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

Project title: The quantum chemistry methods in spatial confinement regime.

1.1. Project goals

One of the most crucial points when analyzing quantum confined systems is the choice of accurate model and quantum chemical method which allow to describe correctly the changes in the electronic wavefunction due to the effect of confinement. In recent years in most studies, the electronic wavefunction of the system subjected to confinement was span by a set of Gaussian-type orbitals (GTO) belonging to the most widely utilized basis sets in the quantum chemical codes. This allows to study systems in soft confinement regimes by various wave function theory (WFT) and density functional theory (DFT) methods. The spatial electron confinement, in turn, is usually modeled by isotropic 3D, 2D, or 1D harmonic oscillator potential (with small oscillatory strength parameter ω) introduced to N-electron Hamiltonian. However, for larger values of confinement strength (strong quasi-1D/2D regime) or when harmonic potential becomes anisotropic, the common strategy is to supply standard GTOs with, specially designed anisotropic GTOs in order to guarantee that the wavefunction spans both Culombic and harmonic oscillator eigenstates. We note that these basis sets are not implemented in any of the popular codes, thus not allowing to routinely study of systems under various confinement with standard WFT and DFT methods. The first goal of the project is to implement the anisotropic GTOs in libint library what will allow their general utilization in novel quantum chemistry codes such as PSI4. Using accurate WFT methods (e.g. the coupled-cluster methods) we will create a database of confined chemical systems, which will be used to assess and improve the performance, and develop new, advanced DFT methods describing correctly the crossovers from 3D to 2D and 1D (second goal).

1.2. Outline

The quantum confinement substantially alters the electronic structure of quantum systems (e.g. atom, molecules, and solids) as compared to their corresponding free state counterparts. This is exhibited in the changes in electronic energy levels, electronic shell filling, orbitals what, in consequence, affect their physical as well as chemical properties such as energetics, reactivity, response properties, etc. Therefore, the chemistry of confinement systems may drastically change. In recent years interest, both physicists and chemists in the study of the physical properties of confined quantum systems have increased with advances experimental techniques which allow to study e.g. atoms or molecules encapsulated in cages like fullerenes, nanotubes or zeolites, atoms, and molecules under pressure or quantum dots or simple molecules in quasi-2D or 2D regimes. The reduction of spatial dimensionality from three dimensions (3D) to 2D and 1D has been often used as an efficient strategy to promote the occurrence of new phenomena. Despite the large scientific effort on this topic, most of the studies and practically all applications have concerned confined extended systems, even if the practical realization of electronic confinement in chemical applications can also be achieved. The study of chemistry under electronic confinement is a challenging topic because the dimensional crossovers (from 3D to 2D and 1D) are one of the most difficult theoretical and computational problems.

1.3. Work plan

- Design and development of new methods and theoretical mathematical and numerical tools for quasi-1D/2D systems
- Numerical implementation of developed methods.

- Performing test calculations for small and medium-sized atomic and molecular systems.
- Study of quantum chemistry in 2 dimensions

1.4. Literature

[1] W. Jaskólski, Phys. Rep 271, 1 (1996).
[2] H. Moritz and et al., Phys. Rev. Lett. 94, 210401 (2005).
[3] A. T. Sommer and et al., Phys. Rev. Lett. 108, 045302 (2012).
[4] P.-F. Loos and et al., Phys. Chem. Chem. Phys. 17, 3196 (2015).

1.5. Required initial knowledge and skills of the PhD candidate

- Basic knowledge about quantum mechanics and quantum chemistry
- Basic knowledge about quantum chemical methods at the level of exchange and correlation effects
- Basic knowledge about Density Functional Theory and Wave Function Theory methods
- Programming skills (e.g.,FORTRAN, C, Python)
- Basis and/or advanced numerical methods knowledge
- Involvement in scientific work
- Good knowledge of written and spoken English

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

- Deep knowledge and understanding quantum-chemical methods ranging from DFT methods up to *ab initio* HF, Coupled Cluster, Perturbation Theory
- Acquiring extensive knowledge of description of many-electron systems including electron correlation effects
- Efficient programming at the advanced level, making parallel code, running quantum chemical calculations
- Ability to analyze the results and to draw conclusions
- General knowledge about calculating different properties of many electron system
- Ability to prepare, present and defend own scientific hypotheses and theses