1. Report on research work of the Austrian (sub) project

1.1 Information on the development of the research project

Overall scientific goals. The goal of this proposal was to set photoemission orbital tomography (POT). With a team consisting of surface scientists (Ramsey in Graz and Bocquet, Soubatch and Tautz in Jülich), synchrotron radiation and metrology experts (Richter, Gottwald, PTB Berlin) and theoretical solid state physicists (Puschnig, Graz), we have explored the limits of validity of the plane wave final state approximation and provided benchmarks for theoretical improvements beyond the plane wave final state. In particular, we have contributed to the following five research questions: (i) How does the experimental geometry and the polarization of the incident UV light influence the applicability of the plane wave final state approximation? (ii) Can photoemission tomography also be applied to molecular film geometries containing tilted molecules and/or to molecular orbitals other than π-orbitals of planar molecules? (iii) How important is the size of the molecule for photoemission tomography approach to work, for instance, would it be applicable for smaller molecules such as benzene? (iv) Does the photon energy dependence of ARPES reveal information on absolute electron density distributions? (v) Is photoemission tomography able to recognize new molecular species formed by chemical interactions on the surface?

Comment on possible changes in research orientation. All research questions formulated in the original proposal have indeed been tackled and have either already been published or are currently in preparation for publication (see below). Additionally, through a couple of new collaborations also new research directions have been opened. This includes the extension of POT to the time-domain (with U. Höfer, Marburg), the theoretical description via time-dependent density functional theory (with A. Rubio in Hamburg), the application of POT to the geometric and electronic structure of longer acenes (with G. Koller, Graz and T. Chasse, Tübingen), or the investigation of spin-states in porphyrins (with M. Cinchetti, Dortmund and C. M. Schneider, Jülich). It should also be noted that the COVID-19 pandemic has led to severe delays, mainly regarding the experimental part of the project owing to the lock-downs and travel restrictions to the synchrotron facilities in Berlin and Trieste, but also the theoretical parts of the project have been affected. Fortunately, through additional funds, the University of Graz has extended the employments of the PhD students Hurdax, Kern and Schwendt by five months each, so at least partially these delays could be compensated.

1.2 Most important results and brief description of their significance

Important scientific advances. The project has led to a number of scientific advances in the photoemission orbital tomography (POT) approach and in the field of organic molecular films. Regarding the POT technique, it has been demonstrated that a plane wave final state can also be applied to smaller molecules such benzene [Egger et al., NJP 2019] and that it may also provide useful insights for three-dimensional molecules such as C60 [Haag et al., PRB (2020), Metzger et al., PRB (2020)]. Using the calibrated beamline at the Metrology Light Source (MLS) in Berlin, comprehensive photon energy dependent as well as polarization dependent measurements, both, for molecular monolayers as well as for 2D-extended layers (epitaxial graphene on SiC) have been performed. When it comes to photon-energy dependent cross-sections, the plane wave final state is demonstrated to lack important aspects observed in the experiment, but requires an improved description of the final state. Here, we have found excellent agreement within our time-dependent density functional theory (TDDFT) calculations and the so-called surface-flux method (see

manuscript in preparation [3]). The same TDDFT description has also been applied successfully to account for the measured circular dichroism in the angular photoemission distribution which has been studied for two model systems (tetracene and pentacene) on two substrate systems (Cu(110) and Ag(110)). These results are currently in preparation for publication [5] also disprove earlier claims that the circular dichroism in molecules reveals the phase of the orbital. In summary, the project has put POT onto firmer grounds and the range of validity and limitations of the simple plane wave final state are now more clearly defined.
When applying POT to various organic molecule / substrate systems, a number of scientific questions could be answered. POT has contributed in understanding the physical mechanisms governing the charge state of molecules on thin insulating layers [Yang et al, JPCL (2019), Hurdax et al., Beilst. J. Nanotechn. (2020), Hurdax et al., Adv. Mater. Int. (2020), Egger et al. Angew. Chem. Int. Ed. (2021)]. The combination of POT experiments with density functional calculations has also been utilized to clarify the chemical state of molecules after undergoing surface chemical reactions [Yang et al., Nat. Commun. (2019), Haags et al., ACS Nano (2020), Cojocariu et al., Chem. Commun. (2021), Haags et al., Science Advances (2022)], the geometric and electronic structure of longer acenes [Bone et al., JPCC (2021), Sättele et al., JPCC (2021), Sättele et al., JPCC (2022)] and the spin structure of adsorbed transition-metal porphyrins [Sturmeit et al., J. Mater. Chem. (2020), Sturmeit et al., Small (2021), Stredansky et al., Angew. Chem. Int. Ed. (2022)].

