

Wave Function Based
Relativistic Multi-Reference
Electron Correlation Methods.
Development and Application
to Atomic and Molecular
Properties.

HABILITATIONSSCHRIFT

zur Erlangung der *venia legendi*
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for my beloved wife and children

[about thought and deception; science defined]

We conclude, therefore, that the argument from religious experience is altogether fallacious. The fact that people have religious experiences is interesting from the psychological point of view, but it does not in any way imply that there is such a thing as religious knowledge, any more than our having moral experiences implies that there is such a thing as moral knowledge. The theist, like the moralist, may believe that his experiences are cognitive experiences, but, unless he can formulate his "knowledge" in propositions that are empirically verifiable, we may be sure that he is deceiving himself. It follows that those philosophers who fill their books with assertions that they intuitively "know" this or that moral or religious "truth" are merely providing material for the psycho-analyst. For no act of intuition can be said to reveal a truth about any matter of fact unless it issues in verifiable propositions. And all such propositions are to be incorporated in the system of empirical propositions which constitutes science.

Alfred Jules Ayer [1]

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List of relevant own publications

1. T Fleig and A Sadlej:
Electric Dipole Polarizabilities of the Halogen Atoms in $^2P_{1/2}$ and $^2P_{3/2}$ States: Scalar Relativistic and 2-Component CI Calculations. [2]
2. M Ilias, V Kelloe, T Fleig, and M Urban:
Electric properties of the hydrogen iodide: Reexamination of correlation and relativistic effects. [3]
3. T Fleig and J Olsen, and L Visscher:
The generalized active space concept for the relativistic treatment of electron correlation. II: Large-scale configuration interaction implementation based on relativistic 2- and 4-spinors and its application. [4]
4. T Fleig and L Visscher:
Large-Scale Electron Correlation Calculations in the Framework of the Spin-Free Dirac Formalism. The Au₂ Molecule Revisited. [5]
5. F Neese, A Wolf, T Fleig, M Reiher, and B A Hess:
Calculation of Electric Field Gradients based on Higher-Order Generalized Douglas-Kroll Transformations. [6]
6. T Fleig:
Spin-Orbit Resolved Static Polarizabilities of Group 13 Atoms. 4-Component Relativistic Configuration Interaction and Coupled Cluster Calculations. [7]
7. J Thyssen, H J Aa Jensen, and T Fleig:
A Direct Relativistic 4-Component Multi-Configuration Self-Consistent-Field Method for Molecules. [8]
8. T Fleig, H J Aa Jensen, J Olsen, and L Visscher:
The Generalized Active Space Concept for the Relativistic Treatment of Electron Correlation. III. Large-Scale Configuration Interaction Implementation in a Kramers-Restricted Multi-Configuration Self-Consistent-Field Program. [9]

9. L K Sørensen, T Fleig, and J Olsen:
Implementation of a Four-Component Spin-Orbit Free Multi-Reference Coupled-Cluster Method with Application to CsLi. [10]

Introduction

The smallest building blocks of matter are comprised — at the level above elementary particles — by atoms and small molecules. A detailed understanding of these systems is highly desirable, both for the sake of knowledge about the small systems themselves as well as the implications of this knowledge for larger molecules. Fundamental understanding of molecular structure, therefore, commences with the study of small molecules¹. Much has been accomplished for light systems in the past, whereas small molecules containing heavy elements, i.e. atoms from the fifth row of the periodic table and beyond, are much less well understood.

The first and foremost piece of information relevant to chemistry and molecular physics is delivered by the investigation of the electron “cloud” surrounding the nuclei, the electronic structure. The theoretical framework for such investigations is provided by quantum mechanics, and the quantum mechanical methodology for carrying out the relevant calculations is at the heart of quantum chemistry.

An understanding of the electronic structure of atoms and molecules is based on the solution of the quantum mechanical equations for the electronic many-body problem, yielding ground- and excited-state energies. Nuclear structure is typically neglected in these treatments, and the nuclei are considered as point charges or simple charge distributions. Going beyond the “pure energetics”, derived properties can be obtained such as the equilibrium bond distances of molecules (and the molecular geometry), harmonic vibrational frequencies of the nuclei in the electronic potential, and dissociation energies. Beside the excitation energies, these spectroscopic properties are primarily sought for in theoretical spectroscopy, and form an important source of information — apart from their predictive power — e.g. for the correct assignment and interpretation of experimental data. An even more detailed understanding is achieved by the consideration of vibrational and rotational states and the various possible couplings such as rovibronic couplings, most of which is beyond the scope of this thesis.

Of similar importance as the determination of energies and spectral constants is the investigation of the electron density in atoms and molecules and its response to external strain, e.g. electric and magnetic fields. The electric polarizability, the extent to which the electron cloud responds to an external electric field, is a basic

¹A “small” molecule will in this thesis be understood as consisting of not more than six or seven atoms.

quantity in the study of scattering processes and is also valuable for the understanding of chemical reactions. The electric dipole moment provides information about molecular bonding and mirrors the shift of electron density in the formation of a molecule from its constituents.

Accurate electronic structure methods must go beyond Hartree-Fock theory where the electron-electron interaction is approximated by a mean field. Instead, the full interaction of electrons needs to be taken into account. There is a wealth of such “correlated” electronic structure methods available for small molecules containing only *light* elements. These methods, in particular new implementations of general-order coupled cluster theory, are able to produce results of arbitrary accuracy within a given physical framework (Hamiltonian). This is not the case for heavy elements. Obtaining accurate electronic structure data for heavy elements necessitates the explicit consideration of the theory of special relativity, a fact which has hampered the development of such quantum chemical methods.

Special relativity reveals itself in two principal ways in heavy systems: It explains the orbital contractions affecting chiefly *s* and *p* shells of heavy elements owing to the increased observed mass of electrons with high velocities and the connected self-consistent expansion mainly of *d* and *f* shells [11]. The corresponding changes of electron density and associated changes of atomic and molecular properties can be considered as perturbations in the 1st through 4th and sometimes also the 5th row of the periodic table, respective to a non-relativistic description of these systems. In the 6th row and beyond, however, a non-relativistic theory in general yields results which are often not even in qualitative agreement with experiment. Striking examples are the shorter and stronger molecular bonds of gold as compared to silver [12], the participation of 5*f* electrons in the chemical bonds formed by actinide atoms [13], and the volatility of mercury [11], to name but a few properties which are ill-described in a non-relativistic framework. These “effects”² are commonly termed “scalar” relativistic. The terminology refers to the structure of the Hamiltonian which here only acts in coordinate space and not in spin space, allowing for a one-component formulation of the wave function. This is the reason why scalar relativistic modifications are today available in many quantum chemistry program packages.

The second important phenomenon in heavy elements which is only described through special relativity is the occurrence of internal magnetic fields arising from the motion of charged particles — the electrons — in the electric fields of the nuclei and other electrons. In the inertial frame of an electron, this leads to a coupling of the magnetic field to magnetic momenta of the electron, its spin and orbital momentum, giving rise to spin-orbit, spin-spin, and orbit-orbit interactions. Of particular importance in heavy elements is the spin-orbit interaction, which beside further

²Some care should be taken with the term “effect” here: In the present context, it has become customary to call the difference between non-relativistic and relativistic view of a phenomenon an “effect” which in strict linguistic terms is improper.

contraction/expansion effects of orbitals partially lifts the non-relativistic energetic degeneracies of states. The consequences in heavy elements can be as drastic as the change of a ground state (PtH, [14]), the qualitatively different description of a dissociation process (Tl_2 , [15]), or the variance of an atomic electric polarizability in the order of 35% (Tl, [7]). The description of magnetic couplings necessitates the use of spin-dependent and therefore at least 2-component Hamiltonians. Consequently, the implementation of the spin-orbit interaction into a quantum chemical method requires severe structural modifications.

The most rigorous theoretical framework to account for all these relativistic effects is Dirac's relativistic quantum mechanics [16, 17, 18]. Here, the Hamiltonian and the wave function obtain 4-component form, the additional components owing to the description of anti-matter, which for electrons are positrons. In 4-component relativistic theory, scalar relativistic and magnetic effects are intertwined and consistently included. The work discussed in this thesis is based on 4-component theory and approximative ansatzes within the 4-component framework, both with respect to method development and application, and solutions are obtained to the Dirac (-Coulomb), not the Schrödinger equation. Many implications related to the level of relativistic treatment and the consequences in application are discussed in the appropriate sections.

The rigorous treatment of relativity is necessary but not sufficient in obtaining high-precision properties for heavy-element systems. Essential is also to account for electron correlation, the static part in the near-degeneracy case and the dynamic part reflecting the explicit electron-electron interaction. The methods presented in this thesis are all based on non-relativistic precursor methods which allow for the highest-level treatment of correlation, i.e. approaching the exact solution of the relevant many-particle equations with a given one-particle basis set (Full Configuration Interaction, General-Order Coupled Cluster), if desired and computationally feasible. This is seldomly done in practice, but these wave-function based methods allow for a systematic improvement of the correlation level and therefore a detailed assessment of electron correlation contributions.

Two specific further complications occurring in heavy-element systems are important to mention, and they cannot be neglected if high precision of properties is to be obtained. First, particularly d and f elements and their compounds often exhibit states, even ground states, which are characterized by several unpaired electrons, i.e. open shells. The treatment of such states surpasses the use of a single Hartree-Fock determinant as a reference function for the correlation step of the calculations. Instead, the multi-reference character of the states must be accounted for, and this calls for methods going beyond standard single-reference implementations (this applies in particular to coupled cluster approaches). Second, many common approaches assume additivity of electron correlation contributions and contributions due to spin-orbit interactions to a given property. This is sometimes reasonable, but restricts those methods in their applicability. A quite impressive example of failure

is the thallium dimer [19], where an additive calculation of the ground state vibrational frequency results in a deviation of more than 35% from the corresponding simultaneous treatment of correlation and spin-orbit coupling. All methods introduced in this thesis treat electron correlation and magnetic couplings simultaneously and on the same footing.

Summarizing, the central objectives of this thesis are to provide *universally applicable* quantum chemical methodology for small heavy-element systems, which in application have the potential of carrying the precision obtainable for properties of light molecules over to the domain of small systems containing heavy elements. *Universal* refers to both the system itself, the state (ground or excited), and properties which can either be derived directly from the energetics (spectroscopic properties) or application of weak external electric fields (electric properties). The reported applications demonstrate the present-day margins of attainable precision for spectroscopic and electric properties of such systems, which are within or often clearly better than chemical accuracy ($1 \frac{\text{kcal}}{\text{mol}}$ for energy differences). In direct comparison, it is shown how the presented methods improve on available approaches. The fact should not be suppressed, however, that the application of rigorous relativistic electronic structure methods is highly demanding on the computational side, which does not allow for exhaustive “scans” of compounds across the periodic table, but rather for studies devoted to the detailed analysis of problem cases.

This thesis provides a snapshot of the methodological and applicational achievements I have contributed to. Despite the completion of many projects, there are just as many, if not more, loose ends remaining. It is to some degree intended to give an overview of a field of quantum chemistry rather than a mere summary of accomplished work. Therefore, part I reviews the state-of-the-art, disregarding own contributions. In part II, the new relativistic quantum chemical methods are described, and part III is devoted to the application of these methods.

Part I
State of the Art

Properties of Small Heavy-Element Molecules

At the other end of the spectrum are the opponents of reductionism who are appalled by what they feel to be the bleakness of modern science. To whatever extent they and their world can be reduced to a matter of particles or fields and their interactions, they feel diminished by that knowledge [...] I would not try to answer these critics with a pep talk about the beauties of modern science. The reductionist worldview is chilling and impersonal. It has to be accepted as it is, not because we like it, but because that is the way the world works.

Steven Weinberg [20]

Small heavy-element molecules were already subject to theoretical studies in the early days of quantum chemistry. These investigations were, however, either of qualitative character or the reliability of quantitative results was rather limited. In the last two decades progress has been made mainly along two lines: The development of modern relativistic quantum chemical methods has improved both the range of applicability and the obtainable accuracy of properties. Second and indirectly, the enormous increase in computational power over the last decades opened for applications of higher and higher precision with available techniques.

The initial section of this thesis is meant to give an overview of modern relativistic electron correlation methods and their application to heavy-element systems. Naturally, such an account cannot make a claim for completeness, so I resort to a summary of methods which have recently been applied and which allow for an assessment of their accuracy through available experiments. The selection is intended to be as objective as possible and not biased towards specific failures. Nevertheless, it serves as a motivation for the development work described in this thesis.

Chapter 1

Heavy-Element Properties and Methods

1.1 Spectroscopic Properties

The majority of all published results in quantum chemistry is today obtained by application of density functional theory (DFT) [21]. The reason lies in the great efficiency of DFT in the treatment of electron correlation which makes it applicable even to very large molecules. For small molecules, pure *ab-initio* methods play a more prominent role. As the methods presented in this thesis are solely based on the wave function, the two different “world views” are discussed separately.

1.1.1 Density Functional Theory

The minimization of the energy expectation value formulated as a functional of the electron density instead of the wave function comprises the central idea of DFT. The resulting equations are structurally equivalent to the Hartree-Fock equations, but in addition accounting for dynamic electron correlation. This efficiency comes with a price, namely the obstacle that the true exchange-correlation density functional is unknown. Commonly, density functionals are calibrated on a series of atoms and small molecules, rendering the approach semi-empirical. Most DFT applications to small molecules are therefore carried out to test the various density functionals and to investigate basis set effects on selected molecular properties with a given functional (“chemist’s functionals”). Although it is seldomly claimed that DFT can systematically provide results of high accuracy, comparable to that attainable with pure *ab-initio* methods, it is imperative to make this evident here for different types of molecules and properties.

A number of “fully relativistic” 4-component as well as 2-component DFT implementations is available today. The 4-component Beijing DFT package (BDF [22, 23]) has been applied to properties of the gold dimer, a system which in its ground state is characterized by strong scalar relativistic but weak spin-orbit effects

(see subsection 5.2.3.1 for a detailed study). Both Local Density Approximation (LDA [24]) and BP/BP86 [25, 26] functionals perform quite well for the equilibrium bond length R_e , the deviations remaining within 4 pm [27, 28]. Harmonic vibrational frequencies are off by roughly 10 cm^{-1} (5%), dissociation energies D_e by almost 0.1 eV (4%) save for the Local Density Approximation which generally fails to describe molecular dissociation satisfactorily. In part, the studies contain extrapolation to the basis set limit. The results of Anton et al. using collinear and non-collinear 4-component Kohn-Sham DFT and the same functionals are significantly better [29] for the gold dimer, although the error for R_e remains at 3 pm. The authors also report calculations on the mercury dimer, a van-der-Waals system which is known to be a difficult case; here BP and PW91 [30] functionals give dramatically different results for all investigated properties.

Matveev et al. [31] studied a series of diatomic molecules where spin-orbit interaction plays a more important role in spectroscopic properties, the lead and bismuth dimers as well as PbO and TIH. Their implementation is based on a 2-component Douglas-Kroll approximation to the Dirac-Coulomb Hamiltonian, which generally do not introduce large errors for valence properties. Despite the consideration of spin-orbit interaction and the use of gradient-corrected functionals (BP), the results are rather poor for the D_e , where Pb_2 is off by 0.3 eV (25%) and PbO by 0.4 eV (11%). Bond lengths, on the other hand, are reproduced satisfactorily, and this is valid also for the LSDA functional VWN [32].

Particularly interesting are the studies carried out by Fossgaard et al. [33, 34] on a test set of 14 molecules of the type HX and XY (X,Y = halogen atoms) and molecules formed from Cs and the coinage metals. The DFT program used [35] is incorporated in the DIRAC quantum chemistry program package [36], and the values are systematically compared to high-level 4-component coupled cluster results. For the test set, LDA functionals perform well, but GGA functionals overestimate bond lengths and underestimate harmonic frequencies by 5-10%. On the more positive side, non-relativistic density functionals seem to perform well also in relativistic calculations, although this issue was not considered closed. Relativistic density functionals would have to be calibrated on heavy-element systems to account for the strongly modified electron density in “relativistic” systems. For CsAu, a molecule with high ionicity and partial negative charge on the gold atom, the error for the dissociation energy amounts to roughly 0.1 eV, whereas the deviation from experiment is an order of magnitude smaller in a coupled cluster calculation.

The Amsterdam Density Functional (ADF [37]) package provides the possibility of calculating excited-state properties via time-dependent (TD) DFT. Wang et al. [38] report vertical excitation energies of the closed-shell diatomics I_2 , AgI, AuH, Au_2 , TIH, and Bi_2 . The Hamiltonian employed is the 2-component spin-dependent zeroth-order regular approximation (ZORA) [39, 40]. With only a few exceptions, the deviations from experimental excitation energies vary between 0.1 and 0.5 eV (roughly 3-15%). Some systematic dependency with respect to the type of exci-

tation (involving only valence s and p orbitals or also d orbitals) and the applied exchange-correlation functionals (VWN, LB94 [41], and SAOP [42]) is made out. The number of excited states which may be obtained to this accuracy, however, is quite impressive, and up to 20 lowest-lying states are reported for the gold dimer.

Density functional methods are widely applied to complexes of lanthanide and actinide atoms, where *ab-initio* approaches are less efficient. A wealth of results also exists for a few actinide molecules which are of particular experimental interest, the actinyl cations. Some of these are studied by comparing different methods in reference [43], where especially the bond length of the uranyl ion received attention. Various DFT results using large-core and small-core relativistic pseudopotentials are compared to benchmark relativistic coupled cluster calculations. With the more accurate small-core pseudopotentials the results scatter around the benchmark value in a range of 2 pm. Vibrational frequencies are produced at significantly reduced accuracy compared to experiment.

A number of neutral systems has also been investigated using DFT approaches, e.g. OUCO, OThCO [44], NUO, NThO [45], and PuN₂ [46]. The data set for the uranium and thorium compounds does not allow for a critical judgement, but the error margins for vibrational frequencies appear to be the same as in the above-mentioned cases. The PW91 calculations on PuN₂ yield results in agreement with the Complete Active Space Perturbation Theory 2nd Order (CASPT2) approach [47, 48] for the bond lengths and semi-quantitative agreement for the excitation energies of lower excited states. However, the precision of the CASPT2 method for the properties of actinide species is yet unknown (see further comments in subsection 1.1.2). Souter et al. [49] find a vibrational frequency for the UH molecule of 1353 cm⁻¹ using ADF along with a BP functional, where the experimental value obtained is 1423.6 cm⁻¹.

The series of uranium trihalogenides has been investigated by Joubert et al. [50] using ADF/ZORA and quasirelativistic effective core potentials [51] within the Gaussian98 [52] package. For the heaviest homologue, UI₃, the various functionals (BP, B3LYP [53, 54], B3P [26, 53], and PBE0 [55, 56]) give equilibrium bond lengths within 3 to 10 pm from experiment. Both theoretical and experimental studies suggest that the molecules prefer a pyramidal C_{3v} arrangement, and the DFT calculations produce bond angles deviating by 20-30° (20-30%) from the experimental value.

In conclusion, DFT approaches do not comprise the method of choice for small molecules containing heavy elements. Although successful in some cases using distinct density functionals, high accuracy (errors smaller than 1% or 1 kcal/mole for energy differences) cannot be achieved systematically. Furthermore, DFT is not universally applicable, as e.g. states characterized by a significant amount of charge transfer from one system entity to another are typically ill-described. This relates to the additional Coulombic potential arising in such cases and the inherent self-interaction deficiency of conventional density functionals [57, 58]. This also explains

the errors in dissociation energies of highly ionic systems such as the CsAu molecule mentioned above.

1.1.2 Wave Function Based Correlation Methods

Quantum chemical models based on the electronic wave function allow for a systematic improvement of the level of calculation and therefore a more complete understanding of electronic structure in general. Figure 1.1 displays this alongside an increasing one-particle basis set, a more exact Hamiltonian ranging from non-relativistic to “fully” relativistic, and an improvement of the treatment of electron correlation. For DFT, variations are possible only on the lower 2 axes, but the method axis remains fixed, save for the possibility of employing different density functionals which is not a systematic procedure to the date.

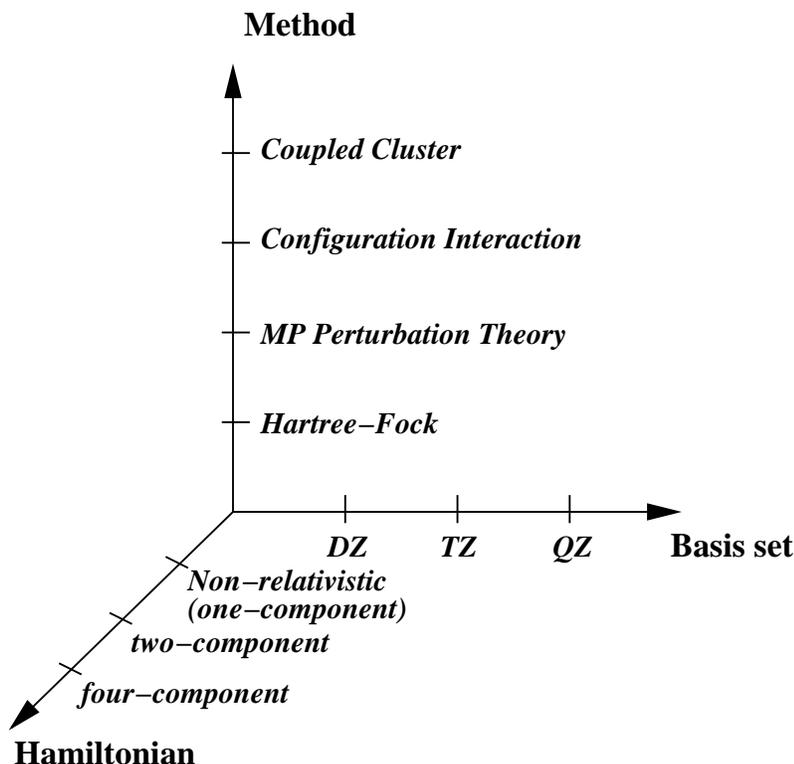


Figure 1.1: The three axes along which a quantum chemical model based on the wave function may be improved: Basis set, Hamiltonian, and the treatment of electron correlation

With respect to the work presented in this thesis, the Hamiltonian axis is mostly at highest precision¹, with the possibility of introducing approximations in specific cases. A general discussion of relativistic Hamiltonians in theory and application

¹Corrections from quantum electrodynamics and terms of higher order in the fine-structure constant are not taken into account.

can be found in a number of recent review articles [59, 60, 61]. Various basis sets are used, in part reaching the level of quadruple zeta (QZ) quality. In general, a basis set of at least triple zeta quality should be used to avoid artefacts in the treatment of electron correlation and to be reasonably sure that the errors due to basis set truncation are smaller than those arising from an approximate treatment of electron correlation [62]. For some of the studies reported here which focus on the influence of electron correlation and/or relativistic effects on properties an improvement of the basis set is a requirement for more accurate results. Approaching the basis set limit is very often computationally intractable when highly-correlated wave-function based methods are used, whereas such studies are significantly easier to carry out with DFT approaches. The optimization of relativistic basis sets is a tedious task, but extensive sets have become available for most heavy elements in recent years [63, 64, 65, 66, 67]. The method axis, however, is the one of major interest in the present context. The electron correlation problem plays the prominent role also in heavy-element chemistry and physics. Therefore, the methods for its treatment, in conjunction with exact relativistic Hamiltonians, are of crucial importance for guaranteeing high precision in obtained properties. The hierarchy of the models on the axis is of course overlapping, but at a given order/excitation level the coupled cluster model provides the most accurate approach. Detailed surveys of available relativistic correlation methods and some results for spectroscopic properties are given in the appropriate sections of this thesis. It is imperative, however, to mention a few general issues here.

A variety of relativistic core potentials/pseudopotentials, e.g. [68, 69], is in use for heavy-element systems, where the inner regions of heavy atoms are typically modelled by a potential fitted to all-electron structure data. This approximation is useful for larger molecules where the orbital optimization step (Dirac-Coulomb Hartree-Fock) becomes computationally impracticable. For atoms and small molecules, however, the correlation step becomes the more demanding in general, and the orbital optimization can always be carried out with the all-electron treatment, even for systems containing 4 or 5 heavy atoms. At the correlation stage, a frozen core is formed from inner electron orbitals and pseudopotentials comprise an unnecessary approximation. Thus, all calculations reported here are carried out explicitly considering all system electrons. The introduced methods, however, allow for the use of core or model potentials in principle, but such an implementation has not been carried out for the mentioned reasons.

Most quantum chemical implementations which can account for magnetic interactions treat correlation and spin-orbit interaction separately, to a larger or smaller degree. The separation takes place at different stages of the calculation. In most instances, orbital optimizations are carried out neglecting spin-orbit coupling. Advancing the same argument as above, the computational cost is much higher in the correlation step, which justifies the more costly spin-dependent orbital optimization. In general, spinors from such a calculation form a significantly improved one-particle

basis in heavy-element calculations [4] and facilitate as well as improve the subsequent correlation treatment. Regarding 4-component methods in this respect, the explicit treatment of the small component degrees of freedom can indeed become too inefficient here if the impact of the small component functions is negligible. Approximate 2-component Hamiltonians e.g. [70, 71, 72], then become a favorable choice. Upon correlating, however, this advantage disappears as the negative-energy states are usually and to a very good approximation neglected in the 4-component correlation treatments (no-pair approximation²) [73].

Another place to separate correlation and spin-orbit coupling is in this later step of the calculation. There exist a number of different “shadings” of how rigorous the separation is carried out, and many of these are mentioned in the following sections. The models seem to work well in many cases where the coupling between correlation and spin-orbit interaction is not decisive. To name but one example, the spin-orbit-(SO-) CASPT2 method [74, 75] draws advantage from its efficient (perturbative) treatment of electron correlation, but spin-orbit interaction is considered only after the orbital optimization and not simultaneously with (dynamic) electron correlation³. The method is successful but not universally applicable to small molecules. An assessment of its accuracy remains an open issue and will rely on the direct comparison with rigorous methods as the ones presented here (see subsection 5.2.2.2 for an example).

