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

**Project title: The Fine and Hyperfine Structure in Molecules – Calculations in the Explicitly Correlated Gaussian Functions**

**1.1.** **Project goals:** The aim of the project is the development and computational implementation of methods for very accurate calculations of fine and hyperfine splittings in the spectra of diatomic molecules. In the approach, we will not assume the Born-Oppenheimer approximation, i.e. we will treat all particles forming the molecule (the nuclei and electrons) on a equal footing. In the calculations we will employ all-particle explicitly correlated Gaussian functions (ECGs) to expand the wave function of the system. As these functions explicitly depend on the interparticle distances, they very effectively describe the inter-particle correlation effects. These effects include the electron-electron correlation, as well as the nucleus-nucleus correlation and the nucleus-electron correlation. The calculation of the fine and hyperfine interactions will be carried out using the perturbation-theory approach.

**1.2.** **Outline:**Calculations in the bases of explicitly correlated Gaussian functions allow to obtain accurate values of the non-relativistic energy of the atomic system, taking full account of the effects of electronic correlation. Currently, this is achievable for several-electron systems. These calculations can be performed by treating atomic nuclei as quantum particles, i.e. going beyond the Born-Oppenheimer approximation. The very accurate functions describing molecular states obtained in this way allow for the determination of precise energy corrections representing relativistic and QED effects. A special class of relativistic corrections is associated with operators dependent on the electron spin and/or nuclear spin, which generally lead to the splitting of molecular states. Magnetic interactions between spin-orbit and spin-spin electrons cause the so-called fine structure, while magnetic interactions between the nucleus and electrons lead to the hyperfine structure.

**1.3.** **Work plan:** Derivation of matrix elements for operators representing relativistic first-order corrections to energy in molecules leading to fine and hyperfine structure. Implementation

of these expressions as a module into an existing Fortran program. Performing test calculations. Performing calculations for selected several-electron molecules. Writing a doctoral thesis.

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

*Angular Momentum Theory for Diatomic Molecules, BRIAN R. JUDD (1975),*
*Operator Techniques in Atomic Spectroscopy, BRIAN R. JUDD (1998),*
*Rotational Spectroscopy of Diatomic Molecules, John Brown, Alan Carrington (2003)*

**1.5.** **Required initial knowledge and skills of the PhD candidate:** Knowledge of quantum mechanics and programming. Knowledge of Racah algebra preferred.

**1.6.** **Expected development of the PhD candidate's knowledge and skills:**acquiring extended knowledge in the field of quantum mechanics and relativistic quantum mechanics. Efficient use of tensor operator algebra. Development of programming methods, mainly in Fortran