DOCTORAL PROJECT PROPOSAL
DOCTORAL SCHOOL OF EXACT AND NATURAL SCIENCES AST
NICOLAUS COPERNICUS UNIVERSITY IN TORUŃ
Contest 007, May 2025

<table>
<tr><td colspan="3">Project discipline: chemistry/physics</td></tr>
<tr><td colspan="3">Project title (in English)</td></tr>
<tr><td colspan="3">Rozwikłanie tajemnicy przenoszenia ładunku w związkach o mieszanej wartościowości.</td></tr>
<tr><td colspan="3">Project title (in Polish)</td></tr>
<tr><td colspan="3">Unraveling the charge transfer mystery in mix-valence compounds.</td></tr>
<tr><td colspan="3">Project submitter(s)/Contact person</td></tr>
<tr><td rowspan="2">dr hab Paweł Tecmer, prof. UMK
degree/title, first and last name</td><td colspan="2">ptecmer@fizyka.umk.pl, +48 56 611 2491
e-mail, phone number</td></tr>
<tr><td colspan="2">Institute of Physics, Faculty of Physics, Astronomy and Applied Informatics
organizational unit</td></tr>
<tr><td colspan="3">Suggested supervisors and mentors</td></tr>
<tr><td colspan="3">1) main supervisor*</td></tr>
<tr><td rowspan="3">dr hab Paweł Tecmer, prof. UMK
.....
degree/title, first and last name</td><td colspan="2">ptecmer@fizyka.umk.pl
.....
e-mail, phone number</td></tr>
<tr><td colspan="2">Faculty of Physics, Astronomy and Applied Informatics
.....
organizational unit</td></tr>
<tr><td>field:</td><td>Physics</td></tr>
<tr><td colspan="3">2) co-supervisor*</td></tr>
<tr><td>Dr
degree/title, first and last name</td><td colspan="2">marta.galynska@umk.pl , 883483341
.....
e-mail, phone number</td></tr>
</table>

	Faculty of Chemistry ..... organizational unit	
	field:	Chemistry
3) auxiliary supervisor* A short justification for the need for auxiliary supervisor in this project Due to the primary supervisor's numerous professional commitments and limited availability, the involvement of an auxiliary supervisor is essential to ensure continuous academic support and effective oversight of the project.		
dr Marta Gałyńska ..... degree/title, first and last name	..... e-mail, phone number	
	..... organizational unit	
	field:	Chemistry

*According to the Regulations of the Doctoral School of Nicolaus Copernicus University in Toruń (Resolution No. 30 of 23.04.2024), the scientific supervision of the preparation of the doctoral dissertation is provided **by the supervisor or supervisors** OR **the supervisor and the auxiliary supervisor**.
Meaning, you can provide the data of **a maximum of 2 people**: **2 co-supervisors** OR **the main supervisor and auxiliary supervisor.**

1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Unraveling the charge transfer mystery in mix-valence compounds.

1.1. Project goals

The primary goal of this project is to deepen our understanding of charge transfer mechanisms between donor and acceptor units at the molecular level. Specifically, the project aims to:

1. **Investigate charge migration** in mixed-valence compounds, particularly diamine molecules and their cations, whose conformers exhibit different degrees of charge localization.
2. **Evaluate the performance of quantum chemical methods** in describing the transition between localised and delocalised states of small diamine molecules.
3. **Establish computational protocols** that can be applied to larger, technologically relevant systems, such as photoactive molecules in photovoltaics.
4. **Provide theoretical insights** that complement experimental observations of ultrafast charge transfer processes occurring on the femtosecond timescale (10^{-15} s).

1.2. Outline

Charge transfer is a fundamental chemical process in which an electron or hole moves from a donor site, characterized by excess charge, to an acceptor site, where a charge deficiency exists. This phenomenon plays a critical role in key biological processes that govern life on Earth, such as photosynthesis, and is also essential to various modern technologies, including photovoltaics.

The systems in which charge transfer occurs are often called mixed-valence compounds. These encompass various chemical entities, including organic and inorganic molecules, metal complexes,

and solid-state materials. Studying such systems is vital for advancing our understanding of charge transport mechanisms and improving the design and performance of technologies that rely on these processes.

Quantum chemistry provides a powerful theoretical framework for investigating charge transfer at the molecular level. It enables detailed insight into molecular geometries and precise characterization of electronic structures. This allows for the determination of charge localization—whether it resides predominantly on the donor or acceptor, or is delocalized between the two of them.