The methods presented in this thesis are capable of computing properties with in principle arbitrary precision, as far as electron correlation is concerned. Coupled cluster as well as configuration interaction calculations may be carried out to any order/excitation level, and extensive (typically uncontracted) basis sets can be used, so that the feasibility of a calculation merely depends on the available computer power. Regarding the Hamiltonian axis, the use of the Dirac-Coulomb-Breit operator is not possible currently⁴. This limits the treatment of spin-orbit interaction to the one-electron spin-orbit and the spin-same-orbit two-electron terms in correlated calculations. However, this is a good approximation for the great majority of heavy-element properties, where the one-electron spin-orbit terms become clearly dominant due to the increasing nuclear charge [4, 77]. Corrections due to quantum electrodynamics like the self-energy and the vacuum polarization (constituting the Lamb shift) are very small for valence properties (less than 1 kcal/mole for atomization energies for instance [78]) and therefore not taken into account.

²As the positive- and negative energy solutions are not decoupled a priori in the 4-component formalism, a realistic screened nuclear potential is used here to define the no-pair approximation.

³A spin-orbit Hamiltonian is diagonalized in the basis of CASSCF (see section 3) wave functions with shifts from spin-orbit free CASPT2 calculations of dynamic electron correlation applied to the diagonal elements.

⁴The Gaunt term is implemented within a local version of the DIRAC program package [76] but cannot be used in correlation approaches due to the lacking integral transformation for Gaunt integrals.

1.2 Electric Properties

The electric properties considered in this work are limited to the static domain, implying that perturbing external fields are always time-independent. Static electric properties may be obtained either analytically, e.g. by applying response theory or by evaluating expectation values of the relevant property operators, or by numerical procedures (see chapter 6). The methods introduced here employ the latter approach. Thus, the attainable accuracy is determined by the precision to which the respective total energies may be calculated, and therefore the same arguments apply as in the preceding chapter on spectroscopic properties.

The focus here lies on electric dipole moments of molecules and electric dipole polarizabilities of both atoms and molecules. Reference [79] provides an excellent state-of-the-art account of atomic polarizabilities. These are required for instance in the study of scattering phenomena, chemical reactions, or electric processes under exposure to irradiation. Quite surprisingly though, accurate polarizabilities — both experimental and theoretical — are available only for a minority of atoms, typically the closed-shell and lighter atoms. Reliable polarizabilities for heavy open-shell atoms and/or excited states are rare if they can be found at all. Most calculations on heavy elements are carried out using DFT with LDA functionals, and the residual errors are in the order of 25% [80]. The magnitude of the errors can be related to the fact that the major part of the atomic polarizability is determined by the outermost electrons. Only a small selection of atoms has been treated with the more reliable CASPT2 (Sb, Re, Bi, Am) or coupled cluster methods (Cd, Xe, Cs, Ba, Au, Hg, Pb, Rn, Fr). The principal difficulty in calculating atomic (and of course also molecular) polarizabilities of heavy elements to high accuracy lies in the sensitivity of the property to electron correlation, necessitating the inclusion of many electrons in the correlation treatment. In addition, large and diffuse basis sets are required to describe the response of the electron density in the valence region to the external perturbation. A particular difficulty is encountered in open-shell systems where spin-orbit interaction often needs to be accounted for consistently. Moreover, the high-accuracy Fock-space coupled cluster methods available become difficult to apply when the number of open shells of a given state exceeds 2 [81]. Open-shell systems may be treated with standard coupled cluster approaches if the open-shell reference function is comprised by a single determinant to a good approximation, e.g. in the study of Ln^{3+} ion polarizabilities [82].

Only a few recent applications to molecular polarizabilities of heavy-element systems (Au_2 [28], AlAu [83], PbO [84]) shall be mentioned here, as such properties are not discussed at length in this thesis. The methods presented here do allow for finite-field calculations also of molecular static polarizabilities. The referenced approaches cover 4-component DFT, scalar relativistic coupled cluster, and 2-component SO-CASPT2. However, no experimental data are available for an assessment of the accuracy of these calculations.

The calculation of molecular dipole moments is somewhat easier than that of polarizabilities, mainly because the dipole moment is only a first-order property. The range of approaches which have been used so far is similar, though. Recent studies report dipole moments of Al-coinage metal compounds (coupled cluster [83]) and group 13-17 heavy diatomics (Dirac-Coulomb Hartree-Fock [85]). A molecule of particular interest is lead oxide (PbO) which has been investigated several times in the past. The most recent work confirms the strong dependency of the property on spin-orbit interaction which varies significantly as a function of the distance between the atoms [84]. Again, 2-component SO-CASPT2 is applied yielding results very close to coupled cluster with perturbative triple excitations (CCSD(T)) when spin-orbit coupling is excluded. An estimate of the spin-orbit contribution gives a result farther away (lower) but still within the error margin of the experimental result [86]. The authors conclude that the inclusion of excited-state configurations relevant for describing spin-orbit interaction decreases the dipole moment due to the smaller polarity of these configurations. Another specific problem case is the HI molecule which is addressed in detail in subsection 6.3.1. For obtaining a quantitatively correct dipole moment value of this molecule, all three axes in figure 1.1 require special attention [87].

Frequency-dependent electric polarizabilities (for the coinage metal dimers [88] and for the series of furan homologues XC_4H_4 , $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$ [89]) have been determined for heavy-element compounds at the Dirac-Coulomb Hartree-Fock level using the DIRAC package in the framework of response theory. No such properties are reported here, but as linear and non-linear response properties can be determined within 4-component Hartree-Fock calculations already, the extension to the correlated quantum chemical methods discussed here comprises an issue of future development work.

Part II

Method Development

Relativistic Multi-Reference Electron Correlation Methods

So the other afternoon I knocks at the door of Dr. Dirac's office in Sterling Hall and a pleasant voice says "Come in." And I want to say here and now that this sentence "come in" was about the longest one emitted by the doctor during our interview.

[...]

Then we sat down and the interview began.

"Professor," says I, "I notice you have quite a few letters in front of your last name. Do they stand for anything in particular?"

"No," says he.

"You mean I can write my own ticket?"

"Yes," says he.

"Will it be all right if I say that P.A.M. stands for Poincaré Aloysius Mussolini?"

"Yes," says he.

"Fine," says I, "We are getting along great! Now doctor will you give me in a few words the low-down on all your investigations?"

"No," says he.

Roundy interviews Professor Dirac [90]

The methodological work described in this thesis encompasses the development or generalization of tools central to quantum chemistry and based on the optimization of the electronic wave function. The development has been and is carried out entirely within a local version of the DIRAC quantum chemistry program package. One of the new modules (LUCITA) has been included in a released version [36] and is accessible to a wider public.

Before embarking on a discussion of the 3 different models which have come to implementation, figure II depicts the hierarchy of the methods and their interrelations. The methods cover static (MCSCF) and dynamic (CI, CC) electron correlation and can make use of fully relativistic 4-component Hamiltonians. The elaboration in the

following 3 chapters emphasizes major issues of theory and implementation as well as important implications concerning application, whereas a great deal of details is omitted and left to the published material.

New Multi-Reference Electron Correlation Programs in DIRAC

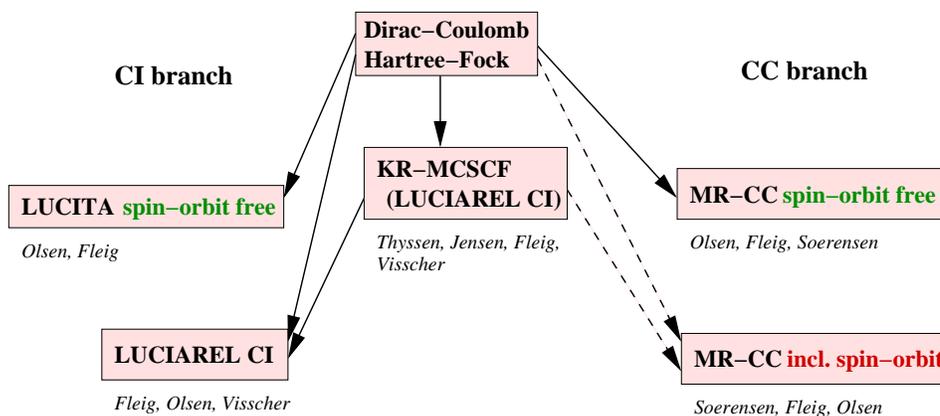


Figure 1.2: An overview of the new relativistic 4-component electron correlation programs in DIRAC and the main authors of the modules.

Color code (**green**, black): Completed; (**red**): Under development

Chapter 2

Relativistic Multi-Reference Configuration Interaction (CI)

2.1 General Remarks

The configuration interaction approach is the oldest and also a conceptually very simple and straightforward method to go beyond the Hartree-Fock model in many-particle theory. There is hardly any quantum chemical program package that does not include a CI module of some type.

Despite this theoretical simplicity, however, the linear parameterization of the wave function in the CI model comprises a quite inefficient approach to the electron correlation problem. The exact solution of the Schrödinger equation given a basis set expansion of the wave function, the Full (F) CI solution, for 20 electrons in 100 spin orbitals spans a Fock space of more than $5 \cdot 10^{20}$ terms disregarding spatial or spin symmetry reductions. Practical applications are therefore limited to restricted CI expansions, very often including only single and double excitations out of a single- (or multi-) reference space. This approach has two severe drawbacks: On one hand, the CI energy converges slowly to the FCI solution with the excitation level [91]. On the other, owing to the linear parameterization, truncated CI models no longer conserve the property of size-extensivity/size-consistency with the number of correlated particles/non-interacting subsystems [92].

Regarding molecular (and atomic) properties, finite-field approaches (6.1.2) based on CI wavefunctions are as easily applied as in other correlation methods and are used quite frequently. The application of analytical procedures (6.1.1) like response theory, on the other hand, have received rather little attention. This is due to the size-consistency problem and to the fact that the one-particle functions are not re-optimized with respect to the external perturbation introduced for obtaining the property, which is the case for instance in the Multi-Configuration Self-Consistent-Field (3) approach.

Nonetheless, CI theory has some striking advantages. Unlike the coupled cluster

approach (4) excited states are straightforwardly obtained and do not essentially depend on a specific reference function, like e.g. a closed-shell electronic configuration. Moreover, CI methods are generally based on the variation principle leading to an upper bound for determined energy eigenvalues. On the technical side, the generalization of existing CI technology to the relativistic domain can be carried out using the same specialized algorithms (e.g. for direct CI procedures) but the required modifications are substantial. These are chiefly the generalization to complex algebra due to the use of spin-dependent Hamiltonians, the implementation of double point group symmetry, and a structural modification to account for the increased number of types of relativistic integrals. The latter point in particular will deserve special attention in subsection 2.2.2.

Non-relativistic CI programs are typically based on expansions in Configuration State Functions (CSF) which are spin eigenfunctions [93], because S comprises a “good” quantum number for the total electronic spin of the many-particle system. However, determinant- (or more precisely string-) based implementations are more efficient as the time-consuming comparison of configurations in the evaluation of CI coupling coefficients is not required [94]. Advances in CI technology have made the treatment of huge CI expansions possible [95] which opens for large-scale applications of relativistic CI programs based on these improved codes [4, 96].

2.1.1 Previous relativistic implementations

A common classification of relativistic CI approaches is comprised by the one-step and the two-step methods. The distinction refers to at what stage of the algorithm spin-orbit coupling is treated. The less general two-step procedures typically involve a scalar relativistic determination of the wave function followed by an optimization including the spin-orbit Hamiltonian. In physical terms, these approaches rely to some extent on the separation of electron correlation and relativistic effects, in particular the spin-orbit interaction, and are therefore intrinsically approximate¹.

In the Restricted Active Space State Interaction (RASSI) [75] program of the *MOLCAS* package [97] matrix elements of scalar relativistic RASSCF wave functions are evaluated over a spin-orbit Hamiltonian in atomic mean-field approximation [98]. This approach provides results of considerable accuracy but is difficult to apply when many open shells are involved or/and many states have to be coupled. Moreover, it is not a classical CI approach and only accounts for a small fraction of dynamic electron correlation. In combination with the perturbative CASPT2 method for dynamic electron correlation, the afore-mentioned SO-CASPT2 method has become a tool of increasing popularity in relativistic quantum chemistry (see also sections 3.1 and 5.2.2.2).

The Effective and Polarized Spin-Orbit CI (EPCISO) code published a few years ago [99] can be best described as a mixture of a one-step and two-step proce-

¹Except in the FCI limit where the method becomes independent of the one-particle basis

ture. Dynamic correlation is accounted for by an effective Hamiltonian and spin-orbit coupling introduced by including single excitations out of a determinantal model space predefined by non-relativistic *LS*-coupled wave functions of the different spatial symmetries. The method thus becomes applicable also to medium-sized molecules [100] but lacks rigor in general. The implementation by Kleinschmidt et al. [101, 102] which can be run as a genuine one-step procedure uses non-relativistic Multi-Reference (MR) CI starting vectors to form a model space in which subsequently a SOCI calculation in the given CSF basis for the coupling spin multiplets is performed. The program is currently applicable to lighter elements only (as it is based on an integral interface to the TURBOMOLE [103] program package lacking auxiliary basis sets for heavy elements). Single excitations with respect to all model space functions can be considered, but an explicit selection of configurations with respect to spin-orbit coupling contributions is not performed.

Other implementations are purely based on effective core potentials, e.g. the Graphical Unitary Group Approach (GUGA) CI in the Columbus program package [104] which is programmed as a one-step double group CI. The use of relativistic effective core potentials aims at molecules containing several or many heavy centers, because there the Hartree-Fock step can already become prohibitively expensive in all-electron approaches. Otherwise, core potentials are not required as given a successful Hartree-Fock or Multi-Configuration SCF calculation, the uncorrelated electron orbitals form a frozen core in the subsequent correlation treatment which does not contribute to the computational expense of the method.

Of the purely one-step methods, two recent ones shall be mentioned here which have been successfully applied in molecular electronic structure calculations: The 4-component direct double group CI program DIRRCI from the MOLFDIR package [105] is now also part of the DIRAC [36] program system and is capable of performing relatively small CI expansions of up to a few million Slater determinants [106]. A previous generalization [107] of the LUCIA program system [108] works with scalar relativistic orbitals only and RAS expansions of the wave function. The code exploits non-relativistic symmetry as far as possible and thus cannot be applied in general spinor calculations. Another drawback is the limitation to 3 active orbital spaces. The CI code described in this thesis can use an arbitrary number of spaces, denoted as Generalized Active Spaces (GAS) with arbitrary occupation constraints (2.2.1). The great potential and use lying in this generalization will become apparent also in the methodology and applications of relativistic MCSCF (3) and the coupled cluster approach described in (4).

The relativistic CI implementation reported earlier [96, 109] which is the precursor to the here-described programs already bears the generality with respect to the one-step approach, the associated one-particle basis and double group symmetry in the one- and many-particle spaces. Furthermore, LUCIAREL is an all-electron implementation. The following sections are concerned with the theoretical implications and the practical aspects of the generalization of this method [4] to 4-component

relativistic methodology. It is to be emphasized that the implementation described in [109] and [96] was only used in connection with a scalar orbital basis and in 2-component relativistic approximation. The latter aspect is more of a technical issue, because the difference between 2- and 4-component versions merely lies in the interface to the respective transformed integrals after the Hartree-Fock step and did not require significant modifications of the CI code as such. A distinction of much greater importance is the advance from using a scalar orbital basis to a spinor basis, as the symmetry and associated quantum numbers are changed. However, the implementation described in this thesis is also general with respect to the one-particle basis, and applications employing both approaches will be reported in the appropriate section (6).

Two common features of all the varieties of CI implementations reported in this thesis shall receive special attention at this point. Apart from the GAS concept, these are

1. *String-driven algorithm.* Configuration interaction (and also e.g. coupled cluster) procedures require the multiplication of some coupling coefficients with integrals and the model parameters, here the CI coefficients (or CC amplitudes). The most efficient way of performing these transformations is to represent the involved determinants (or CSFs) by strings of creation operators in second quantization and to replace the loops over (spin-) orbitals by loops over strings [94, 110]. By this, the evaluation becomes independent of the number of occupied (spin-) orbitals in the occupied/virtual subspaces.
2. *Arbitrary excitation level.* As a direct consequence of the above, the implementation of arbitrary excitation levels is greatly facilitated, because the evaluation of coupling coefficients and the contractions is independent of the excitation level of the occurring determinants. This provides CI codes which can straightforwardly perform up to FCI expansions [95, 108] if the computational demand allows this.

2.1.2 Scope of the Method

With the large-scale implementation of relativistic CI theory presented here, I pursue the following purposes:

1. *Relativistic generality.* The program can be used with scalar relativistic orbitals or general spinors. The former computations are generally less time- and resource-consuming because the orbital optimization step can be done in 1-component approximation. Full 4-component calculations as well as using 2-component spinors from the Barysz-Sadlej-Snijders (BSS) Hamiltonian [72] as implemented in the DIRAC program package [111] can be carried out. The 4-component scheme is important in property calculations where the wave

function in the vicinity of the nucleus changes, e.g. core excitations or nuclear spin-spin couplings. The 2-spinor approach is preferred over the scalar relativistic environment due to reduced truncated CI expansion lengths when spin-orbit coupling is large in the one-particle basis, rendering the scalar approach inefficient. This occurs in heavy p elements with open shells, but also the lanthanides and actinides and their compounds (see subsections 5.1.1 and 5.1.2 for examples).

Currently, 4-component calculations use the Dirac-Coulomb Hamiltonian which lacks spin-other orbit 2-electron terms. For heavy elements, this is a valid approximation, but not satisfactory if a rigorous framework is desired. The implementation of the required Gaunt operator is under development in DIRAC [76] and completed for the Hartree-Fock step.

2. *Excited states.* The iterative methods implemented² allow for the determination of many eigenstates. The program can therefore be applied to complicated open-shell compounds as well as closed-shell molecules. Beside excitation energies, spin-orbit splittings/shifts in ground and excited states can be determined. On the technical side, excited states become accessible in relativistic MCSCF calculations by constructing specific active spaces; this feature will be explained in the section on MCSCF (3).
3. *High precision calculations on small systems.* Spectroscopic properties like equilibrium bond lengths, harmonic frequencies, and dissociation energies can be obtained both for ground and excited states at high precision using multi-reference CI wave functions³. As CI expansions are almost always truncated, the determination of electric properties also for small systems is carried out via finite-field techniques (6.1.2). Not all of these properties can be accessed by these means, as one is often limited by implemented operators in the respective program packages or technical obstacles. Typical applications involve perturbing electric fields yielding static electric dipole moments and polarizabilities.
4. *CI module for relativistic MCSCF program.* One of the most important uses of LUCIAREL finally lies in the conjunction with MCSCF methodology, where beside the integral storage the efficiency of the CI module crucially determines the applicability of the method. With the extended implementation including LUCIAREL active spaces with up to roughly 50 Kramers-paired orbitals and configuration spaces with several tens of millions of determinants are feasible in relativistic MCSCF calculations. Details are discussed in subsection 3.3 and relevant applications are reported in 5.2.2.2.

²Complex Davidson algorithm, see e.g. [112].

³In Active Space sense described below (2.2.1)

2.2 Relativistic CI Theory

The present relativistic CI implementation is based on Slater determinants formed from two separate sets of creator strings, one for spin-up type orbitals, the other for spin-down type orbitals. This concept allowed for generalizations to relativistic Hamiltonians by introducing the additional determinant coupling types in the relativistic case and by accounting for the additional types of relativistic integrals. The underlying one-particle functions are assumed to be pairwise related through time-reversal symmetry. Both one-particle functions and strings are classified fully in terms of double point group symmetry, a consequence of the symmetry reductions due to spin-orbit interaction.

The initial steps of generalizing the non-relativistic precursor program LUCIA [95, 108] to relativistic Hamiltonians has been described earlier [96, 109]. The obtained version is capable of performing large-scale all-electron applications in a one-step procedure, i.e. optimizing the wave function by a fully variational treatment in configuration space including the full spin-dependent Hamiltonian, e.g. in reference [2]. Both one- and many-particle functions are classified according to irreducible representations of double groups here. Kramers symmetry is formally included, but as this initial implementation works from scalar spin orbitals only, the relations reduce to the well-known restrictions induced by spin symmetry like in non-relativistic implementations. As an example, consider the two-particle integral $[ij|\bar{k}\bar{l}]$ in Mulliken notation for spin orbitals. The action of the time-reversal operator \hat{K} is defined as

$$\begin{aligned}\hat{K}\varphi_{i\alpha} &= \varphi_{i\beta}^* \\ \hat{K}\varphi_{i\beta} &= -\varphi_{i\alpha}^* \\ \hat{K}\varphi_i &= \varphi_i^* \\ \hat{K}\varphi_{\bar{i}} &= -\varphi_i^*\end{aligned}$$

where in the last two lines the index i denotes a general spinor. These one-particle functions are *per constructionem* Kramers pairs, and spin orbitals are but a special case of spinors. In a Kramers basis of spin orbitals the mentioned integral fulfills $[ij|\bar{k}\bar{l}] = (ij|kl) = (ij|lk) = [ij|\bar{l}\bar{k}]$, where spin integration is carried out leading to the orbital notation $(pq|rs)$. If the functions are Kramers-paired spinors, however, merely the identity $[ij|\bar{k}\bar{l}] = [ij|lk] \neq [ij|\bar{l}\bar{k}]$ holds (beside similar relations via time-reversal symmetry for the other types of integrals). The use of Kramers symmetry in the present implementation is more involved and will be dealt with in the subsection on excitation classes (2.2.2).

The general difference between the previous and the present implementation does not lie so much in the Hamiltonian employed in the actual CI procedure itself but rather in the Hamiltonian used for obtaining the respective one-particle basis. Thus, the CI procedure starting from a relativistic spinor basis will be elucidated in

the following. Common features are a complex modification of the inverse-iteration Davidson algorithm (reference [91], pp. 544) and a vector partitioning technique which will be described here.

2.2.1 Generalized Active Spaces (GAS)

The GAS formalism imposes extensive implementational requirements on a wave function optimization procedure, but it leads to a program with great generality in application. Restricted Active Spaces (RAS) have been used earlier (e.g. in the RASSCF module of the *MOLCAS* package [113]). GAS can be considered as the complete generalization of this approach, where the one-particle functions are divided into an arbitrary number of subspaces, e.g. as shown in figure 2.1.

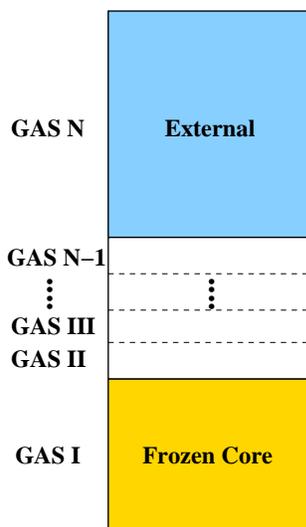


Figure 2.1: Division of the one-particle space into Generalized Active Spaces. The 'Frozen Core' space can be omitted when a core Fock matrix is generated for these orbitals.

To make the scope of the procedure clearer and also to prepare for the discussion of the excitation class formalism, I will focus on a simple atomic example here, the Arsenic atom. Its valence configuration is $4p^3$, the outer core can be described as $3d^{10}4s^2$.

Assuming now that all other electrons form a frozen core, the CI trial wave function is constructed via the scheme in table 2.1. The setup employs 5 GAS, the last of which contains an unspecified number (m,n) of virtual functions. The first column of the Kramers pairs denotes the functions transforming as to the E_g irrep, the second column those transforming as to the E_u irrep of the symmetry group. The first column of the electron occupations denotes the minimum number of electrons taken into account *after* this GAS has been considered, the second the maximum number of electrons *after* this GAS. Thus, GAS I and II remain completely occupied. Single, double, and triple excitations are performed out of GAS III, and combined

GAS	GAS Kramers pairs	Accum. electron occupation	Function type
I	5 0	10 10	3 <i>d</i> , outer core
II	1 0	12 12	4 <i>s</i> , outer core
III	0 3	12 15	4 <i>p</i> , valence
IV	0 3	13 15	5 <i>p</i> , valence correlating
V	m n	15 15	rest, virtual

Table 2.1: Generalized Active Spaces and occupation constraints for the As atom, valence correlation, symmetry double group C_i^*

with single and double excitations out of GAS IV into the virtual space. In other words, GAS III carries between 0 and 3 electrons in all constructed determinants, GAS IV between 1 and 3, and GAS V between 0 and 2 electrons. The so-defined wave function is comprised by all configurations which can be constructed from

$$4p^3, 4p^25p^1, 4p^2V^1, 4p^15p^2, 4p^15p^1V^1, 4p^1V^2, 5p^3, 5p^2V^1, 5p^1V^2. \quad (2.1)$$

The calculation therefore refers to a complete expansion (FCI) in a valence space defined by the 4*p* and 5*p* functions, and single and double excitations with respect to each of these CAS configurations. By these means, Multi-Reference (MR) CI calculations can be modelled: active spaces with varying excitation levels are defined and a virtual space is branched off and restricted to, e.g, a maximum of 2 electrons.

GAS	GAS Kramers pairs	Accum. electron occupation	Function type
I	5 0	9 10	3 <i>d</i> , outer core
II	1 0	10 12	4 <i>s</i> , outer core
III	0 3	12 15	4 <i>p</i> , valence
IV	0 3	13 15	5 <i>p</i> , valence correlating
V	m n	15 15	rest, virtual

Table 2.2: Generalized Active Spaces and occupation constraints for the As atom, valence correlation and core polarization/correlation, symmetry double group C_i^*

To demonstrate the power of the method, I will discuss a second example. Following the setup in table 2.2, where the outer core shells are opened for excitations, the following *additional* configurations arise:

$$3d^{10}4s^1(III - V)^4, 3d^{10}4s^0(III - V)^5, 3d^94s^2(III - V)^4, 3d^94s^1(III - V)^5 \quad (2.2)$$

Triple excitations out of the combined spaces I and II are not allowed, so the configurations $3d^94s^0(III - V)^6$ do not occur⁴. The combined spaces III-V may now

⁴This could be achieved by replacing the 10 with a 9 in the GAS II minimum occupation

carry up to 5 electrons instead of 3 as in table 2.1, and the additional electrons have to be distributed in accordance with the predefined occupation constraints. In the present example this means that the single and double excitations out of the outer core shells are *not* combined with excitations from the valence shells into the correlating or virtual functions because of the minimum constraints of 12 and 13 in GAS III and IV, respectively. Again, if combined excitations were desired, this could be achieved by lowering the minimum occupations in GAS III and IV accordingly.

