Final Report

Theoretical studies of novel material surfaces

NKFIH(NRDIO)-FK-124100

Duration: 01.12.2017-30.04.2024 (77 months)

Principal Investigator (PI): Dr. Krisztián Palotás

Participants: Dr. Arnold Péter Farkas, Balázs Nagyfalusi, Ivan Contini Abilio

Total FTE: 6.44

1. Short summary

During the project we performed extensive **theoretical studies on various novel material surfaces** and surface atomic and molecular structures in accordance with the Work Plan and going beyond that. Particular emphasis was put on the training of young researchers. These activities were mostly conducted in forms of national (Hungary) and a **wide range of international collaborations** (Australia, Austria, Belgium, China, Czech Republic, France, Germany, Japan, Poland, Portugal, Russia, Slovakia, South Korea, Spain, Taiwan, UK, USA), mostly involving experimental research groups. Our **strong international network** including EU COST Actions provides a great visibility of the research activities undertaken and the scientific results obtained within this NKFIH(NRDIO)-funded project. Our research methodology is based on density functional theory in combination with scanning tunneling microscopy and spectroscopy.

2. Scientific output

As a quantitative summary of our research outputs till 28 May 2024, cumulatively **43 journal articles have been published and 2 accepted** (total journal impact factor (IF): >260; of those **8 articles in high-impact journals** (IF>10): 2x Nature Communications, 1x Science Advances, 1x ACS Nano, 1x Journal of Materials Chemistry A, 1x NPG Asia Materials, 1x Nano Letters, 1x Journal of the American Chemical Society; total independent citations: >510); **4 manuscripts are submitted** (1x Surface Science Reports (IF: 9.8), 1x npj 2D Materials and Applications (IF: 9.7), 1x 2D Materials (IF: 5.5) (also on arXiv), 1x Physical Review Research (IF: 4.2) (also on arXiv)); 1 further arXiv preprint, **1 book chapter**; **26 invited talks** (4 significant ones are listed in the List of Publications), 45 contributed talks, and 4 conference posters were presented by the participants, and 46 co-authored conference contributions have been delivered by the PI.

3. Participants of the project and student supervision of the PI

Dr. Arnold Péter Farkas (Szeged) participated in the project since 01.01.2019, and he has been working on the hexagonal boron nitride nanomesh, acting as a bridge between experiment and theory. (4 publications + 2 submitted)
Balázs Nagyfalusi (doctoral candidate, BME) joined the project 01.01.2022, and he has been working on the Gilbert damping part of the project. (2 publications + 1 in preparation)
Ivan Contini Abilio (PhD student, BME) joined the project 01.09.2021, and he has been working on his PhD thesis entitled "Scanning tunneling microscopy of novel materials surfaces", involving the following topics: nitrogen-doped corrugated graphene, scanning tunneling microscopy (STM) imaging with functionalized asymmetric tips, scanning tunneling spectroscopy (STS) developments in the BSKAN code. He successfully passed his comprehensive examination at the BME Doctoral

School of Physical Sciences in July 2023. (1 publication + 3 in preparation; conference presentations: 1 poster achieving the Best Poster Award at YOURHETCAT-2022 (Szeged, Hungary), and 2 talks: DPG-2023 (Dresden, Germany), GEWP-2023 (Cluj Napoca, Romania))
On 30.03.2021 **Gábor Mándi (BME)** successfully defended his **PhD dissertation** entitled "Simulation of scanning tunneling microscopy from first principles". (no publication related to this project)
Zsombor Szabó (BSc student, BME) is working on new developments in the 3D-WKB-STM code since 01.02.2024.
Benjámin Szász (BSc student, BME) has worked on STM code developments and calculations in the period 01.09.2021-31.03.2022.
Ádám Marcell Varga (BSc student, BME) has worked on STM code developments and calculations in the period 01.02.2020-30.09.2020.

4. Summary of scientific results

4.1. Surface oxides and iodides

Oxide interfaces and thin films grown on metal surfaces have wide applications in catalysis and beyond, owing to their unique surface structures compared to their bulk counterparts.

4.1.1. Copper oxides and iodides

Various copper oxides (bulk surfaces and ultrathin films) have been investigated. The $Cu_2O(111)$ surface has been studied in collaboration with Korean groups (Yonsei University, University of Ulsan). Our combined scanning tunneling microscopy (STM) and density functional theory (DFT) studies show that $Cu_2O(111)$ has a stoichiometric surface where the coordinately unsaturated Cu atoms appear with a hexagonal lattice. DFT-based STM simulations reflecting the orbital contributions of the STM tip present a good agreement with experimental STM topography, unveiling the fine structures of $Cu_2O(111)$ surfaces that arise from coordinately saturated Cu atoms. Beside the possibility of kinetically formed oxygen vacancies reported in a previous work, two intrinsic defects identified in this work as a Cu vacancy and Cu adatoms commonly exist on $Cu_2O(111)$ surfaces. [Ly et al. J. Phys. Chem. C 123, 12716 (2019), 10 independent citations]

