

Abstract

This thesis deals with topics belonging to quantum and computational chemistry.

The calculation of electron repulsion integrals is a mandatory task in modern electronic structure theory. This is very demanding since the effort to calculate the needed electron repulsion integrals increases with the fourth power of the basis set size. If one wants to do calculations on large molecular systems with basis sets of reasonable size, the generation and processing of the integrals is a crucial step. The "Quantum Objects Library" is a collection of classes and programs that is written mainly in C++. The foundations of this thesis are set up by an existing efficient integral calculation machinery of the Quantum Objects Library which is a specialized code-generated module that calculates the integrals on the basis of an optimized Obara–Saika scheme. The focus of the first part of the present work is on the implementation of an efficient transformation of the raw integrals so that they can be used in a subsequent quantum chemical calculation. The transformation from the Cartesian to the contracted spherical-harmonic basis is a mandatory step in the scheme to calculate the integrals. The performance of different algorithms and the limitations are discussed. The timings of the subprograms of different algorithms lead to an average speed-up factor of 6 for test calculations with quadruple-zeta basis sets which contain up to g -functions. In addition, it is found that the code-generated Obara–Saika integral calculation machinery needs less than 20 % of the total computer time that is needed to calculate the non-redundant electron repulsion integrals.

The second part of this thesis focuses on two applications of computational quantum chemistry. The sizes of the discussed organometallic systems range from 45 up to 110 light atoms that contain a single metal atom. The first application is a computational investigation of a thermo-optical molecular switch that bases on the haptotropic rearrangement of a chromium fragment on a naphthalene-like system. The particular difficulty was the description of excited states which is necessary due to the occurrence of photon absorption processes. The calculations manifest the hypothesis that the photon absorption initiates the decarbonylation as well as the haptotropic shift towards the thermodynamically unfavoured compound. The second application deals with a stability analysis of chiral titanocene complexes which are used in organometallic catalysis. The analysis is expanded to the kinetic resolution of racemic mixtures of these complexes with the help of different chiral ligands that belong to the family of diols. The calculations point out that BINOL is a proper agent for the separation of the chiral titanocene complexes.