The improved wave function now also contains core-valence correlation of the $3d$ electrons and outer core correlation of the $4s$ electrons along with the valence correlation given by the original space. In practice, employing a reasonable contracted basis set, the first setup gives rise to 10.552 determinants whereas the second spans 2.187.570 determinants.

In summary, GAS spaces allow for a very flexible definition of the wave function in view of the physical or chemical problem aimed at. In particular, it may be and has been applied in the following contexts:

1. *Core-valence and core-core correlation.* These contributions can efficiently be taken into account through the GAS scheme. Likewise for molecules, the outer core orbitals can be divided into a few spaces and the desired excitation level defined for each of the shells. A typical example is the atomic study in reference [2]. Similar to the above setup, the polarization effect of the $(n-1)p$ shell of the halogen atoms is taken into account in highly correlated estimations of the atomic static electric polarizabilities in the J, M_J components of the ground state. In this calculation based on spin orbitals, the $(n-1)p$ polarization serves the purpose of giving a better spin-orbit splitting in the valence shell. In a spinor basis, this is seldomly necessary and the outer core is rather opened for obtaining correlation contributions.
2. *Complete and near-complete valence spaces.* In molecular applications the orbitals or spinors which come to lie in the energetic vicinity of the valence functions most often comprise the antibonding correlating functions required for modelling static correlation. In cases where a complete expansion in such a subspace is desired, a single complete active space (CAS) may be constructed. This type of expansion becomes very extensive rather quickly if one faces a large number of valence orbitals. Then 2 spaces — one from the occupied bonding, the other from the unoccupied antibonding orbitals — with a high excitation level, e.g. up to Triples or Quadruples, may be constructed to consider as many reference configurations of the valence space as possible.
3. *Excited states in MCSCF calculations.* The GAS formalism is also implemented in the presented MCSCF program (3). Here it becomes particularly useful for obtaining excited state wave functions, as described in the applications section (5). In the non-relativistic domain, excited states are very often

obtained from calculations in a different irreducible representation of the point group in MCSCF applications. In relativistic MCSCF, however, the spatial symmetries are mixed and desired excited states most often are found in the same double group representation. If the MCSCF implementation does not open for multi-root optimizations (like the presented one), GA spaces provide a means of converging to an excited state of a given symmetry by ruling out precisely the ground state configuration from the CI expansion.

4. *Core holes.* Employing a restricted space for a core shell enables straightforward and precise construction of core excited states. The energetically following orbitals can be placed into completely filled GA spaces from which excitations are disabled.

As a closing remark, the GAS procedure should not be mistaken for a type of internal contracted CI, as was introduced and refined earlier [114, 115]. CI calculations based on internal contractions diagonalize the Hamiltonian in a model space and in a second step consider excitations from this model space into external orbitals. The GAS CI is, also in this respect, a purely one-step procedure⁵.

2.2.2 Excitation Class Formalism

The creation of excitation manifolds based on a reference state — be it single- or multi-reference — is a substantial issue both in coupled cluster and CI theory. The concept of excitation classes applies to both the wave function, where the type of excitation relative to the reference state is characterized, as well as the Hamiltonian which in second quantization carries out one- and two-particle displacements. The introduction of GA spaces calls for an efficient and transparent handling of the arising excitation types because the excitation level is linked to the chosen occupations of the active spaces. In the second quantization picture this is ideally achieved by labelling all unique excitation types and bookkeeping the number of creation and annihilation operators referring to that excitation type. As a simple example, consider table 2.3.

Excitation class A represents an annihilation of an electron in GAS I and a creation in GAS III, where both operators refer to the Kramers unbarred set of one-particle functions. The type of excitation therefore generates determinants with an occupation lowered by one spinor in the first space and increased by one spinor in the third space and the same Kramers projection M_K as the reference state. This projection value can be understood as the remainder of spin symmetry in the relativistic formalism and is defined as $M_K := \frac{N_p - N_{\bar{p}}}{2}$ with N_p the number of Kramers unbarred and $N_{\bar{p}}$ the number of Kramers barred electrons.

⁵The option of internal contraction is implemented in the spin-free precursor program LUCIA

Exc. class	Elementary operator	GAS			
		I	II	III	
A	\hat{a}_i^\dagger	Creation of unbarred spinor	0	0	1
	$\hat{a}_{\bar{j}}^\dagger$	Creation of barred spinor	0	0	0
	\hat{a}_k	Annihilation of unbarred spinor	1	0	0
	$\hat{a}_{\bar{l}}$	Annihilation of barred spinor	0	0	0
	\vdots				
E	\hat{a}_i^\dagger	Creation of unbarred spinor	0	1	1
	$\hat{a}_{\bar{j}}^\dagger$	Creation of barred spinor	0	0	0
	\hat{a}_k	Annihilation of unbarred spinor	1	0	0
	$\hat{a}_{\bar{l}}$	Annihilation of barred spinor	1	0	0
	\vdots				

Table 2.3: Two exemplifying excitation classes of a one- and a two-particle operator

An excitation class for a two-particle operator is shown in the lower half of table 2.3. Two electrons in an unbarred and a barred spinor of space I⁶ are annihilated and created in two unbarred spinors of spaces II and III, respectively. The complete operator in normal ordering and the associated integral read

$$\hat{a}_{iII}^\dagger \hat{a}_{jIII}^\dagger \hat{a}_k \hat{a}_{\bar{l}} (i\bar{l}|jk). \quad (2.3)$$

Therefore, this operator may be classified as flipping the Kramers projection by one unit, according to $\Delta M_K = +1$. It becomes clear that the first limitation to the excitation classes generated is comprised by the number of spinors per active space and the allowed occupations given by the GAS setup. Within these constraints, the program generates all possible excitation classes already in the setup. The second limitation is imposed to account for different relativistic frameworks. Five commonly occurring cases, labelled by the excitation class manifold M, are implemented and displayed in table 2.4.

M=1 refers to a non-relativistic Hamiltonian and therefore disallows for a change in the Kramers projection. As this environment always implies the use of (restricted) spin-orbitals, the Kramers pairs are simply comprised by a pair of α and β spin functions and a common spatial function. This Hamiltonian class is only used for testing purposes.

M=2 defines a widely-used type of operators where the spin-dependent two-particle terms are approximated by an atomic mean-field [98]. The interface of LUCIAREL to a spin-orbital environment (like in the *MOLCAS* implementation [96]) would refer to this Hamiltonian type, but as the mentioned interface was written prior to the introduction of the excitation class formalism, it is currently not in use.

⁶Not necessarily forming a Kramers pair!

M	excitation classes		
	1-particle terms	2-particle terms	Environment
1	$\Delta M_k = 0$	$\Delta M_k = 0$	Non-relativistic
2	$\Delta M_k = 0, \pm 1$	$\Delta M_k = 0$	Orbitals, mean-field spin-orbit
3	$\Delta M_k = 0, \pm 1$	$\Delta M_k = 0, \pm 1, \pm 2$	Orbitals, full spin-orbit
4	$\Delta M_k = 0, \pm 1$	$\Delta M_k = 0, \pm 2$	Spinors, real/complex double groups
5	$\Delta M_k = 0, \pm 1$	$\Delta M_k = 0, \pm 1, \pm 2$	Spinors, quaternion double groups

Table 2.4: Manifolds of excitation classes depending on the relativistic Hamiltonian and framework

M=3 comprises the generalization of M=2 to a fully spin-dependent Hamiltonian, especially its two-particle terms, but still referring to a scalar one-particle basis. This line of development has been abandoned for the time being, for two reasons: It would go beyond the atomic mean-field approximation for the spin-orbit terms, but as this approach has proven to be extremely reliable and precise both for heavy [61] and also light elements [4, 116], there is little motivation for this kind of implementation. Second, the interface to a spinor environment which is completed [4] and presented in this thesis opens for the use of fully spin-dependent operators in the orbital optimization step. Beside this generalization as such, spinors form an improved one-particle basis for subsequent excitation-restricted correlation calculations.

When a spinor basis of Kramers pairs is used the type of Hamiltonian depends on the double group: The groups currently implemented are the binary groups (with an atmost twofold rotation axis). These can be subdivided into 3 classes by applying the Frobenius-Schur test [117], namely real matrix groups (D_{2h} , D_2 , and C_{2v}), complex matrix groups (C_{2h} , C_2 , and C_s), and quaternion groups (C_i and C_1)⁷. Unbarred and barred spinors transform according to *different* irreducible representations in the real and complex groups. This makes integrals with an odd number of bars vanish in these cases giving rise to the class M=4. In the quaternion groups the partners of a Kramers pair belong to the *same* symmetry, so all possible non-redundant integral types must be considered (M=5).

In the current implementation Kramers symmetry is exploited in the following fashion: Transformed integrals are initially stored over a full spinor list, meaning no reduction through Kramers symmetry is used at this stage. The excitation class formalism requires a distinct ordering of integrals, so a sorting (and reduction) step follows and the spinor list of integrals is deleted afterwards. The formalism furthermore allows for *implicitly* exploiting Kramers symmetry. Reference [4] gives details on the implemented types of excitation classes. As an example, the integral type

⁷The classification can best be understood in the context of quaternion algebra [118, 119, 8] where in the case of real matrix groups the quaternion degrees of freedom of represented quantities become scalar, those of complex groups become twofold, and those of quaternion groups remain fourfold.

$[ij|\bar{k}\bar{l}]$ is never explicitly referred to. In a conventional implementation of Kramers symmetry [96], one can relate $[ij|\bar{k}\bar{l}]$ to $[ij|lk]$ and fetch the corresponding integral from a reduced list. In the new implementation, the corresponding second quantization operator $a_i^\dagger a_k^\dagger a_{\bar{l}} a_j$ does not form a non-redundant excitation class, because $a_i^\dagger a_k^\dagger a_l a_{\bar{j}}$ referring to the integral $[i\bar{j}|\bar{k}l]$ is used in its stead. The essential difference between the mentioned operators is merely a sign. Thus, reference to most Kramers redundant integral types is intrinsically avoided and these are not stored on the integral list used in the CI procedure. The storage requirements have been further reduced by loading only a reduced list of integrals where quaternion symmetry is exploited (as described in reference [8]).

The implications of the excitation class formalism are twofold:

1. *Scientific.* Apart from the facilitated implementation of different Hamiltonian types in relativistic CI technology – as demonstrated above –, the formalism opens for general coupled cluster models where the use of multiple active spaces defines multi-reference approaches (4.2).
2. *Technical.* In the present implementation the evaluation of projected vectors and density matrices (2.2.3) is greatly simplified and generalized through the use of excitation classes. The incorporation of a new operator type is almost trivial now, as it merely requires a modification of a single setup routine. Moreover, the classes define a distinct ordering of integrals (associated with the string of elementary second-quantized operators) and density matrix elements, and allow for a concise storage of the quantities required in an individual calculation.

The precursor program code for the implementation has been taken from the non-relativistic coupled cluster version of LUCIA (in [120]) and extended to account for the relativistic environment. The excitation class formalism will thus be addressed with the according implications in the context of CC theory (section 4).

2.2.3 Projected Vectors and Density Matrices

The treatment of large CI expansions where at the same time only a few (lowest) eigensolutions are required calls for devoted iterative optimization procedures. In the present context, the decisive step of the afore-mentioned complex Davidson algorithm is the linear transformation acting on the CI coefficient vector of a given iteration. The principles and performance of this approach are described elsewhere [91, 95].

The appearance of a wider class of integrals (and density matrices!) in the spinor basis calls for modifications of existing program code that can best be tackled by a complete generalization. The projected vectors are required for plain CI calculations, but for MCSCF problems (3) active density matrices for Kramers-paired spinors

need to be computed in addition. Two aspects of this generalization are of particular importance; A more detailed account can be found in reference [4]:

2.2.3.1 Excitation class driven algorithm.

As an example, I will discuss the evaluation of a projected (sigma) vector fragment from the linear transformation (in matrix notation)

$$\boldsymbol{\sigma} = \mathbf{H}\mathbf{C}.$$

Large calculations make it impossible to store the entire Hamiltonian matrix \mathbf{H} or even a single reference vector \mathbf{C} of expansion coefficients. The occurring vector quantities are therefore split up into batches and processed one at a time. Hierarchical criteria for the construction of a batch are

- Real/imaginary part of coefficients
- Kramers projection M_K of corresponding determinants
- Symmetry and GAS occupation type of the corresponding unbarred and barred creator strings
- A maximum subblock size which is input-driven

The fragments of the sigma vector can be labelled with an M_K and a real/imaginary index, e.g. as $\boldsymbol{\sigma}_r^{M_K}$. A specific example might be

$$\sigma_r^{+1}(\mathcal{T}, \bar{\mathcal{T}}) = \sum_{ijkl} \sum_{\mathcal{S}, \bar{\mathcal{S}}} (i\bar{j}|kl)^{r/i} A_{i\bar{j}kl}^{\mathcal{T}\bar{\mathcal{T}}, \mathcal{S}\bar{\mathcal{S}}} C_{\mathcal{S}, \bar{\mathcal{S}}}^{r/i} \quad (2.4)$$

where $\mathcal{S}\bar{\mathcal{S}}$ denote unbarred and barred creation strings and $A_{i\bar{j}kl}^{\mathcal{T}\bar{\mathcal{T}}, \mathcal{S}\bar{\mathcal{S}}} = \langle \mathcal{T}^\dagger \bar{\mathcal{T}}^\dagger | a_i^\dagger a_k^\dagger a_l a_{\bar{j}} | \mathcal{S}^\dagger \bar{\mathcal{S}}^\dagger \rangle$ is the CI coupling coefficient for the batch types of bra ($\mathcal{T}\bar{\mathcal{T}}$) and ket ($\mathcal{S}\bar{\mathcal{S}}$) determinants. Given a batch type of these for both the bra and the ket side, the excitation classes (of the operator) leading to a non-vanishing coupling coefficient are determined. If a coupling is detected, the code enters a set of routines that is entirely independent of excitation class or the above-mentioned labels⁸, carrying out the matrix operations. The introduction of excitation classes therefore makes these evaluation procedures very transparent and easy to modify, because a new operator would not call for modifications in the involved inner parts of the program.

⁸It would, e.g., even evaluate a sigma vector over a 3- or n-particle operator

2.2.3.2 Equivalence of evaluation.

The true power of the method but unfolds in the fact that the computation of sigma vectors and density matrices can now be carried out with the *same* inner set of routines, respectively. Replacing the integrals $(i\bar{j}|kl)^{r/i}$ used in the contraction for the sigma vector (2.4) with expansion coefficients of the bra determinants $C_{T,\bar{T}}$, a density matrix fraction

$$\rho^r(2) (i\bar{j}|kl) = \sum_{S,\bar{S}} \sum_{T,\bar{T}} C_{T,\bar{T}}^{r/i} A_{i\bar{j}kl}^{T\bar{T},S\bar{S}} C_{S,\bar{S}}^{r/i} \quad (2.5)$$

is evaluated. The computation of general relativistic density matrices is now possible in the recent implementation. This possibility opens for the incorporation of LUCIAREL in a relativistic MCSCF program (3.3.2) where such density matrices are required.

The here-described features are in essence of technical nature, but the implementation allows for extensions and interfaces in a straightforward and transparent manner and thus comprises a cornerstone for improved scientific methodology as elucidated in the following sections on MCSCF and coupled cluster theory.

2.2.4 Relativistic GASCI in an overview

Figure 2.2 displays the schematic Hamiltonian matrix for a 6-particle system.

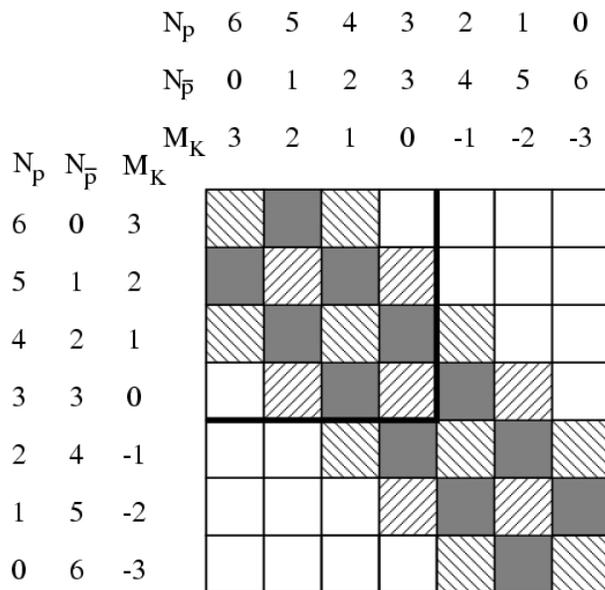


Figure 2.2: Hamiltonian matrix for a 6-particle system. N_p is the number of electrons in unbarred Kramers pairs, $N_{\bar{p}}$ the number of electrons in barred Kramers pairs.

The first CI iteration is the Hartree-Fock determinant in the closed shell case and a simple linear combination of a few determinants in the open-shell case. Assuming

that the initial wave function corresponds to a non-relativistic or scalar relativistic Hamiltonian, this initial wave function has a well-defined Kramers projection value M_K . In the second iteration, all possible couplings from the initial determinants to all singly and doubly excited determinants are included, necessarily having Kramers projection value from M_K to $M_K \pm 2$. This step can be viewed as a first order coupling in terms of perturbation theory. The third iteration includes all the determinants that can be obtained from the initial wave function with up to quadruple excitations and Kramers projection from M_K to $M_K \pm 4$. In the case depicted in figure 2.2 this comprises the full determinant space, but in cases with more open orbitals, a larger number of iterations may be required to include the full determinant space.

An additional feature can be seen from figure 2.2 (further details can be found in reference [121]): The box in the upper left corner symbolizes the reduction of non-redundant contributions in the case of an even number of electrons. This corresponds to exploiting time-reversal symmetry in the many-particle wave function (see also the discussion of this point in the context of coupled cluster theory, subsection 4.3.2), the implementation of which would require changes in the linear transformation (sigma vector) evaluations. In the odd-fermion case, time-reversal symmetry is more easily exploited at the many-particle level if Kramers partners fall into different fermion irreducible representations, which is the case in complex matrix groups. Real matrix groups are treated by switching to the highest complex subgroup thus ensuring the same symmetry blocking. Here in addition, it is exploited that all integrals are purely real [118].

2.3 Approximate Schemes: Spin-orbit Free CI

4-Component Dirac theory does not essentially distinguish between internal magnetic interactions (like spin-orbit coupling) and spin-independent relativistic phenomena. These become apparent only when 4-component operators are transformed to an approximate, 2-component framework [122]. The obtained operators may then be identified as those describing magnetic interactions leading to level splittings and those referred to as “scalar relativistic” contributions which include the mass-velocity term giving rise to relativistic orbital contractions and associated energy shifts. Using only the latter allows for a one-component formalism and the use of point group symmetry for orbitals and many-particle functions just as in non-relativistic implementations.

Unfortunately, there are multiple ways of carrying out the separation into spin-dependent and spin-free terms. A good overview is given in [123] which also includes a numerical comparison of the different approaches. A very elegant variant has been proposed by Dylla [124] where the Dirac identity and a formalization of the kinetic balance relation are used to obtain a spin-free 4-component Dirac Hamiltonian. Based on this separation scheme and its implementation in the DIRAC program

package, both “scalar relativistic” CI (2.3.3) and CC (4.4) implementations are described and applications reported (5.2.3.1 and 5.2.2.3) in the following.

2.3.1 General Remarks

When spin-orbit coupling is omitted from the relativistic formalism regular non-relativistic point group symmetry can be used in program implementations. Moreover, the program package DIRAC [36] supplies algebraically real molecular integrals in the spin-free limitation, despite the use of a 4-component formalism. This is achieved by employing quaternion algebra [119], in particular a formulation based on the quaternion-modified Dirac equation [118]. In view of the fact that the correlation stage of a quantum chemical calculation usually is the cost determining, the increased expense by carrying out a 4-component orbital optimization prior to the CI is hardly relevant. The present implementation therefore allows for large-scale scalar relativistic CI calculations.

2.3.2 Previous Implementations

To my present knowledge, the only configuration interaction program capable of running spin-free Dirac calculations is the DIRRCI (see [105]) module of the Dirac program package. This implementation is based on the threefold RAS concept and allows for arbitrary excitations out of the hole space (RAS 1), arbitrary excitations into the particle space (RAS 3), and CAS CI expansions in the active space (RAS 2). The need for improvement becomes obvious when comparing performance with the present implementation which is reported in subsection 2.3.5. Many other CI programs are used in 1-component approximation where most often the required integrals are evaluated over the Douglas-Kroll-Hess Hamiltonian [125, 126, 127].

2.3.3 Implementation

The precursor CI code for this development work is the spin-free Hamiltonian CI code LUCITA [128] which is the *MOCCAS*-adapted version of LUCIA, mentioned earlier. The existence of a general input and integral interface section in this modification was the reason for using LUCITA as a set-out for the adaptation to the DIRAC package. The adaptation includes

1. A modification of the concise input section to DIRAC standards, documented in the manual of the DIRAC04 release [36]. Like the LUCIAREL program described above, the program exploits the concept of general active spaces (2.2.1). Beside this most general specification, the standard CI models of Singles and Doubles CI (SDCI), Singles, Doubles, Triples, Quadruples CI (SDTQ), Restricted Active Space (RAS) CI, and full CI (FCI) are automatic input options, all based upon the GAS representation of the wave function.

2. An integral interface to transformed integrals over point group symmetry orbitals. Integrals with the same symmetry properties are delivered also in the Lévy-Leblond formalism of the DIRAC package. This opens for applications studying the effect of scalar relativistic contributions directly by comparison with the 4-component non-relativistic Lévy-Leblond scheme [129].

Further details on the implementation are mentioned in the references [5, 10].

2.3.4 Scope of the Method

2.3.4.1 Scientific

The range of applicability of a large-scale spin-free relativistic CI method is somewhat limited. Spin-orbit coupling often plays an important role in heavy-element compounds, and for all such electronic spectra which either have large spin-orbit splittings or states in which second-order spin-orbit contributions become sizeable, the method does not apply. However, many molecules have closed-shell (ground) states with rather small second-order spin-orbit contributions, e.g. the gold dimer [5], the CsLi molecule [10], or the hydrogen halogenides [130]. In most of these cases, single-reference CC methods are better suited due to their greater efficiency as compared to CI techniques. There are systems, though, where the singlet states have significant multi-reference character, like the heavier sulfur analogue trimers [131] in linear geometry. Here multi-reference approaches are required. Moreover, LUCITA provides a straightforward means of describing also excited states with the mentioned character.

2.3.4.2 Technical

There are two main technical motivations for the discussed CI implementation:

1. *Higher excitations.* Singles and Doubles CI calculations do not provide high accuracy and fail to predict e.g. dissociation energies even of closed-shell compounds due to the unbalanced description of bonded and dissociated system. Multi-reference CI expansions typically contain triple and quadruple excitations relative to the reference state, but also higher excitations than Quadruples are desirable for achieving high accuracy [132].
2. *Long CI expansions.* The high-precision treatment of dynamic electron correlation by CI methods requires the inclusion of many determinants (or CSFs), often up to several billion even in smaller molecules. The DIRRCI program can efficiently handle only roughly up to 1 million determinants.

2.3.5 Performance

A timing comparison of the two CI modules given in table 2.5 demonstrates the achievements of the current implementation.

	# of dets	Energy E_H	DIRRCI	LUCITA
SD8:	23.169	-2605.6739629466	794 s	54 s
SdT8:	1.575.409	-2605.6780714925	124.2 h	0.8 h
SdTQ8:	56.025.807	-2605.6849961265	–	24.5 h
SD18:	118.728	-2605.8559825571	5.085 s	130 s
SdT18:	21.704.728	-2605.8611977183	⁹	11.3 h

Table 2.5: CPU Timings for CI calculations on the HBr molecule, distance $2.5 a_0$, virtual cutoff 100 a.u., point group C_{2v} . A single processor type Pentium IV Xeon, 2.4 GHz was used. SD8 denotes a single-reference CI calculation with Single and Double replacements and correlating 8 electrons.

The calculations employ the *MOLCAS* 6.1 [97] basis sets of type ANO-S in an uncontracted fashion, where the small component functions are generated via the restricted kinetic balance prescription [133]. Small component integrals are neglected and their effect modelled by the Coulombic interaction of atomic small component charges [134]. The virtual orbital space is truncated at 100 a.u.¹⁰.

It becomes obvious that DIRRCI cannot compete even in small calculations involving only up to double excitations. Correlating 18 electrons, the Singles and Doubles calculation (118.728 determinants) gains a speed-up of a factor of almost 40 in the LUCITA run. The discrepancy becomes even more drastic when triple excitations are included (correlating 8 electrons). Here, the string-based algorithm of LUCITA has the great advantage of being entirely independent of the excitation type, resulting in a 155 times shorter calculation time. At the larger scale (SdT18), DIRRCI runs cannot be completed in a decent amount of time, whereas LUCITA requires merely 11.3 hours for a calculation involving more than 20 million determinants. As demonstrated in the calculation including also all quadruple excitations and correlating 8 electrons, LUCITA converges to the ground state in about a day.

2.3.5.1 Further Remarks

Large-scale calculations involving hundreds of millions of determinants require a few days of computing time, as reported in reference [5]. Most of the time (more than 80%) is spent in the linear transformations to obtain sigma vectors which opens for efficient parallelization schemes based on the batching of transformation tasks.

⁹After 13 days a single iteration has completed. The required disk space amounts to roughly 20 GB.

¹⁰The use of uncontracted basis sets justifies such truncations as virtual orbitals of high energies either hardly contribute at the correlated stage or are of core-correlating type.

A performance comparison of the fully relativistic implementation LUCIAREL (see 2.1.2), where the relativistic GAS implementation leads to a somewhat increased overhead, with the DIRRCI code gives a similar picture. The speed-up is not as dramatic, but still amounts to a factor of 2 in an SD18 calculation and the same orders of magnitude as the scalar relativistic speed-ups for calculations involving higher than double excitations.

