

**International Conference on Development of
Nanocrystal Materials Through Computational
Modelling // COST 18234 Meeting in ISRAEL**

ABSTRACTS

Table of Contents

Structural and Electronic Key Features of Perovskite Solar Cells From First-principles (<i>Adriana Pecoraro</i>)	3
Insights to the Morphology of Fe ₂ O ₃ Clusters Using Computational Methods (<i>Anders Hellman</i>)	4
Micro-kinetic Approach to Photo-electrochemical Water Splitting: Uncovering Novel Reaction Pathways Toward Efficient Solar Fuel Production (<i>Arik Yochelis</i>)	5
Tuning the Properties of Janus van der Waals Hetero Structures by Varying Interface Terminations (<i>S. Assa Aravindh</i>)	6
Ru-pincer Complexes as Charge Transfer Mediators in CO ₂ Reduction (<i>B.M. Szyja</i>)	7
Titanium Dioxide: Bridging Photocatalytic Processes and Antibacterial Activity (<i>Dmitry Bocharov</i>)	8
Geometric Effects on Platinum Electrocatalysts (<i>Federico Calle-Vallejo</i>)	9
Multi-scale Simulation of Large-scale Nanostructures: Combining Tight-binding and DFT (<i>Florian Libisch</i>)	10
Insights Into the Structure and Behavior of Materials From Classical Molecular Dynamics Simulations (<i>José R. B. Gomes</i>)	11
Novel Nanometric Phases of the Monochalcogenides: Theory Meets Experiment (<i>Guy Makov</i>)	12
First Principles Study of Rb Adsorption on Single-Layer Graphene/ α -Al ₂ O ₃ (0001) Interface (<i>Jonny Bernstein</i>)	13
First Principles Prediction of the Low Frequency Behavior of Perovskite Materials and Solar Cells (<i>Juan A. Anta</i>)	14
Effects of Oxide Supports on Metal Particles in Catalytic Nanomaterials (<i>Konstantin M. Neyman</i>)	16
Making Green Hydrogen Even More Sustainable – the Substitution of Pfas in Fuel Cells and Electrolyzers (<i>Leonhard Mayrhofer</i>)	18
Accelerating Molecular Dynamics Simulations With Enhanced Gromacs Algorithms and Mpi Parallelization (<i>Luliana Marin</i>)	19
Early-stage Frost Formation and Its Effect on Heat Transfer: a Fundamental Approach to Understand Crystalline Structure (<i>Mehmet Arik</i>)	20
High-Performance Bifunctional Oxygen Electrocatalyst derived from bimetallic Mn/Co-MO (<i>Nadezda Kongi</i>)	21
Developments in Multiscaling Simulations (<i>Nicolea Goga</i>)	22
Organic Bulk Heterojunction Nanoparticles for Water Splitting (<i>Nigel Clarke</i>)	23
Role of Surface Chemistry in Tuning Oxygen Red-ox Catalysis at Transition Metal Oxide Surfaces (<i>Michele Pavone</i>)	24
Unique Electronic Properties of Rhombohedral Graphite Thin Films (<i>Peter Vancso</i>)	25
Singlet-triplet Inversion in Organic Photoactive Materials (<i>Piotr de Silva</i>)	26
Designing Nano-structured Chalcogenides for Thermoelectric Applications Using Density Functional Theory and Machine Learning (<i>Ricardo Grau-Crespo</i>)	27
Study of the Nucleation of Zifs via Machine Learning Potentials (<i>Said Hamad Gómez</i>)	28
Excited-state Dynamics of Photo-sensitizers Containing Heavy and Earth Abundant Transition Metals. Quantum Mechanical and Molecular Dynamical Study (<i>Stanislav Zális</i>)	29
Excited State Phenomena and Structural Properties of Nano-materials (<i>Tamar Goldzak</i>)	30
Pushing the Limits of Time Scales in Molecular Simulation (<i>Titus van Erp</i>)	31
Frozen-density Embedding Theory Based Multi-scale Simulations of Electronic Structure of Solvated Species (<i>Tomasz A. Wesolowski</i>)	32
Quantifying the Growth Order in "Artificial" Crystallization (<i>Vesslin Tonchev</i>)	33
Linear Scaling Coupled-Cluster Methods with Molecular Fragmentation Approaches (<i>Uğur Bozkaya</i>)	34
Ab Initio Calculations of the Raman Spectra of Thin Strontium Titanate Films with and without Adsorbates (<i>Veera Krasnenko</i>)	35

Structural and Electronic Key Features of Perovskite Solar Cells From First-principles

Adriana Pecoraro

Department of Physics "E. Pancini", University of Naples Federico II, Naples, Italy
adriana.pecoraro@unina.it

The swift efficiency surge of perovskite solar cells (PSCs) in the last decade has demonstrated their potentiality to both compete and work in synergy with traditional inorganic photovoltaics.¹ Such a rapid development has been unquestionably driven by the outstanding opto-electronic features of perovskite materials, the archetypal methyl-ammonium lead iodide (MAPbI₃, MAPI) perovskite and the more recent triple cation lead halide formulation (CsMAFAPb(IBr)₃, TriLHP) whose chemical stability however still remains a big challenge. Interfaces with the charge transport layers (CTLs) ultimately play a key role in ruling device performance and stability. We present a density functional theory (DFT)-based roadmap aimed at guiding the careful choice of CT materials and the search for effective strategies to engineer these multi-component devices' interfaces. We show several examples of investigation of both CTLs and their interfaces with the perovskite in which we assess the structural and electronic effects of some of the most common optimization design strategies such as doping, composition-tuning or interlayer engineering on both performances and stability.^{2,3} We cover several fundamental aspects such as the stability-related adhesion between layers, the interface band alignment and the mechanism underpinning charge transfer dynamics,⁴ all crucial to boost efficiencies and to guarantee long-term operational devices.

REFERENCES

1. J.Y. Kim, J.-W. Lee, H.S. Jung, H. Shin, and N.-G. Park, "High-Efficiency Perovskite Solar Cells," *Chem. Rev.* **120**(15), 7867–7918 (2020).
2. A. Pecoraro, A.D. Maria, P.D. Veneri, M. Pavone, and A.B. Muñoz-García, "Interfacial electronic features in methyl-ammonium lead iodide and p-type oxide heterostructures: new insights for inverted perovskite solar cells," *Phys. Chem. Chem. Phys.* **22**(48), 28401–28413 (2020).
3. C. Coppola, A. Pecoraro, A.B. Muñoz-García, R. Infantino, A. Dessì, G. Reginato, R. Basosi, A. Sinicropi, and M. Pavone, "Electronic structure and interfacial features of triphenylamine- and phenothiazine-based hole transport materials for methylammonium lead iodide perovskite solar cells," *Phys. Chem. Chem. Phys.* **24**(24), 14993–15002 (2022).
4. A. Pecoraro, F. Fasulo, M. Pavone, and A.B. Muñoz-García, "First-principles study of interfacial features and charge dynamics between spiro-MeOTAD and photoactive lead halide perovskites," *Chem. Commun.* **59**(34), 5055–5058 (2023).

Insights to the Morphology of Fe_2O_3 Clusters Using Computational Methods

Anders Hellman

Chalmers University of Technology, Gothenburg, Västra Götaland, Sweden

Fe_2O_3 clusters exhibit a high surface-to-volume ratio, providing increased reactivity and catalytic activity compared to their bulk counterparts. Furthermore, their small size enables interactions with molecules at the atomic scale, making them suitable for diverse applications such as gas sensing, environmental remediation, and biomedical research. Additionally, their optical properties make them promising candidates for optoelectronics, including photovoltaics, photocatalysis, and sensors. Here, we will use model potentials, Neural network-generated potentials, and DFT to investigate their structure and understand the fundamental principles governing their size, shape, and surface properties.