In another work, combined experimental and theoretical studies of ultrathin Cu-oxide structures on the Cu(111) surface have been performed in collaboration with the same Korean groups as before. Several reconstructed Cu-oxide surface structures ("8", "29" and "44") were investigated by a combination of STM/STS and DFT methods. It is pointed out that the Tersoff-Hamann approximation is not sufficient to obtain all fine details of the STM/STS experiments, and higher level electron tunneling theories are needed to grasp such subtle effects in the calculations. Furthermore, a newly proposed complete atomistic model for the so-called "44" surface oxide is provided. The agreement between experimental and theoretical STM images is very good (Figure 1). [Lee et al. Appl. Surf. Sci. 562, 150148 (2021), 9 independent citations]

Ultrathin Cu-oxide structures on the Au(111) surface have been investigated by using STM, atomic force microscopy (AFM), DFT and Monte Carlo simulations in collaboration with Chinese groups (ShanghaiTech, Shaanxi Normal University). We demonstrated an approach for structural determination of oxide surfaces using element-specific STM imaging enhanced by functionalized tips (CuO_x and O-terminated W tips). Employing this approach, we reinvestigated the so-called "29" and "44" Cu-oxide surface structures on Cu(111), where new surface stoichiometries and atomic structures with non-conventional pentagonal motifs were obtained, and overall, a long range vacancy ordering has been identified: Cu vacancy ordering in the "44", and a combined ordering of Cu and O vacancies in the "29" surface structures. [Zhu et al. **J. Am. Chem. Soc., IF>10**, accepted for publication, 20.05.2024]

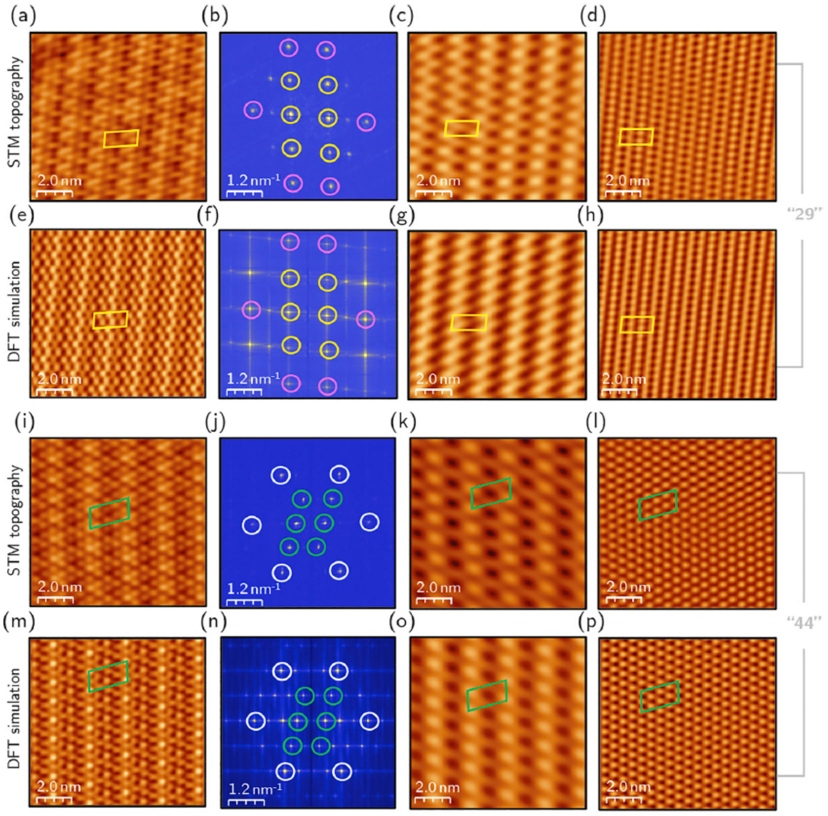

Fig. 1. STM analysis of "29" (top) and "44" (bottom) surface oxide structures: comparison between experiment (STM topography) and theory (DFT simulation). The obtained STM images, their 2D Fourier transforms, and the Fourier-filtered image components are shown. [Lee et al. Appl. Surf. Sci. 562, 150148 (2021)]

Subatomic resolution in scanning probe microscopies (SPM) of Co adatoms on oxidized Cu(110) has been studied in collaboration with Slovak and Japanese groups (Slovak Academy of Sciences, Osaka University). A series of STM images were produced taking different combinations of tip apex atomic orbitals and more realistic tip models (W, Cu) to study their effect on the STM contrast. Depending on the Co spin state and electron orbital symmetries, different subatomic features have been observed. By performing STS simulations for the differential conductance (dI/dV), the energetic origins of the STM contrast from the contributing Co electron orbitals were revealed. Based on calculations of AFM, we proposed that subatomic features can be observed in both AFM and STM. [Turansky et al. Nanotechnology 30, 095703 (2019), 2 independent citations]