Chapter 3

Relativistic Multi-Configuration Self-Consistent Field Technique

3.1 General Remarks

MCSCF theory comprises the most general optimization procedure of the wave function in both the N-electron sector of Fock space and its one-particle subspace [135]. Orbital transformations and excitations in configuration space are parameterized and simultaneously optimized which in particular aims at the treatment of near-degeneracies of states as they occur in molecular dissociation processes. The method contains the Hartree-Fock Self-Consistent Field (SCF) method and Configuration Interaction theory as special cases. Consequently, its high generality makes it applicable for describing the electronic structure of virtually any molecule or atom. The method has therefore been established as a central technique in many quantum chemical program packages, e.g. [113, 136, 137, 138], and is used for obtaining orbitals for subsequent (dynamic) electron correlation treatments or/and property calculations including the so-called static correlation effects arising from near-degenerate electronic valence configurations. Examples of modern applications involve the calculation of ground and excited state potential energy surfaces like in the geometry optimization of the $\text{HMn}(\text{CO})_3(1,4\text{-diazabuta-1,3-diene})$ molecule [139] and frequency-dependent polarizabilities and hyperpolarizabilities using MCSCF response theory [140]. When the configuration space expansion in the selected active space includes all possible determinants or CSFs, the CI becomes a Full CI expansion and the method is referred to as Complete Active Space (CAS) SCF [141]. It is the most widely used variant of MCSCF methods, and in conjunction with the CAS Perturbation Theory 2nd order (CASPT2) approach [47, 48], where dynamic electron correlation is assessed by second-order perturbation theory based on the CASSCF reference function, the method has become a powerful tool for carrying out correlated calculations. Sample applications cover excited states of adenine and uracil [142] or auride ions embedded in He clusters [143].

The range of applicability in view of the size of a molecule is difficult to discuss. In principle, MCSCF applies to any system that can also be treated by a Hartree-Fock calculation. The limiting factors strongly depend on the efficiency of a given implementation. In the present case, they are the size of the corresponding CI expansion (see section 2.1), which in turn is determined by the number of active electrons and the number of active orbitals required, and the hard disk requirements for molecular integrals over 2 general and 2 active orbital indices¹. Due to the large basis sets required in 4-component relativistic theory, which moreover are usually uncontracted, this issue implicitly leads to another practical limitation: The iterative MCSCF procedure involves an integral transformation step in each of the macro-iterations, and this step becomes very time-consuming in larger-scale calculations.

3.1.1 Previous Relativistic Implementations

Two types of "relativistic" MCSCF programs will be excluded from the following summary:

1. *Scalar relativistic implementations.* Based on scalar relativistic approximations of the Hamiltonian (like the DKH approximation excluding spin-dependent terms or a perturbational account of the mass-velocity and Darwin terms) any non-relativistic MCSCF program can in principle make use of these contributions in molecular calculations (e.g. [113]).
2. *Purely atomic codes.* A number of typically numerical finite-difference programs is reported which are restricted to atoms only; a full account is given in a recent review [60].

The MCSCF approach in the framework of quasidegenerate direct perturbation theory of relativistic contributions [144, 145] is not genuinely relativistic MCSCF in the sense used here as relativistic effects in their approach are added on top of a non-relativistic MCSCF. Furthermore, the implementation has not been pursued further so as to allow for a full inclusion of spin-orbit coupling in the optimization, although the method is applicable to general molecules. The molecular code presented by Kim and Lee [146] is restricted to two-component approximation, and furthermore, is based on relativistic effective core potentials. Their work documents some of the benefits of a fully variational KR-MCSCF method for static correlation. To my present knowledge, the implementation described in this thesis is the first all-electron 4-component MCSCF method of general applicability to any molecule or atom. The

¹The basis for the latter argument is the commonly encountered case that the virtual orbital space is much larger than the active and the inactive spaces. In HF theory then, the largest number of two-particle integrals occurs in the virtual-virtual Fock matrix elements, containing 2 virtual and 2 inactive indices. Likewise in an MCSCF, the 2 inactive indices are replaced by 2 indices which run over the inactive and active orbital spaces.

philosophy adopted here is to have maximum generality available and then in view of specific applications “activate” particular approximations. Currently, the aforementioned (see 2.1.2) 2-component BSS Hamiltonian may be used which speeds up the time-consuming integral transformation step significantly² and is a very good approximation for electronic valence properties. In the framework of the quaternion modified Dirac equation [118] the two-component ZORA approximation [39, 40] is parameterized in the program package DIRAC, constituting a further — but as of yet unused — alternative.

3.1.2 Scope of the Method

The aim of this method development work is mainly directed at properties of heavy-element systems where spin-orbit contributions are important and the states of interest cannot be described sufficiently by a single electronic configuration. In particular, the following areas are of interest:

1. *Spectroscopic Properties.* Open-shell and multi-reference molecular systems containing heavy elements require a simultaneous treatment of electron correlation and spin-orbit coupling. Typical examples are the dimer of thallium [19] and many lanthanide and actinide-containing molecules [147]. A more exotic case is the dimer of the superheavy element 111 [27]. The static correlation level adopted in MCSCF methodology is an ideal starting point for the study of these systems. The most important contributions can be accounted for by selecting active spaces appropriately. In cases where dynamic electron correlation is essential, the spinors obtained from an MCSCF calculation serve as a one-particle basis for subsequent correlation treatments, already including spin-orbit coupling in the valence shells. MCSCF further allows for the calculation of full potential curves (surfaces).
2. *Electric and magnetic properties.* Numerical finite-field evaluations of such properties can (almost) always be applied (see 6.1.2). In combination with response theory, (4-component) MCSCF allows for a fully variational relaxation of the wave function with respect to the external perturbation [148]. In the 4-component framework, the calculation of magnetic response properties is facilitated as there is only one perturbing operator, linear in the vector potential [149]. The MCSCF implementation therefore will be useful for linear and non-linear response properties in later developments.

²as small component integrals are eliminated.

3.2 Relativistic MCSCF Theory

A full account of the underlying formalism of relativistic MCSCF theory can be found in the references [8, 121, 150]. I therefore refrain from repetition and instead focus on and discuss important aspects from both a theoretical and a practical point of view, especially with respect to the scope of the method and potential and actual applications.

3.2.1 Furry picture

The adopted physical picture in the present MCSCF implementation [121] is based upon the traditional view of Dirac-Fock theory [119]. Here, the negative-energy states³ are considered unoccupied and, therefore, belong to the secondary orbital space. These eigenstates are not re-interpreted as is done in Quantum ElectroDynamics (QED) by renormalization, where the negative-energy states are occupied allowing for the creation of electron-positron pairs by excitation from the negative- to the positive-energy branch [151, 152]. Instead, excitations are allowed *into* the negative-energy states and the energy is *maximized* with respect to such orbital rotations, whereas it is *minimized* for orbital rotations involving the unoccupied positive-energy (electronic) solutions. This procedure is called *minmax* principle, a generalization of the variation principle. It is implemented as a generalization to the MCSCF procedure of what Talman describes [153] for the Dirac-Coulomb Hartree-Fock (DC-HF) case. In the QED picture, on the other hand, the optimization follows a minimization principle. In effect, retaining the additional degrees of freedom (the orthogonal complement to the electronic orbitals) allows for the complete relaxation of the electronic ground state [119].

The MCSCF approach employs an iterative procedure corresponding to a multi-configurational extension of the procedure in a DC-HF program. The averaged Fock potential for the electron-electron interaction changes from iteration to iteration, until convergence. This potential *implicitly* contains — beside the plain Coulombic interaction term of the electrons — the spin-same-orbit interaction which separates off upon applying a transformation to a 2-component framework [122].

3.2.2 MCSCF Parameterization

The wave function explicitly depends on the vectorial set of parameters in configuration space ($\boldsymbol{\delta}$) and the one-particle subspace ($\boldsymbol{\kappa}$) and together with the complex conjugates forms a parameter manifold $\boldsymbol{\lambda} = [\boldsymbol{\Gamma}, \boldsymbol{\Gamma}^*] = [\boldsymbol{\delta}, \boldsymbol{\kappa}, \boldsymbol{\delta}^*, \boldsymbol{\kappa}^*]$. Interest lies in

³Most often, these states are referred to as positronic states, and this expression will be used in the following for convenience. It has been pointed out by Visscher and Saue [59], however, that due to the definition of one-particle solutions with respect to the *electronic* charge, all states are actually electronic. Positronic states are obtained from the negative-energy states by charge conjugation.

the stationary variational value derived by minimization/maximization of the energy expectation value functional over this wave function, i.e. the variation of

$$E(\boldsymbol{\lambda}) = \langle \Psi(\boldsymbol{\delta}, \boldsymbol{\kappa}, \boldsymbol{\delta}^*, \boldsymbol{\kappa}^*) | \hat{H} | \Psi(\boldsymbol{\delta}, \boldsymbol{\kappa}, \boldsymbol{\delta}^*, \boldsymbol{\kappa}^*) \rangle \quad (3.1)$$

with the parameter set. The Hamiltonian \hat{H} remains general at this point. The implementation has been tested with the Dirac-Coulomb and the BSS Hamiltonians, but other operators, for instance the spin-free Dirac or the ZORA Hamiltonian, can in principle also be invoked.

In contrast to non-relativistic MCSCF theory [135] where spin-independent Hamiltonians lead to formalisms of real arithmetic, the parameter set here becomes twice as large, containing also the complex conjugate parameters accounting for the imaginary degrees of freedom of the system. Consequently, the relativistic implementation has to consider all possible additional savings in order to be efficient. In particular, these are the use of Kramers symmetry, quaternion symmetry, and fully direct iterative techniques, both in the integral transformation step as well as in the construction of the second-derivative matrix (Hessian) with respect to the parameter set. Implications of these will be addressed in appropriate subsections.

3.3 Implementation

3.3.1 Optimization algorithm

Expanding the energy expression (3.1) in a Taylor series $q(\boldsymbol{\lambda})$ around the current expansion point $\boldsymbol{\lambda}$ and applying variation $\frac{\partial q(\boldsymbol{\lambda})}{\partial \boldsymbol{\lambda}}$ to the expression truncated after the second-order term yields the Newton step equation

$$\boldsymbol{\lambda} = - (\mathbf{E}^{[2]})^{-1} \mathbf{E}^{[1]}, \quad (3.2)$$

where

$$\mathbf{E}^{[1]} = \begin{pmatrix} \frac{\partial E}{\partial \Gamma^*} \\ \frac{\partial E}{\partial \Gamma} \end{pmatrix} \quad \text{and} \quad \mathbf{E}^{[2]} = \begin{pmatrix} \frac{\partial^2 E}{\partial \Gamma^* \partial \Gamma} & \frac{\partial^2 E}{\partial \Gamma^* \partial \Gamma^*} \\ \frac{\partial^2 E}{\partial \Gamma \partial \Gamma} & \frac{\partial^2 E}{\partial \Gamma \partial \Gamma^*} \end{pmatrix} \quad (3.3)$$

are the complete gradient and Hessian matrices.

In contrast to non-relativistic MCSCF calculations, the Hessian must not be positive definite but must rather display one negative eigenvalue per electron-positron orbital rotation parameter to avoid variational collapse, according to the minmax principle. The number of negative eigenvalues of the Hessian can be controlled efficiently within the implemented Norm Extended Optimization (NEO) algorithm [154]. It includes a ‘‘level-shift’’ parameter ν resulting in a Newton-type equation with a modified Hessian matrix:

$$\boldsymbol{\lambda} = - \left(\mathbf{E}^{[2]'} - \nu \mathbf{I} \right)^{-1} \mathbf{E}^{[1]}, \quad (3.4)$$

Moreover, the NEO algorithm conserves quadratic convergence and even guarantees convergence to the lowest state of a given symmetry by restricting the step vector to a trust region inside a hypersphere. The major advantage of the procedure in comparison with conventional second-order Newton-Raphson optimization techniques [135, 155] lies in the algorithm-contained specification of the level shift parameter which in the Newton-Raphson scheme has to be determined by explicitly obtaining the Hessian eigenvalues at the beginning of each macro-iteration.

3.3.2 Direct MCSCF algorithm

In view of large-scale applications and the increased number of parameters in the relativistic domain, it is imperative to exploit direct techniques for solving eqn. (3.2). By analogy to the complex generalization of the Davidson algorithm [112] the Hessian matrix is not set up explicitly but, instead, the step vector is expanded in a set of trial vectors \mathbf{b} . Separate sets of these trial vectors for the electronic-electronic, electronic-positronic, and configurational parameters, respectively, are introduced to assure the correct number of negative Hessian eigenvalues for a given state. The introduced expansion coefficients are then obtained by solving a set of projected linear equations, as described in detail in the literature [8, 121, 150]. Converging this “inner” type of iterations yields the optimal step vector $\boldsymbol{\lambda}$ which comprises the walk on the hypersurface towards the optimized MCSCF wave function.

The successive linear transformations comprising the micro-iterations read

$$\boldsymbol{\sigma}_j = \mathbf{E}^{[2]}\mathbf{b}_j \quad (3.5)$$

where the $\boldsymbol{\sigma}$ vectors include both orbital and configurational contributions. The off-diagonal parts comprising orbital contributions to configurational vectors and vice versa are also treated, yielding an algorithm which optimizes on the complete expansion space simultaneously. This procedure is more efficient than, e.g., the one adopted in [146] where successive optimizations in configuration and orbital space are carried out. The configurational (Hessian) sigma vectors (both orbital and configurational contributions) require the evaluation of CI sigma vectors with either the current expansion point CI vector or a trial vector. The orbital sigma vectors, on the other hand, require the evaluation of active density matrices, both of regular and transition density type (details in subsection 3.3.4). The recent implementation [9] makes use of the large-scale CI program LUCIAREL in these steps, allowing for the treatment of large CI expansions and a rapid evaluation⁴. This is important, as the inner loops of the iterative procedure are carried out quite often in a complete calculation. Moreover, the excitation class formalism described in detail in subsection 2.2.2 allows for the calculation of general density matrices using

⁴A CI sigma vector calculation including 25 million Slater determinants requires less than 30 minutes on a single Pentium IV Xeon 2.4 GHz processor.

the same inner code routines as for the CI sigma vectors, ensuring the same high efficiency in the computation of density matrices.

Before elaborating on the large-scale MCSCF implementation, the optimization procedure is described in figure 3.1.

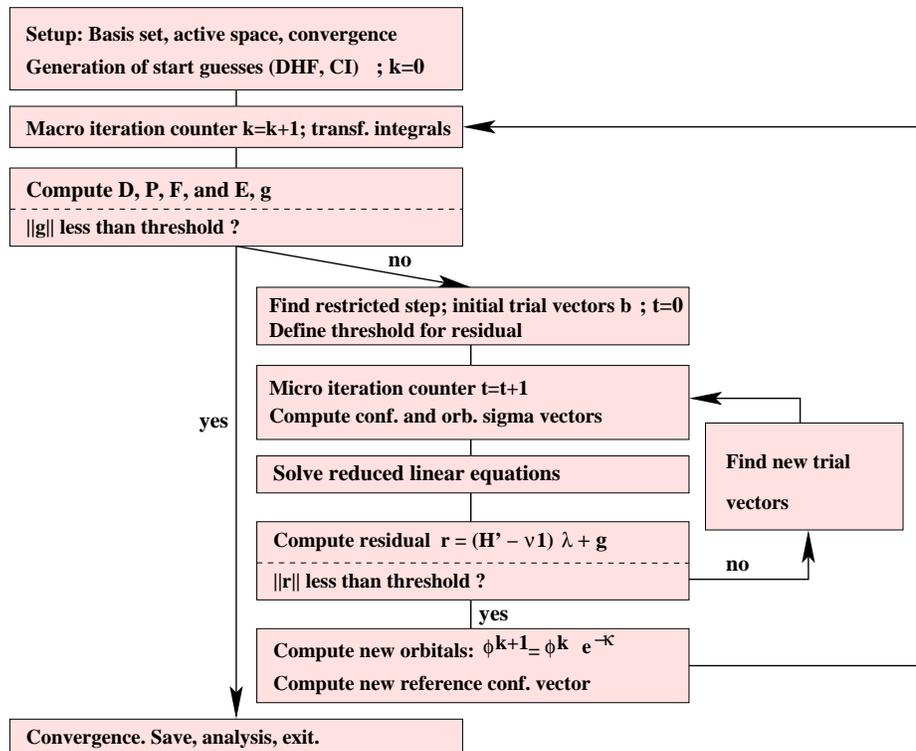


Figure 3.1: Schematic MCSCF optimization procedure

1. Setup of the calculation. Selection of basis set, generalized active space(s), convergence threshold t_{MC} , wave function symmetry (D_{2h}^* and subgroups), and state s to converge to ($s = 1$ for lowest state of specified symmetry, $s = 2$ for first excited state, etc.). Generation of start guess. Macro iteration counter set to zero, $k := 0$.
2. Incrementing macro iteration counter $k := k + 1$. If $k > k_{max}$ then JUMP TO STEP 8 (exit, not converged).
3. Transformation of integrals to the molecular orbitals of the current expansion point. Two-electron integrals with 2 general (electronic and positronic) and 2 active indices are needed.
4. Calculation of Kramers-reduced active one- and two-electron density matrices and the generalized Fock matrices; calculation of the total energy and the gradient. check the norm of the gradient for convergence $\|\mathbf{E}^{[1]}\| < t_{MC}$; if converged, **exit** the macro iteration loop (JUMP TO STEP 8).
5. Step control (when $k > 1$). A large ratio between the actual energy change and the second-order prediction indicates an incorrect description of the hypersurface structure; decrement the macro iteration counter in this case and resume in STEP 7 with the solution vector for a reduced trust radius calculated from the saved trial vectors from previous iteration; otherwise delete trial and sigma vectors from previous iteration.

6. Find the restricted step iteratively: the micro iterations. Project the Hessian onto the set of trial vectors \mathbf{b} ; Find the initial trial vectors using the generalized Davidson-Liu algorithm [112, 156]; set micro iteration counter to zero, $j := 0$, and set electron-positron (e-p) orbital rotation counter to zero, $p := 0$.
 - 6.1. Increment micro iteration counter ($j := j + 1$) and compute the sigma vector(s) for the trial vector(s) (of either configurational, e-e orbital, or e-p orbital type): ($\boldsymbol{\sigma}_n = \mathbf{E}^{[2]}\mathbf{b}_n$). For each trial vector of e-p orbital type, $p := p + 1$.
 - 6.2. Diagonalize the reduced Hessian $\mathbf{E}^{[2]j}$, eigenvalues $\{\epsilon_i\}$. Solve the reduced linear equations: find the optimal level shift parameter $\epsilon_{p+s-1} < \nu^j < \epsilon_{p+s}$ and the current approximate solution $\boldsymbol{\lambda}^j$ within the trust radius.
 - 6.3. Calculate the residual according to $\mathbf{R}^j = (\mathbf{E}^{[2]} - \nu_j \mathbf{I})\boldsymbol{\lambda}^j + \mathbf{E}^{[1]}$; if the norm of the residual is less than convergence threshold t_{micro} , then **exit** the micro iteration loop and jump to STEP 7; if not, new trial vectors are generated and the program continues with STEP 6.1.
7. Obtain new orbitals and new configuration coefficients.
Jump to STEP 2.
8. Exit, print requested information about final KR-MCSCF wave function.

3.3.3 Large-scale MCSCF implementation

The main interface points to LUCIAREL for obtaining a large-scale implementation are the linear transformations of given vectors and the computation of density matrices from CI vectors. A short summary follows, and further details can be found in reference [9].

3.3.3.1 Sigma vectors

The evaluation of the complete electronic gradient $\mathbf{E}^{[1]}$ calls for derivatives with respect to the configurational parameters in a given macro-iteration. As an example, the term for a determinant $|\Phi_\mu\rangle$ reads (eqn. (3.12) from reference [121])

$$\left. \frac{\partial E}{\partial \delta_\mu^*} \right|_{\lambda=0} = \langle \Phi_\mu | \hat{H} | c^{(k)} \rangle - E^{[0]} c_\mu^{(k)} \quad (3.6)$$

meaning a sigma vector type expression $\hat{H} | c^{(k)} \rangle$ needs to be determined from the current expansion point vector $|c^{(k)}\rangle$.

The second place where computations of sigma vectors are required is in the calculation of orbital and configurational contributions to the configurational Hessian sigma vectors. Expressed in terms of configurational (c) and orbital (o) parameters, the matrix equation 3.5 reads

$$\begin{pmatrix} \boldsymbol{\sigma}^c \\ \boldsymbol{\sigma}^o \\ \boldsymbol{\sigma}^{c^*} \\ \boldsymbol{\sigma}^{o^*} \end{pmatrix} = \begin{pmatrix} \mathbf{E}^{[2]c^*c} & \mathbf{E}^{[2]c^*o} & \mathbf{E}^{[2]c^*c^*} & \mathbf{E}^{[2]c^*o^*} \\ \mathbf{E}^{[2]o^*c} & \mathbf{E}^{[2]o^*o} & \mathbf{E}^{[2]o^*c^*} & \mathbf{E}^{[2]o^*o^*} \\ \mathbf{E}^{[2]cc} & \mathbf{E}^{[2]co} & \mathbf{E}^{[2]cc^*} & \mathbf{E}^{[2]co^*} \\ \mathbf{E}^{[2]oc} & \mathbf{E}^{[2]oo} & \mathbf{E}^{[2]oc^*} & \mathbf{E}^{[2]oo^*} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{b}^c \\ \mathbf{b}^o \\ \mathbf{b}^{c^*} \\ \mathbf{b}^{o^*} \end{pmatrix}, \quad (3.7)$$

of which the different elements $E^{[2]c^*c} \cdot b^c$ etc. can be expressed as eqns. (3.29-32) in reference [121])

$$\sigma_{\mu}^{cc} = \langle 0 | \hat{H} | B \rangle - E^{[0]} b_{\mu}^c \quad (3.8)$$

$$\sigma_{\mu}^{co} = \langle \mu | \tilde{H} | 0 \rangle \quad (3.9)$$

$$\sigma_{pq}^{oc} = (\tilde{g}_{pq}^o)^* \quad (3.10)$$

$$\sigma_{pq}^{oo} = (\tilde{g}_{pq}^o)^* + \frac{1}{2} \sum_r g(r) b(r). \quad (3.11)$$

where \tilde{H} and \tilde{g} refer to the one-index transformed Hamiltonian and gradient, respectively, and $g(r)b(r)$ is an abbreviated expression involving products of gradient elements and expansion coefficients.

The first two expressions (3.8) and (3.9) correspond to a sigma vector step with the trial vectors $|B\rangle$ (Hessian solution expansion vector) and $|0\rangle$ (current configurational C vector), respectively. These linear transformations are now efficiently carried out by LUCIAREL on the basis of the string-based algorithm. The remaining two orbital terms (3.10) and (3.11) are derived from the orbital gradient, the evaluation of which will be discussed in the following subsection 3.3.3.2.

As an efficient option, integrals with two positronic indices may be neglected in the calculation of sigma vectors. As long as these are included in the gradient, the KR-MCSCF wave function is fully relaxed with respect to electron-positron rotations. Although this is not a fully second-order optimization, it gives satisfactory convergence at a significantly lower cost in the integral transformation [8, 121].

3.3.3.2 Density matrices

Both the orbital part of the gradient and of the direct Hessian evaluation require one- and two-electron density matrices over the active space indices (active in the sense of the GAS concept 2.2.1). Excitations between all orbital spaces including the inactive and secondary spaces are considered and the spinor gradient element reads

$$\left. \frac{\partial E}{\partial \kappa_{pq}^*} \right|_{\lambda=0} = - \langle c^{(0)} | [\hat{X}_{qp}^-, \hat{H}] | c^{(0)} \rangle = F_{qp} - F_{pq}^* = f(\rho_1^+, \rho_2^{++}). \quad (3.12)$$

F_{qp} here is a generalized Fock matrix [8, 150] and $f(\rho)$ a function of the one- (ρ_1^+) and two-electron (ρ_2^{++}) density. The \hat{X} operators are unitary second-quantized excitation operators adapted to time-reversal symmetry (defined in [157, 158], see also subsection 4.3.3). The introduction of Generalized Active (GA) spaces makes the classification of orbital rotations non-trivial. To exclude redundant orbital rotations between two GA orbital spaces it is examined whether the chosen CI space is invariant with respect to rotations between these two GA spaces. Redundant orbital rotations are subsequently removed from the parameter space.

In each iteration, the density matrices are constructed to calculate the orbital part of the gradient. The second type of call occurs inside the micro-iteration loops in the evaluation of the orbital contributions to the orbital sigma vectors. Here, transition density matrices are required for expressions of the type

$$\langle c^{(0,k)} | [\hat{X}_{qp}^-, \hat{H}] | B \rangle$$

where B is a trial vector expansion in terms of determinants Φ_μ required for the direct update procedure

$$|B\rangle = \sum_{\mu} b_{\mu} |\Phi_{\mu}\rangle.$$

Full details can be found in the references [8, 9].

Density and transition density matrices are again computed efficiently also for large CI expansion vectors by LUCIAREL as described in subsection 2.2.3.2.

3.3.4 Further technical remarks

Full formal details on the technical quantities involved in the implementation can be found in reference [8]. The gradient and Hessian are expressed, like in regular MCSCF theory, in terms of generalized Fock matrices accounting for the different subspaces occurring (inactive, active, virtual). Unlike non-relativistic theory, the amount and classes of integrals and density matrix elements is now increased, owing to the separate treatment of unbarred and barred spinors. An efficient means of handling is comprised by quaternion algebra, which in combination with time-reversal and double group symmetry allows for a concise formulation and computational savings [119]. By means of specific choices of quaternion phase factors, all integrals (also spin-orbit type) can be brought to real form for the real matrix double groups (D_{2h}^* , D_2^* , and C_{2v}^*), allowing for real algebra in the entire formalism. This is exploited in part in LUCIAREL, but a full implementation would require to adapt the entire vector handling of the program to real algebra. The current implementation makes use of the corresponding storage reductions on integrals.

Chapter 4

Relativistic Multi-Reference Coupled Cluster (CC) Theory

4.1 General Coupled Cluster Theory

Full CI calculations become computationally intractable even for systems with less than 20 electrons when moderate basis set expansions (like a triple-zeta basis) are used. The most efficient many-body theory to approach the FCI energy is today comprised by coupled cluster theory¹. The main advantages of the CC model lie in the much higher compactness of the wave function and its termwise size-extensivity. The former leads to a rapid decrease of the error as compared to the FCI energy with increasing cluster excitation level which is due to the product (or equivalently exponential) parameterization of the wave function. In contrast to CI theory, this decrease also pertains at the odd excitation levels. The size-extensivity property makes CC methods favorable in the treatment of extended molecular systems and when correlating many electrons. A perturbative treatment of triple excitations on top of the iterative CC Singles and Doubles (CCSD) model (called CCSD(T) [161]) has become a standard model of electron correlation methods. Very often in molecular property calculations, the accuracy of more approximate treatments of electron correlation is calibrated by using the CCSD(T) result as a reference point (see subsection 5.2.3.1 for an example).

