A. Li, B. Gumhalter, and H. Petek.Phys. Rev. Lett. 123, 017404 (2019) [3] A. Li, M. Reutzel, Z. Wang, D. Novko, B. Gumhalter, and H. Petek. ACS Photon. 8, 247 (2021).*

Ab Initio Excited State Dynamics in Metallic Nanostructures

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Abstract: Metallic structures exhibit strong plasmonic light absorption and act as efficient catalysts, but they have no bandgap, and energy can be dissipated rapidly to heat. The collective nature of excitation and the large number of carriers create challenges for modeling excited state dynamics in metallic systems. By combining real-time time-dependent density functional theory for the evolution of electrons with nonadiabatic molecular dynamics for coupling with phonons [1,2], including explicitly charge-charge Coulomb interactions [3], and developing methods to evolve ensembles of electrons [4], we have studied excited state dynamics in metallic systems. We have shown that coupling of plasmonic excitations to phonons is much weaker compared to regular excitations [5-6], that strong chemical interaction between metal and semiconductor can result in instantaneous plasmon driven charge separation during the photoexcitation process [7-9], that there exist special relatively long-lived states in metallic particles [10-11], and that plasmon excitation can result in both efficient charge and energy transfer [12-13].

Reference: *[1] C. F. Craig, W. R. Duncan, O. V. Prezhdo. Phys. Rev. Lett., 95 163001 (2005). [2]A. V. Akimov, O. V. Prezhdo. J. Chem. Theor. Comp., 9, 4959 (2013). [3] G. Zhou, G. Lu, O. V. Prezhdo. Nano Lett., 21, 756–761 (2021). [4] Y. Wang et al. J. Phys. Chem. B, 124, 4326-4337 (2020). "Peter J. Rossky Festschrift" [5] Z. Guo, W.-Z. Liang, O. V. Prezhdo. Phys. Rev. B, 81, 125415 (2010). [6] A. J. Neukirch, Z. Guo, O. V. Prezhdo. J. Phys. Chem. C, 116, 15034 (2012). [7] R. Long, O. V. Prezhdo. J. Am. Chem. Soc., 136, 4343 (2014). [8] Z. S. Zhang et al. Chem, 4, 1112-1127 (2018). [9] J. Zhang, M. X. Guan, J. Lischner, S. Meng, O. V. Prezhdo. Nano Lett., 19, 3187-3193 (2019) [10]O. Ranasingha et al. J. Phys. Chem. Lett., 7, 1563-1569 (2016).[11] W. Chu, W. A. Saidi, O. V. Prezhdo. ACS Nano, 14, 10608 (2020). [12]T. F. Lu et al.J. Phys. Chem. Lett., 11, 1419-1427 (2020).[13] J. A. Tomko et al. Nature Nanotech., 16, 47-51 (2021)*

Ab Initio Excited State Dynamics in Metallic Nanostructures

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Abstract: Localized surface plasmon resonances (LSPRs) have a broad technology potential as an attractive platform for surface-enhanced spectroscopies, non-bleaching labels, hyperthermal cancer therapy, waveguides, and so on. Most plasmonic metals studied to date are composed of either copper, silver, or gold. The former two can pose significant challenges related to oxidation, the latter is often perceived as cost-prohibitive, and all three are rare. Aluminum has emerged over the past two decades as an earth-abundant alternative; its performance in the UV is exceptional but its LSPR quality factor sharply decrease in the red region owing to losses attributed to interband transitions.

One of the newest metals for plasmonics is magnesium. It is earth-abundant, biocompatible, and has a higher plasmonic quality factor than aluminum across the visible (and than gold and copper in the blue). In the past ten years, several fabricated magnesium structures have emerged, demonstrating the optical behaviors expected of plasmonic metals. Our group has chosen a different approach: we have developed colloidal, scalable batch and flow syntheses capable of size control from 50 to 1000 nm. This enabled to study the fascinating size and shape-dependent optical, chemical, crystallographic and catalytic properties of these novel structures.

This talk will review the advances we have made over the past four years on magnesium plasmonics. The unusual shapes of single crystal and twinned magnesium crystals, owing to its HCP structure, will first be discussed, followed by the formation and stability of the native oxide layer. Then, approaches to control nanoparticle shape will be presented, followed by experimental and numerical results on the plasmonic properties of colloidal magnesium, both far-field and near-field techniques such as optical spectroscopy and electron-energy loss spectroscopy. Finally, our approach to exploiting the chemical reactivity of magnesium for galvanic replacement, and the bimetallic plasmonic-catalyst structures obtained, will be reviewed.