This project will apply a range of quantum chemical methods to study potential energy surfaces of small diamine molecules, their excited and cationic states that exhibit different degrees of charge localization. Charge migration within these systems leads to changes in both geometric and electronic structure. The research will focus on characterizing the initial, transition, and final states along the charge transfer pathway in selected diamine cations, with the aim of elucidating the detailed mechanism of charge transfer in these systems.

1.3. Work plan

Comparative Study of Diamine Cations:
Explore the potential energy surfaces of the electronically excited and cationic states of small diamine using different quantum chemistry methods (single- and multi-configurational) to provide a reliable protocol for investigating this kind of system. (24 months)

Extension to Larger Systems:
Apply the established computational protocol developed for the studied diamine cations to a more complex molecular system, such as an organic dye relevant to photovoltaic applications. This step will test the transferability and robustness of the methodology and provide practical insights into real-world charge transfer materials. (24 months)

1.4. Literature *(max. 7 listed, as a suggestion for a PhD candidate preliminary study)*

1. Deb, S., Cheng, X., Weber, P. M. Structural dynamics and charge transfer in electronically excited N,N'-dimethylpiperazine. *J. Phys. Chem. Lett.* **4** (16), 2780–2784 (2013)

2. Cheng, X., Zhang, Y., Jónsson, E. *et al.* Charge localization in a diamine cation provides a test of energy functionals and self-interaction correction. *Nat Commun* **7**, 11013 (2016)

3. Gałyńska, M., Asgeirsson, V., Jonsson, H., Bjornsson R. Localized and delocalized states of a diamine cation: resolution of a controversy. *J. Phys. Chem. Lett.* **12** (4), 1250-1255 (2021)

4. Reimann, M., Kirsch, C., Sebastiani, D. *et al.* Rydberg electron stabilizes the charge localized state of the diamine cation. *Nat Commun* **15**, 293 (2024)

5. Comment on “Localized and Delocalized States of a Diamine Cation: Resolution of a Controversy” Phun, G. S., Wong, B. M. *J. Phys. Chem. Lett.* **15** (45), 11415-11418, (2024)

6. Szczuczko, L., Gałyńska, M., Kriebel, M. H., Tecmer, P., Boguslawski, K. Domain-Based Charge-Transfer Decomposition and Its Application to Explore the Charge-Transfer Character in Prototypical Dyes, *J. Chem. Theory Comput.* (2025)

7. Tecmer, P., Gałyńska, M., Szczuczko, L., Boguslawski, K., Geminal-based strategies for modeling large building blocks of organic electronic materials. *J. Phys. Chem. Lett.* **14** (44), 9909-9917 (2023)

1.5. Required initial knowledge and skills of the PhD candidate

The ideal candidate for this doctoral project should meet the following qualifications:

Foundational Knowledge in Quantum Chemistry:
A basic understanding of quantum chemistry and computational chemistry methods is essential. The candidate should be familiar with concepts such as electronic structure theory, molecular orbitals, and standard approaches to modeling chemical systems.

Proficiency in Unix-Based Systems:
The candidate should be comfortable working in Unix-based environments (e.g., Linux or macOS), including using the command line, managing files, and navigating the terminal. These skills are important for running quantum chemistry software and handling data analysis tasks efficiently.

Strong English Communication Skills:
Written and spoken English proficiency is required for effective communication within the research team and with external collaborators. The candidate should be able to articulate scientific ideas and engage in academic discussions.

1.6. Expected development of the PhD candidate's knowledge and skills

Advanced Competence in Quantum Chemistry:
The candidate will gain hands-on experience in single- and multi-configurational quantum chemical methods used to study complex electronic structures and charge transfer processes.

Computational Proficiency:
The candidate will become proficient in using advanced computational chemistry software packages and high-performance computing environments. They will learn to design, execute, and interpret simulations of chemical systems.

Interdisciplinary Perspective and Application Awareness:
Working at the intersection of theoretical chemistry, materials science, and physical chemistry, the candidate will gain a broader scientific perspective and a deeper understanding of how fundamental research can inform technological applications, particularly in areas like photovoltaics and molecular electronics.