The problems unfold when the method is to be applied to open-shell states, in particular in multi-reference situations. In the non-relativistic case, pure spin states are not straightforwardly obtained, and the solutions proposed (spin-restricted CC theory [162], and for excited states [163]) fulfill this requirement in part. A full spin

¹Recent advances in the field of the Density Matrix Renormalization Group (DMRG) suggest an alternative methodology, but the current demands on resources both in time (weeks for a single-point calculation on the water molecule) and space (several hundreds of gigabytes of disk and memory) remain formidable [159]. A recent study [160] shows improvement of the DMRG technique which becomes more favorable than high-order single-reference CC at stretched geometries of the nitrogen molecule.

adaptation in the open-shell case leads to a theory where the cluster operators no longer commute, in turn rendering an efficient implementation a difficult task.

The calculation of excited states in CC methodology is nowadays carried out along three different lines: 1) Equation-of-Motion (EOM) ansatz, 2) CC response theory, and 3) Fock-space CC approach. Recent applications of the EOM-CC method include excited states of formaldehyde [164], but the method is by definition not strictly size-extensive. Linear response approaches based on CC expansions have become very popular both for the determination of various molecular properties and excitation energies, e.g. [165, 166, 167, 168, 169]. These approaches, however, are not applicable to multi-reference problems. The Fock-space CC approach is a genuine multi-reference technique and provides — beside excitation energies — especially ionization energies and electron affinities of the system and its positive and negative ions [170, 171, 172]. Fock-space CC has, on the other hand, so far not been used for the analytic determination of properties other than spectroscopic. Here it is worth mentioning that FSCC can describe a molecular dissociation process properly, but implementational as well as practical difficulties (convergence, intruder states) occur when this process involves more than two open shells [173]. Finite-field electric properties like dipole moments have been reported [174].

4.1.1 Previous Relativistic Implementations

The CC model currently witnesses rapid progress, with modern developments concerning iterative excitation levels higher than CC Doubles [110, 120, 164, 175] and various multi-reference approaches [120, 176, 177, 178]. However, none of these methods have been generalized to a relativistic formalism. The 4-component implementations by Visscher et al., Kramers-restricted [179] and unrestricted [180], respectively, are not generally applicable to open-shell/multi-reference states. The only relativistic multi-reference approaches reported to the date are the Fock-Space CC implementations by Landau et al. [181] and Visscher et al. [81]. These methods, as the Fock-space approach in general, suffer from the use of a common orbital basis for all of the occurring ionized systems. When the Fock space sector is increased to higher than ± 2 , the calculations become increasingly difficult to converge. Calculations with 4 or 5 open shells are therefore not possible in general with current FSCC implementations.

4.1.2 Scope of the Method

The multi-reference approach described here is capable of treating an arbitrary number of open shells and is therefore generally applicable, e.g. to heavy d and f elements. The state-selective MRCC approach (see 4.2) provides a means for treating general multi-reference problems including bond-breaking by proper choices of the reference space. Therefore, the current goal is the precise determination of spec-

scopic properties of small heavy-element molecules from calculations of complete ground-state potential energy curves (surfaces). The latest version of the program can treat scalar relativistic contributions “exactly”, i.e. in the spin-orbit free formalism (subsection 4.4) as discussed in the framework of CI (2.3). This limits the current applicability to systems with small contributions from spin-orbit coupling in the ground state, e.g. closed-shell compounds or open-shell systems with σ_s bonding orbitals (see 5.2.2.3). The full spin-dependent implementation is in progress, and theoretical issues are discussed in the following (4.3). The general-order implementation allows for calculations of benchmark precision on diatomic molecules, including cluster excitations of full iterative Triples or even Quadruples.

The implementation is carried out in the DIRAC framework which straightforwardly allows for the introduction of approximations, e.g. by the already-mentioned spin-orbit free formalism or by using the “exact” 2-component BSS Hamiltonian [72, 111]. Even though the computational expense at the correlated level is not reduced by a 2-component approximation, the orbital optimization and integral transformation steps are strongly reduced in demand which allows for the treatment of systems with more than 2 heavy atoms.

As the implementation is strongly facilitated by available relativistic CI technology, an EOM-CC implementation is considered for the calculation of excited states and their properties.

4.2 State-Selective Multi-Reference Approach

The original idea for this type of multi-reference CC approach is ascribed to Oliphant and Adamowicz [182, 183]. In the present approach [120, 132] the projection manifold is extended to simulate excitations from additional reference functions beside those from the Fermi vacuum state. The reference state is formally re-interpreted as a multi-configuration state including the additional reference functions. The parameters of the reference functions which are kept fixed in the implementations by Oliphant et al. are reoptimized in the present approach. The procedure retains the advantages of the single-reference formalism, although higher excitations than those arising from a standard single-reference ansatz are included in the amplitude equations. The drawback of this formalism — in contrast to FSCC or the state-universal ansatz [177, 184] — is the variance with respect to the choice of the Fermi vacuum, because despite the multi-determinantal nature of the reference state a “memory” of the occupied and unoccupied orbitals in the original reference state is retained in the cluster expansion. This also explains the term “state-selective”. The remedy, a separate cluster expansion for every reference function, leads to the state-universal Hilbert-space CC theory which is far less efficient [184]. The loss of Fermi vacuum invariance is, however, not of crucial importance in application and problems can be avoided by proper choices of reference spaces.

The relativistic CC method developed and applied presently is based on the state-selective implementation by Olsen [120, 132], where CAS or even GAS expansions (see 2.2.1) form the formal reference state. Three different implementations of the non-relativistic precursor code are being pursued also in the relativistic implementation:

1. Scheme 1: Based on CI expansions and very general, but without optimal scaling of the method (published in [120]) with respect to the number of occupied/unoccupied orbitals.
2. Scheme 2: Based on a similarity-transformed Hamiltonian and a completely revised evaluation of the CC vector function. This scheme offers the optimal scaling but does not allow for all types of MRCC expansions (published in part in [132]).
3. Scheme 3: Code which is based on the evaluation of commutators. It is completely general, efficient (on scaling and memory), but the current non-relativistic version is not fully stable, yet [185].

The generalization to a fully relativistic framework is carried out in different fashions, the theoretical foundations of which are explained in the following.

4.3 Spin-Dependent MRCC Implementation

The decisive aspects of the complete relativistic implementation are the inclusion of spin-orbit coupling, both at the one- and the many-particle level. The former requires the interfacing of the code to molecular (or atomic) integrals over general spinors, which in the current framework of the DIRAC package are Kramers-paired. The latter calls for a generalization of the cluster operators and the Hamiltonian to include Kramers flip terms. Moreover, time-reversal symmetry may be implemented at the many-particle level or not. These arguments lead to 3 implementation lines, an unrestricted, a Kramers restricted, and a Kramers adapted formulation.

4.3.1 Unrestricted Generalization

Extending the cluster excitations straightforwardly to include Kramers flip terms yields the operators in a Kramers-paired spinor basis

$$\begin{aligned}
 \hat{T}_1 &= \sum_{ia} \{ t_i^a \hat{\tau}_i^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_i^{\bar{a}} \hat{\tau}_i^a + t_i^a \hat{\tau}_i^{\bar{a}} \} \\
 \hat{T}_2 &= \sum_{\substack{i < j \\ a < b}} \{ t_{ij}^{ab} \hat{\tau}_{ij}^{ab} + t_{ij}^{ab} \hat{\tau}_{ij}^{\bar{a}\bar{b}} + t_{ij}^{\bar{a}\bar{b}} \hat{\tau}_{ij}^{ab} \dots + t_{ij}^{\bar{a}\bar{b}} \hat{\tau}_{ij}^{\bar{a}\bar{b}} + t_{ij}^{\bar{a}\bar{b}} \hat{\tau}_{ij}^{ab} \dots \} \\
 &\dots
 \end{aligned} \tag{4.1}$$

etc. for \hat{T}_n , with e.g.

$$\hat{\tau}_i^a := \hat{a}_a^\dagger \hat{a}_i$$

This straightforward formulation has the advantage of the relative ease of implementation and the conservation of the commutativity of the excitation operators \hat{T}_n . The reason for this is that the active (multi-reference) spaces are kept as active hole and active particle spaces analogous to the non-relativistic implementation in [120]. The drawbacks are the expense of the approach (no implemented savings through time-reversal symmetry at the many-particle level) and the expected Kramers contamination (see below) of amplitudes for many-particle states which would theoretically be related by time-reversal symmetry.

4.3.2 Kramers-Restricted Formalism

Non-relativistic open-shell and therefore multi-reference CC theory suffers from the imperfection of spin contamination (pp. 704 in [91]). Several possibilities of solution have been explored, and the most promising appears to be the spin-restricted scheme by Szalay and Gauss [162]. Here, spin equations in a subspace of the excitation manifold are fulfilled, yielding cluster amplitude restrictions ensuring the correct spin expectation value of the CC state. However, the CC wave function is not fully spin adapted and consequently, the energies of, e.g., the M_S components of a triplet state may still differ. The great advantages lie in the usual truncation of the spin-orbital CC amplitude equations and the possibility for computational savings by exploiting the amplitude relations.

In the relativistic case the problem of spin contamination remains, but as spin itself is not conserved there is no obvious way of curing spin contamination. However, as the employed one-particle basis is Kramers paired, there exists the possibility of a partial remedy.

In CI theory, the Kramers pairing of one-particle functions ensures certain time-reversal relations between the coefficients of many-particle functions formed from the one-particle functions, i.e. with Φ a many-particle wave function and $\hat{K}\Phi = \bar{\Phi}$ it follows that $\hat{K}\bar{\Phi} = (-1)^N\Phi$ with N the number of particles (see also reference [121]), giving rise to identities for expansion coefficients of the functions Φ and $\bar{\Phi}$. The deep reason for this lies in the fact that the CI solutions obtained are eigenfunctions of the Hamiltonian and $[\hat{K}, \hat{H}] = 0$. The latter is also true for CC theory, but here the common way of proceeding is to solve the equation system by projection instead of variational techniques². As a consequence, the optimized CC wave function is no longer an eigenfunction of the Hamiltonian, and the property of parameter relation through time-reversal symmetry is lost in general. Thus, the CC amplitudes do not reflect the time-reversal relations inherent in the many-particle states, in essence

²Variational CC theory is possible in principle, but highly inefficient because a truncation of the cluster expansion is no longer possible (see reference [91], p. 652).

due to the product parameterization of the wave function and the non-variational solution procedure. I will dub this symmetry breaking of the amplitudes *Kramers contamination*, accordingly. Two possibilities of removing Kramers contamination are explored in this thesis, the second of which involves a complete adaptation of the formalism to time-reversal symmetry which is discussed in the following subsection (4.3.3). The first possibility is motivated by the spin-restricted formalism of Szalay and Gauss and leads to the following conclusions:

From basic manipulations with the time-reversal operator \hat{K} acting on many-particle states the following condition is derived:

$$\langle \mu \mid [\hat{K}, e^{\hat{T}}] \mid \text{RHF} \rangle = 0 \quad (4.2)$$

with μ the excitation manifold and $\mid \text{RHF} \rangle$ some Kramers-restricted Hartree-Fock reference state. Given the commutativity of the Kramers operator with the (expanded) cluster excitation operator, this equation would be trivially fulfilled. For the closed-shell CCSD case, Visscher et al. showed that a set of amplitude conditions is *fulfilled* within the CC amplitude equations [179] and that these conditions could be exploited for computational savings. In the general open-shell case, however, where $[\hat{K}, \hat{T}] \neq 0$, eqn. (4.2) delivers the following amplitude relations:

$$\begin{aligned} t_i^a &= \bar{t}_i^{a*} & \bar{t}_i^a &= -t_i^{a*} \\ t_{ij}^{ab} &= \bar{t}_{ij}^{ab*} & t_{ij}^{ab} &= -\bar{t}_{ij}^{ab*} & \dots \\ t_{ijk}^{abc} &= \bar{t}_{ijk}^{abc*} & \dots & \end{aligned} \quad (4.3)$$

These are obtained by evaluating the commutator in eqn. (4.2) and comparison of coefficients, so that the total expression vanishes. The general pattern for higher amplitudes is that pairwise related amplitudes are found by barring all indices in a given amplitude and assigning a minus sign for every barred index that is barred a second time (turning it into an unbarred index). This of course reflects the properties of the time-reversal operator acting on one-particle states.

Similar to the approach proposed by Szalay and Gauss for the non-relativistic spin case, the Kramers conditions may be imposed to recover the Kramers relations between many-particle states in the CC optimization. To which extent this leads to computational savings and amends the Kramers contamination problem is subject of further investigation. The advantage of this approach lies in the fact that the structure of the cluster operators remains unchanged, i.e., a commuting formalism for the cluster operators can be retained. It may furthermore be possible to exclude redundant amplitudes (by eqn. 4.3) from the optimization thus reducing the number of independent parameters.

4.3.3 Kramers-Adapted Formalism

The complete spin adaptation of non-relativistic CC theory can be carried out by introducing linear combinations of spin-orbital excitation operators, the singlet operators \hat{E}, \hat{e} . These were implemented for the general open-shell case [186] in a unitary group framework and have the advantage of automatically ensuring exact spin states and a reduction of the number of free parameters. However, the expense is vastly increased by the complexity of the formalism, as non-commuting cluster operators lead to a theory where Baker-Campbell-Hausdorff (BCH) expansions of the wave operators truncate only after the the 8th-order commutator (instead of the 4th as in standard commutative CC approaches). An efficient non-relativistic implementation along these lines is in progress [187] which would be available for relativistic generalization.

The introduction of spin-orbit coupling to the formalism necessitates the use of Kramers instead of spin-adapted operators to remove Kramers contamination and to reduce the number of free parameters. The natural choice would be the \hat{X}, \hat{x} operators as introduced by Aucar et al. [157] (only the one-particle operators are shown here)

$$\begin{aligned}\hat{X}_{pq}^{\pm} &= p^{\dagger}q \pm \bar{q}^{\dagger}\bar{p} \\ \hat{X}_{\bar{p}q}^{\pm} &= \bar{p}^{\dagger}q \mp \bar{q}^{\dagger}p \\ \hat{X}_{p\bar{q}}^{\pm} &= p^{\dagger}\bar{q} \mp q^{\dagger}\bar{p}\end{aligned}$$

but they contain de-excitation terms $\bar{q}^{\dagger}\bar{p}$ etc. leading to the so-called unitary CC theory [188]. As a consequence, the BCH expansion of the amplitude equations even with a truncated excitation manifold μ

$$\langle \mu | e^{-\hat{T}(X)} \hat{H}(X) e^{\hat{T}(X)} | \text{HF} \rangle$$

does not truncate at all. The reason lies in the fact that the de-excitation terms undermine the rank reduction mechanism in the commutators which are obtained by expansion. Alternatively, the excitation operators (and the Hamiltonian) may be formulated in terms of the modified \hat{E} operators

$$\begin{aligned}\hat{E}_{pq}^{+} &:= p^{\dagger}q + \bar{p}^{\dagger}\bar{q} \\ \hat{E}_{\bar{p}q}^{+} &:= \bar{p}^{\dagger}q - p^{\dagger}\bar{q} \\ \hat{E}_{p\bar{q}}^{+} &:= p^{\dagger}\bar{q} - \bar{p}^{\dagger}q \\ \hat{E}_{pq}^{-} &:= i(p^{\dagger}q - \bar{p}^{\dagger}\bar{q}) \\ \hat{E}_{\bar{p}q}^{-} &:= i(\bar{p}^{\dagger}q + p^{\dagger}\bar{q}) \\ \hat{E}_{p\bar{q}}^{-} &:= i(p^{\dagger}\bar{q} + \bar{p}^{\dagger}q)\end{aligned}$$

which do not contain de-excitation terms. For ensuring time-reversal symmetry, an option is to treat real and imaginary parts of the \hat{E} operators separately, casting a

general one-electron operator \hat{W} in the following form:

$$\begin{aligned}\operatorname{Re}(\hat{W}) &= \sum_{pq} \operatorname{Re}(W_{pq}) \hat{E}_{pq}^+ + \operatorname{Re}(W_{\bar{p}q}) \hat{E}_{\bar{p}q}^+ \\ \operatorname{Im}(\hat{W}) &= -i \sum_{pq} \operatorname{Im}(W_{pq}) \hat{E}_{pq}^- + \operatorname{Im}(W_{\bar{p}q}) \hat{E}_{\bar{p}q}^-\end{aligned}$$

The so-defined \hat{E} operators fulfill $[\hat{E}^\pm, \hat{K}] = 0$ and therefore ensure a fully time-reversal symmetry adapted formalism, given that the Hamiltonian and the cluster excitation operators are expanded in them. Using the generic expressions of the many-particle excitation operators (with the help of reference [189]) as

$$\begin{aligned}\hat{E}_{pq}^+ &= (1 + \hat{K}_{pq}) p^\dagger q \\ \hat{e}_{pq,rs}^{+,+} &= (1 + \hat{K}_{pq}) (1 + \hat{K}_{rs}) p^\dagger r^\dagger s q \\ \hat{e}_{pq,rs,tu}^{+,+,+} &= (1 + \hat{K}_{pq}) (1 + \hat{K}_{rs}) (1 + \hat{K}_{tu}) p^\dagger r^\dagger t^\dagger u s q \\ &\dots\end{aligned}$$

where \hat{K}_{pq} is a Kramers replacement operator acting as

$$\hat{K}_{pq} p^\dagger q := \bar{p}^\dagger \bar{q},$$

cluster operators and the Hamiltonian can be expressed. As an example the one-particle cluster operator takes the form

$$\hat{T}_1 = \sum_{ia} \left\{ \operatorname{Re}(t_i^a) \hat{E}_{ai}^+ + \operatorname{Re}(t_i^{\bar{a}}) \hat{E}_{\bar{a}i}^+ - i \operatorname{Im}(t_i^a) \hat{E}_{ai}^- - i \operatorname{Im}(t_i^{\bar{a}}) \hat{E}_{\bar{a}i}^- \right\}.$$

Clearly, the redundant amplitudes identified in (4.3) have vanished. However, the separate treatment of real and imaginary terms is a complication which requires a careful implementation, because due to the exponential their admixture is much more intricate than in CI theory where simple loop structures suffice.

It is easily shown that for the general (open-shell) case, these \hat{E}, \hat{e} operators (like the \hat{X}, \hat{x} operators) are non-commuting. An efficient implementation will rely on the availability of a non-relativistic version employing non-commuting spin singlet operators.

4.4 Spin-Free MRCC Implementation

An intermediate stage of the development work is achieved by the incorporation of the CC implementation by Olsen [120] into the DIRAC program package and the interfacing to the integrals based on the quaternion modified Dirac equation and the spin-free formalism. The same arguments as advanced in sections 2.3 and 2.3.1 apply here. Presently, the resulting CC implementation is the only one that includes scalar relativistic contributions “exactly” and can perform general-order CC calculations.

4.4.1 Previous Implementations

To the best of my knowledge, the only CC program capable of performing spin-orbit free Dirac calculations is the RELCCSD module by Visscher et al. [179, 180]. This program does not allow for the treatment of general open-shell states (in particular multi-reference states) and is furthermore limited to a maximum of full iterative double excitations (CCSD) and perturbative Triples corrections (CCSD(T)). A variety of CC implementations make use of approximate scalar relativistic Hamiltonians like the DKH Hamiltonian, e.g. in the *MOLCAS* [113] and *DALTON* [137] program packages.

4.4.2 Implementation

The spin-orbit free version of the CC program, called ARDUCCA, uses the same integral interface as described in section 2.3.3. Due to the classification of one-particle functions as in non-relativistic frameworks according to point group symmetry, no further modifications to the CC code were necessary. Details can be found in reference [10].

4.4.3 Scope of the Method

Although limited to applications where spin-orbit contributions are of minor importance, ARDUCCA enables for the high-precision treatment of an interesting class of (diatomic) molecules. The molecules formed from two heavy group 1 and/or group 2 atoms have Σ ground states originating in a bonding σ_s -type of molecular orbital. Spin-orbit contributions to such states enter only in second order and are therefore small. Systems like Rb_2 [190] or KCs [191] exhibit large scalar relativistic contributions to their spectroscopic properties and are typically weakly bound. Extensive correlation treatments, preferably beyond the level of single and double replacements, are required for obtaining properties of high accuracy. Such a study is reported in reference [10] on the CsLi molecule (see section 5.2.2.3). Other examples are the heavy homologues of ozone Te_3 and Po_3 , the ground states of which have quite pronounced multi-reference character [131].

4.4.4 Performance

The final paragraph concerns a timing comparison of the spin-free RELCCSD and ARDUCCA modules in table 4.1, again carried out on the HBr molecular ground state.

³The energy of the perturbative Triples CCSD(T) calculation with RELCCSD is $-2605.66451358 E_H$.

⁴Due to increased memory requirements this calculation was carried out on a single IBM shared-memory processor, type Power4+, 1.7 GHz, and with a cutoff value of 10 a.u. for virtual orbitals.

	# of amplitudes	Energy E_H	RELCCSD	ARDUCCA
CCSD8:	23.168	-2605.66038918	18 s	77 s
CCSDT8:	1.575.408	-2605.66484157 ³	not possible	42 m
CCSDTQ8:	13.277.367	-2605.66413080	not possible	7.5 h ⁴
CCSD18:	118.727	-2605.85738898	51 s	194 s
CCSDT18:	21.704.727	-2605.86390631	not possible	11.1 h

Table 4.1: CPU timings for spin-orbit free CC calculations on the HBr molecule, distance $2.5 a_0$, virtual cutoff 100 a.u., point group C_{2v} . A single processor type Pentium IV Xeon, 2.4 GHz was used. CCSD8 denotes a CC calculation with Single and Double excitations and correlating 8 electrons etc.

CCSD runs with 8 and 18 correlated electrons, respectively, are somewhat faster with RELCCSD. This is likely to be due to the higher generality of ARDUCCA (implementation of GAS) as compared to RELCCSD which is a single-reference implementation. However, even the demanding calculations including full iterative Triples (CCSDT8/18) or even Quadruples (CCSDTQ8) can be performed in a decent amount of time using ARDUCCA. A CCSDT calculation correlating 22 electrons on the CsLi molecule (60.8 million amplitudes, see subsection 5.2.2.3) takes less than 3 days.

Part III

Application

Spectroscopic and Electric Properties of Small Heavy-Element Systems

We are all, each in our own way, seekers of the truth [...]. As we collectively scale the mountain of explanation, each generation stands firmly on the shoulders of the previous, bravely reaching for the peak.

Brian Greene [192]

The methods presented in this thesis have been applied to a variety of heavy atoms and molecules. All of these applications go beyond mere testing of methods. Some of the calculations served the purpose to calibrate and to compare approaches, e.g. the study of the effects of electron correlation on atomic polarizabilities comparing CI and CC in subsection 6.2.1. Others are mentioned to show the applicability and the performance of a method in cases where principal difficulties arise, for instance in the calculation of excited states of the uranium atom in subsection 5.1.2.2. However, the majority of studies has scientific impact, and many of the obtained results are the most precise theoretical values available for these systems (e.g. Au₂, UO₂, AuO, CsLi, Tl, I, At).

The chapters are subdivided into atomic and molecular sections, and particular issues regarding the application of molecular methods to atoms are addressed. The largest molecule reported here is triatomic, but all methods can be applied to molecules of roughly twice the size also. Beyond that, the rigor implemented into the methods becomes the limiting factor, in particular the treatment of two-particle integrals. For larger applications, these should be included in approximative ways (e.g. by the resolution of the identity method) or calculated on the fly (integral-direct techniques), all of which comprises work for future development.

Chapter 5

Spectroscopic Properties

Theoretical spectroscopy in the first place seeks the energy differences between the electronic states of atoms and molecules. In the great majority of calculations here, this is achieved by solution of the Dirac-Coulomb equation, for molecules in the Born-Oppenheimer approximation. In the case of atoms, the electronic spectrum is the final piece of information in the scope of this thesis. For molecules, potential energy curves are determined by pointwise calculations at different molecular nuclear geometries, yielding the spectral parameters of equilibrium bond lengths and harmonic vibrational frequencies. Where possible and desired, the calculations are carried out to the dissociation limit or, alternatively, dissociation energies are determined by atomic calculations at the same level as a corresponding molecular calculation (e.g. Au_2). Both vertical and adiabatic molecular excitation energies are reported (e.g. UO_2).

The goals pursued by these studies are twofold: First, especially in the case of molecular spectra, predictions of yet unknown spectral parameters are made. Even when experimental data are at hand, precise theoretical results are of great importance as the assignment of experimental bands, e.g., often relies on a trustworthy calculation of the corresponding electronic states. Second, and an always important issue when new approaches have been developed, the methods are applied to system properties known from experiment with high confidence to probe the reliability and the applicability of the different approaches. As a general motivation, the methods allow for a detailed understanding of the electronic structure of atoms and small molecules, and this is demonstrated in numerous cases.

5.1 Atoms

The introduced methodology offers the refined calculation of atomic spectra at high precision. Albeit the efficiency is not optimal in such calculations — due to the implementation of binary double groups instead of the full atomic symmetry group — the simultaneous treatment of electron correlation and spin-orbit coupling combined

with the possibility of constructing appropriate GA spaces and long CI expansions opens for calculations of high quality. Computational problems arise when the degeneracy in the lower states of atoms becomes very high, as for instance in the uranium atom. As the CI program determines every M_J component of an atomic state J as a distinct eigenvector, excited-state calculations become extremely time-consuming. The implementation of full atomic symmetry would be somewhat of an improvement, but the problem pertains when several states of the same total angular momentum are desired. CC calculations are not possible for excited states, currently, so these studies are carried out using the MCSCF and CI programs. Experimental atomic spectra are available for all but the heaviest atoms, and a wealth of excitation energies is tabulated [193, 194, 195].

5.1.1 Main group atoms

Main group atoms of the first two groups exhibit no spin-orbit splitting in their S ground states¹. The first excited states typically are $^{2,3}P$ states arising from $ns \rightarrow np$ single excitations, with the exception of Ba where the first excited state is 3D from $6s \rightarrow 5d$ [193, 194, 195]. The trend of stabilizing the $(n-1)d$ shell by many-particle effects is counteracted in the heavy atom Ra, where the relativistic stabilization (contraction) of the $7p$ shell makes the excitation $ns \rightarrow np$ more favourable.

