6. Summary and conclusions


The non-relativistic valence-only method, using a frozen relativistic core combined with first order perturbation theory for the relativistic effects on the valence electrons, has been applied to Sn and SnH₄. The results show that the relativistic corrections to the valence properties are mainly direct relativistic valence effects, and that there is a large difference between the atomic and molecular relativistic effects. In view of these results, relativistic effects should not be calculated by the inclusion of a relativistic pseudopotential without further study if accurate results are required.

The feasibility of all-electron open-shell molecular Hartree-Fock-Dirac calculations on chemically interesting systems has been demonstrated by the calculations reported in chapter 4 and 5. The general contraction method, using kinetic and atomic balance for the small components of molecular basis sets, reduces the computational effort while retaining sufficient accuracy.

The average of configuration open shell method followed by a complete open shell configuration interaction calculation (the COSCI method) has proven to be useful to obtain total energies for the states of interest. The calculations on EuO₆⁻ clusters show that the method is extremely useful in obtaining all the individual states of the open shell manifold. In that case, it yields an ab initio intermediate coupling description of the f⁶-like manifold.

The results of calculations on an Eu³⁺ impurity in the Ba₂GdNbO₆ crystal (modelled by an EuO₆⁻ cluster in a Madelung potential) show that the splittings due to relativistic effects, which are much larger than the splittings due to the surroundings, can be calculated within about 10 cm⁻¹. We have also found that both a pure Madelung field and a bare EuO₆⁻ cluster significantly over-estimate the splittings introduced by the surroundings. The detailed form of the orbitals is important in the calculation of these
6. **Summary and conclusions**

splittings, so the preferred approach should be to use relativistic orbitals from the outset.

In our calculations on the hydrides, we have verified that the Breit interaction leads to small corrections to the relativistic results both for light and heavy atoms (a small bond length expansion for PbH$_4$). For the lighter systems the relativistic bond length contractions are very small. However, in such cases the neglect of the Breit interaction when studying relativistic effects leads to contractions which are significantly overestimated (for CH$_4$ by about a factor 3).

For the PbH$_4$ molecule the relativistic effects are much more important than the correlation effects.

6.2. **Conclusions.**

In general, we conclude that it is important to use relativistic orbitals from the outset when one wants to calculate properties which depend on the details of the orbitals (like the small crystal field splittings in lanthanide impurities). We have demonstrated that open-shell Hartree-Fock-Dirac calculations are feasible for some chemically interesting systems, and that the open shell CI method yields reliable results. It has also proven to be possible and important for valence properties to include the Breit interaction. The inclusion of correlation effects remains of course important. But in the case of heavy systems, like the PbH$_4$ molecule, relativistic effects are at least as important so that the use of a relativistic method from the outset leads to a better set of zeroth order orbitals, which can be used as a basis for CI or MBPT calculations.

In the near future, more work remains to be done to reduce the computational effort. It will probably be possible to improve the SCF convergence significantly. Also, significant gains can be obtained by further reducing the number of two-electron integrals. This could be accomplished by reducing the small component basis. It might be worthwhile to study the use of molecular basis sets which are atomically balanced only, and to study whether (SSI) integrals with an absolute value smaller than 10$^{-3}$ might be neglected without degrading the accuracy of the results.

An important extension of the method is the inclusion of correlation effects. This can be done using techniques similar to those used to handle correlation effects in non-relativistic calculations, like many-body perturbation theory of configuration interaction calculations. The main difference is the Hamiltonian used, the presence of negative
According to the work of Sucher [1], the CI calculations based on the positive energy MO's solves the relativistic problem within the no-pair approximation. It will be interesting to study corrections to this approximation by perturbation theory.

6.3. References.