Micro-kinetic Approach to Photo-electrochemical Water Splitting: Uncovering Novel Reaction Pathways Toward Efficient Solar Fuel Production

Arik Yochelis

Ben-Gurion University of the Negev, Israel

The oxygen evolution reaction in photo-electrochemical water splitting presents a critical challenge for solar fuel production. This reaction involves four photo-generated holes that oxidize two water molecules to produce an oxygen molecule and four protons. The multihole reaction gives rise to different oxidized intermediates at the surface of the photocatalyst that may lead to electron-hole recombination which degrades the photoconversion efficiency. Thus, understanding the reaction mechanism presents experimental and theoretical challenges.

Motivated by experiments on hematite photoanodes, we developed micro-kinetic framework and uncovered counterintuitive, yet generic, mechanisms that shed new light on the photo-electrochemical reactions: (i) coexistence of two surface reaction paths (bi-stability) in a certain range of potentials and H_2O_2 concentrations, and (ii) dominance of parallel rather than sequential reaction steps under potentiodynamic discharge. The results fundamentally broaden the paradigm of the water photo-oxidation reaction mechanism, suggesting that interactions between coexisting pathways may lead to complex self-organized kinetic effects.

Tuning the Properties of Janus van der Waals Hetero Structures by Varying Interface Terminations

S. Assa Aravindh

Nano and molecular systems research unit, University of Oulu, Finland
Assa.Sasikaladevi@oulu.fi

The ever-growing energy needs demand technological development related to photo catalysis. Conventional photo-catalytic materials suffer from low quantum efficiency, charge-recombination, and chemical back-reactions. Janus van der Waals hetero structures, are 2D materials where a metal atomic layer M is sandwiched between layers X and Y of two different chalcogen, halogen, or pnictogen atoms owing to finite out-of-plane dipole moments, and possess enhanced photo catalytic properties due to their intrinsic Rashba effect, strongly bound excitons, and strong interaction with light [1]. In this study, two dimensional (2D) GaAs/MoSSe Janus interfaces were investigated using first principles calculations. The effect of different atomic terminations on the interface stability, electronic properties and charge transfer at the interfaces were analyzed and found that conducting properties are altered with respect to different terminations. Metallic states are formed at the stable MoSSe/GaAs interface due to the presence of 2D occupied anti-bonding states in MoSSe and the band alignment at the interface. We demonstrate that the non-symmetric structure of MoSSe Janus material plays a key role in controlling the electronic properties of the stable Janus interface, which will be crucial deciding factor for practical applications [2].

REFERENCES

1. Pan, Linfeng, et al. "Boosting the performance of Cu₂O photocathodes for unassisted solar water splitting devices." *Nature Catalysis* 1.6 (2018): 412-420.
2. Albar, Arwa, and S. Assa Aravindh. "Emergence of metallic states at 2D MoSSe/GaAs Janus interface: a DFT study." *Journal of Physics: Condensed Matter* 33.47 (2021): 475701.

Ru-pincer Complexes as Charge Transfer Mediators in CO₂ Reduction

B.M. Szyja, J. Zasada, E. Dziadyk-Stopyra

Institute of Advanced Materials, Wroclaw University of Science and Technology

In this work we unravel the role of the system components in the charge transfer (CT) processes occurring in the 2-electron reduction of CO₂.

We focus our analysis on the pincer-complex/graphene composite system in order to explain the role of the donors of the pincer ligands on the elementary charge transfer processes. To achieve this goal, we have used the unique combination of the constrained DFT method and computational hydrogen electrode approach.

The results obtain this way allowed us to conclude that the catalytic performance of the system depends to a great extent on the electron donating properties of the Ru-pincer complex. We have determined, that the optimal charge transfer in the system is due to the easy, single step transfer to the activated CO₂ molecule and the energies required for such transfer are comparable to the overpotential of the reaction.

We have observed the trend in which the first coordination sphere of the Ru cation directly influences the CT energy – the more imine ligands coordinating the Ru, the lower ECT is, regardless on the transfer direction. This trend fits in the HSAB theory, according to which imine ligands are considered the harder donors than carbenes. On the contrary, the overpotentials determined for the Ru-CCC, Ru-CNC, Ru-NCN and Ru-NNN pincers did not show the same trend, what implies that the interactions of the Ru site and the CO₂ reactant do not change linearly, but rather are characterized by the optimum interaction strength.

Titanium Dioxide: Bridging Photocatalytic Processes and Antibacterial Activity

Elina Neilande¹, Alise Podelinska¹, Uladzislau Shapel¹, Hanna Bandarenka², Sergei Piskunov¹ and Dmitry Bocharov¹

¹Institute of Solid State Physics, University of Latvia, Kengaraga 8, Riga, LV-1063, Latvia

²Belarusian State University of Informatics and Radioelectronics, P.Brovka St., Minsk, 220013, Belarus

Titanium dioxide (TiO₂) is a compound that has garnered significant attention due to its distinctive photocatalytic properties, which not only stand out in various applications but also underpin its antibacterial capabilities. It is primarily through this photocatalytic activity that TiO₂ antibacterial functionality emerges.

When TiO₂ is exposed to ultraviolet light with a wavelength less than roughly 390 nm, it undergoes an excitation process that generates pairs of electrons and holes. These pairs engage in redox reactions on the TiO₂ surface, thereby manifesting its photocatalytic nature. Subsequently, the excited electrons and holes can react with water and oxygen molecules, resulting in the production of highly reactive oxygen species such as superoxide ions (O₂⁻) and hydroxyl radicals (•OH). This sequence of events elucidates the dual facets of TiO₂ photocatalytic and antibacterial attributes.

The reactive oxygen species spawned from TiO₂ photocatalytic process carry potent destructive capabilities. They can degrade organic matter and infiltrate bacterial cell walls and membranes. Once inside, they cause oxidative damage to key cellular components such as proteins, lipids, and nucleic acids. This damage has the potential to culminate in cell death, and it is this process that imbues TiO₂ with its antibacterial qualities.

Current research endeavors are exploring the possibility of enhancing TiO₂ photocatalytic activity under visible light. These advancements include doping TiO₂ with various elements, such as nitrogen, sulphur, carbon, or metals, or implementing specific modifications to its structure. In this presentations we observe the mechanisms of TiO₂ antibacterial properties related to the photoexcitation and explain the ways for antibacterial properties first principles modelling.

This research was funded by the Latvian Scientific Council grant LZP-2021/1-0464.

Geometric Effects on Platinum Electrocatalysts

Federico Calle-Vallejo^{1,2}

¹Nano-Bio Spectroscopy Group and European Theoretical Spectroscopy Facility (ETSF), Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, University of the Basque Country UPV/EHU, Av. Tolosa 72, 20018 San Sebastián, Spain.

²IKERBASQUE, Basque Foundation for Science, Plaza de Euskadi 5, 48009. federico.calle@ehu.es

Platinum is simultaneously one of the scarcest and most promising electrocatalysts for a number of reactions, which calls for the design of optimal Pt electrocatalysts with maximal utilization. To do so, it is necessary to unambiguously determine and exploit the most active sites for each reaction. A computational tool for that purpose are “generalized coordination numbers” (GCNs).