Opening of new promising research agendas. In a first proof-of-principle experiment it could be shown that POT can also be applied to study the ultrafast dynamics in optically excited molecular orbitals [Wallauer et al., Science (2021)]. By combining time-resolved photoemission using high laser harmonics and a momentum microscope, a tomographic, femtosecond pump-probe experiment of unoccupied molecular orbitals could be demonstrated. By measuring the full momentum-space distribution of transiently excited electrons, their excited-state dynamics could be connected to real-space excitation pathways. This offer the possibility of observing ultrafast electron motion in time and space. In the course of the project, we have also undertaken the first steps in simulating such pump-probe ARPES experiments by applying a real-space, real-time TDDFT approach employing the surface-flux method to simulate the angular distribution of transiently emitted electrons.

Development of new research methods or instruments. The project has led to the versatile simulation and analysis tool “kMap.py: A Python program for simulation and data analysis in photoemission tomography” [Brandstetter et al., Comp. Phys. Commun. (2021)] available under the open GPLv3 license. This simulation tool “kMap.py” is also closely connected to an open, online data base containing molecular orbitals that has been developed in the course of this project. Within a collaboration with G. Koller’s FWF-project (I4145, Photoemission Tomography of Excited Molecular States), also situated at the University of Graz, a momentum microscope (Nano-ESCA), connected to a He-lamp source and a high-harmonic generation laser source, could be established and has provided first, very promising results.

Relevance for related areas of research. Within this project, POT has been further developed with the aim to become another surface science approach for the investigation of the adsorbed layers. While this technique is quite specialized it yields results that impact a wider range of topics beyond organic molecular layers, including 2D van-der-Waals materials, molecular magnets and it can be further extended from the static applications to study the temporal and spatial evolution of electronic excitations on ultrafast (femto-second)

time scales. The latter may have implications for a number of opto-electronic applications ranging from energy harvesting to catalysis.

Added value of the international collaboration. The cooperation within the DFG-part of the project, i.e., the close collaboration with the groups at the FZ Jülich (Posseik, Soubatch, Tautz) and at the PTB Berlin (Richter) was essential for the success of the project. First, the toroidal electron energy analyzer operated by the FZ Jülich at the Metrology Light Source at the PTB synchrotron in Berlin is a unique instrument to perform the POT experiments outlined above. Second, the absolutely calibrated photon flux provided at the synchrotron beamline at the MLS was crucial for the photon energy dependent measurements of the photoemission cross sections. On the other hand, the Austrian part of the project has offered the essential expertise for growing highly oriented films and has asso provided all the theoretical input to analyze and understand the experimental data, ranging DFT calculations for gas phase molecules and organic/metal interfaces with POT simulations using a plane wave final state to more involved calculations beyond a plane wave final state description, i.e., TDDFT simulations and finals states from solving the Lippmann-Schwinger equation.
In summary, the this joint FWF/DFG project with the three involved nodes (Graz, Jülich, Berlin) has provided the ideal framework to conduct this research. Without this international collaboration, it would hardly been possible to achieve the research goals.

1.3 Information on the execution of the project, use of available funds and (where appropriate) any changes to the original project plan

Duration. The Austrian part of the project has started on September 1st, 2018 and ended on 31st of March 2022.