Van der Waals-corrected DFT calculations were performed in collaboration with a Korean group (Yonsei University) to examine the initial stages of CuI (p-type transparent semiconductor at room temperature) ultrathin film formation on Cu(111) within the framework of ab initio atomistic thermodynamics. Simulated STM images are in good agreement with experimental results. Moreover, it was found that the surface electron work function is modulated by a competition between charge transfer and polarization effects, which is determined by the local surface structure. [Lee et al. J. Phys. Chem. C 124, 16362 (2020), 4 independent citations]

4.1.2. Iron oxides

Ultrathin FeO Films on Ag(111) have been studied with a combination of experimental (STM, low energy electron diffraction (LEED) and X-rax photoelectron spectroscopy (XPS)) and theoretical (DFT, STM) tools in collaboration with Polish groups (Adam Mickiewicz University Poznań, University of Wrocław). We observed the formation of a previously unreported Moiré superstructure with 45 Angströms periodicity, as well as other reconstructed and reconstruction-free surface species. The results indicate that the structure of FeO films on the Ag(111) support critically depends on the film preparation conditions. DFT calculations were also performed on a model FeO film on Ag(111). The results indicate that such a film should exhibit tunable thickness-dependent properties. [Lewandowski et al. Nanomaterials 8, 828 (2018), 10 independent citations]

Extensive simulations of STM images of hematite and magnetite surfaces in various terminations were performed in collaboration with Polish and USA groups (University of Wrocław, Arizona State University). The exact match with experimental STM results has been difficult to achieve. For some terminations an extreme dependence of the simulated STM image on the tip-sample distance and on the bias voltage has been found. Results for hematite have been published and the difference between STM simulations of metal and insulator/semiconductor surfaces was also discussed. [Ossowski et al. J. Phys. Chem. C 125, 26711 (2021), 3 independent citations]

4.1.3. Molybdenum oxides

Ultrathin Mo-oxide films on a Au(111) surface were theoretically studied in collaboration with Korean and Australian groups (Yonsei University, University of Sydney). Various polymorphic structural models were proposed and compared with previous experimental results. We found that the oxidation state of Mo atoms in the O/Mo layers can be modulated and reduced without intentional creation of oxygen vacancies. This is also assisted by a charge transfer mechanism from the Au substrate to these oxidic films, providing a direct means to tune the surface electronic properties of ultrathin oxide films on metal substrates. [Lee et al. Nanoscale 11, 6023 (2019), 1 independent citation]

4.1.4. Titanium oxides

A machine learning-based approach was employed for the prediction of complex polaron-vacancy structures and patterns on the rutile TiO_2(110) surface. In particular, the inhomogeneous distribution and interaction of surface oxygen vacancies and induced small polarons was investigated in a combined theoretical-experimental work in collaboration with Austrian groups (University of Vienna, Vienna University of Technology). An analysis of the experimental STM mages yielded a direct validation of the theoretical predictions through STM simulations. [Birschitzky et al. npj Comput. Mater. 10, 89 (2024)]

4.1.5. Sodium iridate

The direct visualization of the spin-dependent orbital geometry on the Na_2IrO_3 surface with ultra-high resolution has been achieved within a collaborative theoretical-experimental work with a Chinese group (Shaanxi Normal University). This honeycomb iridate surface is a candidate for the realization of the Kitaev model by exhibiting strongly correlated, topologically nontrivial band structure that may have protected quantum spin Hall states. Our combined STM+DFT work revealed a novel relativistic Mott insulator character rather than Slater-like states. We demonstrated that the Ir-O-Ir bonds and the subtle local density of states variation of Ir atoms induced by spin correlations can be imaged in real space in ultra-high resolution utilizing a spin-polarized oxygen-functionalized iridium STM tip. [Zhang et al. Microstructures, accepted for publication, 22.04.2024]

4.2. 2D materials

4.2.1. Charge density waves in niobium diselenide

In collaboration with a Korean group (APCTP, Pohang), DFT and STM calculations were employed to investigate the strain-induced structural instabilities between triangular and stripe charge density wave (CDW) phases in a pristine single layer 1H-$NbSe_2$, and to analyze the energy hierarchy of the structural and charge modulations. A phase separation between triangular and stripe CDW phases was obtained, in agreement with earlier experiments. The observed wavelength of the stripe-associated 4x4 charge modulation is reproduced with a good accuracy in comparison with experiments. [Cossu et al. **NPG Asia Mater.** 12, 24 (2020), **IF>10**, 8 independent citations]

The interplay of CDWs in bilayers of 2H-$NbSe_2$ was further investigated depending on the DFT description (exchange correlation functionals and van der Waals parametrizations) and on the structural matching (periodic lattice distortions) of the individual layers in collaboration with the same group as above. We found CDW combinations in the bilayers with a lowered symmetry due to the lateral displacements of the individual 1H-$NbSe_2$ layers. The interlayer coupling plays a crucial role in determining the CDW patterns. Using STM simulations we identified a trend of the detection limits of the different CDW combinations. [Cossu et al. Phys. Rev. Res., submitted for publication, 29.03.2024, arXiv:2404.01807]

4.2.2. Doped graphene

The synthesis of nitrogen-doped single-layer graphene on Cu(111) substrate, its doping properties, and doping-induced variation of local work function (LWF) of graphene have been investigated on the atomic scale by combining STM/STS, X-ray photoelectron spectroscopy (XPS), and DFT calculations in collaboration with an USA group (California State University Northridge). Most nitrogen dopants are at the edges of graphene islands and the graphene domain boundaries with the pyridinic configuration. Graphitic nitrogen dopants arrange into curved lines within graphene islands after multiple growth cycles. The LWF strongly depends on the atomic bonding configuration and concentration of the nitrogen dopants: it decreases for graphitic nitrogen doping and increases for pyridinic nitrogen doping [Neilson et al. J. Phys. Chem. C 123, 8802 (2019), 6 independent citations].

