Abstract/Objectives:

We advance audacious revisiting of backgrounds of computational chemistry, by key revisions of basis set conceptual and technical aspects and innovative contributions to the Density Functional Theory (DFT).

The Gaussian Type Orbitals (GTOs) were drawn at dawn of computational chemistry as replacement of Slater type functions. Initial compromises done in this view became, in meanwhile, hidden and overlooked, since the intense routine with GTOs seemed to act are quality warrantor. However, the drawbacks and limitations of GTOs are serious, denounced in actual project, altogether with a plan of rationales to cure the situation. A major issue is the tacit limitation of radial factors to r^l powers related with the l secondary quantum number of a given shell, impeding the account of radial profile at superior orbital levels. A good part of the rich bases are unnecessarily oversized patches to these limitations, while introducing the higher radial monomial factors is a better alternative. We also devised a strategy to tailor basis sets by equating the spectral terms with the help of Slater-Condon integrals, done by radial-angular factorization (a regularity obscured in GTO practice).

In DFT, we point the inconsistencies emerging from Local Density Approximation (LDA), assuming spherical symmetry of exchange hole, valid for homogenous electron gas, but offending the symmetry in atoms, when placed in general acentric position. The gradient corrected methods are only partly alleviating the effect. We propose a new principle, imposing, for atoms, exchange-correlation hole devised as spherical crust with sharp cusp profile. Conceiving the atomic body energy as continuous function of shell populations, we draw unprecedented strategies to asses DFT-alike energy derivatives based on experimental spectroscopy or multi-configuration calculations. The principle leads to a new generation of Density Functional Tight Binding (DFTB) approximate methods, best suited for nanoscale system.

Objectives

The project revisits and revises fundamental parts of the computational chemistry, consisting in two branches, dedicated to basis sets (ascribed in text as D.2.1.1-D.2.1.5) and density functionals, also formulated as functions of electronic charge and populations (Obj. D.2.2.1-D.2.2.4).

The envisaged goals are:

-Critical evidence of the flaws of Gaussian bases in use. The problem does not stay in exponential part, but merely in the limitation of the radial factors to the r^l powers, where l is the shell secondary quantum number, being demanded a larger range of r^k terms (at least k=0…l).

-Conceiving the algorithms and writing the codes (in various programming languages) for producing new Gaussian and Slater type basis sets. Initial will approach the case of hydrogen type atoms, treating then, successively, other series from periodic table.

-In the frame of Density Functional Theory (DFT) we try to eliminate the dependence on the local density approximation, unsuited for atomic case, proposing a spherical crust

shape of the Fermi hole. We will elaborate the new theory, implement the codes and test the results.

-Elaborating and testing a semiempirical DFT version where the density dependence is simplified to functions of charge and populations, on the shells of the atoms in molecules.

The results will consist in computer codes, ISI articles and participation to scientific manifestations.

Objectives for 2017

Critical verification of the current used basis sets.

Testing the limits of Density Functional Theory (DFT) methods.

Act 1.1 – Stating the problems existing with the currently used bases. Testing the spectral

performances of the Gaussian bases for the hydrogen atom.

Act 1.2 – Verifying the performances of existing bases and the DFT limits for the metal ions d and f. Non-standard calculations for Ligand

- Field and exchange interactions by CAS and DFT methods d-f systems. Correlations with Slater-Condon parameters.

-1 ISI article

- Participation to conferences.

Objectives for 2018

Act.2.1 – Conceiving and writing the algorithms for the treatment of many-electrons atom in the wave-function and density functional theories. (Obj. D.2.1.1 and D.2.1.2)

Act.2.1 – Optimizing new Gaussian-type basis sets for the series of first light atoms. (Obj. D.2.1.2)

Act.2.2 – Optimizing new Slater-type basis sets for the series of first light atoms. (Obj. D.2.1.3) Relationships with numeric basis sets. (Obj. D.2.1.5)

Act.2.3 – Realizing correlations between basis sets and the Slater-Condon parameters. (Obj. D.2.1.4)

Act.2.4 – Adjusting basis sets for the d and f elements by optimization to experimental atomic spectra and Slater-Condon parameters. (Obj. D.2.1.4)

Act.2.5 – Correlations between computed and experimental structural data. (molecular geometry, spectra, magnetism). (Obj. D.2.1.4)

-1 ISI article.

- Book chapter published in an international publishing house.

-Participation to conferences.

Objectives for 2019.

Act 3.1 – Elaboration the theory of a new density functional type, relating to the spherical symmetry of the atom. (Obj. D.2.2.1).

Act 3.2 – Elaboration the codes for the atom treatment with the new forms of the density functional in basic sets of Gaussian, Slater or numerical type for extended series of atoms. (Obj. D.2.2.2)

Act 3.3 – Implementation of new types of density functional in the routines of an open source code. (Obj. D.2.2.1 - D.2.2.2)

Act 3.4 – Correlation between calculated and experimental structural data (molecular geometry, magnetism spectra). Relation with the Slater-Condon parameters. (Obj. D.2.2.3)

Act 3.5 – Elaboration the theory of semiempirical versions of DFT, based on the atomic energies (ionizations and populations). (Obj. D.2.2.4)

Act 3.6 – Parameterization of semiempirical DFT theory with atomic spectroscopy data, experimental and calculated. (Obj. D.2.2.4 - D.2.2.5)

Act 3.7 – Implementation of the new basic sets types in the routines of an open-source code. (Obj. D.2.1.2)

-3 ISI articles

- Participation to conferences.