Of greater interest in the present context are the p block atoms where spin-orbit coupling leads to level splittings² already in the ground state. These lowest splittings increase as the nuclear charge increases and are largest at the end of the p block (group XVII). For instance, indium having a nuclear charge of 49 exhibits a $J = \frac{1}{2} - J = \frac{3}{2}$ splitting of 2212 cm^{-1} where the much lighter bromine (nuclear charge 35) has 3685 cm^{-1} (for $\frac{3}{2} - \frac{1}{2}$). The reason for this is the increased effective nuclear charge along a row in the p block, as nuclear charge is added and the additional electrons only partially contribute to the screening. When switching to the next row of the periodic table, on the other hand, the closed subshells screen the nuclear charge more effectively for the early p atoms.

The publications [2, 7] mainly concern atomic static polarizabilities of group-13 and group-17 atoms (in 6.2.1), but for obtaining these in J, M_J resolution a detailed study of the ground-state splittings in terms of electron correlation effects is required.

5.1.1.1 Group-13 atoms

The excitation energy of the $\frac{3}{2}$ state is to a large degree determined by the description of the $p_{1/2}$ and $p_{3/2}$ valence spinors. Spinor methods, i.e. approaches in which spin-orbit coupling is already included in the optimization of the one-particle functions,

¹Merely a level shift is caused by higher-order couplings.

²The term 'level splitting' takes levels as a reference point which have been recorded without spin-orbit coupling. In the following, the term 'excitation energy' will be used when the picture has been changed and $j - j$ coupling or correspondingly $\omega - \omega$ coupling is adopted.

have a great advantage in such cases, because the correlation step need not account for the radial difference of the valence spinors by additional terms in the determinant expansions (like in SOCI methods based on spin orbitals [96, 99, 101]). In the latter approaches, triple excitations may become important when spin-orbit interaction affects the “shape” and radial extent of the one-particle functions significantly. For the thallium atom, the ground state splitting in plain valence CI calculations using spin orbitals amounts to 6599 cm^{-1} [96] (6330 cm^{-1} with a different basis set [4]) whereas the value obtained using 4-spinors is 7709 cm^{-1} which is very close to the experimental value of 7792.7 cm^{-1} [195]. However, electron correlation plays a profound role as explained in the following.

For the lighter atoms, B and Al, the excitation energy is determined by either FCI or calculations of near FCI quality including more than 50 million Slater determinants, yielding errors of only a few inverse centimeters [7]. The remaining correlation (and basis set) errors are in this case even smaller than the one stemming from the approximate Hamiltonian through neglect of the Gaunt interaction (spin-other-orbit terms, see [122]). The Gaunt interaction accounts for the residual error, quenching the splitting by a few inverse centimeters. Ongoing work in the DIRAC package [196] involves the implementation of the Gaunt integrals which will make studies of highest precision possible on systems of this type.

For the heavier atoms, Ga, In, and Tl, the error can be reduced to within 100 cm^{-1} by using large CI expansions [4, 7, 96]. These calculations are model cases for studying error cancellation. DC-HF (or CASCI) calculations deliver $J = \frac{1}{2} - J = \frac{3}{2}$ splittings in close agreement with experiment, but it is the right answer for the wrong reason. Correlating the 3 valence electrons results in splittings too small by about 10%. The reason for this is an unbalanced coupling of states to the $\frac{1}{2}$ and $\frac{3}{2}$ components leading to differential correlation effects [4]. The intershell correlation effects can be investigated by including a GAS per subshell and restricting the number of holes to 1 (core-valence (CV) correlation) or 2 (core-core correlation). Several shells may also be treated simultaneously with different numbers of holes. Adding the $(n-1)d$ shell in CV correlation improves the results to errors of less than 5% of the total splitting. This is explained by the depopulation of more compact shells and population of more diffuse shells through the correlation treatment. Consequently, the effective nuclear charge experienced by the valence electrons increases, and with it the spin-orbit splitting. Adding the $(n-1)p$ electrons in CV correlation further increases the spin-orbit splittings, in line with the above arguments.

The inclusion of double excitations from outer core shells has only small effects on the splittings. However, they become important in the calculation of dipole polarizabilities, as discussed in subsection 6.2.1.

5.1.1.2 Group-17 atoms

Similar to the group-13 atoms, the difference in radial extent of the $p_{1/2}$ and $p_{3/2}$ valence spinors to a large degree determines the ground state spin-orbit splitting, despite that the present atoms have a p hole instead of a p particle ground state. In fact, in iodine the difference is even more pronounced than in thallium. The spin-orbital plain valence CI yields a splitting of 5862 cm^{-1} [2], the 4-spinor result is 7765 cm^{-1} which again comes very close to experiment (7603.15 cm^{-1} [195]). When a spinor basis is used, the excitation energy of the $J = 1/2$ state is obtained to high precision already upon correlating only the p valence electrons (SDTQ 5, 7590 cm^{-1}). The effect of correlating outer-core shells is of rather low significance here, as the above-described depopulation impact on the valence shells is decreased in the case of hole states.

5.1.2 Lanthanide and actinide atoms

The calculation of excited states of f elements is a demanding undertaking. Many of the atoms have states in which configurations from several subshells are mixed among each other. This is due to the energetic vicinity of ns , np , $(n-1)d$ and $(n-2)f$ shells [197]. Spin-orbit coupling is strong and leads to a considerable term mixing, both from the same and from different configurations. It therefore necessitates the designation of states in terms of the total angular momentum J in most cases. A simultaneous and high-level treatment of electron correlation is indicated, and a further complication arises due to the frequently occurring large number of open shells. This is no problem for MCSCF/CI methods in principle³, but the high angular momentum values lead to high (M_J) degeneracies which calls for the calculation of many eigenvectors to obtain but a few lower-lying excited states. Two representatives are discussed in the following.

5.1.2.1 Lanthanides: Thulium

Among the most important observations made in lanthanides is the lanthanide contraction — a large fraction of which is ascribed to direct relativistic effects [198] — and the participation of f electrons in bonding [147]. A question of interest arising in this context is the description of states formed from open f shells, e.g. the $^2F_{7/2}$ and $^2F_{5/2}$ components of the Tm atom ground state which is described by a $4f^{13}$ configuration. The study carried out in reference [4] focusses on the spin-orbit splitting obtained at a given level of electron correlation and depending on whether a one-particle basis of spin orbitals or spinors already including spin-orbit coupling have been used. Even though the radial extents of the underlying $f_{7/2}$ and $f_{5/2}$ spinors of the Tm atom do not differ greatly, the spinor basis proves much more

³In contrast to e.g. Fock-space CC methods where the number of open shells is limited typically to 2 or 3 [173, 196], as mentioned earlier.

efficient in reproducing the experimental splitting between the ground state components. Excluding dynamic electron correlation, the $J = \frac{5}{2}$ excitation energies do not differ greatly in the spin-orbital and the spinor treatment. Upon correlating the 15 valence electrons (from $6s^2 4f^{13}$) in a Singles and Doubles CI treatment, however, the spin-orbital basis yields an excitation energy of 9817 cm^{-1} whereas the spinor basis gives 9280 cm^{-1} which reduces the error by roughly 50% (the experimental value is 8771.243 cm^{-1} [199]). The remaining deviation is ascribed to basis set and correlation errors. This finding underlines that the use of spinors in particular in open-shell heavy-elements is favorable in general as compared to scalar relativistic spin orbitals also in the f elements. This situation may also occur in molecules formed from the f elements, but it is not necessarily so. An example where a spinor basis does not comprise a major improvement is the UO_2 molecule which is discussed in subsection 5.2.2.2.

5.1.2.2 Actinides: Uranium

Uranium and plutonium compounds have for a long time been at the center of interest among the heavy f elements due to their importance in the nuclear fuel cycle [200]. The lowest electronic states of the uranium atom are derived from the odd-parity configurations $s^1 f^3 d^2$ and $s^2 f^3 d^1$, resulting in quintet and septet states (LS coupling picture) of high angular momentum. Spin-orbit coupling mixes the lowest terms 7M , 5L , 5K , 7I , 5H , 7L , and 7K arising from these configurations, yielding lowest states of $J = 5, 6, 7$ [201].

The basis set for the present study is the ANO-DK3 set described in [202], but used without contraction and augmented by 3 additional g functions and 1 h function especially for correlating the f electrons. All calculations are fully 4-component. The one-particle spinor basis for the correlated calculations is obtained by averaging over the odd-parity configurations mentioned above and imposing restrictions with 3 electrons in the *gerade* and 3 electrons in the *ungerade* spinors. This ensures a balanced description of the lowest excited states which all originate from these configurations. The results of the correlated calculations are compiled in table 5.1 and compared to those from the Multi-Configuration Quasi-Degenerate Perturbation Theory with Spin-Orbit coupling (SO-MCQDPT) method and experiment.

Upon accounting for dynamic electron correlation, the correct ordering of the lowest excited states is obtained and the excitation energies improve significantly. The 'corr. CASCI' values are comparable to those in the column 'Valence', where a large set of many-particle states is included in the QDPT procedure. A closer agreement with experiment requires the consideration of correlation contributions from the outer core shells of uranium, which becomes evident from column 'CC+Valence'. A corresponding calculation with the current implementation of LUCIAREL is possible, but the time required for converging on a large number of excited state compo-

⁴Obtained without the additional $3g1h$ basis functions.

State (J)	LUCIAREL		SO-MCQDPT [201]		Exp. [203]
	CASCI	corr. CASCI	Valence	CC+Valence	
6	0	0	0	0	0
5	1741	1109	1069	607	620
7	2920	3333 ⁴	3958	3267	3801
6	2205		6155	3768	4276

Table 5.1: Lowest excited states of the uranium atom without (CASCI) and with (corr. CASCI) dynamic electron correlation, cutoff for virtual Kramers pairs: 1 a.u. 'Valence' denotes a correlated calculation including only the 6 valence electrons, whereas in 'CC+Valence' also the $6p, 6s, 5d, 5p, 5s, 4f$ outer core electrons are correlated. Excitation energies given in cm^{-1} .

nents is not acceptable. The key problem lies in the extraordinarily high degeneracy of the atomic states in uranium, requiring the optimization of at least 17 eigenvectors to obtain but the 2 lowest excited states ($J = 5$ and $J = 7$). Important improvements of the program for atomic calculations of this type would be the implementation of atomic symmetry and parallelization. The latter project has been started and upon completion will allow for a much more efficient calculation of a large number of excited states. The present code is more efficient in the treatment of heavy-element molecules, which is the topic of the following section.

5.2 Molecules

5.2.1 Small Molecules with Light Atoms

Due to the few electrons that generally need be correlated, bond lengths, harmonic frequencies, and dissociation energies in the ground state of such systems can be determined to a high precision with the available methodology. The calculation of spin-orbit splittings and excitation energies comprises a more difficult task, as the size of basis sets needs to be increased and the computational demand grows with the number of eigenvectors to be optimized on.

Properties of light systems are not in the focus of this thesis, so only a brief account shall be given here. For light molecules, the lack of the Gaunt interaction in the 4-component DIRAC package gives rise to larger errors than those typically introduced by basis set or correlation deficiencies. A good example is the ClO molecule, discussed in [4] with summarized results in table 5.2. The non-relativistic ground state splits into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states including spin-orbit coupling, with a splitting energy of 318 cm^{-1} experimentally. Neglecting the spin-other-orbit terms (column in table 5.2 denoted 'spinors'), which are non-negligible in lighter systems where the nuclear charge is small, leads to an overshoot of the splitting by 18.4

cm^{-1} at the CCSD(T) level, which is almost 20% of the total splitting. Including the Gaunt interaction (spinors+G) brings the splitting down to 315.3 cm^{-1} , an error of less than 1%.

Approach	orbitals ⁵	orbitals+G	spinors	spinors+G ⁶
CAS 9 in 5	224.3	206.9	245.1	
CAS 13 in 8	229.6	212.2	252.1	
SD9-3au	291.9	274.3	313.1	est. 293
CCSD			324.4	303.5
CCSD-T			336.4	315.3
Exp ⁷		318		

Table 5.2: ${}^2\Pi_{3/2}$ - ${}^2\Pi_{1/2}$ level splittings of the ClO molecule in cm^{-1} at different correlation levels and using different one-particle functions. CAS 9 in 5 is a CASCI calculation without virtual orbitals with 9 electrons in 5 Kramers pairs, comprising the $2p$ electrons in the occupied σ , π , and π^* orbitals. In CAS 13 in 8 the $2s$ electrons are added as well as the remaining p -type σ^* orbital. SD9-3au denotes a correlated SDCI calculation with 9 electrons and a cutoff for virtual orbitals of 3 a.u. The estimate in the last column is obtained by adding the Gaunt (G) contribution which is found to additive at the various correlation levels.

Obviously, the largest fraction of the remaining deficiency can safely be ascribed to the number of correlated electrons (9 in this case) and the basis set. Beside this, using a spinor basis of one-particle functions proves more efficient than a spin-orbital basis, with deviations on the same scale as the Gaunt interaction, as to be seen by comparison of the columns 'orbitals' vs. 'spinors' in table 5.2. This deviation is less pronounced when shifts on closed-shell (ground) states are investigated.

5.2.2 Molecules with One Heavy Atom

The electronic structure of these systems is to a large degree determined by the heavy atom, both with respect to electron correlation and relativistic effects. A common approach to the understanding of chemical bonding is to commence by investigating the diatomic hydrides of heavy atoms. The importance of scalar relativistic contributions very often is striking; E.g., the bond of the TIH molecule contracts by more than 5% upon including relativistic kinematics [61, 205], that of the also closed-shell AuH molecule even by more than 11% [206]. Whereas spin-orbit coupling is small in the ground states of AuH and also the group 17 hydrides [3, 77, 130], it is important for understanding the dissociation energy of TIH [207]. In open-shell molecules,

⁵Computed with a modified version of the AMFI code including only the one-electron and the two-electron spin-same-orbit terms [204]

⁶Reference [180]

⁷Reference [86]

spin-orbit coupling may even lead to a change of ground state, like for instance in PtH [8, 14, 208] where $^2\Sigma^+$ changes to $^2\Delta_{5/2}$ upon inclusion of spin-orbit coupling.

In the following, the spectroscopic and bonding properties of more complicated heavy-element oxides and the CsLi molecule will be discussed.

5.2.2.1 Coinage Metal Oxides

Coinage metal compounds are ideally suited for initial and benchmark applications of new methods, for two essential reasons: (1) The heteronuclear diatomics are small enough not to make the calculations too costly, and (2) within group 11 relativistic contributions can readily be investigated due to the large effects for gold. Element 79, where a valence s shell is starting to be filled, comprises a maximum of relativistic effects in the periodic system. It is explained by the strong contraction of inner “wiggles” of the valence s orbitals due to the high electron speed near the heavy nucleus accompanied by a contraction of the complete orbital [12, 209]. The same effect is observed for the $6p_{1/2}$ orbital of Au.

Beside the relativistic contraction/decontraction of orbitals, spin-orbit coupling leads to a splitting of the coinage metal oxide $^2\Pi$ ground states into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components. Whereas the scalar relativistic effects in gold compounds are well-investigated [5, 210, 211] (see also subsection 5.2.3.1) calculations including spin-orbit coupling are scarce. Given the new methodology here, it is interesting to study the sole effect of spin-orbit coupling in the coinage metal oxides. In reference [8] AuO is discussed at some length, and the most important results are summarized here.

Figure 5.1 shows the ground-state potential curves calculated by a 4-component CASSCF including the full valence space and by an equivalent run using the Douglas-Kroll-Hess Hamiltonian correct up to the second order in the external potential for the one-electron terms and with uncorrected two-electron terms⁸ excluding spin-orbit terms.

By these means, scalar relativistic effects are considered in both cases and the bond contraction through spin-orbit coupling becomes apparent. This contraction, amounting to $-0.055 a_0$ for AuO at the CASSCF level, increases by nearly an order of magnitude in AuO as compared to the lighter homologue (see table 5.3), pointing to the relativistic maximum at this element. It is interesting to note that this bond contraction is far more pronounced including static electron correlation than in a DC-HF calculation where it only amounts to $-0.013 a_0$. A closer look reveals that the singly-occupied bonding π -type orbital obtains more and more contribution from Au $5d$ as the bond is formed. In the CASSCF calculation, this open-shell character of the Au $5d$ is increased as compared to the Hartree-Fock-type calculations, leading to enlarged spin-orbit effects on bonding. Though the spin-orbit contraction of the AuO bond is remarkable, it is still an order of magnitude smaller than the complete

⁸The induced picture-change error is negligible here.

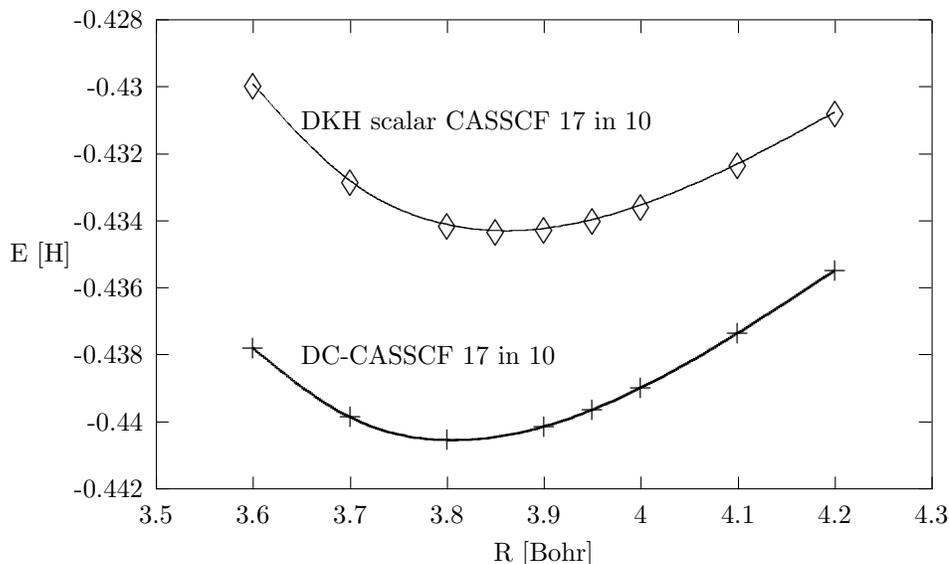


Figure 5.1: Potential curves of the AuO $^2\Pi_{3/2}$ ground state at the CASSCF level with 17 electrons in 10 Orbitals/Kramers pairs. Comparison of scalar relativistic (DKH) vs. fully relativistic (DC) calculation.

relativistic contraction of Au bonds, which is typically around $-0.4 a_0$ [211].

Table 5.3 compiles bond lengths, harmonic frequencies, and correlated adiabatic excitation energies for the two heavier coinage metal oxides. Including dynamic correlation with a CAS reference space (CASCI17) based on the 4-component DC-HF orbitals brings the results for AuO quite close to the experimental values. The agreement is somewhat reduced in case of AgO which is ascribed to the relatively small basis set and correlation errors. A Coupled Pair Functional (CPF) correlation calculation by Bauschlicher et al. [216] gives a result of $3.908 a_0$ for the $^2\Pi_{3/2}$ ground state, close to the one obtained here. A Fourier Transform Spectroscopic investigation by O'Brien et al. [217] reports a slightly larger value of $3.908 a_0$ than the one from an earlier experiment given in table 5.3. The 4-component density functional theory results (DFT BDF) by Liu et al. yield properties with significantly larger errors, despite the moderate basis set (DZ quality) used in the present study. To my knowledge, these results are the best obtained so far in a study of the AuO molecule including spin-orbit coupling, although it is expected that in particular the use of a more extensive basis set would lead to further improvement.

5.2.2.2 Uranium Dioxide (UO_2)

Owing to the dangers and difficulties arising in experiments conducted with actinide compounds, in particular the often toxic and radioactive uranium and plutonium materials, experimental spectra are rather scarce. On the theoretical side, a number of closed-shell compounds has been investigated in the past [218, 219, 220, 221], but

Approach	AgO			AuO		
	R_e [a_0]	ω_e [cm^{-1}]	T_e [cm^{-1}]	R_e [a_0]	ω_e [cm^{-1}]	T_e [cm^{-1}]
DC-HF SOF	3.910	518		3.753	567	
DC-HF	3.909	518		3.740	572	
DKH CAS 17 in 10	4.044	362		3.861	407	
DC-CAS 17 in 10	4.037	367		3.806	427	
CASCISD17 ^{DC-HF} ($^2\Pi_{3/2}$)	3.915	460	0	3.673	520	0
CASCISD17 ^{DC-HF} ($^2\Pi_{1/2}$)	3.922	459	219	3.715	516	805
DFT BDF [27]				3.460	695	
Exp. ($^2\Pi_{3/2}$)	3.776 [212]	490.5 [213]	0 [214]	3.604 [215]		
Exp. ($^2\Pi_{1/2}$)	3.781 [212]	489.9 [213]	270 [214]			

Table 5.3: Equilibrium bond lengths, harmonic frequencies, and adiabatic excitation energies of coinage metal oxides using different approaches. CASCISD17 denotes MRCI calculations with single and double excitations out of the CASSCF reference space correlating 17 electrons. DC-HF Kramers pairs and a cutoff value of 5 a.u. for virtual orbitals is used. SOF: Spin-orbit free.

calculations on open-shell molecules from this regime are more demanding and only few methods for carrying them out have been available, e.g. [75, 99, 104].

A case study on the UO_2 molecule is reported in reference [9]. Due to the availability of recent experimental data [222, 223], it is suited for comparison of modern theoretical approaches. Two open-shell electrons form an odd-symmetry state manifold arising from the $\text{U}(5f\ 7s\sigma_g)\text{O}_2$ configuration and an even manifold from the $\text{U}(5f^2)\text{O}_2$ configuration. The molecule is linear and symmetric in the ground state [222]. The splitting between the lowest u and g states is of interest because the shifts in the asymmetric stretch vibrational frequency going from a neon to an argon matrix (experiment in reference [224]) may be explained by assuming a change of ground state in the argon matrix. This viewpoint is supported by the theoretical work of Li et al. [225] which indeed indicates a significant lowering of the *gerade* states upon coordination with argon. This interaction could be strong enough to cause a matrix-induced change of ground state, similar to the one observed in CUO [226]. This explanation is, however, not in agreement with the electronic spectra of UO_2 in argon reported by the group of Heaven [222, 223]. The latter investigation renders an assignment of the ground state as *gerade* unlikely.

In DC-HF calculations, it is found that spin-orbit coupling has only a very small effect, leaving the equilibrium U-O bond distance nearly unchanged at $3.315 a_0$. This is supported by a close analysis of the bonding spinors/orbitals. Upon including spin-orbit interaction, the deviation of the orbital angular momentum projection values of the spinors from integer values is found to be very small. The bond is elongated to $R_e = 3.348 a_0$ upon including static correlation in a restricted GASSCF calculation yielding $(\Omega = 2)u$ as the molecular ground state.

The configuration space for correlated calculations is based upon the restricted GASSCF expansion and all single and double excitations into a virtual space truncated at 2 a.u., amounting to 44 virtual Kramers pairs and a total expansion length of almost 10 million determinants. The results are compiled in table 5.4.

State	T _e [cm ⁻¹]		R _e [a ₀]		
	present	Exp.[222]	present	SO-CASPT2[227]	SOCI [228]
2 <i>u</i>	0	0	3.372	3.375	3.401
3 <i>u</i> ^{MC}	417	360	3.379		
3 <i>u</i> ^{DC-HF}	-		3.375		

Table 5.4: Equilibrium bond lengths and adiabatic excitation energies of low-lying electronic states of UO₂ using DC-MCSCF orbitals (MC) or DC-HF spinors (DC-HF) and comparison with experiment and other approaches.

All presented methods find 2*u* as the ground state also at the correlated level. The adiabatic excitation energy for the 3*u* state is in good agreement with experiment, given the small splitting between the two states. The bond lengths hardly differ for the 2*u* and 3*u* states and the two curves are nearly parallel. Using DC-HF spinors, this correspondence is even better as the averaging eliminates the state-specific (here 2*u*) character of the orbitals in the (MC) calculation. The agreement between the present value and the SO-CASPT2 result obtained with a similar basis set and active CASSCF space is excellent. The deviation of the SOCI result obtained with the COLUMBUS program is somewhat larger. The two most likely explanations for this deviation are the use of an effective core potential and/or the higher restriction on the multi-reference space in the SOCI treatment as compared to the present calculations.

Single-point results for the states of *u* symmetry are collected in table 5.5. The SO-CASPT2 results which are very close to the gas phase experiment in case of 3*u* are off by more than 1000 cm⁻¹ for the excited states 1*u* and 2*u*. A shift along the (nearly parallel) potential curves yields a modification of roughly 300 cm⁻¹ which is too little to reconcile the results. Further, the U 6*p* electrons are correlated in a fashion depicted in figure 5.2 and denoted CV in table 5.5. In total, 24 electrons are correlated yielding a configuration space of more than 50 million determinants. The significant increase of the 2*u* excitation energy indicates the importance of the 6*p* electrons in correlated calculations on uranium compounds.

The present calculations have been improved further by extending the basis set with functions of high angular momentum mainly to account for angular correlation of the *f* electrons on uranium. The 2*u* excitation energy is hereby increased to 2042 cm⁻¹. Preliminary results of 4-component coupled cluster calculations on UO₂ [230] indicate that this excitation energy is even further increased upon including *double* excitations from the U 6*p* orbitals. The shift from the argon matrix, in which

State	SDT-SD	CV-SDT-SD	SOCI [228]	SO-CASPT2[229]	Exp.
U-O sep.	3.372 a_0		3.402 a_0	3.452 a_0	
$2u$	0	0	0	0	0 [222]
$3u$	427		431	378	360 [222]
$1u$	1089		1088	2567	1094 [223]
$2u$	1542	1814	1566	2908	1401 [223]

Table 5.5: Excitation energies of u electronic states of UO_2 from different approaches and compared with experiment. SDT-SD denotes SDT excitations from 7 occupied valence orbitals to the U(7p,5f) orbitals and a σ_g^* orbital and SD excitations into the virtual space from all reference determinants so created.

the $1u$ and $2u$ excited state transitions have been measured, can hardly account for such a deviation which ranges from at least 800 to at most 1400 cm^{-1} in the different approaches. The highest confidence can be drawn from the fact that CI excitation energies approach the preliminary CC result systematically, suggesting a $2u$ excitation energy in the range between 2200 and 2500 cm^{-1} . It is likely that the assignment of the experimental bands is in error as it is based on the lower-level SOCI calculations from reference [228] and earlier SO-CASPT2 calculations [227] which both are proven to be off substantially by the investigations reported here.