In my talk, I will show that GCNs capture adsorption-energy trends for Pt sites on extended surfaces and nanoparticles of different sizes and shapes.^[1]

I will also exemplify the use of “coordination-activity plots” based on GCNs to outline the geometric configuration of optimal Pt sites for three important reactions: O₂ reduction,^[2, 3] H₂ evolution,^[4] and CO electro-oxidation.^[5]

In addition, I will show how GCNs can be used to rationalize the intricate selectivity of organic reactions depending on Pt electrodes.^[6]

Finally, I will show that GCNs can be used on strained Pt electrodes^[7] and Pt alloys.^[8] Time permitting, I will illustrate the use of GCNs on other transition metal catalysts.^[2, 9, 10]

REFERENCES

1. F. Calle-Vallejo, J.I. Martínez, J.M. García-Lastra, P. Sautet, D. Loffreda. *Angew. Chem. Int. Ed.* **2014**, 53, 8316–8319.
2. F. Calle-Vallejo, J. Tymoczko, V. Colic, Q.H. Vu, M.D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A.S. Bandarenka. *Science* **2015**, 350, 185–189.
3. F. Calle-Vallejo, M.D. Pohl, D. Reinisch, D. Loffreda, P. Sautet, A.S. Bandarenka. *Chem. Sci.* **2017**, 8, 2283–2289.
4. M.D. Pohl, S. Watzele, F. Calle-Vallejo, A.S. Bandarenka. *ACS Omega* **2017**, 2, 8141–8147.
5. F. Calle-Vallejo, M.D. Pohl, A.S. Bandarenka. *ACS Catal.* **2017**, 7, 4355–4359.
6. C.J. Bondue, F. Calle-Vallejo, M.C. Figueiredo, M.T.M. Koper. *Nat. Catal.* **2019**, 2, 243–250.
7. F. Calle-Vallejo, A.S. Bandarenka. *ChemSusChem* **2018**, 11, 1824–1828.
8. R. M. Kluge et al. *Energy Environ. Sci.* 2022, 15, 5181–5191.
9. O. Piqué, Q. H. Low, A. D. Handoko, B. S. Yeo, F. Calle-Vallejo. *Angew. Chem. Int. Ed.* **2021**, 60, 10784–10790.
10. A. M. Reichert, O. Piqué, W. A. Parada, I. Katsounaros, F. Calle-Vallejo. *Chem. Sci.* **2022**, 13, 11205–11214.

Multi-scale Simulation of Large-scale Nanostructures: Combining Tight-binding and DFT

Florian Libisch

Institute for Theoretical Physics, Vienna University of Technology

I discuss our recent models for simulating large-scale nanostructures with different length scales by combining density functional theory with tight binding. I focus on moiré superlattices, which emerge when stacking various two-dimensional materials such as graphene with a relative twist angle between the layers. The resulting moiré supercells contain ten thousands of atoms, making their simulation challenging.

Nevertheless, strain and lattice relaxation effects profoundly affect electronic, and thus catalytic, properties.

The size of the moiré supercell, electronic properties, the role of strain and even the phonon band structure vary with twist angle. Indeed, bilayer graphene becomes superconducting at the right angle. I present a momentum-based approach to treat these effects as a continuous function of twist angle, and compare our predictions with recent measurements of optical and transport properties.

Insights Into the Structure and Behavior of Materials From Classical Molecular Dynamics Simulations

José R. B. Gomes

CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
*Corresponding author e-mail: jrgomes@ua.pt

The continuous developments in computer hardware and algorithms have been enabling the consideration of realistic models in molecular simulations of different classes of materials with remarkable success [1].

Compared to quantum mechanics (QM) methods, which have electronic detail, molecular mechanics (MM) methods and classical molecular dynamics (MD) simulations neglect electronic degrees of freedom and treat molecules as a collection of atoms, with atomistic detail, or a collection of interaction sites mimicking several atoms, hence, with coarser detail. MM methods have been widely employed to optimize the structures of large molecular systems or to provide an adequate embedding of the inner QM region in QM/MM calculations, while MD methods have been used to understand the dynamic evolution with time of complex systems with many degrees of freedom. The MM and classical MD methods describe interatomic interactions by means of a force field and, in the case of the latter, they also integrate the Newton's equations of motion to provide the position and speed of each species over time. Generally, classical MD simulations with atomistic detail can be applied to thousands of atoms and hundreds of nanoseconds of simulation time, while simulations employing coarse models allow the study of systems composed of millions of molecules and to attain simulation times in the order of tens of microseconds.

In this talk, I will present selected examples of application of classical MD simulations to the understanding of the structure of materials [2], including a novel strategy using the so-called sticky particles to handle on-the-fly studies of chemical reactions within a MM formalism [3].

REFERENCES

1. M. Bordonhos, T. L. P. Galvão, José R. B. Gomes, J. D. Gouveia, M. Jorge, M. Lourenço, J. M. Pereira, G. Pérez-Sánchez, M. L. Pinto, C. M. Silva, J. Tedim, B. Zêzere, *Adv. Theor. Simul.*, (2023) 2200628.
2. G. Novell-Leruth, A. Kuznetsova, J. Tedim, José R. B. Gomes, T. L. P. Galvão, *Nanomaterials*, 12 (2022) 4039.
3. A. P. Carvalho, S. M. Santos, G. Pérez-Sánchez, J. D. Gouveia, J. R. B. Gomes, M. Jorge, *npj Comput. Mater.*, 8 (2022) 49.

Novel Nanometric Phases of the Monochalcogenides: Theory Meets Experiment

Guy Makov

Dept. of Materials Engineering, Ben-Gurion University

Tin and germanium monochalcogenide binary compounds, $M(=Ge,Sn)X(=S,Se)$, are earth-abundant, low-toxicity material families relevant for energy applications. They have very recently been found to present multiple novel phases with new functional properties at the nanoscale. These phases belong to an extended family of metastable phases in the bulk. Since they have been synthesised experimentally, it was hypothesised that they are stabilised as nanometric particles by size effects, or by solution ligands, or by the substrate surface. To identify the controlling mechanisms in the stabilisation of metastable phases, we modelled the surface energies, effects of ligand absorption and the interactions with substrate surfaces, focusing on the low-symmetry cubic- π - and γ - phases of SnS and SnSe. Our results explain the experimental conditions and elucidate the role of ligands and substrate effects on these processes. This approach can help design ab-initio syntheses of metastable states.

REFERENCES

1. E. Segev et al., CrystEngComm 20, 4237 (2018)
2. R.E. Abutbul et al., Nanoscale 11, 17104 (2019)
3. R.E. Abutbul et al. ACS Crystal Growth & Design (2022)
4. N. Mishra et al. ACS Crystal Growth and Design (2023)
5. N. Zakay et al. ACS Applied materials and Interfaces (2023)

First Principles Study of Rb Adsorption on Single-Layer Graphene/ α -Al₂O₃ (0001) Interface

Noy Galron^{1,2}, Jonny Bernstein² & Yaron Amouyal¹

¹Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

²Rafael – Advanced Defense Systems, Israel

Alkali-metal-vapor cells made of sapphire (α -Al₂O₃) are used in physics in a range of applications such as hyperfine atomic clocks, optical magnetometers, atomic gyroscopes and noble-gas hyperpolarization. A common problem in such systems is change in transparency of the sapphire surface due to adsorption of alkali metal atoms, that eventually reduces cell functionality.