Use of personnel. On the Austrian part of the project, the PhD students Mathias *Schwendt* and Christian *Kern* were responsible for the theoretical aspects of the project and they have been employed from 09/2018 to 11/2021 with additional 5 months added at the end (until 03/2022) from COVID-19 funds of the University of Graz. While Schwendt developed a code employing a final state from solving the Lippmann-Schwinger equation, Kern has focused on the TDDFT description of the photoemission process in collaboration with Angel Rubio (MPI Hamburg), where Kern spent also a 6 week research visit. Both PhD students were also strongly involved in the experimental part of the project and contributed to five joint publications. Philipp *Hurdax* (04/2019 – 12/2020) and Larissa *Egger* (02/2019 – 09/2019) have been employed as PhD students for the experimental part of the project, where Hurdax has also been employed additional five months from COVID-19 funds of the KFU Graz until 05/2021). Both, Hurdax and Egger, have been conducting several beamtime experiments at the MLS in Berlin and also performed in-house experiments leading to 10 joint publications with the Jülich and Berlin groups. In addition, to these 4 PhD students, also Xiaosheng *Yang*, the experimental PhD student from FZ Jülich, has been working in Graz on the analysis of measurement data and on writing two joint publication between 09/2109 and 12/2019. During that time, Yang was also closely working together with the student assistant D. *Brandstetter* on the development of the python analysis tool “kMap.py” published in Comp. Phys. Communications. Moreover, the Master’s students A. Reichmann, L. Reicht and C. Dösinger have been employed as student assistants and contributed to the project goals (1 paper published, 2 more in preparation). Lat but not least, the PhD student *A. Windischbacher (*mainly employed in G. Koller’s FWF project I4145-N36, Photoemission Tomography of

Excited Molecular States) has also been working for the project (02/2022 – 03/2022) and has actually made significant contributions to four joint publications.

No equipment has been purchased.

2. Personnel development – Importance of the project for the research careers of those involved (including the project leader)

Peter Puschnig. The project's output, including scientific publications, invitations to conference and seminar talks, education of Master and PhD students, is an important aspect in the qualification process of the PI which involves an evaluation every six years (the next evaluation will be in 2026). The project has also initiated new collaborations (U. Höfer, A. Rubio) which led to the ERC-synergy grant consortium consisting of F.S. Tautz, P. Puschnig, U. Höfer, R. Huber who have been invited to the final interview round on September 5th, 2022.

The PhD students **Larissa Egger** (defense 06/2020), **Philipp Hurdax** (defense 08/2022), **Mathias Schwendt** (planned defense 12/2022) and **Christian Kern** (planned defense 12/2022) have been trained in state-of-the surface science and ab-initio electronic structure methods, respectively. Moreover, they have gained international experience, for instance, through mutual research visits with partners, by attending synchrotron beamtimes, or through various conference participations where they could present their research results. Their main career achievements have been (Egger, now PostDoc at the Materials Center Leoben) or soon will be (Hurdax, Schwendt, Kern) the doctoral degree.

All involved Master's students (Reichmann, Reicht, Dösinger) are currently employed as PhD students working in the field of ab-initio electronic structure theory at the Graz University of Technology and the University of Leoben, Austria, certainly benefiting from their experience with the present project at the Master's level. D. Brandstetter, as a student assistant, contributed also to four publications and is currently pursuing a Master's Thesis in Puschnig's group planning to continue as a PhD student.

3. Effects of the project beyond the scientific field

On several occasions, project publications have been accompanied by press releases and have been covered in media, thereby informing the public about our research results:

July 2019: Nano-Graphene formed on Copper
September 2020: Control over interfacial charge transfer
November 2020: Superaromatic or not?
February 2021: Charge makes the difference
February 2021: Ultrafast in Space and Time
May 2021: Momentum Microscopy at Work
March 2022: Inspired by Nature
July 2022: "Alles im Blick"

4. Other important aspects

Publications in preparation / submitted / accepted.