Two sources for the deviations between the different theoretical approaches are possible but have not been investigated further: The SO-CASPT2 calculations are carried out using spin orbitals instead of spinors as one-particle basis. An analysis would require running the present calculations with spin orbitals in the 2-component implementation of LUCIAREL [4]. It is unlikely, however, that the use of spinors can make up for such large a difference in excitation energies, given the above analysis of the influence of spin-orbit coupling at the one-particle level. The second and more probable possibility concerns the assumption of additivity of spin-orbit coupling and dynamic electron correlation in the SO-CASPT2 approach. Simulating this kind of treatment is not possible with our current CI implementation. It remains to be shown whether an additive treatment of spin-orbit coupling and electron correlation can deviate from the simultaneous treatment on such a scale for excitation energies. Furthermore, a careful study of basis set effects would be of value.

Table 5.6 shows our results for the lowest set of g states, calculated at an inter-shell correlation level and compared to SO-CASPT2. The same ordering of states is found and the excitation energies are in good agreement for the $4g$ and $2g$ states after shifting along the potential curve. For the $1g$ state a deviation of at least 600 cm^{-1} remains. The $0g$ state from the $7s^2$ (U) configuration is found as the second vertically excited state of g symmetry, and was not calculated in reference [229]. Due to the small intensities for the $7s$ to $5f$ excitation these states have not been observed experimentally so that the accuracy of the calculation cannot be

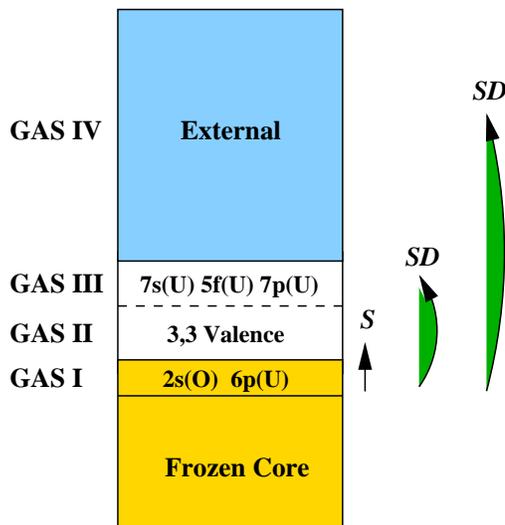


Figure 5.2: Generalized Active Spaces for core-valence-type of correlation treatment on UO_2 . Single (S) excitations from space I are combined with Single and Double (SD) excitations from space II with a combination maximum of Double excitations into the correlating valence and virtual spaces.

verified. Presuming that the reasonable agreement with the SO-CASPT2 values is not fortuitous, it may in this case be assumed that differential correlation is small and that the computed energies comprise reasonable predictions of the excitation energies. Without explicitly calculating the UO_2Ar interaction energies it remains, however, impossible to predict whether the lowest of these states may fall below the $2u$ state in an argon matrix.

The experience gained in this study clearly points out that the rigorous methodology of the combined application of MCSCF and MRCI including spin-orbit coupling is capable of producing results of high reliability on such systems. However, an extensive study of the spectrum of UO_2 would require the calculation of a larger number of excited states, inclusion of outer-core electrons in core-valence correlation, and an increase of the (truncated) virtual orbital space. Ongoing work aims at these goals, e.g. by parallelism of the CI program and implementation of linear symmetry for reduction of the determinant expansions (and facilitated assignment of states).

5.2.2.3 CsLi

The CsLi molecule is a sample system of molecules studied in ultracold and Bose-Einstein condensation experiments. Its electronic structure in the ground state is determined in particular by the scalar relativistic contraction of the Cs $6s$ orbital forming the σ -bonding molecular orbital and dynamic electron correlation.

The study in reference [10] closely investigates correlation effects, resolved into

State	SO-CASPT2[229]	S12C2 – SD ^{DC-HF}
U-O separation	3.452 a ₀	3.481 a ₀
4g	3330	3102
0g(s ²)	-	5862
1g	6823	7243
2g	12073	11648

Table 5.6: Excitation energies of g electronic states of UO_2 at different correlation levels and comparison with other approaches. S12C2-SD denotes single (S) excitations of 12 valence electrons, a CAS with 2 electrons in the $\text{U}(7s,7p,5f)$ orbitals and single and double (D) excitations into the virtual space from all reference determinants so created.

lower and higher CC excitation level and valence and outer core correlation, and the influence of scalar relativistic effects on ground state spectroscopic properties. The most important results are summarized in table 5.7. An uncontracted basis set is used with $\{24s18p13d3f\}$ functions for Cs and $\{11s5p2d1f\}$ functions for Li [231].

<i>Method</i>	Corr. El.	R_e [Å]	ω_e [cm ⁻¹]	D_e [eV]
LL-HF	0	3.979	170.3	-
SFDC-HF	0	3.909	173.9	-
CCSD	10	3.669	187.3	0.838
MRCCSD-SF	10	3.670	186.3	0.792
CCSDT-LL	10	3.703	183.8	0.767
CCSDT-SF	10	3.642	186.2	0.743
CCSD-SF	22	3.656	187.9	0.880
CCSDT-SF	22	3.623	186.5	0.752
MELD ⁹		3.65	183	0.72
CIPSI1 ¹⁰		3.615	187.1	
CIPSI2 ¹¹		3.604		0.717

Table 5.7: Spectroscopic properties of the CsLi molecule at various correlation levels and approaches to relativity. LL: Non-relativistic 4-component Lévy-Leblond; SF: Spin-orbit free 4-component relativistic; otherwise: Dirac-Coulomb Hamiltonian

The most striking observation is the large bond contraction upon correlating electrons. It is explained by a shift of electron density predominantly from the delocalized bonding orbital to the more diffuse and localized low-lying $3p_x$ and $3p_y$

⁹Reference [232]

¹⁰Reference [233]

¹¹Reference [191]

orbitals on Li but not the $3p_z$ thereby making the molecule more ionic. The effect of the outer core correlation is about 10% of the total correlation contraction and about one third of scalar relativistic contributions. The increase in the dissociation energy can be explained by the better description of the system near the equilibrium bond distance compared to the separated atoms, a deficiency which is engrained in any single-reference method. Inclusion of the outer-core electrons makes this unbalanced description even more noticeable. Increasing the correlation level, on the other hand, results in a more balanced description of the entire potential curve and in particular yields improved dissociation energies. This is true for both the multi-reference (MR) as well as the iterative Triples (CCSDT) treatments as compared to plain CCSD. Spin-orbit contributions are found to be negligible. To summarize, a hierarchy of contributions can be deduced, as shown in figure 5.3.

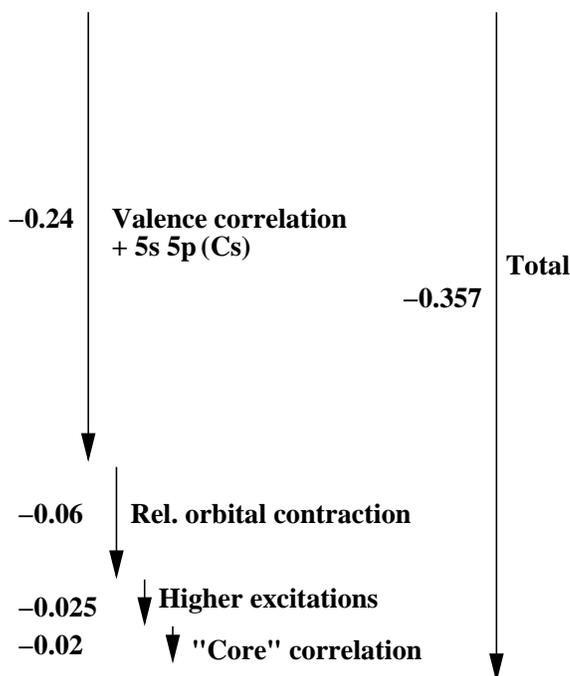


Figure 5.3: Relativistic and correlation effects on the equilibrium bond length in CsLi (atomic units).

The final equilibrium bond length at the spin-free CCSDT level with 22 electrons correlated is 3.6225 Å. The various contributions are found to be decoupled to a large degree, and the same trends apply to the values for harmonic frequencies. The findings also point to the importance of correlation effects for the molecular dipole moment [191], which should be calculated preferably at the CC level. In contrast to many other heavy-element molecules (e.g. the gold compounds, see subsection 5.2.3.1), correlation effects are more important than relativistic effects in this and similar molecules.

An attempt to perform a more extensive multi-reference coupled cluster calcu-

lation including 22 electrons in the reference space failed, i.e. the results were in conflict with the expected trend. A deeper analysis revealed a deficiency in the employed basis set: The larger MR space strongly correlates the Cs d electrons, and the Cs basis set does not contain appropriate angular correlation functions. Therefore, a series of calculations is under way where the f and g spaces of the basis set are extended (ANO-RCC [97]). Preliminary results indicate that apart from improving on all the other approaches, the large MRCC expansions lead to results in agreement with the expected trend.

5.2.3 Molecules with Two Heavy Atoms

High-precision theoretical spectroscopy on heavy-element diatomics remains a difficult undertaking. In most cases, even the ground states of these systems are of the open-shell type, necessitating the inclusion of spin-orbit coupling and dynamic (and often also static) electron correlation at best on equal footing. There is considerable interest in gold diatomics, due to the large relativistic effects in the gold atom. In general, most studies are concerned with the electronic ground state, e.g. [27, 85, 234, 235]. Whereas TlAt is dominated by scalar relativistic bond contraction, the superheavy homologue Tl[117] exhibits some spin-orbit contributions due to the increased spatial extent of the [117] $7p_{3/2,1/2}$ spinor [85]. It is a general trend that spin-orbit coupling does not affect bond lengths to a large degree, but dissociation energies may change significantly upon including internal magnetic couplings, as demonstrated on the halogen dimers and interhalogen diatomics [234]. Excited states of PtAu and PtAu₃ are investigated in references [236] and [237], where the participation of Au d electrons in the ground state bonding and excitation processes is demonstrated. Again, this is explained by the relativistic stabilization of the Au 6s orbital, decreasing the energetic separation between the 6s and 5d orbitals.

5.2.3.1 Au Dimer (Au₂)

The work carried out in reference [5] primarily aims at a methodological comparison of MRCI and CC in the case of a closed-shell heavy diatomic. Furthermore, an attempt is made to investigate the truncation and picture-change error introduced by a DKH approach truncated at the second order in the external potential and completely neglecting the transformation for the 2-electron terms (DKH2/0). All calculations reported here have been carried out using the 4-component spin-orbit free Dirac-Coulomb Hamiltonian, except where noted otherwise.

Table 5.8 clearly displays the large effort required in the MRCI treatment to approach the quality of CC calculations of the bond length, harmonic frequency, and even dissociation energy, the latter of which for CC is determined from an atomic calculation at the same correlation level. This is due to the pronounced closed-shell character of the gold dimer. The multi-reference spaces required for

including the important set of quadruple excitations involving the gold $5d$ electrons lead to unmanageably large calculations (several tens of billions of determinants).

Method	Number of determinants	R_e [pm]	ω_e [cm^{-1}]	D_e [eV]
Hartree-Fock	1	253.5	175.4	—
CISD	1.457.150	249.8	185.3	5.03
MR CISD	155.343.054	250.9	180.0	1.93
CCSD		248.4	190.4	2.06
CCSD(T)		247.7	192.1	2.28
Exp. [238, 239, 240]		247.2	190.9	2.29

Table 5.8: Spectroscopic properties of the gold dimer, (MR)CI and CC calculations. All electrons from the $6s$, $5d$, and $5p$ shells (34 in total) are correlated

Using the same uncontracted basis set and the DKH instead of the Dirac-Coulomb (DC) Hamiltonian, a CCSD(T) 34 value for R_e of 248.4 pm is obtained as compared to 248.0 pm with DC¹². The deviation can be attributed to two possible sources: On one hand, the DKH2/0 level of theory contains a picture-change error in the two-particle integrals. This picture-change correction has been estimated by Park and Almlöf [241] to quench the bond length by 1.1 pm at the SCF level. At the correlated level, the effects of scalar relativity are reduced, in part through the depopulation of compact shells. At the SCF level, the contraction of the Au_2 bond amounts to -32.8 pm when comparing a non-relativistic with a DKH2/0 calculation. At the correlated level (SDCI34), it is only -27.1 pm, so the quenching of relativistic one-electron effects amounts to roughly 15% through electron correlation in this molecule. A similar quenching for the two-particle corrections can be expected, so the picture-change error reported by Park and Almlöf will be reduced. It is therefore difficult to assign a quantitative residual deviation coming from higher-order terms in the DKH transformation without an explicit elucidation of the two-electron picture-change effect at the correlated level or a complete general-order calculation.

Starting out from the best bond length value from table 5.8 and applying further corrections, the estimate in table 5.9 can be made.

CCSD(T) 34	247.7 pm
near-complete basis set -0.1 pm
Counterpoise correction $+0.7$ pm
Spin-orbit coupling -0.4 pm
Best estimate	<hr/> 247.9 pm

Table 5.9: Approaching the exact equilibrium bond length of the gold dimer.

¹²The cutoff for virtual orbitals was increased to 60 a.u. here for greater rigor.

The estimate for the basis set completeness has been taken from reference [242]. The counterpoise correction and the shift from including spin-orbit interaction are own calculations and are in agreement with the results obtained by other approaches (mentioned in reference [5]). The different corrections are additive to a large degree. The residual deviation of 0.7 pm (0.3%) from the experimental value is attributed to the overshoot of the counterpoise correction and small correlation errors from the Hartree-Fock treatment of inner-shell electrons.

The study demonstrates that very accurate results can be obtained for the ground state geometries of heavy-element diatomics, provided a CC treatment is feasible. The analysis of the influence of higher-order terms in the DKH expansion is hampered by the unknown effect of the 2-electron picture-change error in these calculations, which only could be estimated.

Chapter 6

Electric Properties

6.1 Methods for Property Calculations

Different approaches for obtaining atomic and molecular electric properties are employed in this thesis, and therefore a brief overview of the techniques shall be given here.

6.1.1 Analytical Methods

The Hellmann-Feynman theorem allows statements on how the total energy of a system changes with a varying Hamiltonian. With both the total Hamiltonian $\hat{H}(P) = \hat{H}^{(0)} + \hat{H}^{(1)}(P)$ and the solution depending on some parameter P , the variation of the expectation value $E(P) = \int \Psi^* \hat{H} \Psi d\tau$ of the normalized state Ψ delivers three terms:

$$\frac{\partial E}{\partial P} = \left\langle \frac{\partial \Psi^*}{\partial P} \left| \hat{H} \right| \Psi \right\rangle + \left\langle \Psi^* \left| \frac{\partial \hat{H}}{\partial P} \right| \Psi \right\rangle + \left\langle \Psi^* \left| \hat{H} \right| \frac{\partial \Psi}{\partial P} \right\rangle \quad (6.1)$$

Assuming the wave function Ψ has been optimized with respect to the full Hamiltonian, one is left with the Hellmann-Feynman theorem:

$$\frac{\partial E}{\partial P} = \left\langle \Psi^* \left| \frac{\partial \hat{H}}{\partial P} \right| \Psi \right\rangle \quad (6.2)$$

Under these circumstances the energy dependence on the parameter P may be found by the computationally simple task of evaluating an expectation value over the derivative of the complete Hamiltonian with respect to the perturbation.

This situation is given in Hartree-Fock optimizations, where the variational space is comprised by the orbital rotation parameters, and the approach is applied in calculations of electric field gradients in subsection 6.3.3. By these means, first-order properties can also be evaluated as expectation values of MCSCF wave functions over the Hamiltonian [243].

Upon including dynamic electron correlation in the calculation, the optimization of the full wave function with respect to the perturbation is mostly out of reach in practice, so the so-called “non–Hellmann–Feynman” terms in equation (6.1) are non-vanishing. As will be described for more specific cases, one is usually in an intermediate situation, the two extremes being the full validity of the Hellmann–Feynman theorem and the other having obtained a solution wave function for the zero-order Hamiltonian only. Thus, the partial accounting for the external perturbation in the wave function optimization comprises an approximation. Such approximations include, e.g., neglecting the orbital optimization in a truncated CI or CC calculation.

The most sophisticated analytical approach to arrive at general-order properties is comprised by response theory [244, 168]. The implementation of CC and MCSCF response methods in the 4-component framework, however, comprise future work.

6.1.2 Numerical Methods

It is also possible, mostly due to the lack of appropriate implementations of analytical procedures, to obtain electric (and magnetic) properties by applying the external field at a set of given finite and small strengths and to compute the total field-dependent energy of the considered system at these different points. This type of procedure will in general be called a finite-field technique. Its application to electric properties is rather wide-spread (e.g. [245, 246]) and with appropriate choices of the external field points and “hard” convergence of the iterative wave-function methods leads to precise and reliable results.

The total field-dependent energy ϵ of the system may be expanded as a Taylor power series around the point of zero electric field strength. For simplicity, only the z component of the electric field will be used in the following:

$$\begin{aligned} \epsilon(E_z) &= \sum_0^{\infty} \frac{1}{n!} \left(\frac{\partial^n \epsilon}{\partial E_z^n} \right)_{E_z=0} E_z^n \\ &= \epsilon_0 + \left(\frac{\partial \epsilon}{\partial E_z} \right)_{E_z=0} \cdot E_z + \frac{1}{2} \left(\frac{\partial^2 \epsilon}{\partial E_z^2} \right)_{E_z=0} \cdot E_z^2 + \frac{1}{6} \left(\frac{\partial^3 \epsilon}{\partial E_z^3} \right)_{E_z=0} \cdot E_z^3 \\ &\quad + \mathcal{O}(E_z^{n>3}) \end{aligned} \tag{6.3}$$

By using the Hellmann–Feynman theorem (6.2) for this particular case

$$\frac{\partial \epsilon(E_z)}{\partial E_z} \Big|_{E_z=0} = \left\langle \frac{\partial \hat{H}(E_z)}{\partial E_z} \right\rangle_{E_z=0} \tag{6.4}$$

specific relations for the desired system properties may be found.

Continuing the argument above and representing the perturbing external (electric) field by a Hamiltonian $\hat{H}^{(1)} = -\mu_z E_z$ added to the complete Hamiltonian $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$, where μ is the complete dipole moment of the system, so including

the permanent and the induced moment, the Hellmann-Feynman theorem becomes

$$\frac{\partial \epsilon(E_z)}{\partial E_z} = -\langle \mu_z \rangle_0 \quad \text{with} \quad \frac{\partial \left(\hat{H}^{(0)} - \mu_z E_z \right)}{\partial E_z} = -\mu_z. \quad (6.5)$$

Evaluating this expression for the above Taylor series expansion of the total energy (6.3) one obtains

$$\langle \mu_z \rangle_0 = - \left(\frac{\partial \epsilon}{\partial E_z} \right)_{E_z=0} - \left(\frac{\partial^2 \epsilon}{\partial E_z^2} \right)_{E_z=0} \cdot E_z - \frac{1}{2} \left(\frac{\partial^3 \epsilon}{\partial E_z^3} \right)_{E_z=0} \cdot E_z^2 + \mathcal{O}(E_z^{n>2}). \quad (6.6)$$

Comparing this expression with a basic expansion as known from electrodynamics the occurring derivative terms can be identified with the electric system properties of ascending order, so

$$- \left(\frac{\partial \epsilon}{\partial E_z} \right)_{E_z=0} = \mu_z \quad \text{permanent electric dipole moment} \quad (6.7)$$

$$- \left(\frac{\partial^2 \epsilon}{\partial E_z^2} \right)_{E_z=0} = \alpha_{zz} \quad \text{electric dipole polarizability} \quad (6.8)$$

$$- \left(\frac{\partial^3 \epsilon}{\partial E_z^3} \right)_{E_z=0} = \beta_{zzz} \quad \text{electric first dipole hyperpolarizability} \quad (6.9)$$

The total energy of the perturbed system can thus be expressed as

$$\epsilon(E_z) = \epsilon_0 - \mu_z E_z - \frac{1}{2} \alpha_{zz} E_z^2 - \frac{1}{6} \beta_{zzz} E_z^3 - \mathcal{O}(E_z^{n>3}). \quad (6.10)$$

The properties are therefore the coefficients of a power series of the total energy in the electric field. In the general case, the dipole moment becomes a vector, the polarizability a second-rank tensor etc.

By determining the total energy at a sufficient number of finite-field strength points, the resulting function can be interpolated by a fitting procedure, and the coefficients are directly obtained from the polynomial function (e.g., program WFFIT [247] which is applied for all results obtained in this fashion). It is important for this numerical procedure to carefully consider the energy convergence in the iterative optimization of the wave function when the perturbation is included. For first-order properties like the dipole moment this is less crucial, but for second-order properties like electric polarizabilities, the Hartree-Fock and correlated energies have to be converged to at least within $10^{-10} E_H$. This becomes of utmost importance when spin-orbit interaction is included and the resulting level splittings are small, as is the case for the lighter atoms in subsections 6.2.1.1 and 6.2.1.2.

6.2 Atoms

6.2.1 Electric Dipole Polarizabilities

Accurate polarizabilities of heavy atoms with open p , d , or f shells require the use of extensive and diffuse basis sets and the treatment of dynamic electron correla-

tion and spin-orbit interaction on the same footing. The methods described here thus allow for such studies, in particular also of excited-state polarizabilities. In the following, the heavy p block elements where spin-orbit coupling becomes very important are investigated.

6.2.1.1 Group 17 Atoms

The study in paper [2] is the first of its kind, in the sense that the impact of spin-orbit coupling on individual J, M_J state polarizabilities of atoms is resolved. The sample calculations are carried out on the halogen atoms where for iodine and astatine large spin-orbit splittings between the $J = \frac{3}{2}$ ground state and the $J = \frac{1}{2}$ excited state occur. As polarizabilities strongly depend on the radial distribution of valence electron density, the values for $J = \frac{3}{2}$ and $J = \frac{1}{2}$ states are expected to differ significantly. The results are of limited accuracy, for two reasons: 1) The spin-free polarizabilities are determined at high correlation level but only for the ground state ($M_L = 0$) component. These values are — due to the lower p_z occupation in field direction — smaller than the M_L -averaged values usually reported in such studies (e.g. [248]). 2) The spin-dependent calculations are carried out in restricted subspaces and resulting spin-orbit shifts added to the spin-free values. Therefore, the spin-orbit resolved results are of lesser quality than the spin-free ones. The fact that 2-component instead of 4-component CI calculations are carried out leads to a picture-change error which is analyzed and found to be smaller than 1.5% of the total polarizability of At. The most important finding is comprised by the difference in polarizabilities between the values for the (averaged) $J = \frac{3}{2}$ ground state and the $J = \frac{1}{2}$ excited state. For iodine, this difference amounts to 2.8% (or 0.14 \AA^3) and for astatine to 8% (or 0.54 \AA^3) of the total polarizability. The most important results are summarized in table 6.1.

	F	Br	I	At
Correlation level	SDTQ	SSDTQ	SSDTQ	SSDTQ
Scalar rel. reference	0.510	2.795	4.405	5.165
$J = \frac{3}{2}, M_J = \frac{3}{2}$	0.533	2.835	4.568	5.475
$J = \frac{3}{2}, M_J = \frac{1}{2}$	0.486	2.735	4.148	4.495
$J = \frac{1}{2}, M_J = \frac{1}{2}$	0.510	2.815	4.498	5.525

Table 6.1: Polarizabilities in different J, M_J components, given in \AA^3 , scalar relativistic CI and 2-component spin-orbit CI calculations.

SSDTQ: Singles from sub-valence p shells, combined with SDTQ excitations from the valence orbitals into the external space.

As the external electric field is applied in one (z) direction, one of the $\frac{3}{2}, M_J$ components has an increased, the other a decreased polarizability value, in line with the z character of the corresponding atomic spinors. As the nuclear charge increases,

however, relativity comes into play, contracting the $p_{1/2}$ spinor and resulting in an increased (!) polarizability for the $\frac{1}{2}$ state which has the hole in the $p_{1/2}$ spinor. In the extreme case of astatine, the $\frac{1}{2}$ state even has a larger polarizability than the $\frac{3}{2}, \frac{3}{2}$ state.

A final word about the importance of spin-orbit coupling calls for determining the deviation of the (averaged) $J = \frac{3}{2}$ ground state value from the M_L -averaged value. Along with an analysis of polarizability anisotropy components, this is elucidated in a more rigorous and complete study on the group 13 atoms (subsection 6.2.1.2).

6.2.1.2 Group-13 Atoms

The group-13 atoms have a p particle instead of a p hole valence state, reducing the spin-orbit splittings somewhat compared to the group-17 elements and relative to the nuclear charge. On the other hand, polarizability anisotropies are largest at the beginning of the p block. Paper [7] reports benchmark values of predictive quality for the heavier elements Ga, In, and Tl in the $J = \frac{1}{2}$ ground states at the 4-component CCSD(T) level, shown in table 6.2.

Correlated electrons		Ga	In	Tl
CCSD(T)	19		9.11	7.64
CCSD(T)	21	7.36		

Table 6.2: Coupled cluster benchmark polarizabilities of the $\frac{1}{2}, \frac{1}{2}$ ground states of the group-13 atoms, in \AA^3 .

These coupled cluster results are also used for calibrating CI calculations for obtaining excited-state polarizabilities of high accuracy. Further calibration is obtained by examining the influence of the cutoff value for virtual orbitals and the correlation treatment on the spin-orbit splittings. Table 6.3 compiles all static polarizabilities for the group 13 atoms.

The line $\bar{\alpha}_{J=\frac{3}{2}} - \alpha_{J=\frac{1}{2}}$ can be understood as the effect of both spin-orbit coupling and the contraction of the $p_{1/2}$ spinor/decontraction of the $p_{3/2}$ spinor, so a measure of the importance of relativistic contributions in total. In the last line, the effect of spin-orbit coupling is displayed as the difference of the M_L -averaged polarizability including scalar contributions and the value for the $J = \frac{1}{2}$ ground state.