In collaboration with the same group as above, we studied the formation of various nitrogen-doping (graphitic, pyridinic, pyrrolic) configurations within a corrugated graphene layer on Ir(111) and Ru(0001) metal substrates by means of a combined experimental-theoretical approach. Five different N-containing solid sole precursors were considered, and their effect on the formation of N-doped graphene was investigated by XPS, STM and DFT. Atomic scale insights on the N-bonding configurations were achieved by DFT and STM calculations, in combination with high-resolution STM experiments. We identified a great variety of experimentally observed N-doping configurations. Pyridinic-N configurations were found the most abundant. STM calculations revealed the importance of the local carbon environment in the STM contrast formation of the N defects. [Yang et al. J. Phys. Condens. Matter 35, 405003 (2023), 2 independent citations]. Further extensive DFT calculations have been conducted, and a theoretical analysis of the physical properties of the nitrogen defects is performed. [Abilio et al. manuscript in preparation]

Nitrogen- and boron-doped free-standing single layer graphene sheets were considered as demonstrative cases for the newly implemented STS theoretical method employing the revised Chen's derivative rules, see section 4.5.1. [Abilio et al. manuscript in preparation]

4.2.3. Hexagonal boron nitride

4.2.3.1. Effect of substrate surface alloying

The structural and electronic properties of a gold-rhodium surface alloy on the Rh(111) substrate, and the morphology of a hexagonal boron nitride (hBN) layer depending on the Au-alloying of the surface layer of Rh have been studied by DFT and STM simulations in collaboration with experimental partners at the University of Szeged and ELI-ALPS (Szeged). Based on total energy calculations it was found that an earlier experimentally observed 2x1-striped Au-Rh surface is composed of a perfectly ordered suface alloy layer of 50% Au and 50% Rh rather than Au adatom rows on Rh(111). STM calculations revealed bias-voltage-dependent contrast differences among selected corrugated surface layer structures at various Au coverages, which, however, are difficult to resolve in STM experiments due to the theoretically predicted low apparent corrugations. [Palotás et al. J. Phys. Chem. C 122, 22435 (2018), 2 independent citations]

Surface alloying of the Rh(111) substrate with gold resulted in the tuning of the hBN nanomesh morphology. We demonstrated that a gradual increase of the Au amount in the surface layer gradually reduced the pore diameter of the hBN nanomesh, which flattens out at about 1 monolayer Au coverage [Gubó et al. Phys. Chem. Chem. Phys. 20, 15473 (2018), 7 independent citations]. Furthermore, extensive DFT calculations on hBN/AuRh/Rh(111) surfaces were conducted, where several types of reconstructions of the Au-Rh surface alloy below the BN sheet were considered. It was found that the previously identified 2x1 Au-Rh surface alloy is considerably rearranged in the presence of the hBN overlayer, and the energetically favored structure corresponds to a case where the hBN pore is in strong interaction with underlying Rh atoms, and the Au atoms migrate below the hBN wire region. The experimentally determined (NanoESCA, ELI-ALPS, Szeged) local electron work function variations depending on the Au content are well reproduced in the calculations, and show an enhancement upon Au addition to the pure Rh(111) substrate. The charge transfer mechanisms were also analyzed in great detail by employing DFT that explained the enhanced local electric fields in the modified hBN nanomesh morphology. [Halasi et al. npj 2D Mater. Appl., submitted for publication, 29.01.2024]

4.2.3.2. hBN nanomesh template for metal nanoparticles and molecules

Metal Au and Rh atomic structures (adatom, small atomic island, monolayer) were systematically studied on hBN/Rh(111) by DFT in collaboration with experimental partners at the University of Szeged and ELI-ALPS. It is found that Au and Rh behave remarkably differently that also affect their catalytic properties. For Au/hBN/Rh(111) the importance of low-coordinated negatively charged Au atoms is confirmed by DFT results. The amount of the negative charge on the Au atom depends on its coordination number, as evidenced by model atomic structures studied by DFT [Farkas et al. Appl. Catal. A 592, 117440 (2020), 6 independent citations]. DFT results confirmed that Rh desorption has a larger activation energy than Au desorption. While both Rh and Au atoms prefer adsorption in the pore region, the Rh-N and Au-B bondings are preferred, which act as nucleation sites for the formation of larger metallic clusters. The Rh adatom is found to be negatively charged as well but in a smaller extent than Au. [Vári et al. Appl. Surf. Sci. 623, 157041 (2023)]