In this work we introduce a novel approach to mitigate the phenomenon by pre-adsorption of single-layer graphene (SLG) on sapphire surface. We aim to model, study and quantify adsorption of Rb on α -Al₂O₃ (0001) surface with and without SLG by Density Functional Theory (DFT) and Quantum Molecular Dynamics (QMD).

First Principles Prediction of the Low Frequency Behavior of Perovskite Materials and Solar Cells

Juan A. Anta

Department of Physical, Chemical and Natural Systems, Universidad Pablo de Olavide, Carretera de Utrera km 1, Sevilla 41013, Spain

Hybrid metal halide perovskites are mixed ionic–electronic semiconductors with exceptional optoelectronic properties, ideal for applications in photovoltaics, along with many others like lighting, lasing and x-ray detection. In all these applications, robustness and stability of the material is crucial. Bearing in mind that perovskites are ionic materials, it is expected that ion migration should play a significant role in all stability issues under operational conditions, which often are triggered by irreversible ionic displacements.

It is well-known that most experimental advances and record performances are not obtained with pure perovskites but with mixed compositions, empirically devised. In addition, many key features in photovoltaic perovskites occur at relatively long-time scales due to the relatively slow ionic motion. Description of perovskites using first-principles techniques such as density functional theory (DFT) are limited by their high computational demands, which restricts their use to small systems (hence only pure materials can be studied) and short-time scales (hence ionic motion cannot be properly described). The Holy Grail in photovoltaics would be to be able to predict the expected performance, i.e. the current–voltage curve, starting from materials properties and low-level first-principles atomistic calculations.

In this work we combine atomistic calculations with drift–diffusion (DD) modelling to simulate the current–voltage curve of perovskite solar cells. In order to get around the limitations of DFT, we use classical molecular dynamics (CMD), which is less expensive and enables simulations for larger systems and longer times. We have developed the required force field for CMD by means of a genetic algorithm.¹ The algorithm finds the best parameter set that simultaneously fits the DFT energies obtained for several crystalline structures with moderate degrees of distortion with respect to the equilibrium configuration. Using this strategy we have found a transferable classical force field to describe the mixed hybrid perovskite $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{Br}_y\text{I}_{1-y})_3$ for variable composition ($\forall x, y \in [0, 1]$). The model includes Lennard–Jones and Buckingham potentials to describe the interactions between the atoms of the inorganic lattice and the organic molecule, and the AMBER model to describe intramolecular atomic interactions. The resulting model reproduces correctly the XRD patterns, the expansion of the lattice upon I/Br substitution and the thermal expansion coefficients. From the simulations we have extracted the ion diffusion coefficients of the pure and mixed perovskites, presenting for the first time these values obtained by a fully dynamical method using a transferable model fitted to first principles calculations.

The ion diffusion coefficients obtained are then transferred to a DD model^{2,3} including transport and recombination of charge carriers (electrons and holes) in the perovskite, transport of a single positive ionic species (iodine vacancies in the perovskite), and electron and hole transport in the electron transport layer and hole transport layer, respectively. The charge carriers and ions are fully coupled through including the electron and hole charge densities with the ion charge density in the Poisson's equation. The DD calculation allows to simulate the current-voltage curve and the impedance spectrum. The ionic parameters derived from the atomistic simulations are proven to lead to the correct prediction of the ion-induced hysteresis and the low frequency features of the impedance spectrum for a variety of perovskite compositions.

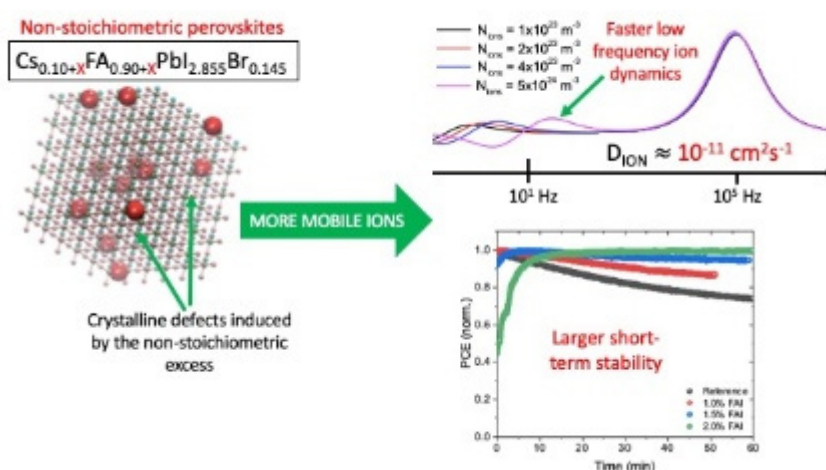


Figure 1: Simulation of the low frequency response of perovskite solar cells from first principles

REFERENCES

1. Balestra, S. R.-G.; Vicent-Luna, J. M.; Calero, S.; Tao, S.; Anta, J. A. Efficient Modelling of Ion Structure and Dynamics in Inorganic Metal Halide Perovskites. *J. Mater. Chem. A* 2020. <https://doi.org/10.1039/D0TA03200J>.
2. Courtier, N. E.; Cave, J. M.; Foster, J. M.; Walker, A. B.; Richardson, G. How Transport Layer Properties Affect Perovskite Solar Cell Performance: Insights from a Coupled Charge Transport/Ion Migration Model. *Energy Environ. Sci.* 2018, 12, 396–409.
3. Riquelme, A.; Bennett, L. J.; Courtier, N. E.; Wolf, M. J.; Contreras-Bernal, L.; Walker, A. B.; Richardson, G.; Anta, J. A. Identification of Recombination Losses and Charge Collection Efficiency in a Perovskite Solar Cell by Comparing Impedance Response to a Drift-Diffusion Model. *Nanoscale* 2020, 12 (33), 17385–17398.

Effects of Oxide Supports on Metal Particles in Catalytic Nanomaterials

Konstantin M. Neyman

ICREA (Institució Catalana de Recerca i Estudis Avançats), Barcelona, Spain
 Departament de Ciència de Materials i Química Física, Universitat de Barcelona, Barcelona, Spain
 konstantin.neyman@icrea.cat
www.icrea.cat/Web/ScientificStaff/Konstantin-M-Neyman-292

Metal-support interactions can dramatically affect the reactivity and related properties of catalytic nanomaterials. However, detail studies of interfaces between metal particles and oxide supports remain scarce due to their challenging experimental characterization. Yet, a deep understanding of interactions at such interfaces can be gained using density-functional calculations [1].

We illustrate this by determining the interfacial charge transfer, the short- or long-range nature of nanoparticle-support interactions and the effects of metal and oxide nanostructuring on the properties of relevant to catalysis supported metals. Calculations of metal particles on regular and nanostructured surfaces of unreducible (MgO , ZrO_2) and reducible (CeO_2) metal oxides help delineating elusive interface effects on the structure and reactivity of catalytic materials [2-8]. The effects identified by modelling are discussed in relation with the experimental observations.