2. INFORMATION ON ACADEMIC ACHIEVEMENTS BY SUGGESTED PROJECT SUPERVISORS (REQUIRED FOR EACH PERSON INVOLVED)

A. Suggested supervisor	Dr hab, Paweł Tecmer ..... degree/title, first and last name
a. Grants obtained in the last 5 years	
1) Towards a reliable and efficient description of electron correlation effects in large molecules: embedding pCCD-type methods, National Science Centre Poland (OPUS), 01.04.2020-31.03.2024, no. 2019/33/B/ST4/02114 2) Development of pCCD-based methods to reliably model electronic structures and properties of building blocks of organic solar cells, National Science Centre Poland (SONATA BIS), 02.11.2022-01.11.2027, no. 2021/42/E/ST4/00302 3) Nowatorskie metody chemii kwantowej do modelowania struktur elektronowych i właściwości organicznych półprzewodników., National Science Centre Poland (Preludium Bis), 01.10.2024-30.09.2027, no. 2023/50/O/ST4/00353.	
b. H-index value	
according to Google Scholar	25
according to Scopus	24
c. Number of quotations	
according to Google Scholar	1960
according to Scopus	1582
d. Value of Field Weighted Citation Impact in the last 5 years (by SciVal database)	0.96
e. List of 4 major academic papers published or accepted for publication in the last 4 years, IFs	
1) K. Boguslawski, A. Leszczyk, A. Nowak, F. Brzęk, P. Sz. Żuchowski, D. Kędziera, and P. Tecmer "Pythonic Black-box Electronic Structure Tool (PyBEST). An open-source Python platform for electronic structure calculations at the interface between chemistry and physics", *Comp. Phys. Comm.*, 264, 107933 (2021) [**IF**: 7.2]	
2) **P. Tecmer**, K. Boguslawski "Geminal-based electronic structure methods in quantum chemistry. Toward a geminal model chemistry.", *Phys. Chem. Chem. Phys.* 24, 23026-23048 (2022) [**IF**: 3.67]	
3) K. Dyall, **P. Tecmer**, and A Sunaga, "Diffuse Basis Functions for Relativistic s and d Block Gaussian Basis Sets", *J. Chem. Theory Comput.*, 19, 198–210 (2023) [**IF**: 6.0]	
4) R. Chakraborty, M. M. F. De Moraes. K. Boguslawski, A. Nowak, J. Świerczyński, and **P. Tecmer,** " Toward Reliable Dipole Moments without Single Excitations: The Role of Orbital Rotations and Dynamical Correlation", *J. Chem. Theory Comput.*, 20, 4689–4702 (2024) [**IF**: 6.0]	
f. List of promoted doctoral candidates: last names, titles of doctoral dissertations, names of universities, year and field of graduation	
Not applicable yet	

g. Information on currently supervised doctoral theses (list of doctoral students, name of the doctoral school, year of education, and topic of the doctoral dissertation, please indicated those on "the fifth year"- extension)

1) Delarm Jahani, 4-year, AC, Orbital energies from pCCD-based methods for OPV materials
2) Rahul Chakrabnorty, 4-year, AST, Embedding pCCD-base methods
3) Zahra Karimi, 2-year, AC, Model Hamiltonians with PyBEST
4) Ram Dhari Pandey, 1-year, AST, charge transfer in organic electronics

h. Description of previous (and potential) scientific cooperation with other academic centers in the last 5 years (max. 1 page)

1) **Wigner Research Centre for Physics, Budapest, Hungary (Prof. Ors Legeza, dr Gergely Barcza)**. The reference calculations will be performed in the Budapest DMRG code developed by Prof. Ors Legeza from the Wigner Research Centre for Physics, Budapest, and his coworkers. Prof. Legeza is an outstanding scientist working across the fields of condensed matter physics, quantum chemistry, and nuclear physics, laureate of the Carl Friedrich von Siemens Research Award of the Alexander von Humboldt Foundation (2018). Prof. Legeza and his research team have already some experience in modeling electronic structures of extended pi-systems using model Hamiltonians and DMRG, small components of organic photovoltaic materials. Thus the Ph. D. student can build upon their knowledge and experience with the parametrization process of model Hamiltonians. In that way, the applicant will get access to the newest version of the DMRG code and easily obtain technical support with convergence difficulties or bug fixes in the code when needed. Up to date, the Budapest DMRG code is one of the most computationally wise efficient DMRG-codes for quantum chemistry and solid-state physics, allowing for efficient and reliable large scale modeling of electronic structures of complex systems. In the past decade, the scientific cooperation with Prof. Legeza was very fruitful and resulted in ten joint high-quality international publications.
2) The methodological progress of the project will be consulted with Prof. Paul A. Johnson from the **University of Laval, Quebec City, Canada**, who has the mathematical background and experience in developing new geminal-based theories. The scientific collaboration of the applicant with Prof. Jonson is documented in several joint peer-reviewed publications. An additional advantage of working with Prof. Johnson is his experience in quantum chemical modeling of novel organic materials.