Ultrafast photoinduced electron dynamics in metallic nanogaps from first principles calculations

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Abstract:A nanoscale gap between two metallic nanoparticles is an ideal platform to exploit the interplay between electron currents and photonic excitations. The capability of a metallic gap to enhance the amplitude of the induced plasmonic field produces a variety of non-linear effects [1,2] which can be exploited in different applications in optoelectronics, such as optical rectification, light emission driven by DC currents, or high-harmonic generation, among others. Furthermore, in ultranarrow gaps, tunneling of electrons at optical frequencies has been found to screen the plasmonic bonding gap resonance, and activate a new distribution of optical modes characterized by optical charge transfer [3]. Here we address the complex ultrafast dynamics of photoelectrons driven by single-cycle optical pulses in nanoscale gaps. By solving Schrödinger equation within the framework of Time-Dependent Density Functional Theory (TDDFT), the currents of the electrons photoemitted across the gap can be monitored, identifying ultrafast electron bursts where electron quiver occurs when the amplitude of the induced field at the plasmonic gap is reversed within the optical cycle. The properties of the amplitude and carrier-envelope phase (CEP) of the incident pulse, together with the gap length determine the complex electron dynamics [4,5,6]. Experimental measurements of the current autocorrelations for pairs of such pulses with controlled relative delay between them, confirms the ultrafast dynamics of the photoelectrons in the gap and its complexity

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Hot-carrier transfer: Insight from atomic scale simulations

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Abstract: Metal nanoparticles are attractive for plasmon-enhanced generation of hot carriers, which may be harnessed in photochemical reactions. While direct hot-carrier transfer can in principle be particular efficient for increasing photo-catalytic activity, it is difficult to discern experimentally and competes with several other mechanisms. In our work, we analyze the coherent femtosecond dynamics of photon absorption, plasmon formation, and subsequent hot-carrier generation through plasmon dephasing using first-principles simulations [1]. We predict the energetic and spatial hot-carrier distributions in small metal nanoparticles and find that the distribution of hot electrons is very sensitive to the local structure. Our results show that surface sites exhibit enhanced hot-electron generation in comparison to the bulk of the nanoparticle. While the details of the distribution depend on particle size and shape, as a general trend lower-coordinated surface sites such as corners, edges, and 100 facets exhibit a higher proportion of hot electrons than higher-coordinated surface sites such as 111 facets or the core sites.

The distribution of hot carriers on a surface is, however, only one part in the transfer process, the other part being the receiving molecule (or semiconductor). To shed light on these aspects, we model from first principles hot-carrier generation across the interface between plasmonic nanoparticles and a CO molecule [2]. We show that the hot-electron transfer probability depends non-monotonically on the nanoparticle-molecule distance and can even be effective at long distances, well outside the region of chemisorption; hot-hole transfer on the other hand is limited to shorter distances. These observations can be explained by the energetic alignment between molecular and nanoparticle states as well as the excitation frequency. The hybridization of the molecular orbitals is the key predictor for hot-carrier transfer in these systems, emphasizing the need to include the effects of ground state hybridization for accurate predictions. Finally, we demonstrate a non-trivial dependence of the hot-carrier distribution on the excitation energy, which could be exploited when optimizing photo-catalytic systems. The present results thereby demonstrate how hot carriers could be tailored by careful design of atomic-scale structures in nanoscale systems.

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Quantum Mechanical Modeling of Plasmon-Like Excited States

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Abstract: Quantum mechanical studies of Ag nanoclusters have shown that plasmonic behavior can be modeled in terms of excited states where collectivity and coherence among single excitations leads to strong absorption. However, typical DFT methods are computationally expensive for large nanoclusters. We have shown that semiempirical INDO/CI approaches with appropriate parameters reproduce the TD-DFT optical spectra of various Ag nanoclusters at 2-3 orders of magnitude lower computational cost. By comparing the INDO/CIS and INDO/CISD excited states, we have provided evidence to support the common assumption that single excitations are typically sufficient to describe the optical spectra of plasmonic excitations quantum mechanically. Among prototypical nanoclusters, the emergence of these collective, coherent plasmon-like states corresponds to the emergence of nonlinear optical properties consistent with those of larger plasmonic nanoparticles. These methods also allow us to identify quadrupolar plasmon-like excited states and quantify the charge-transfer plasmon character in nanocluster dimers.

Electrically Controlled Light Matter Interaction for Metasurfaces at Visible Frequencies

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Abstract: A rigorous evolution from passive to active metasurfaces has been witnessed in nanophotonics recently. This advancement brings forward new physical and practical applications. However,dynamic metasurfaces operating at visible frequencies often featurelow performance due to design and fabrication restrictions at the nanoscale. In this presentation, we demonstrate new concepts for electrically-controlled metasurfaces with high intensity contrast, fast switching rate, and excellent reversibility. We employ liquid crystals as well as conducting polymers that can be locally conjugated on preselected gold nanorods to actively control the phase profiles of the metasurfaces. The optical responses of the dynamic metasurfaces can be in siturecordedand optimized by controlling the growth of electrochromic polymers of subwavelength dimensions during the electrochemical processor the orientation of liquid crystals.In particular, we showcase electrically-controlled anomalous transmission and reflection as well as pixelated holography with good switching performance. Such electrically powered optical metasurfaces lay a solid basis to develop metasurface devices for real-world optical applications

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Band-Structure Anisotropy and Plasmonic Structure in a Two-Dimensional Electron System

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Abstract: We show that the dielectric properties in a two-dimensional electron gas can be profoundly modified by the variation of the shape of the one-electron energy band. Considering the systems with a singleband having triangular, square, or hexagonal shapes, we found anisotropy in the dispersion of a conventional two-dimensional plasmon with a characteristic sqrt(q) behaviour. In the case of the triangular system the strong distortion of the plasmon dispersion from the isotropic behaviour is observed at any momentum transfer. In the cases of higher symmetry at small momentum transfers the plasmon dispersion becomes almost isotropic. The respective symmetry becomes notable at larger momentum transfers. The threshold for the transition from the isotropic to the anisotropic dispersion increases with increasing the symmetry of the system.