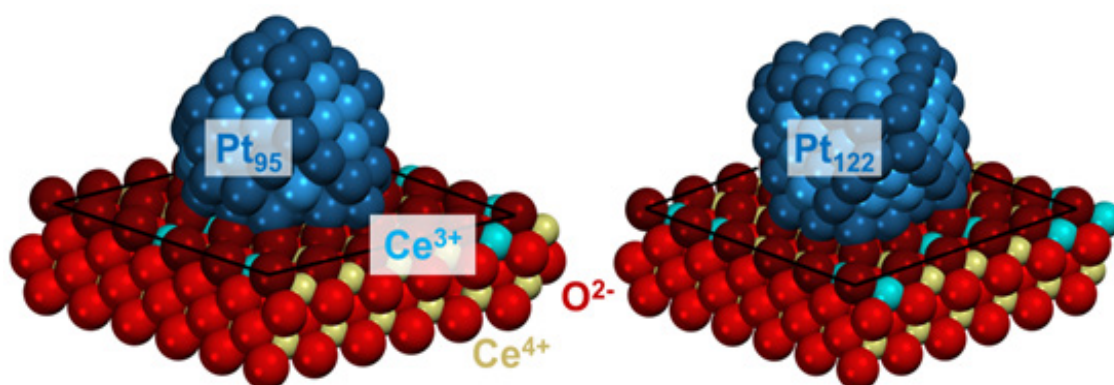


Figure 1: Platinum particles forming $\{100\}/(111)$ and $\{111\}/(111)$ interfaces with $\text{CeO}_2(111)$ [4,5].

REFERENCES

1. K.M. Neyman, S.M. Kozlov. Quantifying interactions on interfaces between metal particles and oxide supports in catalytic nanomaterials. *NPG Asia Materials* 14 (2022) 59
2. G.N. Vayssilov, Y. Lykhach, A. Bruix, F. Illas, K.M. Neyman, J. Libuda et al. Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles. *Nature Materials* 10 (2011) 310
3. A. Bruix, Y. Lykhach, V. Matolín, J. Libuda, K. M. Neyman et al. Maximum noble metal efficiency in catalytic materials. *Angew. Chem. Int. Ed.* 53 (2014) 10525
4. Y. Lykhach, S.M. Kozlov, V. Matolín, K.M. Neyman, J. Libuda et al. Counting electrons on supported nanoparticles. *Nature Materials* 15 (2016) 284
5. S.M. Kozlov, K.M. Neyman. Effects of electron transfer in model catalyst composed of Pt nanoparticles on CeO₂(111) surface. *J. Catal.* 344 (2016) 507
6. Y. Suchorski, S.M. Kozlov, K.M. Neyman, G. Rupprechter et al. The role of metal/oxide interfaces for long-range metal particle activation during CO oxidation. *Nature Materials* 17 (2018) 519
7. J.E. Quinlivan Domínguez, K.M. Neyman, A. Bruix. Stability of oxidized states of free-standing and ceria-supported PtO_x particles. *J. Chem. Phys.* 157 (2022) 094709
8. E.M. Slavinskaya, A.I. Stadnichenko, J.E. Quinlivan Domínguez, A. Bruix, K.M. Neyman, A.I. Boronin et al. States of Pt/CeO₂ catalysts for CO oxidation below room temperature. *J. Catal.* 421 (2023) 285, doi: 10.1016/j.jcat.2023.03.004

Making Green Hydrogen Even More Sustainable – the Substitution of PFAS in Fuel Cells and Electrolyzers

Leonhard Mayrhofer

Fraunhofer Institute for Mechanics of Materials IWM · Business Unit Tribology

Per- and polyfluoroalkyl substances (PFAS) have excellent properties in terms of hydrophobicity, (electro-)chemical stability, etc. Therefore, these materials are widely used in both fuel cells and electrochemical water-splitting systems. A key component is the polymer membrane, which in the case of proton exchange membranes (PEMs) is also usually based on perfluorinated polymers. However, the chemical stability of PFAS causes them to accumulate in the environment, and there is general concern about the health risks of PFAS. As a result, PFAS will be largely banned due to regulations, and substitutes need to be developed. Here we briefly summarize the degradation processes of fluorine-free polymer membranes and provide an outlook on how modeling can contribute to a better understanding of the basic degradation processes of membranes and other components.

Accelerating Molecular Dynamics Simulations With Enhanced GROMACS Algorithms and MPI Parallelization

Luliana Marin

University POLITEHNICA of Bucharest

Molecular dynamics (MD) is a computational method used to study the structure of atomic systems.

However, MD simulations often suffer from long computation times, taking weeks or even months to produce results. In order to overcome this challenge, parallelization techniques such as MPI (Message Passing Interface) have been employed to expedite the simulations. This research paper presents improved GROMACS algorithms, along with the utilization of MPI parallelization, to enhance the efficiency of MD simulations. Additionally, experimental findings and a novel thermostat approach for parallelizing molecular dynamics using MPI are discussed in detail.

Early-stage Frost Formation and Its Effect on Heat Transfer: a Fundamental Approach to Understand Crystalline Structure

Alper Saygin¹, Altug M. Basol¹, and Mehmet Arik^{1,2}

¹EVATEG Research Center, Ozyegin University, Istanbul, 34794, Turkey

²Department of Mechanical Engineering, Auburn University, Auburn, AL, USA

Frosting is a phase change process during which water in its vapor form desublimates and generates solid ice. It is a very widely encountered phenomenon in thermal devices, such as evaporators, heat pumps, precoolers etc. However, frosting negatively affects the performance of these devices, since it possesses very low thermal conductivity and induces a thermal barrier between the medium and surface.

In this study, frost growth over a metal surface is investigated experimentally, especially focusing on the early stage of frosting. The characteristics of frost formed at the early stage are crucial to forecast the heat transfer transparency of the finally formed frost layer. Based on altered environmental conditions of air temperature and speed, frost growth is recorded with a high-speed camera positioned at the side, and heat transfer is continuously monitored for 10 minutes. The results pointed out that, at low air speeds and surface temperatures, frost growth tends to be more columnar and dendritic, whereas lateral growth is more pronounced at high air speeds and surface temperatures. Also, heat transfer is severely decreased with the frost coverage of the test surface, especially for high air speeds. The most porous and the least thermally conductive frost layer is found when air speed and surface temperature is the lowest.

High-Performance Bifunctional Oxygen Electrocatalyst derived from bimetallic Mn/Co-MOF

Gulnara Yusibova¹, Veera Krasnenko², Nadezda Kongi¹

¹*Institute of Chemistry, University of Tartu, Tartu, Estonia*

²*Institute of Physics, University of Tartu, Tartu, Estonia*

Metal-air batteries and fuel cells rely heavily on two crucial processes: the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). To ensure the widespread adoption of these technologies, it is imperative to develop catalysts that are both efficient and cost-effective for ORR/OER. A promising alternative to noble metal catalysts is the use of metal-organic framework (MOF)-based catalysts, which possess desirable properties such as a high surface area and tunability.

In this study, we introduce a novel bifunctional oxygen electrocatalyst, MnO_x/Co-N-C, that is synthesized by carbonizing the dual metal Mn/Co-MOF precursor TAL-42. Our findings demonstrate that the optimized MnO_x/Co-N-C catalyst exhibits remarkable catalytic activity for both ORR and OER, surpassing the performance of state-of-the-art Pt/C and RuO₂ catalysts. Furthermore, this catalyst showcases prolonged stability in zinc-air battery (ZAB) applications. These results underscore the potential of utilizing the dual metal TAL-42.

Developments in Multiscaling Simulations

Nicolea Goga

Multiscale molecular dynamics (MD) simulations are a computational approach that combines different levels of resolution in a simulation to model a system at different scales. The goal is to accurately capture the behavior of a complex system by incorporating multiple levels of detail in the simulation. Fine-grained and coarse-grained molecular dynamics are two different levels of resolution used in molecular simulations. In fine-grained simulations, individual atoms or molecules are explicitly represented, while in coarse-grained simulations, groups of atoms or molecules are combined into larger particles.

