PHD PROJECT DESCRIPTION
(4000 characters max., including the aims and work plan to de published online)

Project title: Non-Born–Oppenheimer Calculations of Fine and Hyperfine Structure in Atomic and Molecular Systems Using NEO-Based Methods

1.1. Project goals

The main goal of the PhD project is the development and implementation of computational methods for calculations of fine structure (FS) and hyperfine structure (HFS) in atomic and molecular systems within the non-Born–Oppenheimer (non-BO) framework. The work will focus particularly on nuclear-electronic orbital (NEO) approaches and hybrid NEO–explicitly correlated Gaussian (ECG) methods.

The project aims to construct and test computational schemes in which electrons and selected nuclei are treated quantum mechanically on equal footing. Particular attention will be devoted to the implementation of relativistic and spin-dependent operators, including spin–orbit, spin–spin, and hyperfine interactions, within internal-coordinate non-BO formulations.

The PhD student will participate in benchmark calculations for selected small atoms and molecules and in exploratory studies of larger systems that are difficult to treat using fully correlated ECG approaches. An important objective will be the comparison of BO-based and non-BO descriptions and the analysis of nonadiabatic effects in spin-dependent spectroscopy.

1.2. Outline

Precision spectroscopy of atoms and molecules requires theoretical methods capable of describing relativistic, nonadiabatic, and spin-dependent effects with high accuracy. While many existing calculations rely on the Born–Oppenheimer approximation, the non-BO framework allows direct inclusion of electron–nuclear coupling already at the wave-function level.

The project concerns the development of computational tools for FS/HFS calculations using orbital-based multicomponent approaches, especially the NEO method. The work will involve derivation and implementation of matrix elements of spin-dependent operators, development of numerical procedures, and testing of computational stability and convergence.

The project is connected with ongoing research on high-accuracy non-BO calculations carried out in the research group of the PI. However, the PhD work will focus mainly on the development and application of NEO-based approaches for systems beyond the practical limits of fully correlated ECG calculations.

The obtained methods will be tested on selected benchmark systems and used to analyze the role of relativistic, hyperfine, and nonadiabatic effects in atomic and molecular spectra.

1.3. Work plan

Year 1

study of theoretical foundations of quantum mechanics, angular momentum theory, and non-BO methods,
introduction to NEO methodology and multicomponent quantum chemistry,
learning numerical and computational techniques used in the group,
implementation of selected basic operator matrix elements.

Year 2

implementation of FS and HFS operators within the NEO framework,
development and testing of computational routines,
validation of the implemented methods using benchmark systems,
participation in calculations for selected atoms and diatomic molecules.

Year 3

extension of calculations to more complex systems,
analysis of nonadiabatic and relativistic contributions,
comparison of BO and non-BO results,
preparation of scientific publications and conference presentations.

Year 4

final calculations and optimization of computational procedures,
interpretation of obtained results,
completion of publications,
preparation and defense of the doctoral dissertation.

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

K. Varga and Y. Suzuki, *Stochastic Variational Approach to Quantum-Mechanical Few-Body Problems*, Springer (1998).
- S. Bubin et al., “Born–Oppenheimer and non-Born–Oppenheimer molecular quantum mechanics with explicitly correlated Gaussian functions,” Chemical Reviews 113, 36 (2013).
- J. Mitroy et al., “Theory and application of explicitly correlated Gaussians,” Reviews of Modern Physics 85, 693 (2013).
- M. Tachikawa and H. Nakai, “A multicomponent molecular orbital theory for electrons and nuclei,” Chemical Physics Letters 290, 437 (1998).
- T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory*, Wiley (2000).
- K. Pachucki, *Theory of the Lamb Shift in Hydrogen and Light Hydrogen-Like Ions*, Springer (2017).
- M. Stanke et al., “Non-Born–Oppenheimer calculations of fine structure in atomic systems,” selected recent papers of the research group.

1.5. Required initial knowledge and skills of the PhD candidate

good knowledge of quantum mechanics and mathematical physics,

- basic knowledge of atomic or molecular physics,
- familiarity with linear algebra and numerical methods,
- programming skills (preferably Fortran, C/C++, or Python),
- ability to read scientific literature in English,
- motivation for theoretical and computational research.

Experience in scientific computing or quantum chemistry will be an additional advantage but is not strictly required.

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

During the PhD project, the candidate will gain advanced knowledge in:

- non-Born–Oppenheimer quantum mechanics,
- relativistic and hyperfine interactions in atoms and molecules,
- multicomponent and NEO-based quantum chemistry methods,
- numerical methods and scientific programming,
- development and validation of computational physics codes,
- analysis and interpretation of spectroscopic data.

The candidate is expected to acquire experience in scientific publishing, conference presentations, and international research collaboration. The project will prepare the student for independent research work in theoretical physics, computational chemistry, and precision spectroscopy.