

Density functional perturbation theory for modeling of weak interactions and spectroscopy in the condensed phase

This thesis deals with the development and application of computational methods for the efficient and accurate calculation of spectroscopic parameters and non-covalent inter-molecular interactions in condensed-phase systems in the framework of density functional perturbation theory. On the one hand, corrections to the Born-Oppenheimer electronic wavefunction were calculated to determine the vibrationally induced magnetic moments necessary for vibrational circular dichroism spectra. On the other hand, electronic polarization effects have been modeled using a new representation of the non-local electronic susceptibility response function.

Vibrational spectroscopy is an experimental method which allows the determination of the configuration of complex molecular systems. Vibrational optical activity allows the determination of the absolute configuration or secondary structure of chiral molecules without the requirement of long-range order. The main goal of this thesis was the development of a deeper theoretical understanding and interpretation of vibrational optical activity spectra. This required a substantial methodological effort, including developments and implementations in the context of quantum mechanics for the calculation of spectroscopic observables of condensed phase systems.

To this end, I have combined molecular dynamics simulations with adiabatic density functional perturbation theory, giving access to vibrational circular dichroism (VCD) spectra for strongly anharmonic systems. The complementary competences of the research groups of Rodolphe Vuilleumier and Daniel Sebastiani have allowed a symbiotic combination of these methods for the calculation of spectroscopic observables beyond the harmonic approximation. The research group of Prof. Sebastiani has a strong background in the modeling of the interactions of matter with magnetic fields by means of adiabatic perturbation theory, especially regarding gauge invariance. The research activity of Prof. Vuilleumier is focused on the modeling of anharmonic effects such as solvation effects and the effective normal mode analysis of molecular vibrations at finite temperature.

In the framework of this French-German cooperation we have, for the first time, rigorously derived the nuclear velocity perturbation theory (NVPT) starting from the exact factorization of the electron-nuclear wavefunction (XF). Furthermore, we are the first to report a successful implementation of the this theory, which has been implemented in the state-of-the-art electronic program package CPMD. Its application to systems in the gas phase can be compared with the established method based on the magnetic field perturbation theory. The results obtained by both approaches are in excellent agreement and have shown that our theory is well suited for the calculation of VCD spectra in the harmonic approximation.

The new methodology has been generalized to systems in the condensed phase. For this purpose, the canonical ensemble has been sampled by molecular dynamics simulations at finite temperature, for which vibrational optical activity observables have been calculated. The results of these calculations show a very good agreement with experimental spectra. In particular, there is no problem with the choice of the gauge in the condensed phase for systems in the liquid phase. We have also shown that our method is able to treat induced chirality from a chiral solute to an achiral solvent.

The NVPT not only allows the calculation of VCD spectra. It also allows to take into account how the electronic mass influences vibrational spectra. We have shown before that, starting from the XF, there are additional vibronic contributions to the vibrational spectra. Based on this work, we have shown that in turn the electrons induce a renormalization of the nuclear mass which depends

on the nuclear positions and allows to integrate non-adiabatic effects in an elegant way.

Furthermore, density functional perturbation theory can be used for the modeling of weak interactions, notably in the condensed phase. We intend to use the non-local electronic susceptibility for the efficient modeling of polarization effects and weak interactions. The non-local electronic susceptibility is a linear response function of the electronic density response due to an external perturbation potential. The aim of this project is to explore the applications of this response function.

The approach is based on an explicit representation of its non-local spatial dependence by means of an iterative spectral decomposition using the Lanczos algorithm. The main result of this study is the derivation of a new representation of the response function based on a multipole expansion, which gives a very condensed representation of the response function. This allows the efficient application of the response function to weak inter-molecular interaction.

In the new representation, the changes of the molecular geometry can be taken into account by a Taylor series in the nuclear coordinates. The new representation can be equally obtained by either a unitary transformation after the diagonalization or a direct, iterative symmetry decomposition.