Additionally, we have found that in the momentum-energy phase regions,that in the isotropic case are dominated by electron-hole pairs, strong inhomogeneityin the Fermi velocities of the carriers causes strong variations in the dielectric function. As a result, additional plasmon modes with characteristic sound-like dispersion can emerge. In the case of the systems with the triangle and square symmetry, one acoustic plasmon isfound and its dispersion in a whole momentum space is determined. In the hexagonal case the number of acoustic plasmons increases to two. We predict that at higher symmetries the number of such plasmons should increase. However, this process is accompanied by a quick reduction of the spectral weight of such modes, which eventually lead to a well-known result that such kind of mode cannot be realized in an isotropic two-dimensional electron gas.

From “strong coupling” to “hot electrons”: Photon-driven molecular dynamics and spectroscopy at nanostructures

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Abstract: In plasmonic nanostructures, at metal surfaces, and / or in cavities, the interaction of molecules with photons is often dramatically enhanced, among other effects by direct “strong coupling” of light-modes to molecular vibrations, or by coupling to “hot electrons” created in the metal. Both coupling channels can affect dynamics and reactivity, and are accompanied by characteristic spectroscopic fingerprints.

In this presentation, we shall first focus on “vibrational strong coupling” (VSC) of quantized light modes in cavities to molecular vibrations, leading to the formation of light-matter hybrid states, “vibrational polaritons”. These leave their signatures in spectra in the form of Rabi splittings and also alter reaction rates in isomerization reactions. Using fully quantum stationary and also dynamical models based on a so-called Pauli-Fierz Hamiltonian, some recent results of our group on spectroscopy and reactivity of cavity-mebedded molecules shall be presented [1].

Second, we consider femtosecond laser (FL) pulse driven chemistry at metal surfaces, promoted by “hot electrons”, e.g., FL-induced desorption, diffusion or reactions. In the examples presented, we mostly use classical Langevin Ab Initio Molecular Dynamics with Electronic Friction (AIMDEF) based on Density Functional Theory (DFT), and random forces obtained from a two-temperature model. Results will be presented for associative desorption of H2 and isotopomers from Ru(0001) and its “dynamical promotion” [2], and for desorption, diffusion, and reactions and (time-resolved) spectroscopic response of CO on CO(O):Ru(0001) [3], respectively

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Injection of hot carriers in molecules: insights from first-principle based multiscale modeling

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Abstract: Hot carriers generated upon metallic nanostructures interaction with light are known to be able to catalyze chemical reactions of nearby molecules. Understanding from a microscopic point of view the overall process poses several challenges, ranging from how the hot carries are generated and transferred to the mechanism of the chemical reaction itself. In this talk, I will focus on our modeling effort aimed at clarifying the injection step of hot carriers into the molecule. For this goal, we have set up a multiscale modeling approach able to incorporate a GW/Bethe Salpeter description of the molecule-metal interface, and to include decoherence and relaxation effects via the stochastic Schroedinger equation technique. Results for a specific system will be discussed, showing how this approach can be used to reveal the underlying chemical picture

Mid-Infrared Radiative Emission from Bright Hot Plasmons in Graphene

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Abstract: The decay dynamics of excited carriers in graphene have attracted wide scientific attention, as the gapless Dirac electronic band structure opens up relaxation channels that are not allowed in conventional materials. I will present the first experimental demonstration of a mid-infrared light-emitting mechanism originating from an ultrafast coupling of optically excited carriers into hot plasmon excitations in graphene. Such excitations show gate-tunable, non-Planckian emission characteristics due to the atom-level confinement of the electromagnetic states. Evidence for bright hot plasmon emission is further supported by a large emission enhancement observed from graphene decorated with gold NDs, which serve as out-coupling scatterers and promote localized plasmon excitation. These findings for plasmon emission in photo-inverted graphene open a new path for the exploration of mid-infrared emission processes, and this mechanism can potentially be exploited for both far-field and near-field applications for strong optical field generation.

Ultrastrong light-matter interaction in 2D nonstructures: cavity photons vs. free photon

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Abstract: The semiconducting 2D crystals support the collective polarization modes called excitons. The excitons, if dipole active, can absorb or emit the photons. However, in some occasions the exciton and photon can interact stronger so that a hybrid mode is created called exciton-polariton. Popular platforms for studying the light-matter interaction are 2D TMDs embedded in the microcavity device. Here the exciton in 2D crystal hybridise with photon 'confined' between reflective metal walls. The hybridisation is stronger, the larger is the exciton oscillator strength and the larger is the overlap between photon and exciton wave functions. Fig.1. demonstrate the ultrastrong exciton-photon binding in hBN microcavity, where exciton-polariton Rabi spliting is =440meV[1]. However, do the strong coupling between 'free' transversal s(TE) photons and excitons exists? Contrary to p(TM) exciton-polaritons, which in non-retarded limit (Q»ex/c) reduces to longitudinal exciton, the s(TE) exciton-polaritons 'do not' exist in non-retard limit, i.e. they are 'trapped photons'; the coexistence of s(TE) photons and exciton, confined to propagate only within nano-structure. The coupling between exciton in single layer TMDs and free photons is very weak [2]. However, this coupling drastically enhances in vdW haterostructures composed from several single-layers. The strong deformation of the photon line (=Qc/M) in thin crystaline C60 film composed of N=9 single-layers can be seen in Fig.2. [3], where the photon bending is S = 670meV. I will present the theoretical simulation of interplay between excitons, cavity and free s(TE) photons in various 2D nanostructures using our Quantum-Electrodynamical-Bethe-Salpeter-Equation approach (QE-BSE)[2].