Multiscale MD simulations can be used to study a wide range of phenomena including water splitting, protein folding, drug binding, and material properties. The approach has become popular in recent years due to advances in computing power and simulation algorithms, as well as the increasing availability of experimental data that can be used to validate simulations. In this presentation we will make a review of several multiscaling molecular dynamics simulations.

Organic Bulk Heterojunction Nanoparticles for Water Splitting

Nigel Clarke

University of Sheffield

We give an overview of recent experimental developments in the design and performance of organic bulk heterojunction nanoparticles which are promising candidates for hydrogen production. A key feature required for efficient water splitting is the internal microstructure of the nanoparticle. We will discuss these developments in the context of mesoscale modelling that we have previously developed for bulk heterojunction solar cells. To highlight the predictive capabilities of these computer simulations we consider the systematic variation of device morphologies and the effect this has on photovoltaic performance. In this manner, we can correlate the device performance with the device's internal structure and predict how the polymer morphology might be tailored to meet hydrogen production needs

Role of Surface Chemistry in Tuning Oxygen Red-ox Catalysis at Transition Metal Oxide Surfaces

Michele Pavone

Department of Chemical Sciences, University of Naples Federico II, Comp. Univ. Monte Sant'Angelo Via Cintia 21, Naples 80126 ITALY – electronic mail: michele.pavone@unina.it

Production of green Hydrogen and its exploitation as fuel in electric vehicles rely on energy conversion devices that undergo electrochemical processes involving Oxygen. In the first case, water splitting demands for efficient (photo)electrocatalyst for oxidation of water to molecular oxygen (Oxygen Evolution Reaction, OER). In the second, the oxidation of molecular hydrogen in fuel cells calls also for efficient and effective cathodes for the Oxygen Reduction Reaction (ORR).

In standard cells, for both OER and ORR processes the workhorse electrode materials have been noble metals as for example platinum. Concerns of costs and sustainability for a widespread deployment of electrolyzer and fuel cells have motivated an extensive research on alternative electrode materials based on transition metal oxides.

In this contribution, we discuss how OER and ORR can be catalyzed by oxides whose formula contains earth abundant or non-critical chemical elements. By applying state of the art DFT calculations, we show that the OER and ORR mechanisms for can be strongly affected by chemical modifications at the surface. In particular, we discuss the effects of oxygen vacancies in tuning both the electronic and the structural features of the exposed electrode surfaces [1, 2]. As well, we show how different possible doping elements can be crucial in activating the electrode surface toward OER/ORR catalysis, with direct or indirect effects [3,4].

Besides helping the correct understanding of experimental outcomes, our results show how the chemistry of transition metal oxide surfaces can be easily tuned for improving the electrocatalytic performance of potential electrodes for highly needed cheap and effective energy conversion devices.

REFERENCES

1. AB Muñoz-García, M Pavone, *J. Mater. Chem. A*, **5**, 12735–12739 (2017)
2. AB Muñoz-García, M Tuccillo, M Pavone, *J. Mater. Chem. A*, **5**, 11825–11833 (2017)
3. P Madkikar, D Menga, GS Harzer, T Mittermeier, A Siebel, FE Wagner, M Merz, S Schuppler, P Nagel, AB Muñoz-García, M Pavone, HA Gasteiger, M Piana, *J. Electrochem. Soc.* **166**, F3032 (2019)
4. A Massaro, A Pecoraro, S Hernández, G Talarico, AB Muñoz-García, M Pavone, *Mol. Catal.* **517**, 112036 (2022)

Unique Electronic Properties of Rhombohedral Graphite Thin Films

Peter Vancso

Centre for Energy Research (CER), Budapest

Twisted bilayer graphene have demonstrated that partially filled flat bands can host a rich variety of quantum ground states, such as superconductivity, or ferromagnetism. In addition, these flat bands also become intriguing for chemistry, because they modulate the electron transfer processes and can tune the chemical reactivity of the surface [1]. Rhombohedral graphite (RG) is perhaps the simplest and structurally most perfect condensed matter system to host a flat band. In this talk, we provide detailed investigation of the flat band in RG by using low temperature Scanning Tunneling Microscopy (STM) measurements combined with electronic structure calculations [2]. We measured the flat surface band of 8, 10 and 17 layers of RG and identified a degenerate ground state, forming a competing domain structure between a sublattice antiferromagnetic insulator and a gapless, correlated paramagnet.

We also investigated the transport properties of few-layer RG by performing wave-packet dynamical calculations with local pseudopotentials, which we used previously for graphene [3]. The detailed electronic and transport properties have revealed the important role of the stacking configurations and correlation effects in RG and could also provide further information for recent experiments, where domain-dependent surface adhesion was observed [4].

REFERENCES

1. Yu et al., Nat. Chem. 14, 267–273 (2022)
2. I. Hagymási et al., Sci. Adv. 8, eabo6879 (2022)
3. P. Vancsó et al., Carbon 64, 101–110 (2013)
4. V. Hsieh et al., Nano Lett. 23, 3137–3143 (2023)

Singlet-triplet Inversion in Organic Photoactive Materials

Piotr de Silva

Department of Energy Conversion and Storage, Technical University of Denmark
Anker Engelunds Vej 301, 2800 Kongens Lyngby, Denmark
e-mail: pdes@dtu.dk

The well-established Hund's rule predicts that the state of higher spin multiplicity has lower energy for a given electronic configuration. Consequently, the singlet-triplet (ST) gap is predicted to be always nonnegative. For a long time, there was little to no evidence that Hund's rule could be violated in molecules. This ground was broken in 2019 when two independent theoretical studies demonstrated ST inversion in azaphenalenenes [1, 2]. They also showed that ST inversion is due to electron correlation and requires a substantial contribution of double excitations in the lowest-lying excited states, an effect that had not been explicitly considered before in molecular design. Such ST-inverted photoactive organic materials have potential applications in a host of technologies, including light-emitting devices and photocatalysts. Interestingly, heptazine, one of the first identified ST-inverted molecules [2], has already been known as an efficient photocatalyst for the water-splitting reaction. The obvious question arises, is the ST inversion beneficial for photocatalysis, and how to rationally design new materials with this property?

I will analyze the problem of gap inversion from the perspective of the electronic structure theory. I will demonstrate that inversion is possible but requires a substantial contribution of double excitations in the lowest-lying states. I will also show that adiabatic TD-DFT, the workhorse excited states electronic structure method, fails to predict negative singlet-triplet gaps and, in general, has questionable accuracy for the calculations of small-gap systems.