In connection to experimental works at the University of Szeged and ELI-ALPS, DFT calculations were employed to study ethanol adsorption and the decomposition product of atomic hydrogen on pristine hBN/Rh(111), and also on pure Au and pure Rh atomic clusters on hBN/Rh(111), the latter two serving as models for metal nanoparticles on hBN/Rh(111). The results on the pristine and Au-covered hBN/Rh(111) are published, where we found strong B-H bonds in the absence of gold, and found that larger negative charges on low-coordinated Au atoms are responsible for their enhanced catalytic activity. Selective transformation of ethanol to acetaldehyde was demonstrated in the experiments. [Farkas et al. Appl. Catal. A 592, 117440 (2020), 6 independent citations]. According to our results ethanol adsorption is less selective on the hBN nanomesh than that found for azobenzene molecules.

Azobenzene molecular switch has been studied on hBN/Rh(111) both experimentally and theoretically in collaboration with the University of Szeged and ELI-ALPS. STM indicated a clear preference for trans-azobenzene adsorption rather than cis-azobenzene in the pores of the hBN nanomesh, manifesting a templating effect, but in some cases one-dimensional molecular stripes also form, implying attractive molecule-molecule interaction. DFT calculations confirmed these experimental findings and provided further details regarding the adsorption energetics, bonding, and intermolecular interactions. Figure 2 schematically shows the templating effect of the hBN nanomesh hosting trans-azobenzene molecules. Based on our results, we explained the mechanism of initial azobenzene molecular growth on the hBN/Rh(111) nanomesh structure. [Szitás et al. J. Phys. Chem. C 124, 14182 (2020), 4 independent citations]

I contributed to the preparation of an extensive review article focusing on the summary and analysis of hBN/metal nanotemplate effects from the literature with a particular emphasis on published results since 2019. [Óvári et al. Surf. Sci. Rep., submitted for publication, 17.11.2023]

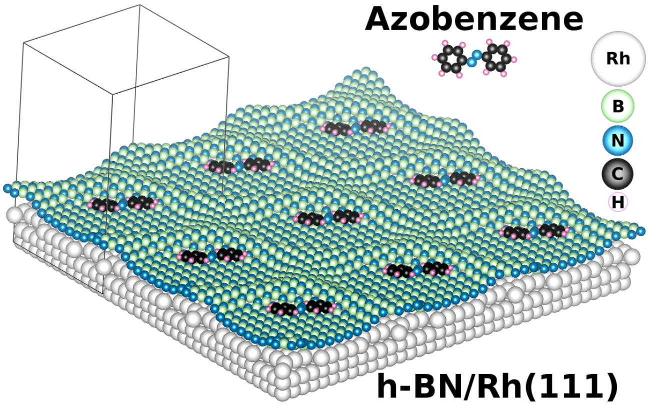

Fig. 2. Schematic image illustrating the templating effect of the hBN nanomesh hosting trans-azobenzene molecules. [Szitás et al. J. Phys. Chem. C 124, 14182 (2020)]

4.2.3.3. hBN defects and metal intercalation

Extensive DFT and STM calculations were performed to study the properties of various defect structures on a hBN layer on Rh(111). Another focus was to study simple atomistic models for metal intercalation below the hBN layer (without and with Rh support). Energetic preference for Rh and Au metal atom intercalation below the hBN layer was found. The role of the hBN surface defects has been identified to be crucial for metal atomic intercalation. Energy barriers for the Rh and Au atomic intercalation were estimated by considering a free-standing hBN layer with various simple defects. We found that N vacancies show generally higher energy barrier for atomic intercalation than B vacancies, and the energy barrier relation between Rh and Au critically depends on the hBN defect type. Intercalation through the middle of a BN-divacancy provided the smallest energy barriers. Our identified trend points to the potential importance of hBN defects with larger spatial extension and hBN edges for metal intercalation processes. It is also anticipated that the presence of the Rh support promotes Rh compared to Au atomic intercalation through the hBN layer. [Vári et al. Appl. Surf. Sci. 623, 157041 (2023)]

4.2.4. Heterostructures of 2D materials

DFT and STM calculations were performed in combination with experimental STM to study the properties of pristine single layer $ReSe_2$ and $ReSe_2$/graphene heterostructure interfaces in collaboration with Korean groups (Yonsei University, University of Ulsan). The presence of trapped charges in the studied van der Waals heterojunctions was demonstrated theoretically, and observed in real space by experimental STM. It was also revealed that electron accummulation occurs at the $ReSe_2$ side and electron depletion at the graphene side within the interface. The trapped charges are even more enhanced at the edge of $ReSe_2$. [Ly et al. Appl. Surf. Sci. 579, 152187 (2022), 1 independent citation]

With extensive STM/STS calculations we contributed to the detailed understanding of another van der Waals heterojunction: $MoTe_2$/graphene. This system turned out to be very sensitive electronically, and non-conventional higher-order Moiré patterns can be observed by STM depending on the applied bias voltage. The electronic sensitivity is attributed to the various energy-dependent electron orbitals contributing to the tunneling in the STM junction. This work has been conducted in collaboration with Hungarian, Belgian, and French groups (HUN-REN Centre for Energy Research, University of Namur, LMPQ CNRS-University of Paris). [Pham et al. npj 2D Mater. Appl. 6, 48 (2022), 6 independent citations]