Comparing with the available experimental values for the ground state, the result for Tl is in excellent agreement. Also, an earlier (preliminary) calculation by relativistic response theory [80] reports a value of 7.5\AA^3 . Given the high level of

¹Reference [248]

²Reference [249]

³Reference [250]

⁴Reference [80]

	$\alpha[\text{\AA}^3]$	B	Al	Ga	In	Tl
α_{L,m_L}	$\alpha_{0,0}$	3.634	10.96	10.72	13.66	16.02
	$\alpha_{1,1/-1}$	2.759	6.85	5.90	8.01	7.57
	$\bar{\alpha}_{m_L}$	3.051	8.22(8.56 ¹)	7.51	9.89	10.38
α_{J,m_J}	$\alpha_{1/2,1/2}$	3.042	8.21	7.39	9.17	7.64
	$\alpha_{3/2,1/2}$	3.340	9.68	9.25	12.41	15.68
	$\alpha_{3/2,3/2}$	2.747	6.90	6.05	8.23	8.40
	Corr. level	MRSDT5 (100)	MRSD13 (100)	SD13 (10)	SD13 (10)	SD13 (10)
	$\alpha_{1/2,1/2}$ (Exp.)	-	6.8 ± 0.3^2	-	10.2 ± 1.2^3	7.6 ± 1.1^4
	$\bar{\alpha}_{J=\frac{3}{2}} - \alpha_{J=\frac{1}{2}}$	0.002	0.08	0.26	1.15	4.40
	$\bar{\alpha}_{m_L} - \alpha_{1/2,1/2}$	0.01	0.01	0.12	0.72	2.74

Table 6.3: Component-resolved static polarizabilities, spin-orbit free (α_{L,m_L}) and spin-dependent (α_{J,m_J}), group-13 atoms. MRSDT5 (100) denotes a multi-reference Singles, Doubles, and Triples calculation with 5 electrons and a cutoff value of 100 a.u. for virtual orbitals. $\bar{\alpha}$ denotes an averaging over the polarizabilities in the index.

electron correlation and the extent of the basis sets in the present study, some reference values for In are questionable. The experimental reference value for In of 10.2 \AA^3 has an estimated error bar of 12%, and the present result is within this error range. The true polarizability is therefore at the lower end of the experimental range. A relativistic density-functional theory calculation yields a value of 9.66 \AA^3 (in [250]) which is likely to be too large. The relativistic response theory result of 9.1 \AA^3 (in [80]), on the other hand, agrees very well with the present value. The experimental result for aluminum is certainly in error. The high-level CI result reported here agrees reasonably well with previous CC calculations by Lupinetti and Thakkar (as reference value in table 6.3) and Fuentealba [251] (8.66 \AA^3).

The values for the lightest atom are near FCI quality. Already here, the difference between $\alpha_{1/2,1/2}$ and that of the other two components is significant, but eliminating the directional dependence from the excited-state component values by averaging, the difference $\bar{\alpha}_{J=\frac{3}{2}} - \alpha_{J=\frac{1}{2}}$ amounts to only 0.002 \AA^3 . Also aluminum is essentially non-relativistic. Apart from the increasing importance of relativity in the gallium atom, the decrease of all property values is remarkable when comparing to aluminum. The reason lies in the smaller screening of the nuclear charge by the d electrons in Ga, resulting in more compact valence shells and a reduced polarizability. A similar argument applies when comparing In and Tl with respect to f electrons in Tl, but here the effect becomes mingled with large relativistic effects and is therefore not directly visible.

The sole effect of spin-orbit coupling on the polarizabilities can now be elucidated: The spin-free calculations yield one-particle basis functions with radial parts modified by relativistic corrections, i.e., valence s and p shells are contracted as compared to the non-relativistic picture. This contraction is the same in all M_L state

components, and it is of course also present in the spin-dependent calculations. In the latter, the $p_{1/2}$ spinor gives rise to a spherically symmetric electron density and, therefore, the polarizability of the corresponding $J = \frac{1}{2}$ state can be compared to the average value of the M_L component polarizabilities from the spinfree calculation. At a given level of electron correlation the difference will be the impact of spin-orbit coupling alone on the polarizability.

Figure 6.1 gives an overview of the spin-orbit effects on static polarizabilities in the group 13 atoms in the upper part. The lower part shows the anisotropy component α_a (also referred to as tensor polarizability [252]) from spin-free and spin-dependent calculations.

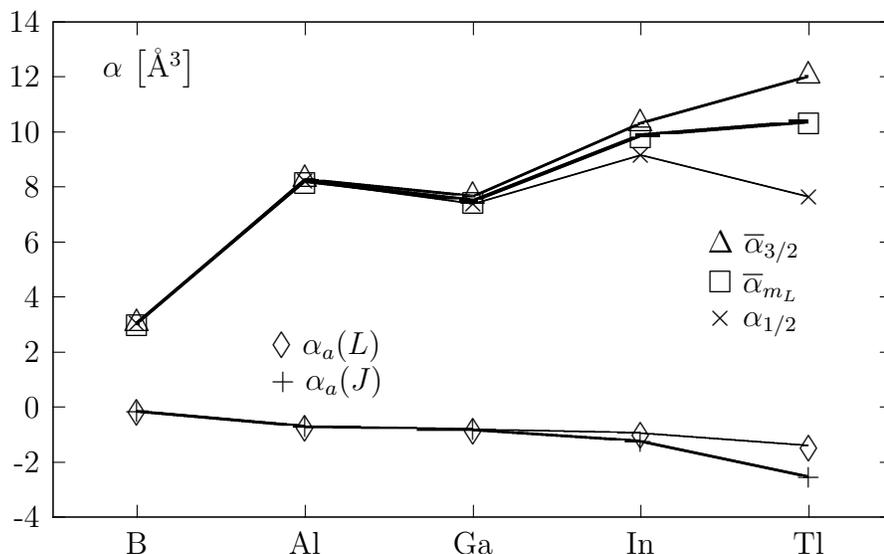


Figure 6.1: Component-resolved group 13 polarizabilities and polarizability anisotropy components. $\bar{\alpha}$ denotes a polarizability averaged over the components in the respective index.

The tensor polarizability increases on the absolute as the nuclear charge increases. The difference between $\alpha_a(J)$ and $\alpha_a(L)$ is due to spin-orbit coupling, because the mixing of spin and spatial degrees of freedom leads to deviations from the purely spatial anisotropies. Again, the impact of spin-orbit interaction is seen to be considerable for In and strong for the Tl atom.

Results are estimated to be within error ranges of 1-4%, depending on the atom and employed basis set, both for ground and excited states. The values for the three heavier atoms are assigned predictive power regarding possible future experiments of the static electric properties of these atoms.

6.3 Molecules

Whereas the studies on atoms were focussed on open-shell systems and resolving the properties in states split by spin-orbit coupling, the molecules studied so far are of the closed-shell type. Orbital contraction by the relativistic description is a major issue in these studies, and the effect of spin-orbit coupling — mainly introduced through singlet-triplet coupling — is presumably of minor importance.

6.3.1 Electric Dipole Moments

HI molecule. The electric dipole moment of hydrogen iodide has been investigated repeatedly both by experimentalists and theoretical groups, yielding a residual discrepancy which could not be reconciled by the most sophisticated approaches. The study in reference [3] employs high-level treatments of electron correlation (CCSD(T), 26 correlated electrons), large and diffuse basis sets, and accounts for scalar relativistic, spin-orbit, and vibrational corrections. The largest effects come from electron correlation and scalar relativistic contraction, quenching the dipole moment by roughly 20%, respectively. The effects are to a large degree additive. The final value obtained from a scalar relativistic CCSD(T) calculation in a large uncontracted basis set and correlating 26 electrons is 0.155 a.u. at the experimental bond length of $R_e = 3.0409$ a.u. A spin-orbit correction to this value is estimated to be -0.01 a.u., which yields a result too far from experiment (0.176 a.u. [253]).

As expected, the dipole moment is sensitive to the extent and the diffuseness of the employed basis set, in particular at the correlated level. Despite the investigation of the impact of various basis sets on the dipole moment and convergence of the property with respect to electron correlation in study [3], an unresolved discrepancy with experiment of roughly 10% remains. A later investigation by van Stralen et al. [87] reports a more systematic study of extending the basis set, including iodine functions with angular momenta up to h . It is these high angular momentum functions which provide the flexibility for the correlated wave function to reproduce the dipole moment in close agreement with experiment.

6.3.2 Electric Dipole Polarizabilities

HI molecule. Paper [3] also reports detailed studies of the static electric polarizability and polarizability anisotropy, depending on the choice of basis set, relativistic contributions, and the effect of dynamic electron correlation. The relaxation of the wave functions through electron correlation leads to an increase in polarizability (α_{zz}) as the electron distribution becomes more diffuse in the valence region. Scalar relativistic contributions are sizeable, cancelling the increase due to electron correlation to a large degree. Spin-orbit coupling, on the other hand, is far less important, leading to only marginal corrections. Similarly, the increase in the number of corre-

lated electrons is rather unimportant, even exhibiting an oscillatory behavior.

The effects of electron correlation and relativity on the perpendicular polarizability component α_{xx} are altered somewhat compared to the α_{zz} component. Whereas the influence of electron correlation is increased, the contraction due to scalar relativistic effects does not affect the polarizability to the same degree as for α_{zz} . This difference is related to the relativistic bond contraction in HI which affects the parallel polarizability component more strongly than the perpendicular one. It is demonstrated that the polarizability in general increases, not unexpectedly, when stretching the bond, and that the anisotropy increases more strongly than the mean polarizability, again reflecting the difference between the behavior of the parallel and the perpendicular components.

A substantial deviation from experiment also prevails here. Although it has not been shown explicitly in reference [87], the use of augmented basis sets will most likely also lead to electric dipole polarizabilities in close agreement with the available experimental values for HI.

6.3.3 Electric Field Gradients

The electric field gradient (EFG) in a molecule is an important property in spectroscopic techniques such as electron paramagnetic resonance (EPR) and nuclear quadrupole resonance (NQR). The coupling of the electrostatic field-gradient tensor to the nuclear quadrupole moment tensor is the most widely applied approach to the determination of nuclear quadrupole moments (NQM). This is an indirect manner of determining the NQM which can also be obtained directly from nuclear structure calculations.

Hydrogen Halides (HX). The study in [6] is devoted to the investigation of the convergence of electric field gradients at the heavy nucleus in the diatomic hydrogen halides when approximate Hamiltonians, here in particular the Douglas-Kroll-Hess Hamiltonian, are employed to the values obtained by fully 4-component approaches. The field gradients are obtained as expectation values at both the Dirac-Coulomb Hartree-Fock and Density Functional Theory level, neglecting (the small) contributions from spin-orbit coupling. The agreement between the 4-component and the DKH results is extremely well, with maximum deviations not larger than 1% of the property value. This applies to calculations where picture-change errors have been eliminated from the approximate-Hamiltonian methods properly. It appears hardly necessary to extend the Douglas-Kroll transformation of the property operator or the Hamiltonian to beyond the second order in the external field, even for the heaviest nucleus At. It is also again shown that the field gradient is not a typical core property, with contributions from the electronic core region limited to roughly 15%.

Zusammenfassung

Im Zentrum dieser Arbeit steht die Entwicklung relativistischer Elektronenkorrelationsmethoden sowie deren Anwendung auf schwere Atome und kleine Moleküle mit schweren Elementen. Elektronische Strukturmethode, die die höchstgenaue Berechnung spektroskopischer und elektrischer Eigenschaften von kleinen Systemen *ohne* schwere Elemente erlauben, sind in der Quantenchemie weitgehend etabliert. Die Möglichkeit zu schaffen, ähnliche Genauigkeit auch für kleine Systeme mit schweren Elementen in elektronischen Strukturrechnungen zu erzielen, ist eine Grundmotivation für die hier vorgestellten Arbeiten. Hierbei richtet sich das Augenmerk wesentlich auf zwei Kernpunkte: Erstens sind alle Methoden universell anwendbar, d.h. sie liefern unabhängig vom betrachteten System oder Zustand zuverlässige Resultate. Zweitens sind die Methoden in der Anwendung systematisch und prinzipiell beliebig weit verbesserbar. Die Methoden erlauben den Einsatz großer, unkontrahierter Basissätze und Hamiltonoperatoren verschiedener Genauigkeit, bis hin zum vierkomponentigen Dirac-Coulomb-Hamiltonoperator.

Methodenentwicklung

Um diese Ziele zu erreichen, wird ein Satz von Elektronenkorrelationsmethoden vorgestellt, der es erlaubt, statische Korrelation bei der Orbitaloptimierung zu berücksichtigen (MCSCF) und dabei alle führenden relativistischen Beiträge zu berücksichtigen, d.h. skalar-relativistische Orbitaleffekte sowie Spin-Bahn-Wechselwirkung. Das Programm wurde in einer ersten Implementierung von Jørn Thyssen und Hans Jørgen Aagaard Jensen vorgestellt und von mir weiterentwickelt. In der Hauptsache besteht diese Weiterentwicklung auf einem verzahnten Zusammenschluss der Methode mit dem von mir entwickelten relativistischen Konfigurationswechselwirkungs- (CI)- Programm LUCIAREL (s.u.), sodass MCSCF-Rechnungen mit großen aktiven Orbitalräumen und Determinantenentwicklungen überhaupt und auf effiziente Weise möglich wurden. Die erweiterte vierkomponentige MCSCF-Methode erlaubt die Berechnung von Molekülen, in denen die Spin-Bahn-Wechselwirkung insbesondere in den Einteilchenfunktionen von Bedeutung ist, die in nachfolgenden Berechnungen dynamischer Elektronenkorrelation verwendet werden. Hierbei ist nun wegen des Einbezugs statischer Korrelation auch die Berechnung voller Potentialkurven oder -flächen von Molekülen mit schweren Elementen möglich. Die

Berechnung von Grundzuständen wird in einigen Fällen diskutiert, aber auch angeregte Zustände können mit Hilfe des Konzeptes generalisierter aktiver Räume (GAS) zugänglich gemacht werden. Die Verwendung vierkomponentiger Hamiltonoperatoren ist in den meisten Fällen, in denen Valenzeigenschaften schwerer Elemente untersucht werden, nicht vonnöten. Daher ist es möglich, mittels des zweikomponentigen BSS-Hamiltonoperators approximative Berechnungen mit ebenso hoher Genauigkeit aber stark reduzierten Rechenanforderungen durchzuführen. Dies spielt im Schritt der Orbitaloptimierung eine wichtige Rolle, weil hier der zusätzliche Basissatz, der für die Beschreibung der zwei kleinen Komponenten benötigt wird, nicht mehr auftritt. Die Verwendung eines genäherten Hamiltonoperators ist jedoch in den üblicherweise nachfolgenden Schritten der dynamischen Korrelationsbehandlung nicht mehr von Vorteil.

Das vorgestellte relativistische CI-Programm **LUCIAREL** bildet sowohl die Grundlage für erweiterte MCSCF-Berechnungen als auch das "Arbeitspferd" für die Behandlung dynamischer Korrelation und kommt in einer Vielzahl von Anwendungen zum Einsatz. Auf der physikalischen Seite ist anzumerken, dass die Methode allgemein konzipiert ist und prinzipiell mit jedem in Frage kommenden Hamiltonoperator (vierkomponentig, zweikomponentig, skalar-relativistisch) sowie mit Spinoren als auch Spinorbitalen verwendet werden kann. Die einzige Einschränkung besteht in der Forderung nach Einteilchenfunktionen, die an Zeitumkehrsymmetrie adaptiert sind, d.h. Kramers-Paare. Eine solche Formulierung ist ohne externe Magnetfelder, die in dieser Arbeit nicht betrachtet werden, grundsätzlich immer möglich. **LUCIAREL** basiert auf einer Erzeugerstring-getriebenen, nichtrelativistischen Implementierung von Jeppe Olsen, die hauptsächlich von mir auf den relativistischen Formalismus verallgemeinert wurde. Die jüngsten Errungenschaften bestehen in der Verwendung von Spinoren statt Spinorbitalen sowie dem Anschluss an ein vierkomponentiges Programmpaket (**DIRAC**). Spinoren bilden einen wesentlich besseren Ausgangspunkt für die Behandlung dynamischer Korrelation, weil der entsprechende Konfigurationsraum weitgehend nach Kriterien der Korrelation selbst aufgebaut werden kann. Werden Spinorbitale hingegen verwendet, so müssen in der Regel auch Anregungen berücksichtigt werden, die nur zur Beschreibung der Spin-Bahn-Wechselwirkung von Bedeutung sind, was die Effizienz dieses Ansatzes verringert. Zu den eher technischen Neuerungen zählt die Programmierung von relativistischen Ein- und Zweiteilchendichtematrizen, die über Spinoroperatoren und relativistische CI-Vektoren ausgewertet werden. Neben der Erzeugung von natürlichen Orbitalen (oder Spinoren) finden diese insbesondere im Anschluss an das erwähnte MCSCF-Programm Verwendung. In der Anwendung auf schwere Atome und Moleküle erweist sich **LUCIAREL** derzeit in der Lage, eine kleinere Zahl (bis zu etwa 5) angeregter Zustände pro irreduzibler Doppelgruppen-Darstellung zu erfassen, wobei der beschränkende Faktor weitgehend in der erforderlichen Rechenzeit besteht. In diesen Rechnungen sind jedoch ausgedehnte GAS-Multireferenzentwicklungen mit insgesamt bis zu etwa 100 Millionen Slaterdeterminanten möglich. Ähnliche Be-

schränkungen gelten auch für die oben diskutierten MCSCF-Anwendungen. In derartigen Berechnungen zahlt es sich aus, dass höhere Anregungen als Doppelanregungen ebenso effizient behandelt werden wie Doppelanregungen selbst, was im Falle von ausgedehnten Multireferenzentwicklungen unabdingbar ist.

Zur Effizienzsteigerung in dynamischen Korrelationsbehandlungen wird ein relativistisches Coupled Cluster (CC)- Programm vorgestellt, das derzeit ohne Einbezug der Spin-Bahn-Wechselwirkung angewendet werden kann. Die nichtrelativistische Vorläufermethode von Jeppe Olsen wird von Lasse Sørensen und mir selbst zur Verwendung allgemein relativistischer Operatoren ausgebaut. Hierzu habe ich den erforderlichen Formalismus ausgearbeitet und ein Konzept entwickelt, wie Zeitumkehrsymmetrie im Allgemeinen in der CC-Theorie implementiert werden kann, was bislang nicht bekannt war. Es zeigt sich, dass eine Implementierung ähnlich dem spinbeschränkten Formalismus von Szalay und Gauss [163] am vielversprechendsten erscheint, weil unter Verwendung einer speziell formulierten Zeitumkehrsymmetriebedingung für die Cluster-Amplitudengleichungen die Vertauschbarkeit der Clusteroperatoren erhalten werden kann. Die voll adaptierte Version, hingegen, bei der zeitumkehrredundante Amplituden vollständig eliminiert werden, führt zu einem nichtkommutativen CC-Formalismus, der aufwendig zu implementieren ist und dessen Effizienz trotz seiner Eleganz fragwürdig bleibt. Die spinfreie Variante ARDUCCA entstand durch Anschluss an das vierkomponentige Programmpaket DIRAC und vermag effizient CC-Entwicklungen allgemeiner Ordnung und mit mehr als 100 Millionen Clusteramplituden durchzuführen, was in einer ersten Anwendung auf das CsLi-Molekül demonstriert wird. Eine analoge Implementierung wird im Falle der CI-Methode ergänzend zur voll relativistischen Variante vorgestellt (LUCITA). LUCITA und ARDUCCA beweisen in der Praxis den Fortschritt in Anwendbarkeit und erreichbarer Genauigkeit für spektroskopische und elektrische Eigenschaften.

Anwendung

Die in dieser Arbeit vorgestellten Anwendungen befassen sich mit der Ermittlung genauer spektroskopischer sowie elektrischer Eigenschaften kleiner Moleküle mit schweren Elementen und schwerer Atome. Die neu entwickelten quantenchemischen Verfahren werden hierbei meist in Kombination eingesetzt.

Die relativistisch vierkomponentige MCSCF-Methode wird einerseits im Vergleich mit einer spinfreien Variante am AuO-Molekül zur Bestimmung des Einflusses der Spin-Bahn-Wechselwirkung auf die Gleichgewichtsbindungslänge angewandt. Es zeigt sich, dass sich besonders unter Einbezug statischer Elektronenkorrelation die AuO-Bindung durch Spin-Bahn-Kopplung stark verkürzt, was auf den erhöhten offenschaligen Charakter der Au-5*d*-Orbitale zurückgeführt wird, die an der partiellen π -Bindung beteiligt sind. Ein spinorbasiertes MCSCF-Verfahren ist folglich nicht allein für die Beschreibung von Dissoziationsprozessen von Bedeutung,

bei denen Spin-Bahn-Wechselwirkung eine entscheidende Rolle spielt, sondern dient auch zur korrekten Beschreibung molekularer Zustände im Bindungsbereich schwerer Moleküle mit ähnlichen Valenzstrukturen wie AuO. Andererseits, und hiervon nicht losgelöst, stellen MCSCF-Spinoren für schwere Elemente eine verbesserte Einteilchenbasis dar, die in nachfolgenden Behandlungen dynamischer Elektronenkorrelation zum Einsatz kommt. Dies wird am Beispiel des UO_2 -Moleküls diskutiert und bei der Berechnung der tiefstliegenden Molekülzustände durchgeführt. Derzeit wird das MCSCF-Programm zur Berechnung der vollen Potentialkurve des TI-Dimers eingesetzt, bei dem die simultane Berücksichtigung statischer Korrelation und Spin-Bahn-Kopplung unabdingbar ist.

Die Berechnung spektroskopischer und elektrischer Eigenschaften angeregter Zustände wird vornehmlich mit dem vorgestellten Multireferenz-CI-Verfahren vorgenommen. Hochgenaue statische elektrische Polarisierbarkeiten wurden mit Hilfe von CC-Kalibrierungsrechnungen an den jeweiligen Grundzuständen für die angeregten Zustände der Atome der dritten Hauptgruppe ermittelt. Hier ist die Verwendung von MCSCF-Spinoren als Einteilchenbasis nicht notwendig, jedoch erweisen sich zustandsgemittelte Dirac-Coulomb Hartree-Fock Spinoren als sehr vorteilhaft, weil die nachfolgenden CI-Berechnungen, insbesondere beim Thalliumatom, auf die Beschreibung dynamischer Elektronenkorrelation beschränkt werden können und keine zusätzlichen Anregungen zur Erfassung von Spin-Bahn-Effekten benötigt werden. Die Resultate haben großenteils geschätzte Restfehler von nur 1-2% und sind somit zuverlässige Daten für Untersuchungen, die auf die Polarisierbarkeiten dieser Atome zurückgreifen. Eine ähnliche Studie, jedoch weniger rigoros, wurde einige Jahre zuvor für die Halogenatome durchgeführt, die ebenfalls vorgestellt wird.

Genaue spektroskopische Eigenschaften mittels relativistischer MRCI-Rechnungen wurden für die Moleküle AuO und UO_2 bestimmt. Für Goldoxid sind insbesondere die Gleichgewichtsbindungslänge und die erste Anregungsenergie zu nennen. Am Urandioxid wird demonstriert, wie das implementierte Konzept generalisierter aktiver Räume bei der Behandlung eines Moleküls mit komplizierten Bindungsverhältnissen vorteilhaft eingesetzt wird. Die Beschränkung der CI-Entwicklungen erlaubt auf diese Weise die Korrelation auch der äußeren "core"-Elektronen des Uranatoms, deren Einbezug zur Berechnung insbesondere von Anregungsenergien hoher Genauigkeit erforderlich ist. Für vertikale Anregungsenergien wird nahegelegt, dass bisherige Berechnungen anderer Gruppen mit weniger rigorosen Methoden (COLUMBUS Spin-Bahn CI [228], Spin-Bahn-CASPT2 [227, 229]) für Anregungsenergien von UO_2 signifikante Fehler (wenigstens 15%) aufweisen und dass hierdurch auch die Zuordnung von Zuständen in experimentellen Spektren fehlerhaft sein könnte. Die Studie an UO_2 macht den derzeitigen Anwendungshorizont des neuen CI-Programms deutlich, der jedoch noch durch technische Verbesserungen (z.B. Parallelisierung, Implementierung linearer und atomarer Symmetrie) erweitert werden kann.

Die effizienteste Weise, hochgenaue Eigenschaften in korrelierten elektronischen

Strukturrechnungen zu erhalten, stellt die CC-Methode dar. Die neue Implementierung, die derzeit nur auf Grundzustände und ohne Spin-Bahn-Wechselwirkung angewandt werden kann, wurde in einer umfassenden Studie am CsLi-Molekül eingesetzt. Die Auswirkungen relativistischer Effekte und dynamischer Elektronenkorrelation wurden hier in Berechnungen höchster Genauigkeit ermittelt, die insbesondere Multireferenz-CC-Entwicklungen und iterative Dreifach-Clusteranregungen beinhalten. Im CsLi- und ähnlichen Molekülen dominieren Korrelationseffekte auf die spektroskopischen Eigenschaften deutlich, während skalar-relativistische Effekte wesentlich schwächer sind und die Spin-Bahn-Wechselwirkung vernachlässigbar klein ist. In einer methodisch vergleichenden Untersuchung am Golddimer wird die Effizienz und Überlegenheit der CC-Methode gegenüber dem CI-Ansatz (wiederholt) demonstriert. Die nach Berücksichtigung weiterer Korrekturen erhaltene Gleichgewichtsbindungslänge weicht nur 0.3% vom experimentellen Wert ab, der mit einer verlässlichen Methode ermittelt wurde [238]. Es ist erstrebenswert, die vorgestellte CC-Implementierung auch auf die Behandlung angeregter Zustände zu erweitern. Derzeit werden die in dieser Arbeit vorgestellten Konzepte zur Verallgemeinerung auf den voll relativistischen Fall implementiert, so dass der Einbezug der Spin-Bahn-Kopplung möglich wird.

Mit Ausnahme der Berechnungen an CsLi und den Wasserstoffhalogeniden, für die elektrische Dipolmomente und Polarisierbarkeiten sowie elektrische Feldgradienten berechnet wurden, sind alle in dieser Arbeit diskutierten Anwendungen von mir selbst durchgeführt worden. An den erstgenannten Untersuchungen habe ich mitgewirkt.

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