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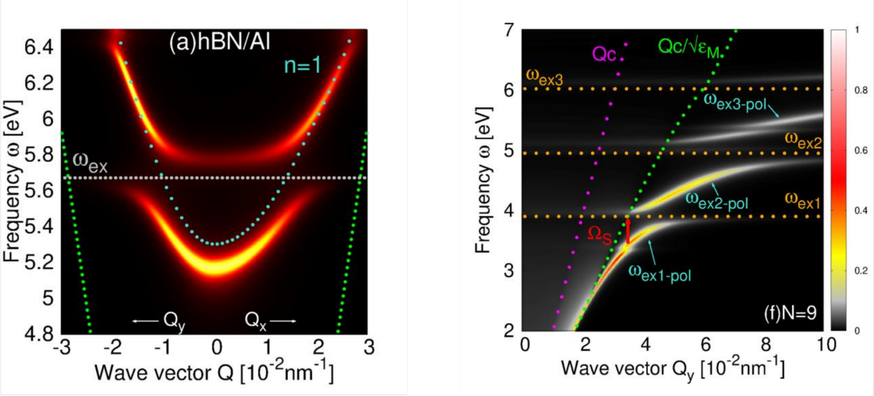

Figure 1: Left Panel: The hybridisation between cavity mode n = 1 (cyan dotted) and hBN exciton (white dotted) in aluminium cavity of thickness d = 90 nm. Right Panel: The spectral intensity of s(TE) polarised exciton-polaritons in fullerene (C60) thin film composed of N=9 single-layers phisisorbed at Al_2O_3 surface.

Differences between photon-induced and plasmon-induced hot electron

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Abstract: Despite the great potential of plasmon-induced hot carriers for photovoltaics and photochemistry, their precise role in the enhancement of the efficiency of these processes is still heavily discussed. Fundamental questions remain on how plasmon-induced hot carriers are generated, how they dissipate energy and momentum, and how the underlying mechanisms come into play in plasmonic energy conversion processes. Many theoretical studies have been conducted in the last years to address these questions. However, it is essentially unresolved if plasmonic enhancement is simply due to the field-enhancement of light at the surface of a metal, or if there is a more fundamental difference between plasmon-induced and photon-induced hot carriers.

A fundamental difference is known for bulk plasmon resonance [1-3], but this is far from clear for technologically important surface plasmons. Direct imaging of surface plasmon induced hot charge carriers could provide essential insights, but separating the influence of the driving laser, field enhancement, and fundamental plasmon decay has proven difficult.

Here we present an approach using a two-color femtosecond pump-probe scheme in time-resolved 2-photon photoemission (PEEM and momentum microscopy), supported by a theoretical analysis of the light and plasmon energy flow. We separate the energy and momentum distribution of plasmon-induced hot electrons from that of photoexcited electrons by following the spatial evolution of photoemitted electrons during the propagation of a surface plasmon polariton (SPP) pulse along a gold surface. We find plasmonic enhancement toward high excitation energies and small in-plane momenta, suggesting a fundamentally different mechanism of hot electron generation previously unknown for SPP [4] .

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Integrated plasmonics: Exotic plasmons from a 2D metal and nonequilibrium photoreaction dynamics

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Abstract: The past decade has witnessed numerous discoveries of two-dimensional (2D) semimetals andinsulators, whereas 2D metals were rarely identified. Borophene, a monolayer boron sheet, has recently emerged as a perfect 2D metal with unique electronic properties. We show that collective excitations in borophene exhibit two major plasmon modes with low damping rates extending from the infrared to ultraviolet regime. The anisotropic 1D plasmon originates from electronic transitions of tilted Dirac cones in borophene, analogous to that in extreme doped graphene. These features enable borophene as an integrated platform of 1D, 2D, and Dirac plasmons, promising for directional polariton transport and broadband optical communication in next-generation optoelectronic devices. We will also present first-principles dynamic simulations of complex pathways and ultrafast interaction dynamics of plasmon-induced photoreactions, which demonstrate a synergic interplay and transition from indirect hot-electron transfer to direct charge transfer enacted by strong localized surface plasmons

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Insights into nanoplasmonics from first-principles time-dependent density functional simulation

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Abstract: Our implementation of time-dependent density functional theory within linear response allows computing the optical properties of systems with several thousands of atoms [1,2]. We applied this method to study the dependence of the near-field enhancement and localization on the structural details of the plasmonic nano-gaps [3,4], the different size dispersion of the plasmon resonance of silver and sodium nanoparticles and how this behaviour correlates with the presence of 4d electrons in the Ag case [2], and more recently to describe valence EELS [5]. In this talk I will concentrate mostly in the correlation between transport properties across sub-nanometric metallic gaps and the optical response of the system. Our calculations show that, due to the conductance quantization in metal nanocontacts, small reconfigurations play a crucial role in determining the optical response. We observe abrupt changes in the intensity and spectral position of the plasmon resonances, and find a one-to-one correspondence between these jumps and those of the quantized transport as the neck cross-section diminishes.