The α-phase of bismuthene on MoS_2 (α-Bi/MoS_2) and graphene/WTe_2 heterostructures were considered as demonstrative cases for the newly implemented STM theoretical method employing the Moiré plane wave expansion model (MPWEM) capable of simulating STM images based on geometric information only, see section 4.5.3. [Le Ster et al. 2D Mater., submitted for publication, 27.03.2024, arXiv:2310.06535]

4.3. Molecules on surfaces and catalysis

The coordination-restricted ortho-site C-H bond activation and dehydrogenative homocoupling of 1,3-BPyB and 1,4-BPyB molecules on different metal surfaces (Cu, Au) were studied by a combination of STM, non-contact AFM, and DFT calculations in collaboration with Chinese and German groups (Peking University, Friedrich-Alexander University Erlangen-Nürnberg). The coupling products on Cu(111) exhibited certain configurations subject to the spatial restriction of robust two-fold Cu-N coordination bonds. Compared to the V-shaped 1,3-BPyB, the straight backbone of 1,4-BPyB helped to further reduce the variety of reactive products. By utilizing the three-fold coordination of Fe atoms with 1,4-BPyB molecules on Au(111), a large-scale network containing single products was constructed. Our contribution was STM/STS simulations. [Zhang et al. **ACS Nano** 13, 1385 (2019), **IF>10**, 27 independent citations)]

In collaboration with a Chinese group (Soochow University), we contributed to the extensive DFT study of finding a favorable transition metal center and pathway of electrocatalytic reduction of nitrogen (N_2) for producing ammonia (NH_3) at relatively low overpotential and high selectivity with respect to hydrogen evolution in single-atom catalytic systems on a 2D phthalocyanine molecular layer. Molybdenum was found the best performing transition metal atom for this purpose. Moreover, we proposed that the dipole of the N-N triple bond in the adsorbed N_2 molecule is a better theoretical indicator for predicting the catalytic performance of active sites in the nitrogen reduction reaction. [Liu et al. **J. Mater. Chem. A** 8, 3598 (2020), **IF>10**, 47 independent citations]

In collaboration with a Chinese group (Shaanxi Normal University), we contributed to the interpretation of DFT results, and based on them we proposed a scheme for the on-surface synthesis of 2D covalent organic frameworks via molecular assembly directed photocycloadditions, a new strategy for the large-scale synthesis of 2D carbon materials. [Niu et al. J. Phys. Condens. Matter 33, 475201 (2021)]

In collaboration with a Polish group (Maria Curie-Skłodowska University Lublin), pentacene molecular adsorption on the Si(553)-Pb surface was investigated by DFT and STM. We contributed with STM+STS calculations. Two pentacene phases have been identified: a low-density and a high-density phase, both showing 1D ordering. Thus, the Si(553)-Pb surface exhibits a novel 1D template effect for the formation of long-range molecular structures. [Nita et al. J. Phys. Chem. C 126, 17738 (2022)]

4.4. Semiconductor surfaces

The Si(331)-(12x1) reconstructed semiconductor surface was studied theoretically (DFT+STM) in collaboration with Portuguese and Russian groups (University of Aveiro, Institute of Semiconductor Physics Novosibirsk) to explain particular features of experimentally obtained STM images, and also provided an improved atomic structural model for this vicinal silicon surface. [Zhachuk et al. J. Chem. Phys. 149, 204702 (2018)]

4.5. STM/STS method developments

4.5.1. Chen's derivative rules for STS

For STM method developments, we included the Chen's derivative rules into the calculation of the electron tunneling differential conductance, dI/dV, and implemented the method into the BSKAN code. We tested the new computational approach on nitrogen- and boron-doped single-layer graphene. [Abilio et al. manuscript in preparation]

4.5.2. Toward machine learning STM

A full automation scheme of high-throughput STM simulations in combination with machine learning techniques has been started, where our collaborative partner in Korea (Yonsei University) developed a graphical user interface (autobskan), with a strong support from our group with developer expertise in the BSKAN code. [Lee et al., poster at the PSI-K conference 2022]

4.5.3. Moiré plane wave expansion model for STM

We contributed to the development of a new non-DFT-based method at the University of Łódź in Poland, which relies on the Moiré plane wave expansion of bilayer heterostructures composed of 2D materials, and allows the simulation of STM images even for incommensurate 2D heterostructures of arbitrary symmetries and twist angles based on lattice geometry information only. [Le Ster et al. 2D Mater., submitted for publication, 27.03.2024, arXiv:2310.06535]