[1] X. Yang, M. Jugovac, G. Zamborlini, V. Feyer, G. Koller, P. Puschnig, S. Soubatch, M. G. Ramsey, and F. S. Tautz,
"Momentum-selective orbital hybridization", *Nature Communications* (accepted).
[2] P. Hurdax, C. Kern, T. Boné, A. Haags, L. Egger, X. Yang, H. Kirschner, M. Richter, S. Soubatch, G. Koller, F. S. Tautz, M. Sterrer, P. Puschnig, P. and M.G. Ramsey,
"Extreme Distortion of Fused Aromatics on Dielectric Interlayers Quantified by Photoemission Orbital Tomography" (in preparation).
[3] C. S. Kern, M. G. Ramsey, P. Puschnig, A. Haags, X. Yang, F. C. Boquet, S. Soubatch, F. S. Tautz, H. Kirschner, A. Gottwald, M. Richter, U. De Giovannini, A. Rubio, and S. Moser
"The photoemission crossection of graphene's horseshoes: a final word on final states?" (in preparation)
[4] P. Puschnig, D. Brandstetter, L. Egger, G. Koller, M. G. Ramsey, A. Haags, X. Yang, F. C. Bocquet, F. S. Tautz, S. Soubatch, H. Kirschner, A. Gottwald, and M. Richter
"Benchmarking electronic structure methods with photoemission orbital tomography" (in preparation)
[5] C. S. Kern, X. Yang, U. De Giovannini, G. Zamborlini, V. Feyer, M. Ramsey, S. Soubatch, F. S. Tautz, A. Rubio, and P. Puschnig
"Circular dichroism in the photoelectron angular distribution of organic molecules" (in preparation)

Conference participations and a list of the most important lectures

Invited lectures:

- University of Göttingen, Physics Colloqium, 06/2022, P. Puschnig
- Materials Metrology Workshop, Berlin, 12/2019: M. G. Ramsey
- Tübingen University, Germany, 2019: S. Soubatch
- Plenary talk at the Workshop on Molecular Electronics, Institute of Molecular Science, Okazaki, Japan, 2019: S. Soubatch,
- 14th European Conference on Surface Crystallography and Dynamics, virtual event, 2021: F. C. Bocquet,
- TU Dortmund, Physics Colloquium: P. Puschnig
- University of Jena, Physics Colloquium, 11/2018: M. G. Ramsey
- Universität Zürich, Physics Colloquium, 11/2018: P. Puschnig

Contributed lectures:

- Gemeinsame Jahrestagung von ÖPG und SPG, 09/2021 (Innsbruck): C. Kern, M. Schwendt
- 33rd Symposium on Surface Science, 03/2020: P. Hurdax
- Gemeinsame Jahrestagung von ÖPG und SPG, 08/2019 (Zürich): C. Kern

Poster presentations:

- *Workshop on Molecular Electronics, Okazaki, Japan, 2019:* A. Haags
- *Wilhelm und Else Heraeus Workshop "Photoemission tomography:* Applications and Future Developments", Bad-Honnef, Germany, 2021: A. Haags, C. Kern, M. Schwendt, A. Winischbacher, and D. Brandstetter

Organisation of symposia and conferences.
In cooperation with F.S. Tautz and M. Richter, P. Puschnig has organized the WE-Heraeus-Seminar *"Photoemission Tomography: Applications and Future Developments"* from October 24th – 27th, 2021 in bad Honnef, Germany. Due to the COVID-19 pandemic, the seminar was held in hybrid format with 36 participants in presence and 21 joining online. In 19 invited talks and more than 20 poster presentations, the current state of the art in the field and future directions in POT have been discussed by the most important players in the field.

List of the most important pending applications for grants.
Building on the results of the proof-of-principle study on time-resolved momenum mapping of molecular orbitals [Wallauer et al., Science 2021], F. S. Tautz (FZ Jülich), P. Puschnig (KFU Graz), U. Höfer (Univ. Marburg) and R. Huber (Univ. Regensburg) have applied for an ***ERC-synergy grant*** entitled "Photoemission Orbital Cinematography: An ultrafast wave function lab". At the time of writing this report, the funding decision is still pending, noting that our consortium has been invited to the final round of interviews taking place in September 2022.