Proposition de stage M2 “Physique de la Matière”

Vibrational spectroscopies for heavy-element containing molecules

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Motivation. Vibrational spectroscopy methods such as the infra-red (IR) spectroscopy, Raman, hyper-Raman, as well as the vibrational circular dichroism (VCD) are important techniques routinely used by chemists to determine and analyze molecular structure elements. The interpretation of such spectra is often only possible in combination with simulated spectra. In this M2 project we will develop the first analytical four-component relativistic (all-electron) implementation of these spectroscopies within the DIRAC [1,2] and OpenRSP programs using the Kohn–Sham (KS) density functional theory (DFT) approach. This will make it possible to simulate vibrational spectroscopies for polyatomic molecules containing heavy elements for the first time at the four-component relativistic level.

Project. a) Work in collaboration with the group of K. Ruud in Tromsø, Norway [3]. b) Extend an existing and operational pilot implementation of IR spectroscopy at Hartree–Fock level to KS DFT using the DIRAC [1,2] and OpenRSP [4] programs. c) Implement polarizability and hyper-polarizability gradients at the KS DFT level to allow Raman and hyper-Raman spectroscopies. d) Implement VCD using the approach of Thorvaldsen *et al.* [5]. e) Test, validate, and publish these implementations with example applications on molecules containing heavy elements.

What you will get. a) Learn about relativstic electronic structure theory. b) Learn how to write professional Fortran 90 quantum chemistry code. c) Learn collaborative programing tools and work-flows and interact with other DIRAC and OpenRSP developers. d) Learn how molecular properties can be computed and how they are implemented. e) Learn how KS DFT works in practice. f) Understanding of the various vibrational spectroscopies in the harmonic approximation.

What you will need. This is an ambitious project but it starts from a solid code base and a theory which is under control. This project will involve programming in Fortran 90. You do not have to be an expert in Fortran but for the project to be fun you should enjoy programming and methodology.

References

[1] http://dirac.chem.vu.nl

[2] http://diracprogram.org

[3] http://www.ctcc.no

[4] R. Bast, U. Ekström, B. Gao, T. Helgaker, K. Ruud, A. J. Thorvaldsen, Phys. Chem. Chem. Phys. 13, 2627 (2011).

[5] S. Coriani, A. J. Thorvaldsen, K. Kristensen, P. Jørgensen, Phys. Chem. Chem. Phys. 13, 4224 (2011).