4.5.4. Effect of the tilting of functionalized STM tips on the STM contrast formation

We investigated the physical mechanisms of the STM imaging of CO molecule and Cu adatom on the Cu(111) surface in a German-Hungarian experimental-theoretical collaboration (Technical University of Ilmenau). The experimentally obtained STM images were interpreted and analyzed based on DFT and STM calculations. We found that the decomposition of the tunneling current in terms of tip orbital contributions explains the obtained STM contrast differences with functionalized STM tips. With the tilting of the axis of the STM tip the corresponding asymmetric experimental STM image contrasts could also be reproduced and explained for a Cu adatom, and deviations on the imaging of a CO molecule have been also investigated. [Abilio et al. manuscript in preparation]

4.5.5. High-resolution tunneling vector spin transport in spin-polarized (SP-)STM

A 3D-WKB theory of combined tunneling electron (scalar) charge and (vector) spin transport has been developed in SP-STM. The high-resolution tunneling electron charge and spin transport (longitudinal spin current and spin transfer torque (STT)) properties of a variety of magnetic skyrmions in ultrathin films at surfaces were investigated. [Palotás et al. Phys. Rev. B 96, 024410 (2017), 8 independent citations; Palotás et al. Phys. Rev. B 97, 174402 (2018); Palotás, Phys. Rev. B 98, 094409 (2018), 4 independent citations; Palotás et al. J. Magn. Magn. Mater. 519, 167440 (2021), 1 independent citation]

4.6. Spin dynamics method developments

The linear-response calculation method of the diagonal elements of the site-nonlocal Gilbert damping tensor (Figure 3) as a Fermi surface quantity has been implemented into the real-space SKKR code. Extensive test calculations for determining their properties have been performed for Fe and Co bulk and their (001)-oriented surfaces [Nagyfalusi et al. Phys. Rev. B 109, 094417 (2024)]. Further extensive calculation of Gilbert damping parameters of Fe and Co overlayers and small atomic (adatom and dimer) clusters on noble metal (Au, Ag, Cu) supports has been performed. [Nagyfalusi et al. manuscript in preparation]

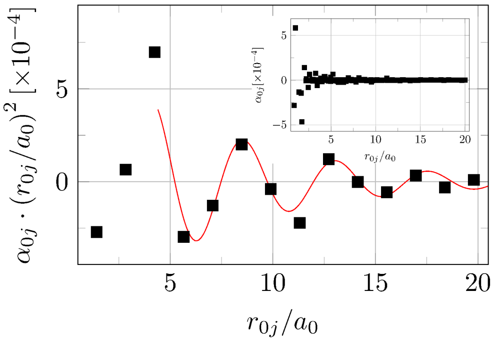

Fig. 3. Asymptotic behavior of the site-nonlocal Gilbert damping times the squared distance in bulk bcc iron. Black square symbols: calculated values, red curve: asymptotic fit. The inset shows the calculated atomic-site-dependent Gilbert damping values in the given distance range. [Nagyfalusi et al. Phys. Rev. B 109, 094417 (2024)]

4.7. Magnetism and superconductivity at interfaces

Adsorbing individual 3d transition metal atoms (Mn, Fe, Co) on the Re(0001) surface, the Kondo coupling, the magnetic anisotropy, and the so-called Yu-Shiba-Rusinov (YSR) states were investigated depending on the d-band filling of the adatoms [Schneider et al. npj Quant. Mater. 4, 42

(2019), 11 independent citations]. A proposition for the usage of linear Fe atomic chains with variable lengths on the Re(0001) elemental superconductor surface to design Majorana fermions with excellent controllability has been published in collaboration with a German group (University of Hamburg) and with the Budapest University of Technology and Economics (BME) [Kim et al. **Sci. Adv.** 4, eaar5251 (2018), **IF>10**, 207 independent citations]. The magnetic ground states of such atomic chains and the emergence of chiral multispin interactions were reported. [Lászlóffy et al. Phys. Rev. B 99, 184430 (2019), 28 independent citations]

Electronic, magnetic and superconducting properties of transition metal (Mn, Fe) adatoms, atomic dimers and monatomic chains were studied on the Nb(110) elemental superconductor surface. Upon Mn dimer formation, the atomic YSR orbitals split for ferromagnetic (fm) and, surprisingly, also for antiferromagnetic (afm) alignment. The numerical calculations attribute the unexpected splitting of atomic YSR orbitals in afm dimers to spin-orbit coupling and broken inversion symmetry at the surface [Beck et al. **Nat. Commun.** 12, 2040 (2021), **IF>10**, 34 independent citations]. A spin-spiral ground state is obtained for Fe chains along the [1-10] direction as a consequence of the frustration of the isotropic interactions. Here, a flat spin-spiral dispersion relation is identified, which can stabilize spin-spirals with various wave vectors together with the magnetic anisotropy [Lászlóffy et al. Nanomater. 11, 1933 (2021), 3 independent citations]. The magnetic ground states of Fe atomic chains on Re(0001), Nb(110) and Rh(111) surfaces were studied theoretically in further details. [Nagyfalusi et al. J. Phys. Condens. Matter (2022)]

