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

Project title: Efficient calculations of intrinsic properties of molecular systems.

1.1. Project goals: The ionization potential (IP) of molecules is a fundamental quantity in contexts such as charge transfer and transport processes, photo-electron spectroscopy, and especially molecular electronics, where, together with electron attachment (EA) and excitation energies (EE) attracts great interest in applied and theoretical research. The ability to accurately predict (with the accuracy in the range of 0.1–0.3 eV) of these intrinsic parameters has become of key importance in the context of new developments in these fields. To date, many useful approaches have been established allowing to calculation EEs, Eas, IPs with various accuracy and cost. Unfortunately, the size of the molecules used limits the application of first-principle ab initio methods in modeling such structures. The utilization of state-of-the-art IP/EA/EE equation-of-motion coupled-cluster(IP/EA/EE-EOM-CC) or electron propagator (EP) [3] theory methods (providing high accuracy results) becomes especially difficult, particularly when one needs to perform calculations in larger basis sets. Thus, the development of affordable and at the same time accurate methods for calculating IP/EA/EE is still an important topic of research. Recently, we have proposed [1,4] extremely simple, practical, reliable, and computationally not expensive (scaling as $O(N^3)$ in post-Hartree–Fock step, where N is the system size) methods denoted as ΔMP2-SCS(IP) and ΔMP2-SOS(IP) for the calculation of vertical ionization potentials (VIP). The comprehensive assessment of the ΔMP2-SCS methods (performed for a large set of small and medium-size molecules, DNA/RNA bases, donor and acceptor organic molecular systems) has revealed that both methods are able to provide IPs comparable in accuracy with state-of-art EP approaches such as OVGF, P3+ or CEP methods with substantially lower computational cost ($O(N^3)$), also outperforming the standard DFT methods. The goal of this project is twofold: 1) develop modified ΔMP2 and EP2 methods for treatment IP, EA and EE energies [2]; 2) the ΔMP2-SCS methods provide results that differ from the reference data i.e. the IP-EOM-CCSD and experimental ones of only 0.1–0.2 eV. However, there is still room for improvement e.g. by utilizing the system-dependent parameters in the working equations. These can be done utilizing the idea of scale amplitudes from Ref. [5].

1.2. Outline: Base on the spin-component-scaled decomposition of second-order self-energy expression [1] we will develop a new method (in the framework of electron propagator methods) for the calculation of IP, EA and EE. Moreover, utilizing the scaled amplitude concept, we will develop the working equations for semi-empirical scaling parameters (c_{os}, $c_{ss,}$) which will increase the accuracy of the predictions and make these methods a fully ab initio approach.

1.3. Work plan

a) development scaled ΔMP2, EP2 and ΔMP2-SCS(EA) and ΔMP2-SCS(EE) methods
b) Utilization of the scale amplitude concept in the context of the ΔMP2-SCS methods
c) numerical implementation of developed methods
d) Application of the developed methods to some interesting systems in quantum chemistry and solid state physics

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

[1] Śmiga S. and Grabowski I., J. Chem. Theory Comput. 14 4780, 2018
[2] Beste A, Vázquez-Mayagoitia A and Ortiz J V 2013 J. Chem. Phys. 138 074101
[3] Öhrn Y and Linderberg J 1965 Phys. Rev. 139 A1063
[4] Śmiga, Siecińska, Grabowski, New J. Phys.22(2020) 083084
[5] Śmiga, Fabiano, Phys. Chem. Chem. Phys.1930249, 2017

1.5. Required initial knowledge and skills of the PhD candidate

- Basic knowledge of quantum mechanics and quantum chemistry.
- Basic knowledge about Density Functional Theory and Wave Function Theory methods.
- Programming skills (FORTRAN, C, Python).
- Basic and/or advanced numerical methods knowledge.
- Involvement in scientific work.

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

- Deep knowledge and understanding quantum-chemical methods ranging from *ab initio* (HF, CC, PT) up to DFT methods
- Acquiring extensive knowledge of description 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 draw conclusions
- General knowledge about calculating different properties of many electron systems