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Ultrafast excitation of electrons in crystals: insights from non-equilibrium band structure calculations

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Abstract: Last decade, understanding of transient excitation of electrons in solids has brought important developments for several classes of materials, at the level of both fundamentals and applications. While laser-excitation of dielectrics induces measurable ultrafast currents in the PHz regime [1], employing few-cycle laser pulses with controlled carrier envelope phase enables a coherent control of the electron dynamics with reduced crystal damage probability [1]. Notably, the possibility of transiently closing the band-gap of solids during their irradiation by linearly polarized ultrashort laser pulses was evidenced and attributed to the light-induced Zener tunneling [1].

The corresponding ultrafast modification of the band structure induced by laser dressing of electronic states can be measured experimentally and analyzed theoretically using the Floquet formalism [2]. Despite its simplicity and limitations, it is applicable to several classes of materials and enables to study the effects of light coupling with electrons in solids for a wide range of experimental conditions [3].

In this work, after preparing the electronic band structures of two metals (Au and Mo), a semiconductor (Si) and a dielectric (-SiO 2) using the density functional theory (DFT), the effects of dressing by a polarized laser light on the corresponding electronic band structures were investigated using the Floquet formalism [3]. While a selective excitation of the electrons can be achieved via a choice of laser wavelength and field strength [3], the Floquet simulations illustrate how the change in crystal orientation affects the electron dynamics in solids.

Overall, the proposed approach outlines promising ways for selecting materials and laser parameters, via a computer-aided manner, broadening perspectives in ultrafast photonics.

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Carrier dynamics and optical nonlinearity in plasmonic hetero-nanostructures

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Abstract: Plasmonic nanostructures, metamaterials and metasurfaces provide unique opportunities to design the enhanced nonlinear optical response in the required spectral range and with required parameters, exploiting free-electron gas properties. In this talk, we will overview second- and third-order nonlinear optical processes in several types of plasmonic nanomaterials allowing to engineer the magnitude and time-response of nonlinearity. Some of the examples to be overviewed include ultrafast Kerr-type nonlinearity in mesoscopic plasmonic CuS nanocrystals with low free-carrier concentration which exhibit a much faster carrier relaxation than in traditional plasmonic materials, plasmonic hetero-nanostructures which allow tailoring the electron dynamics controlled by hot-carriers redistribution, as well as the nonlinear response time controlled by anisotropic geometry of the nanostructures. Ultrafast nonlinearity in an epsilon-near zero material coupled to plasmonic antennas will be reported as well. New designs for enhancing four-wave mixing, harmonic generation and controlling ultrafast pulse propagation will be discussed.

Poster Presentation

Nonequilibrium electron dynamics and controlled surface functionalization in plasmonic metals

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Abstract: We study nonequilibrium electron dynamics in plasmonic metals with the help of a set of complete Boltzmann collision integrals [1,2]. Our description traces the transient electron distribution and the influence of distinct interaction processes. We show that electron-phonon scattering maintains a certain long-lasting nonequilibrium in the electron distribution on picosecond timescales [3]. We calculate the spectral density of electrons in specific energy windows above or below Fermi energy and compare it with pure equilibrium results from the two-temperature model (TTM). Our simulations show a strong influence of nonequilibrium during and after the end of the laser pulse. Strong laser excitations allow for permanent surface modifications. We have studied the role of propagating surface plasmon polaritons (SPP) on nanostructuring, namely the formation of the laser-induced periodic surface structures (LIPSS) [4-6]. Such structures have a very broad area of applications such as optics (coloring, optical data storage, solar cells), chemistry (catalytic activity, chemical sensing), biology (antibacterial surfaces, directional growth of living cells), and mechanics (reduction of friction, wear resistance, fuel injection). We find a good agreement of our theoretical predictions with experimental observations [5].

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Energy transfer to molecular adsorbates by transient hot-electron tunnelling