REFERENCES

1. P. de Silva, "Inverted Singlet-Triplet Gaps and Their Relevance to Thermally Activated Delayed Fluorescence", *J. Phys. Chem. Lett.* **2019**, 10, 5674-5679
2. J. Ehrmaier et al. "Singlet-Triplet Inversion in Heptazine and in Polymeric Carbon Nitrides", *J. Phys. Chem. A* **2019**, 123, 8099-8108

Designing Nano-structured Chalcogenides for Thermoelectric Applications Using Density Functional Theory and Machine Learning

Ricardo Grau-Crespo

University of Reading, UK

Chalcopyrite-structured semiconductors with formula unit ABX_2 , where A is a monovalent cation, B is a trivalent cation, and X is chalcogenide anion (S, Se, Te) represent an important class of potential thermoelectric materials for the conversion of heat to electricity [1, 2]. While the electronic transport properties of these materials are attractive, they often suffer from too high thermal conductivities which limits their thermoelectric behaviour. In order to understand the thermal conductivities of these materials we have carried out a theoretical investigation of the lattice thermal conductivities of 20 chalcopyrite semiconductors with $A = \text{Cu}$ or Ag ; $B = \text{Al}$, Ga , In , or Tl ; $X = \text{S}$, Se , or Te . To afford accurate predictions across this large family of compounds, we solve the Boltzmann transport equation with force constants derived from density functional theory calculations and machine learning-based regression algorithms, reducing by about two orders of magnitude the computational cost with respect to conventional approaches of the same accuracy. The results are in good agreement with available experimental data and allow us to rationalise the role of chemical composition, temperature, and nanostructuring in the thermal conductivities across this important family of semiconductors [3]. We show that the nanoparticle size required to halve the thermal conductivity of one of these compounds is approximately 20 nm for each W/m K of thermal conductivity in the bulk, but some deviations from this law are observed. Focusing then on the material where the nanostructuring strategy is predicted to be the most effective (AgInTe_2), we do a full computational study of the effect of nanostructuring on both electron and phonon transport. We predict figure of merit (zT) values up to 2 for p-type AgInTe_2 at 700 K when the average grain size is in the affordable 10–100 nm range [4].

REFERENCES

1. S Tippireddy, F Azough, Vikram, F Towers Tompkins, A Bhui, R Freer, R Grau-Crespo, K Biswas, P Vaqueiro, AV Powell. Tin-substituted chalcopyrite: an n-type sulfide with enhanced thermoelectric performance. *Chemistry of Materials* 34 (2022) 5860–5873.
2. S Tippireddy, F Azough, V. Vikram, A Bhui, PA Chater, D Kepaptsoglou, Q Ramasse, R Freer, R Grau-Crespo, K Biswas, P Vaqueiro, AV Powell. Local Structural Distortions and Reduced Thermal Conductivity in Ge-Substituted Chalcopyrite. *Journal of Materials Chemistry A* 10 (2022) 23874–23885.
3. JJ Plata, V Posligua, A Marquez, JF Sanz, R Grau-Crespo. Charting the lattice thermal conductivities of I-III-VI2 chalcopyrite semiconductors. *Chemistry of Materials* 34 (2022) 2833–2841.
4. JJ Plata Ernesto, J Blancas, A Marquez, V Posligua, J Fdez Sanz, R Grau-Crespo. Harnessing the unusually strong improvement of thermoelectric efficiency of AgInTe_2 with nanostructuring. Submitted (2023).

Study of the Nucleation of ZIFs via Machine Learning Potentials

Said Hamad Gómez

*Department of Physical, Chemical and Natural Systems
University Pablo de Olavide*

We have studied the nucleation of Zeolitic Imidazolate Frameworks, using machine learning potentials to model a large set of nanoparticles, consisting of Zn atoms and imidazolate molecules. Our study provides information about how the stable crystal topologies change as the size of the nanocrystal changes, before reaching the sizes at which the bulk crystal structure becomes the most stable.

Excited-state Dynamics of Photo-sensitizers Containing Heavy and Earth Abundant Transition Metals. Quantum Mechanical and Molecular Dynamical Study

S. Zálíš,¹ **M. Melčák,**^{1,2} **J. Heyda,**^{1,2} **M. Pižl**^{1,2} and **A. Vlček**^{1,3}

¹J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 182 23 Prague, Czech Republic, stanislav.zalis@jh-inst.cas.cz

²Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, CZ-166 28 Prague, Czech Republic

³Department of Chemistry, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

Excited-state dynamics of systems containing transition metal complexes [Re(bpy)(CO)₃Cl], [Re(L)(CO)₃(phen-)], [Ru(bis(MeO)-bpy)₂(NCS)₂] and [Mn(L)(CO)₃(phen-)] (phen = 1,10-phenanthroline, bpy=1,2-bypiridine, L=Cl, histidine) were modelled. Theoretical (DFT quantum mechanical molecular mechanical (QM/MM) and molecular dynamics (MD)) studies were performed in order to examine how the character central atom influence the electronic structure and corresponding static and dynamic properties.

Different MD approaches have been employed to study the relaxation processes during the ISC of complexes in solvent media. Non-adiabatic spin – orbit including TD DFT molecular dynamics of the relaxation of “molecular spin-orbit wave packet”, and successive vibrational relaxation in non-adiabatic regime was used in fs time-scale. Several relaxation processes have been identified up to 1 ps time. The non-adiabatic simulations were used for interpretation of the experimental fluorescence decay. For times longer than 1 ps adiabatic DFT trajectories in lowest excited state were employed, enabling to describe the relaxation of the solvent sphere. This approach was also used for interpretation of electron transfer within protein chains linked to [Re(L)(CO)₃(phen-)] photosensitizer. Comparison of the excited states characteristics of Re(L)(CO)₃(phen-) and Mn(L)(CO)₃(phen-) shows how the central metal variation influences a photocatalytic behavior.

Acknowledgments

This work was supported by the COST action CA18234 and Czech Science Foundation (GAČR) grant 19-15785S

Excited State Phenomena and Structural Properties of Nano-materials

Tamar Goldzak

School of Engineering, Bar Ilan University

Excited states in molecules and materials are key for understanding their optoelectronic properties, such as quantum yield, absorption and emission spectra and more. These properties are important for the performance of optoelectronic devices such as solar cells, quantum detectors and more. They also play a key role in designing quantum information technologies, such as designing novel qubits. An accurate quantum mechanical description of excited state properties has been a long-time challenge, especially for complex molecular systems, such as colloidal nanocrystals (NC), which are composed of hundreds to thousands of atoms. Using *ab initio* electronic structure methods is desired for a microscopic quantum mechanical chemical understanding of excited state phenomena and structural properties. These calculations incorporate many body correlations effects from first principle, and help in understanding energy and charge transfer mechanisms on the atomic level, and serve as a guide for exploring novel materials and new synthesis pathways.

I am going to present recent research works within the scope of applying and developing electronic structure methods for complex molecular systems that are untreatable with conventional approaches. The main focus of the talk will be on applying Density Functional Theory (DFT) based methods to calculate excited states and absorption spectra in colloidal NC, and explore the role of NC's surface structure on the excited state manifold and the spectroscopic properties.

Pushing the Limits of Time Scales in Molecular Simulation

Titus van Erp

Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Molecular Dynamics (MD) and Monte Carlo (MC) simulations are the two main branches of molecular simulation, both offering powerful tools for exploring thermodynamic properties, and MD allowing us to study kinetics in addition. However, MD simulations face limitations in accessible time scales, spanning from nanoseconds to milliseconds, depending on factors like system size, hardware capabilities, the level of theory, and human patience. These restrictions hinder the investigation of phenomena requiring longer observation periods, such as chemical reactions, membrane permeation, phase transitions, and protein folding. To overcome these limitations, our research group has developed the RETIS method, which combines the strengths of MC and MD.

In this presentation, I discuss several practical applications in various areas, such as water splitting, redox reactions, and membrane permeation. While the applications discussed above would literally require centuries of wall time if performed by standard MD, they are manageable but still costly requiring months of computation with RETIS.

With recent algorithmic enhancements and Machine Learning techniques, our goal is to reduce it to days. This will enable exploration of a broader parameter space and provide valuable guidance for designing catalysts, drugs, and functional materials.