We contributed to a combined experimental-theoretical study of surface Fe atomic structures (adatom, dimer, monatomic chains) on Au/Nb(110) surface in collaboration with a German group (University of Hamburg) and BME. Proximity-induced superconductivity in the Au layer was observed, and the effect of the large spin-orbit coupling of the Au on the YSR states and on the formed YSR bands of the fm Fe chains has been analyzed. It was found that despite the large spin-orbit coupling topological superconductivity does not emerge in the fm Fe states. However, when the magnetic state is artificially changed to a spin-spiral, a superconducting gap is opening, which enables the emergence of Majorana edge states in the Fe chains. [Beck et al. Comm. Phys. 6, 83 (2023)]

A combined experimental-theoretical study of mono- and bilayers of Mn on Nb(110) surface in collaboration with a German group (University of Hamburg) and BME has been conducted. We identified a c(2x2) afm order, which is due to the strong first neighbor intra- and inter-layer afm exchange interaction of Mn. The spin moments of Mn are out of plane. We observed proximity-induced superconductivity in the Mn layers with the presence of YSR states, which were experimentally detected by tunneling spectroscopy. [Lo Conte et al. Phys. Rev. B 105, L100406 (2022), 10 independent citations]

The correlation between magnetic states and their YSR characteristics of small Fe atomic clusters on Pb(111) superconductor surface has been studied in a collaboration with the Technical University of Ilmenau. First-principles simulations of the YSR states reveal which adsorption geometries and magnetic structures of the clusters can reproduce the experimental spectra most accurately. [Amann et al. Phys. Rev. B 108, 195403 (2023)]

We studied the interaction of the magnetic moment of a molecule (TBrPPCo) with a superconducting lead, Pb(111), substrate upon sequential chemical modifications of the molecule induced by the tip of an STM in a German-Hungarian experimental-theoretical collaboration (Technical University of Ilmenau). A distance change of only 8 picometers, i.e. one ten-millionth of the diameter of the human hair, between the magnetic cobalt center of the molecule and the lead substrate resulted in a significant change of the measured characteristics of the YSR states in the tunneling spectrum of the molecule. The results might lead to new developments and applications in various fields of surface physics and chemistry, e.g., in surface chemical reactions, in (molecular) nanoelectronic devices or in ultra-sensitive detectors. The graphical illustration about our discovery was selected for a cover page of the highly prestigious journal Nano Letters. [Schulte et al. **Nano Lett.** 23, 1622 (2023), **IF>10**, 1 independent citation]

4.8. Complex magnetism at surfaces/interfaces

Magnetic properties and complex ground states at material surfaces/interfaces have been studied in collaboration with various groups abroad and with the BME: X/Co/Pt(111) (X=Re,Os,Ir,Pt,Au) ultrathin films (German collaboration) [Simon et al. Phys. Rev. B 97, 134405 (2018), 16 independent citations]; skyrmion formation in Fe double layer on an Ir(111) substrate upon hydrogen exposure (Germany, Taiwan) [Hsu et al. **Nat. Commun.** 9, 1571 (2019), **IF>10**, 29 independent citations]; bulk MnN and the MnN/Fe interface (Austria, Germany, Spain) [Simon et al. Phys. Rev. B 98, 094415 (2018), 4 independent citations]; Ru/Co/Cu in comparison with Pt/Co/Cu interfaces have been studied (Slovakia, Russia) [Ščepka et al. arXiv:1911.02467, 2019, 2 independent citations]. The magnetic properties of sandwiched Au/Fe/Au/W(110) structures were investigated by DFT, taking several model systems (experimenatl collaboration with Maria Curie-Skłodowska University Lublin, Poland). We reproduced well the experimentally observed Curie temperatures in the calculations. [Zdyb et al. Materials 15, 1019 (2022)]

5. Formal research networks and further dissemination

5.1. Participation in EU COST Actions

The PI was acting as a **Member of the Management Committee of two EU COST Actions**, representing Hungary:
- MP1306, "EUSpec: Modern Tools for Spectroscopy on Advanced Materials" (2014-2018)
- CA17123, "MAGNETOFON: Ultrafast opto-megneto-electronics for non-dissipative information technology" (2018-2023)

Furthermore, the PI acted as **co-proposer for two EU COST Actions**, representing Hungary, which were both **selected for funding by the European Commission** as announced 22.05.2024:
- OC-2023-1-26747, "Polytopo: Topological textures in condensed matter"
- OC-2023-1-26762, "CHIROMAG: Magnetism and chirality: twisting spins, light, and lattices for faster-than-ever spintronics"

5.2. Further dissemination

A short book chapter has been published on the screened Korringa-Kohn-Rostoker method. [Palotás and Szunyogh, Springer Proceedings in Physics, Vol. 204, Chapter 28, pp. 381-386 (2018)]
We published an overview article on topological magnetic states in Hungarian language in the journal of the Hungarian Physical Society for the purpose of public outreach. [Rózsa and Palotás, Fizikai Szemle 73, 114-120 (2023), 1 independent citation]
During the project duration, altogether **26 invited talks**, 45 contributed talks, and 4 conference posters were presented at scientific events by the project participants, and 46 co-authored conference contributions have been delivered by the PI.

--- Budapest, 28 May 2024, Dr. Krisztián Palotás, Principal Investigator ---