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Abstract: In the last ten years the study metallic nanoparticles gained a lot of interest because of their optoelectronic features and especially to the presence of Surface Plasmon Resonance (SPR). This peculiar effect makes these nanosystems suitable for a broad variety of applications in biomedicine, catalysis, electronics, optics and more. [1,2] A relatively new and highly promising way by which SPR can be exploited is hot-carriers mediated photocatalysis. As the SPR start to dephases, there is the generation of the so called hot-carriers which are out of equilibrium electrons (and holes) with higher (or lower) energy compared to the unperturbed system. Once formed, these carriers can migrate to the nanoparticle edges and their energy can be transferred to a molecule adsorbed on the surface, activating chemical reactions such as water splitting [3] and CO2 reduction [4]. Although many theoretical advances have been made to determine the physics below this phenomenon [5,6], there still are an open debate on the precise interaction mechanism with the adsorbate. Our work aims to investigate one of the possible HC injection routes which implies the transient tunneling to the adsorbate and further energy release the molecular vibrational states. To do that, we explored the interaction among hot-electrons (HEs) and

a small molecule at the real time Time Dependent Density Functional Theory (rt-TDDFT) level. We represented the hybrid metallic nanostructure-molecule system through a minimalistic model composed on a linear chain of metal atoms interacting with a small molecule adsorbed on the edge. By simulating the real-time dynamics of a set of single HE on the metal chain, we observed that they can interact with the adsorbate by releasing part of their kinetic energy on some specific vibrational modes, with an efficiency strongly dependent on the molecular species and on the HE energies. Our work suggests that, regardless their energy, all generated HE can compete to the activation of the motion involved in the photocatalyzed reaction and this process can cooperate with the currently accepted mechanism involving a direct electron transfer. [7]

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Thermal and non-thermal effects in metal nanostructures

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Abstract: Here, we develop a coupled Boltzmann-heat equations formulation for calculating the electrondistribution in plasmonic nanostructures under continuous wave illumination, taking into accountnon-equilibrium and thermal effects on the same footing [DUbi Sivan, Light Sci. Appl., 2019;Sivan, Un Dubi, Faraday Discuss., 2019]. This is done by ensuring a total energy balance andbasic thermodynamics. This allows us to determine self-consistently and uniquely the increasein electron and lattice temperatures above ambient conditions although the system is inherentlyaway from thermal equilibrium. Our approach also allows us to deduce how the power densitypumped into the nanostructure by the absorbed photons splits into the non-thermal electrons andinto heating the electrons and the phonons. we find that most absorbed power causes heating, andonly an extremely small fraction actually leads to high energy electron generation. Based on thisunderstanding, we develop a simple model based on the Fermi's golden rule and the ArrheniusLaw and show that the enhanced chemical reactions observed experimentally are highly unlikelyto be due to the generation of non-thermal ("hot") electrons; instead, the faster chemistry morelikely originates from a purely photothermal effect [Dubi, Un Sivan, Chem. Sci., 2020]. Finally,we combine the analytic form for the electron non-equilibrium distribution of an illuminated metalwith the standard Landauer theory of transport through MJs, and suggest a scheme that can beused to measure the non-thermal electron distribution in the presence of strong heating and evenlarge thermal gradients (i.e., regardless of the temperature distribution) [Dubi, Un Sivan, NanoLett., 2022]. Using this formulation we hows how non-thermal electrons can be measured directlyand separately from the unavoidable thermal response, and discuss the relevance of our theory torecent experiments.

Mixing the light-spin with plasmon-orbit

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Abstract: The transformation of light carryingspin angular momentum (SAM) to an optical field vortex carrying angular momentum (OAM) has been of wide interest in recent years [1]. In our work, we investigatethe superposition of two fields that each carry one of those degrees of freedom and focus on the transfer of the resulting angular momentum to matter. For this, we measured the interaction between 3Dlight carrying axial SAM and 2D plasmon-polariton vortices carrying high order transverse OAM [2].The interaction is mediated via two-photon absorption on a gold surface, imprinting the resulting angular momentum mixing into matter by excitation of electrons that are photo-emitted into vacuum and detected by photoemission electron microscopy (PEEM). We show experimentally and theoretically that the absorptive nature of this interaction leads to both single and double photon-plasmon angular momentum mixingprocesses which correspond to different quantum pathways of the electron excitation[3].

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Molecular excited states probed by near-field spectromicroscopy at subnanometer scale

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Abstract: Scanning tunneling microscopy-induced luminescence (STML) is an experimental technique capable of detecting light emission of chromophores with submolecular resolution. The interaction between the molecular sample and the plasmonic nanocavity formed between the scanning probe and a metal sample amplifies the molecular emission signal by orders of magnitude (near-field spectroscopy). Therefore STML is an ideal technique to achieve insight in the photophysics of single molecules or their aggregates, allowing to obtain a mapping of the electronic transition in real space with submolecular resolution. Additionally, STML can overcome some limitations of conventional far-field spectroscopy, accessing information otherwise not available, such as forbidden (dark) excited states. A complete rationalization of STML results in terms of the molecular microscopic properties requires to flank experiments with a computational framework combining: (i) quantum-chemical calculations of the molecular electronic structure and (ii) a theoretical description of the molecular optical response in the near-field. The simulated spatial maps of the emission are directly comparable to the experiments, while offering detailed information about the molecular excited states and their photophysical behavior. In this contribution, we present the results from the application of the experimental and theoretical STML setup to small conjugated molecules. First, we will take a close look at the high-resolution luminescence spectra of charged phthalocyanines that manifest a peculiar peaks progression, linked to the coupling between the molecular electronic excitation (trions) and the librational molecular motion on the surface (librons). Interestingly, we could establish a general correlation between the adsorption configuration of the molecule (chiral vs. non-chiral) and the spectral profile appearance.[1] Second we will show recent insight on the delocalized excitonic states of aggregates with controlled geometry, formed by perylene-tetracarboxylic dianhydride (PTCDA) anion molecules. We revealed the involvement of two low-lying excited states of PTCDA anion and their entanglement in the excitonic states. Furthermore, we could demonstrate control over the aggregate emission by switching the assembly charge states, showing the possibility to tailor excitonic properties of organic dye aggregates for advanced functionalities.[2]