i. Scientific resume of the supervisor (can be added as a separate file)

A. Suggested supervisor	dr Marta Gałyńska ..... degree/title, first and last name

a. Grants obtained in the last 5 years

1. Rozwikłanie tajemnicy przenoszenia ładunku w związkach o mieszanej wartościowości. National Science Centre Poland (SONATA 19) 2023/51/D/ST4/02796, 1.10.2024 do 30.09.2027
2. Approaching the quantum-chemical limit in cold and ultracold molecules. Ulam NAWA - Seal of Excellence, BPN/SEL/2021/1/00005, 01.10.2022 - 30.09.2024

b. H-index value	
according to Google Scholar	7
according to Scopus	5
c. Number of quotations	
according to Google Scholar	120
according to Scopus	89
d. Value of Field Weighted Citation Impact in the last 5 years (by SciVal database)	0.60
e. List of 4 major academic papers published or accepted for publication in the last 4 years, IFs	
1) **M. Gałyńska**, K. Boguslawski "Benchmarking ionization potentials from pCCD tailored coupled cluster models", *J. Chem. Theory Comput.*, 20 (10), 4182-4195, (2024)	
2) P. Tecmer, **M. Gałyńska**, L. Szczuczko, K. Boguslawski, "Geminal-based strategies for modeling large building blocks of organic electronic materials", *J. Phys. Chem. Lett.,* 14 (44), 9909-9917, (2023)	
3) **M. Gałyńska**, V. Asgeirsson, H. Jonsson, R. Bjornsson, "Localized and delocalized states of a diamine cation: resolution of a controversy", *J. Phys. Chem. Lett.,* 12 (4), 1250-1255, (2021)	
4) L. Szczuczko, **M. Gałyńska**, M.H. Kriebel, P. Tecmer, K. Boguslawski, "Domain-Based Charge-Transfer Decomposition and Its Application to Explore the Charge-Transfer Character in Prototypical Dyes", *J. Chem. Theory Comput.*, (2025) https://doi.org/10.1021/acs.jctc.5c00186	
f. List of promoted doctoral candidates: last names, titles of doctoral dissertations, names of universities, year and field of graduation	
Not yet applicable.	
g. Information on currently supervised doctoral theses (list of doctoral students, name of the doctoral school, year of education, and topic of the doctoral dissertation, please indicated those on "the fifth year"- extension)	
Not yet applicable.	
h. Description of previous (and potential) scientific cooperation with other academic centers in the last 5 years (max. 1 page)	
i. Scientific resume of the supervisor (can be added as a separate file)	

4. DECLARATION OF TECHNICAL/EXPERIMENTAL/FINANCIAL RESOURCES SUFFICIENT AND NECESSARY TO COMPLETE THE PROJECT

I declare that I am able to provide the technical/equipmental support and financial resources necessary to carry out this doctoral project.

Toruń, 09.05.2025 — Paweł Tecmer

place, date — signature of project submitter

I declare that I HAVE/DO NOT HAVE financial resources for a doctoral scholarship as part of a project from external sources:……

project name/souces name

Toruń, 09.05.2025 — Paweł Tecmer

place, date — signature of project submitter

5. DECLARATION CONCERNING THE AUTHORSHP OF PROJECT IDEA

I declare that the author of the idea for the doctoral project is:

Toruń, 09.05.2025 — Paweł Tecmer

place, date — signature of project submitter

6. DECLARATION CONCERNING CONSENT TO TRANSFER OF PROJECT SUPERVISION IF NEEDED

I declare that should the PhD candidate be accepted to the Doctoral School of Exact and Natural Sciences and started the project but for some reasons a change of the supervisor is necessary, **I AGREE** to transfer the substantive supervision of the project to another person designated by the Director of the Doctoral School of Exact and Natural Sciences of the Nicolaus Copernicus University in Toruń.

Toruń, 09.05.2025 — Paweł Tecmer

place, date — signature of project submitter

7. DECLARATION CONCERNING THE POSSIBILITY OF PUBLISHING THE CONTENT OF THE PROJECT

I declare that the description of the project submitted to the contest from point 1 and basic scientific CV of a prospective supervisor, can be published on the website of Doctoral School of Exact and Natural Sciences, Nicolaus Copernicus University in Toruń.

Toruń, 09.05.2025 — Paweł Tecmer

place, date — signature of project submitter