

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

Project title: Structure of the simplest molecular complexes – accurate quantum mechanical calculations at the frontier of molecular physics and chemistry

1.1. Project goals

- **Understanding the structure of molecular complexes from first principles.**
- **Providing accurate theoretical data to support the interpretation of spectroscopic experiments.**
- **Determination of the positions and, for the first time, intensities of the spectral transitions in weakly bound molecular complexes using a fully quantum approach.**

1.2. Outline

The study of weakly bound molecular complexes, such as hydrogen dimers ($\text{H}_2\text{--H}_2$) and hydrogen-noble gas complexes, addresses fundamental questions at the intersection of molecular physics, chemistry and astrophysics. Due to their inherent simplicity, the energy structures and spectroscopic properties of these weakly bound van der Waals systems can be accurately predicted from first principles [1]. The spectra arising from transitions between bound and quasi-bound states serve as sensitive probes of anisotropic intermolecular interactions [2], and have even been observed in the atmospheres of giant planets within the Solar System, providing critical information about atmospheric composition and physical conditions [3].

Much of the knowledge about the $\text{H}_2\text{--H}_2$ and $\text{H}_2\text{--noble gas}$ complexes stems from pioneering experiments conducted in the early 1990s [4]. Recent advances in experimental spectroscopic techniques have, however, revitalized the field, notably with the recent detection of hydrogen dimer features at room temperature [5]. Our group has also developed a new ultra-sensitive cryogenic experimental setup operating down to 5 K [6], which, with sensitivity surpassing previous setups, promises not only dramatic improvement in accuracy of experimental measurements of transition frequencies, but also for the first time accurate measurements of the line intensities in these weakly bound van der Waals complexes.

Simultaneously, progress in quantum chemistry has led to improved potential energy and dipole moment surfaces that account explicitly for monomer bond stretching [7], which is crucial for a proper interpretation of the dimer spectra. These advancements provide a unique opportunity to rigorously test state-of-the-art quantum chemical calculation against experimental spectra of weakly bound van der Waals complexes.

This project will focus exclusively on the simplest benchmark systems, $\text{H}_2\text{--H}_2$ and $\text{H}_2\text{--noble gas}$ complexes (e.g. $\text{H}_2\text{--He}$), to further develop, validate, and apply quantum theory to describe the energy levels and spectral line intensities, entirely from first principles. Comparing these theoretical results with new experimental data will allow for

a stringent test of quantum chemical methods, enhance understanding of the intermolecular interaction anisotropy, and lay the foundation for studies of increasingly complex van der Waals systems.

1.3. Work plan

- *Literature review and familiarization with state-of-the-art theoretical methods for describing the structure of weakly-bound complexes.*
- *Derivation of equations governing the rovibrational energy structure of weakly-bound complexes.*
- *Derivation of expressions for line intensities of transitions between bound and quasi-bound states in weakly-bound molecular complexes.*
- *Derivation of population distributions of rovibrational states in thermal equilibrium.*
- *Expansion of the potential energy surface and preparation for bound-state calculations.*
- *Numerical calculations of bound-state energies through solving coupled-channel equations in molecule-molecule and molecule-atom systems.*
- *Expansion of the dipole moment surface which determines line intensities of spectral transitions within weakly bound complexes.*
- *Numerical calculation of spectral line intensities using computed wavefunctions and transition dipole moment surface.*
- *Interpretation of the results and comparison with the available experimental data for validation.*

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

- [1] J. Schaefer, A. R. W. McKellar, Z. Phys. D 15, 51-65 (1990)
- [2] A. van der Avoird, P. E. S. Wormer, R. Moszyński, Chem. Rev. 94, 1931-1974 (1994)
- [3] R. Hanel et al., Science 204, 972 (1979).
- [4] A. R. W. McKellar, J. Chem. Phys. 92, 3261 (1990), 95, 3081 (1991)
- [5] H. Fleurbaey, S. Kassi, A. Campargue, Phys. Chem. Chem. Phys. 26, 21974 (2024)
- [6] K. Stankiewicz et al., arXiv:2502.12703
- [7] H. Jóźwiak et al., A&A 687, A69 (2024).

1.5. Required initial knowledge and skills of the PhD candidate

Skills and experience in theoretical physics. Good knowledge of FOTRAN or C (also Matlab and Python). Excellent problem-solving and communication skills. Written and verbal communication skills and presentation skills. Teamwork ability. Good command of the English language.

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

Knowledge, skills and experience in molecular physics, computer coding and numerical methods. Knowledge of molecular physics theory, molecular interactions and molecular spectroscopy.