Frozen-density Embedding Theory Based Multi-scale Simulations of Electronic Structure of Solvated Species

Tomasz A. WESOLOWSKI

Université de Genève, Dept. Physical Chemistry, GENEVA, Switzerland

*Email: Tomasz.Wesolowski@unige.ch <https://www.unige.ch/sciences/chifi/wesolowski>

The interpretation of spectroscopic data for molecules in condensed phase hinges on the quality of the electronic structure derived from simulations. In case of multi-scale simulations such as QM/MM, for instance, the wavefunction representing all electrons in the system is not constructed. Instead, the wavefunction level of description is restricted to the embedded species. Frozen-Density Embedding Theory (FDET) provides **exact relations** between for the multiplicative embedding potential, the embedded wavefunction, and the Hohenberg-Kohn energy functional (1). FDET provides, therefore, the exact formulation of the embedding problem in case of such multi-scale simulation methods which apply multiplicative embedding operators. FDET based simulation methods might differ in: a) the treatment of the electron-electron correlation for embedded electrons, b) the technique to generate the charge density representing the remaining electrons (denoted as P_B in FDET), and c) the functional approximating the FDET embedding potential.

The present paper focusses on such FDET based methods, **in which the continuum field description**, is used for P_B . Numerical examples concern the solvent effect on vertical excitation energies (2). Time permitting, recent applications of the FDET based methods for other properties critically depending on the quality of the embedded wavefunction will be reviewed (3).

REFERENCES

1. For the derivation of the basic FDET relations, see [T.A. Wesolowski, Phys. Rev. A. 77, 012504 (2008)]; for the subsequent additions see [M. Fu and T.A. Wesolowski, J. Phys. Chem. A., **127**, 535 (2023)] and references there.
2. Gonzalez-Espinoza et al., J. Chem. Theor. & Comput. **18** (2), 1072 (2022) and the references there; [Gonzalez-Espinoza et al., to be published]; [Ricardi et al., J. Chem. Theory & Comput., (2023) in revision]
3. M. Fu and T.A. Wesolowski, J. Chem. Theor. & Comput. **17**, 3652 (2021); Gimbal-Zofka et al., to be published

Quantifying the Growth Order in “Artificial” Crystallization

Vesslin Tonchev

Faculty of Physics, Sofia University, Sofia, Bulgaria

The talk is devoted to revealing the proper data patterns of crystallization using a combination of an analytical model and Cellular Automata. It is based on the model equation [1] for the rate of transformation in the case when the supersaturation is not sustained during the process and the growth velocity is assumed to be proportional to the decaying supersaturation raised to power g – the *growth order*. After demonstrating further validation of the model with published experimental results, it is applied systematically to several “artificial” crystallization systems based on Cellular Automata where the spatial dimensionality is known but the growth order is not. The talk ends with a principal discussion on the fit quality and the need of avoiding deceptive data patterns.

REFERENCES

1. V. V. Ivanov, C. Tielemann, K. Avramova, S. Reinsch, and V. Tonchev, *Modelling Crystallization: When the Normal Velocity Depends on the Supersaturation*, arXiv:2304.12402.

Linear Scaling Coupled-Cluster Methods with Molecular Fragmentation Approaches

Uğur Bozkaya¹

¹Department of Chemistry, Hacettepe University, 06800 Ankara, Turkey

The coupled-cluster (CC) singles and doubles with perturbative triples [CCSD(T)] method is generally referred the “gold standard” of modern computational chemistry.

High computational costs of coupled-cluster (CC) methods, such as coupled-cluster singles and doubles (CCSD) and CCSD with perturbative triples [CCSD(T)] prohibit their applications to large chemical systems. To overcome this bottleneck, efficient implementations of linear-scaling coupled-cluster methods, which are taking advantages of the molecular fragmentation approaches, such as systematic molecular fragmentation (SMF) and cluster-in-molecules (CIM) are reported.

Performances of the fragment-based linear-scaled CC approaches are investigated for several sets of molecular systems in comparison with their standard versions. We conclude that the fragment-based CC methods are promising for the study of large-scale chemical systems, where the conventional methods are computationally prohibitive.

Acknowledgments

U.B. acknowledges The Scientific and Technological Research Council of Turkey (TUBITAK) for financial support.

Ab Initio Calculations of the Raman Spectra of Thin Strontium Titanate Films with and without Adsorbates

Veera Krasnenko¹, Leonid L. Rusevich², Aleksander Platonenko², Yuri A. Mastrikov², Maksim Sokolov³ and Eugene A. Kotomin²

¹*Institute of Physics, University of Tartu, Tartu, Estonia*

²*Institute for Solid State Physics, University of Latvia, Riga, Latvia*

³*Theoretical Inorganic Chemistry, University of Duisburg-Essen, Duisburg, Germany*

Various photocatalysts are currently being studied, to improve the photocatalytic efficiency of water splitting and produce hydrogen as a fuel, as a solution to global environmental challenges. Among many other materials, strontium titanate SrTiO₃ (STO) is well known. Recently thin STO films and nanoparticles have also become attractive as photo-electrochemical water-splitting photocatalysts¹. While the bulk STO crystal characteristics are relatively well known, the nanostructure, chemical composition, and crystallinity of ultrathin perovskites are quite complex and challenging to understand in detail.

As is known, the Raman vibrational spectra are extremely sensitive to local deviations from the average periodicity and to different chemical structures (even if they contain the same atoms in different arrangements), which makes them a valuable tool for studying local structures. Furthermore, the defects produced by water adsorption and splitting give the characteristic Raman frequencies that can be used to identify adsorbates and different surfaces promising for effective photocatalysis². Therefore, Raman spectroscopy could serve as an effective tool for the structural characterization of materials/surfaces for water splitting.

Interpretation of the Raman spectra requires accurate matching of Raman peaks to specific vibrations based on independent prior knowledge of the structure. However, the available experimental data for STO thin films based on Raman spectroscopy differ from each other due to different content of defects, film growth conditions, etc. Since the photo-electrochemical properties of the film could depend on film thickness, it is useful to investigate the Raman spectra' dependence on the film thickness. To this end, *tt* calculations are necessary for a reliable peak assignment. In our study, the *tt* DFT methods were used for modelling the Raman spectra of STO films with different thicknesses, with and without adsorbates. This method allows us to identify the Raman frequencies that characterize the bulk STO and new features in the scattering spectra arising with increasing film thickness.

According to our calculations, most of the peaks in the Raman spectra for thin films, due to their very low intensity, differ from the Raman active modes observed in a bulk STO crystal. However, as the film thickness increases, the frequencies of the Raman modes approach to bulk ones, and the intensity of the crystal(bulk)-specific modes becomes higher and, as a result, noticeable in the Raman spectrum. The effects of water splitting products are discussed as well.

The obtained results could help to explain some uncertainties and interpretation in the experimental data for thin STO films. Moreover, our results show that *ab initio* Raman calculations can also help to investigate STO thin films whose composition, morphology, and crystallinity are tuned to improve and optimise their photocatalytic properties.

Keywords: DFT, Raman, SrTiO₃ film, water splitting

REFERENCES

1. Sokolov, M.; Mastrikov, Y. A.; Zvejnieks, G.; Bocharov, D.; Kotomin, E. A.; Krasnenko, V. Water Splitting on Multifaceted SrTiO₃ Nanocrystals: Computational Study. *Catalysts* **2021**, *11*, 1326. <https://doi.org/10.3390/catal11111326>.
2. Krasnenko, V.; Rusevich, L. L.; Platonenko, A.; Mastrikov, Y. A.; Sokolov, M.; Kotomin, E. A. Water Splitting on Multifaceted SrTiO₃ Nanocrystals: Calculations of Raman Vibrational Spectrum. *Materials*. **2022**. <https://doi.org/10.3390/ma15124233>