

Report on the TTU/SPRINT-FAPESP project

High-level Quantum Chemical Investigations of Defect Structures in Model Graphene Systems

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Project start: September 1, 2015

Project end: August 31, 2017

Graphene and related polyaromatic hydrocarbon sheets constitute promising materials for applications in sensors, photovoltaics, optoelectronics and spintronics. Graphene band gap engineering based on chemi- and physisorption processes and development of low-bandgap π -conjugated compounds stand in the forefront of current material research. Defect structures and di- and polyradicals play an increasingly important role for the design of advanced materials. The goal of the present project was to perform theoretical calculations in order to provide insight into the electronic structure of afore-mentioned defects and show the possibilities of stabilizing the high chemical reactivity of the polyradical systems so that they can be used in practical applications.

It is planned to submit a joint research proposal to FAPESP/NSF as soon as there is a respective call open.

The collaboration proceeded in the form of several exchange visits of the PI and of project participants.

Exchange visits:

Francisco B. C. Machado to Texas Tech University (TTU): February 21 – March 04, 2016 and August 31 – September 09, 2016

Hans Lischka to Instituto Tecnológico de Aeronáutica (ITA): April 22-24, 2015, August 12-19, 2016

Adelia Aquino to ITA: August 12-19, 2016

Publications:

- N. J. Silva, F. B. C. Machado, H. Lischka, A. J. A. Aquino, π - π Stacking between Polyaromatic Hydrocarbon Sheets beyond Dispersion Interactions, *PhysChemChemPhys* **18** (2016) 22300-22310
- R. Nieman, A. Das, A. A. J. Aquino, R. G. Amorim, F. B. C. Machado, H. Lischka, Single and Double Carbon Vacancies in Pyrene as First Models for Graphene Defects: A Survey of the Chemical Reactivity toward Hydrogen, *Chem. Phys.* **482** (2017) 346-354
- M. Pinheiro Jr., L. F. A. Ferrão, F. Bettanin, A. J. A. Aquino, F. B. C. Machado, H. Lischka, How to tune efficiently the biradicaloid nature of acenes by chemical doping with boron and nitrogen, *PhysChemChemPhys* **19** (2017) 19225-19233
- A. D. Powell, N. S. Dattani, R. F. K. Spada, F. B. C. Machado, H. Lischka, R. Dawes, Investigation of the ozone formation reaction pathway: Comparisons of Full Configuration

Interaction Quantum Monte Carlo and Fixed-Node Diffusion Monte Carlo with contracted and uncontracted MRCI, *J. Chem. Phys.* **147**, (2017) 094306

- F. Bettanin, L. F. A. Ferrão, M. Pinheiro Jr, A. J. A. Aquino, H. Lischka, F. B. C. Machado, D. Nachtigalova, The singlet L_a and L_b bands for N-acenes ($N = 2$ to 7): An CASSCF/CASPT2 study, *J. Chem. Theory Comput.*, **13** (2017). 13, 4297–4306

Publication in preparation:

- D. V. V. Cardoso, M. Pinheiro Jr, A. J. A. Aquino, F. B. C. Machado, H. Lischka, The Characterization of Electronic Defect States of Single and Double Carbon Vacancies in Graphene Sheets Using Molecular Density Functional Theory
- R. G. Amorim, R. Nieman, A. Das, A. A. J. Aquino, F. B. C. Machado H. Lischka, Graphene reactivity investigation using pyrene and extended pyrene model
- A. Das, M. Pinheiro Jr., F. B. C. Machado, A. J. A. Aquino, H. Lischka, Efficient Modulation of the Singlet Open Shell Character of Heptazethrene by Nitrogen Doping
- M. Pinheiro Jr, A. Das, A. J. A. Aquino, F. B. C. Machado, H. Lischka, The Variation of Singlet Polyradical Character in Polyacenes Induced by Nitrogen Doping Revealed by means of Singlet/Triplet Splittings

Presentations:

Hans Lischka

- “The Polyradical Character in Polyaromatic Hydrocarbons: The Electronic Structure of Zethrenes and Chemical Reactivity of Single and Double Vacancies in Graphene Models”, Argonne National Laboratory, Argonne, Ill, USA, February 18, 2016
- “The Polyradical Character in Polyaromatic Hydrocarbons: The Electronic Structure of Zethrenes and Chemical Reactivity of Single and Double Vacancies in Graphene Models”, Northwestern University, Evanston, Ill, USA, February 19, 2016
- “Chemical Reactivity of Single- and Double Vacancies Toward CH Bond Formation in Graphene Models: A Quantum Chemical Study”, 26th Austin Symposium on Molecular Structure and Dynamics in Dallas (ASMD@D), Dallas, TX, USA, March 3, 2016
- “Excitonic Coupling and Charge Transfer in Organic Semiconductor Polymers: Ab Initio and Density Functional Calculations”, Workshop on Excited-State Electronic Structures and Dynamics, Beijing Normal University, Beijing, China, May 18, 2016
- “The Polyradical Character of Kekulé and non-Kekulé Structures of Polyaromatic Hydrocarbons Localized Orbitals in MRCI calculations”, International Society of Theoretical Chemical Physics (ISTCP) 2016, Grand Forks, USA, July 19, 2016
- “Material Science Combined with Quantum Chemistry: Modeling Defects in Graphene”, FAPESP-TTU Scientific Collaboration: STEM Across Continents Program, Texas Tech University, Lubbock, TX, USA, August 31, 2016
- “Unpaired densities in singlet polyradicals: Local electron correlation treatment in extended multireference approaches in comparison with quasi correlated tight binding”, Invited talk, 253rd ACS National Meeting in San Francisco, California, USA, April 4, 2017
- “Polyradicaloid Character in Polycyclic Aromatic Hydrocarbons: How to Characterize and How to Tune it”, Invited talk, Institute of Chemistry & BioMedical Sciences, University of Nanjing, Nanjing, China, June 6, 2017

- “Polyradicaloid Character in Polycyclic Aromatic Hydrocarbons and Defect Structures in Graphene Nanoflakes”, Invited talk, School of Chemistry and Chemical Engineering, Anhui University, Hefei, China, June 9, 2017

Adelia Aquino

- “A Computational Study of π - π Stacking Interactions Using High-Level Ab Initio and Density Functional Methods”, Argonne National Laboratory, Argonne, Ill, USA, February 18, 2016
- “A Computational Study of π - π Stacking Interactions Using High-Level Ab Initio and Density Functional Methods”, 26th Austin Symposium on Molecular Structure and Dynamics in Dallas (ASMD@D), Dallas, TX, USA, March 5, 2016
- “A Computational Study of π - π Stacking Interactions Using High-Level Ab Initio and Density Functional Methods”, Texas Tech University, Feb 26, 2016
- “The Importance of International Education”, International Program in Foz do Iguacu, PR, Brazil, August 20-23, 2016

F.B.C. Machado

- “Electronic States Generated by Single and Double Carbon Defects in Pyrene, Extended Pyrene and 7a,7z-Periacene as a Model for Graphene Sheet”, XVIII Simpósio Brasileiro de Química Teórica, Pirenópolis, GO, Brazil, November 22-25, 2015.
- “Single and Double Vacancies in Graphene Models: Electronic States and Reactivity”, 21st International Workshop on Quantum Systems in Chemistry, Physics, and Biology (QSCP-XXI), Vancouver, Canada, July 2-8, 2016.

Workshop/School:

“3a Escola de Química Computacional – Theory of new materials at atomistic level: Graphene, Graphene Defects and π -Conjugated Polyradical Systems”, Hans Lischka, Rodrigo Amorim, Francisco B. C. Machado (scientific coordinators), Nelson H. Morgon, Ricardo Vessecchi, (coordinators), Sergio E. Galembeck (general coordinator), Ribeirao Preto, Brazil, December 11 – 14, 2017, project accepted by the University of Sao Paulo and by FAPESP