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Hybridisation of Plasmons, Excitions and Photons in van der Waals Heterostructures Investigated by a Composite RPA/GW/BSE Method

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Abstract: We introduce a first-principles theoretical model for the calculation of optical properties of quasi-2D crystals based on the many-body photon propagator which mediates the interaction between fermionic current fluctuations. Using this model we proceed to calculate the spectra of s(TE) and p(TM) electro- magnetic modes for both free-standing as well as layered crystals composed of weakly bound sheets of graphene and analogous materials. In our work, we perturbatively expand the photon propagator to include both RPA and GW self-energy corrections as well as ladder vertex corrections to correctly describe electron-hole binding. Finally, we solve the Bethe-Salpeter equation and obtain the dispersion relations of electromagnetic modes in the composite systems. Our theoretical model can be applied to both semiconducting/isolating as well as metallic heterostructures, depending on the type of quasiparticle modes we are after. We have investigated exciton-polaritons in semiconducting heterostructures composed of transition metal dichalcogenides (TMD) spaced apart by boron nitride (hBN) layers where the dielectric screening due to hBN is correctly accounted for in the GW-BSE formalism. In particular, we quantify the strength of exciton-photon binding as a function of the number of TMD layers and find a rein-forcing relationship. We theoretically predict the transition from weak to strong exciton-photon binding in vdW layered crys- tals by increasing the number of crystal layers N. An exciton-photon binding enhancement of factor >5 is achieved in hBN multilayers. In addition, we investigated plasmon-polariton modes in graphene/hBN heterostructures by applying a similar formalism, but truncating terms beyond RPA due to diminishing returns for zero bandgap systems. In this system, we identify Dirac and multiple acoustic plasmon-polariton (PP) branches. Their respective dispersions relations were found to be highly dependent on the number of layers in the heterostructure. To bridge the momentum gap between the evanescent SPP modes and infrared photons, we patterned the topmost layer of graphene into nanoribbons. This introduces symmetry breaking and leads to the formation of Bloch plasmon polariton modes. The emerging Bloch band structure is anisotropic and has both radiative and evanescent character, allowing for a wide range of possible applications

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Ultrafast non-equilibrium dynamics of Dirac plasmon in graphene

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Abstract: Exploring low-loss two-dimensional plasmon modes is considered central for achieving light manipulation at the nanoscale and applications in plasmonic science and technology. In this context, pump–probe spectroscopy is a powerful tool for investigating these collective modes and the corresponding energy transfer processes. Here, I present a first-principles study on non-equilibrium Dirac plasmon in graphene [1], wherein damping channels under ultrafast conditions are still not fully explored. The laser-induced blueshift of plasmon energy is explained in terms of thermal increase of the electron–hole pair concentration in the intraband channel. Interestingly, while damping pathways of the equilibrium graphene plasmon are entirely ruled by scatterings with acoustic phonons [2], the photoinduced plasmon predominantly transfers its energy to the strongly coupled hot optical phonons, which explains the experimentally-observed tenfold increase of the plasmon linewidth [3]. The present study paves the way for an in-depth theoretical comprehension of plasmon temporal dynamics in novel two-dimensional systems and heterostructures.

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First principles investigation of plasmonic hydrogen catalysis on metallic magnesium nanoparticles

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Abstract: Plasmon-induced hot-carrier photochemistry is currently a promising avenue to achieve highly selective and efficient chemical transformation on plasmonic metal surfaces. A new class of materials made up of Earth-abundant-elements has gained increasing interest in the plasmonic area, as an alternative to the oft studied late transition metals (Au, Ag and Cu).

Here, we will present our results on the optical and electronic properties of metallic magnesium nanoparticles and their potential use as plasmonic hydrogen catalysts. We explore the optical and electronic properties with time-dependent density functional tight-binding (TD-DFTB) and molecular dynamics with electronic friction (MDEF) simulations. Our results show that Mg nanoclusters can produce highly energetic hot-electrons and they energetically align with electronic states of physisorbed molecular hydrogen, the occupation of which by these hot electrons can promote hydrogen dissociation. The reverse reaction, hydrogen evolution on metallic Mg, may also be promoted by hot electrons, but following a different mechanism.[1]

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Stacking the odds: Distribution-biased generative deep learning for targeted design of organic electronics.

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Abstract: High-throughput screening of excited states in molecules can advance the search for functional organic molecules with potential importance for modern organic electronics. However, time-consuming experiments and high computational costs of accurate quantum chemical calculations severely limit the characterization of such systems and consequently targeted molecular design [1].

