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

Project title: Advancement of unconventional electronic structure methods in the search of efficient organic photovoltaic solar cells

1.1. Project goals

The ultimate goal of the proposed research project is the large scale modeling of electronic structures and properties of small building blocks of organic photovoltaic materials using unconventional electronic structure methods and model hamiltonians. This goal will be achieved by employing unconventional electronic structure methods such as the Density Matrix Renormalization Group (DMRG) algorithm and the Antisymmetric Product of 1-reference orbital Geminal (AP1roG), also known as the pair Coupled-Cluster Doubles (pCCD), and its extensions. The advantage of these approaches over the standard quantum chemistry methods is their ability to reliably account for strong electron correlation effects even in large molecular systems. This is particularly beneficial for the description of electronic structures of many OPVs building blocks, where the multi-reference or biradial nature, limits the applicability of standard electronic structure methods such as Density Functional Theory.

1.2. Outline

One of the limiting factors of large scale quantum-chemical modeling with DMRG is the need to optimize the orbital basis, that is, the DMRG self-consistent field (DMRG-SCF) procedure. Since the rotation of the orbital basis requires a four-index transformation upon each SCF step, the total time for DMRG calculations increases considerably. To avoid the costly step of orbital rotations within the DMRG algorithm, alternative molecular orbital bases will be examined. Only after having found an optimal orbital set for DMRG-(F)CI calculations, that is, the one that yields the DMRG energy closest to DMRG-SCF, and features a rapid convergence in micro-iterations and with respect to the number of renormalized block states, this method will be fully applicable to the modeling of the large OPV building blocks. Furthermore, the Extended Koopmans' theorem will be applied on top of the DMRG-(F)CI and AP1roG-based methods to obtain valence orbital energies. The results of quantum chemical studies with DMRG and AP1roG-based methods of large OPV building blocks will serve as a database for parametrizing the model Hubbard and the Pariser-Parr Pople (PPP) Hamiltonians. Finally, these newly parametrized Hamiltonians will be employed to investigate electronic structures and properties of modern OPV materials, which size prohibits the use of fully ab initio quantum chemical Hamiltonians.

1.3. Work plan

-literature study of modern OPV structures and properties and data collection
-choice of optimal orbitals for DMRG
-quantum chemical modeling of electronic structures and properties of small components of OPV materials
-generation of reference data for small building blocks of OPVs
-creation of unique data set of electronic structures and properties of OPV components
-parametrization and testing of model Hamiltonians in the PyBEST software package
-large scale modeling of OPVs electronic structures and properties with model Hamiltonians.

1.4. Literature

1.5.

-Risko, C, McGehee, M. D., Brédas, J.-L. Chem. Sci., 2, 1200–1218 (2011)

-K. Boguslawski, A. Leszczyk, A. Nowak, F. Brzęk, P. Sz. Żuchowski, D. Kędziera, and P. Tecmer Pythonic Black-box Electronic Structure Tool (PyBEST). An open-source Python platform for electronic structure calculations at the interface between chemistry and physics, Comp. Phys. Comm., 264, 107933 (2021)

-Boguslawski K., Tecmer P., Ayers P.W., Bultinck P., De Baerdemacker S., Van Neck D. Phys.Rev. B 2014, 89, 201106(R)

1.6. Required initial knowledge and skills of the PhD candidate:

-enthusiasm for science and commitment to hard work
-analytical thinking
-good knowledge of English
-basic knowledge of quantum physics and/or chemistry
-basic knowledge of Linux/Unix, computer clusters, modern programming languages (such as Python and C++)

1.7. Expected development of the PhD candidate's knowledge and skill

-scientific independence
-high-quality programming skills
-version control (git) and continuous integration (gitlab)
-expert knowledge on the electronic structure methods
-state-of-the-art computational modeling of electronic structures of organic photovoltaic materials and their properties
-co-authorship in the PyBEST software package
-improved soft and hard skills (presentations, reports, communications, working in the group)
-experience in writing grant applications
- good quality scientific papers, where the Ph.D. student is the first (or leading) author