In this talk, we will show how deep learning can advance this research area by using an automated approach to molecular design that combines two deep learning techniques: The first is based on a physics-inspired deep learning model for high-throughput screening of optical and electronic properties with near experimental accuracy [2]. The second technique we use is generative deep learning, which allows us to generate novel molecules by learning the structural distribution of a dataset. In successive iterations, the output of the generative model is filtered with the spectroscopic deep learning model and then used to retrain the generative model with a bias. In this way, molecules with finely tuned optoelectronic properties can be efficiently generated [3]

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NQCDynamics.jl: Nonadiabatic quantum classical dynamics in the Julia language

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Abstract: Accurate and efficient methods to simulate nonadiabatic and quantum nuclear effects in high-dimensional and dissipative systems are crucial for the prediction of chemical dynamics in the condensed phase. To facilitate effective development, code sharing, and uptake of newly developed dynamics methods, it is important that software implementations can be easily accessed and built upon. Using the Julia programming language, we have developed the NQCDynamics.jl package, which provides a framework for established and emerging methods for performing semiclassical and mixed quantum–classical dynamics in the condensed phase. The code provides several interfaces to existing atomistic simulation frameworks, electronic structure codes, and machine learning representations. In addition to the existing methods, the package provides infrastructure for developing and deploying new dynamics methods, which we hope will benefit reproducibility and code sharing in the field of condensed phase quantum dynamics.

Quantifying the breakdown of electronic friction theory during molecular scattering of NO from Au(111)

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Abstract: The Born-Oppenheimer approximation fails to capture the extent of multiquantum vibrational energy loss recorded during molecular scattering from metallic surfaces. Vibrational state-to- state scattering of NO on Au(111) has been one of the most studied examples in this regard, providing a testing ground for developing various nonadiabatic theories. The exact failings compared to experiment and their origin from theory are not established for any system, particularly since dynamic properties are affected by compounding simulation errors, of which the quality of nonadiabatic treatment is just one. We use a high-dimensional machine learning representation to perform a comprehensive quantitative analysis of the performance of molecular dynamics with electronic friction in describing nonadiabatic state-to-state scattering. We find that electronic friction theory accurately predicts vibrationally elastic and weakly inelastic scattering, but underestimates vibrational inelasticity that involves multi- quantum energy loss and overestimates molecular trapping at high vibrational excitation. Our analysis reveals potential remedies to these issues.

Machine-learning-based models for nonadiabatic dynamics of hydrogen molecule adsorption on copper surfaces

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Abstract: The unique electronic structure of metals may cause significant differences between classical adiabatic molecular dynamics (MD) and experimental results. Traditionally, molecular dynamics methods utilize the Born-Oppenheimer approximation, which assumes separation of electronic and nuclear degrees of freedom and enables that the nuclear dynamics can be described by a single potential energy surface (PES). However, on metallic surfaces often the energy exchange between adsorbate and surface atoms is significant and causes the breakdown of the Born-Oppenheimer approximation. There are multiple methods to include such nonadiabatic effects, with one of the most efficient being molecular dynamics with electronic friction (MDEF) [1]. MDEF introduces the non-adiabatic effects by means of both electronic friction and random forces. However, a meaningful comparison between computational simulations and experiments demands the capability to run thousands of MDEF trajectories which are currently unfeasible through ab-initio MD. In this context, machine learning provides a lighter model to compute the electronic friction tensor and the PES allowing to overcome this computational limitation. Here, we present a general workflow for developing machine-learning-based models that enable simulating nonadiabatic molecular dynamics of hydrogen molecules at different copper surfaces.

Surface plasmon polaritons: Their properties for different metal and the constitutive role in ultrafast laser processing.

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Abstract: Irradiation of metals and semiconductors by intense ultrashort laser pulses leads to a transient change of material optical properties, subsequently inducing a strong increase in optical absorption (losses) and creating favorable conditions for excitation of several types of surface electromagnetic waves (SEW) [1], including Surface Plasmon Polaritons (SPP) [2]. The classical SPP theory was developed for noble metals under the assumption of small perturbations of the free-electron gas and weak plasmonic damping. For intense laser irradiation of materials resulting in out-of-equilibrium conditions, the theory is to be revised by taking into account high optical losses resulting in strong plasmonic damping. Contrary to traditional plasmonic applications, upon intense laser irradiation ofmaterial surfaces even small coupling efficiencies are sufficient to provide a spatial modulation of the deposited laser energy, yielding in the formation of laser-induced periodic surface structures (LIPSS) [1,2]. In Ref. [3], it was predicted theoretically that SPP can efficiently be generated on thesurfaces of a wide range of irradiated metals, thus broadening the range of plasmonic applications. The SPP properties such as their spatial period and the decay length were calculated for metals where the optical losses are considerable.In this work, simulations have enabled to classify plasmonically active metals into several groups in respect of the SPP decay length LSPP. To check the effects of highly non-equilibrium heating of free electrons at ultrashort laser irradiation, the temporal variations of the dielectric permittivity were modeled numerically for titanium and molybdenum as the examples. For these aims, the two-temperature model was supplemented by the computation of the optical properties in the frame of the Drude model. It has been shown that the SPP decay length is decreasing upon laser-induced excitation of these two metals. Physical insights into SPP propagation indicate that preferably materials with short SPP decay lengths, of the order of 10 m, allow the imprinting of highly-regular periodic structures on material surfaces via coherent linking effects in laser scan processing. This theoretical result was successfully verified experimentally for several metals when the laser processing parameters are suitably chosen [4,5].

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