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Towards relativistic quantum chemistry. On the AB INITO calculation of relativistic electron wave functions for molecules in the hartree-fock-dirac approximation.

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CHAPTER I Introduction

1. The aim and scope of this research

Computational Theoretical Chemistry is a research area which, as far as electronic structure problems are concerned, encompasses essentially the development of theoretically sound, yet computationally feasible quantum mechanical models for atoms, molecules and the solid state. Research carried out in this area consists of three closely connected parts : the development of theory, the design and construction of efficient algorithms and computer codes and the performance of state of the art applications. In line with the growth in computational power the models employed show a continuous refinement while also the area of applications is shifting from small molecules built from first and second row elements to larger systems, including (pieces of) proteins and large molecular clusters (solid state models).

A combination of both, systems which are intrinsically large and the need for a refined model, occurs where heavy atoms, i.e. atoms with high nuclear charges are involved in the target system. The need for this refinement lies in the fact that the high nuclear charges are the source of such strong potentials that the most tightly bound electrons possess energies which are no longer small compared to their rest mass energy m_0c^2 (8.187240×10^{-14}J = 18778.871 au). The finiteness of the velocity of light should therefore be taken into consideration explicitly, which introduces so called relativistic effects. Or rather it manifests the non-relativity defects of a non-relativistic model. In particular the rare-earth elements, which have been subject of investigation in the Theoretical Chemistry group of the University of Groningen [1] can be considered heavy in this sense. Van Piggelen concluded [2] that further analysis of the influence of the relativistic effects should be carried out first, before other refinements of the applied model are introduced.

The incorporation of relativistic effects in the non-relativistic models has been worked out theoretically and from several points of view [3, 4] but as will be shown their implementation in existing programs or algorithms is far from trivial if at all possible. Moreover it is far from elegant to proceed along this way even when the relativistic effects are dominant. It therefore seems worthwhile, if not natural, to start from a relativistic model based on the Dirac equation [5].

For the moment bypassing the theoretical traps of the modification of Dirac's equation into a many particle equation, one is left with two types of problems. Firstly, the problems related to the nature of Dirac's equation (with its unbounded spectrum) and secondly those related to the many particle aspect of the model. In quantum chemistry the problems arising in the application of the usual many particle models are dominated by the computational aspects of the particle-particle interaction and considerable know-how exists in attacking this kind of problem. It is therefore not surprising that in early attempts to solve the resulting relativistic equations the emphasis was on the interaction part rather than on the proper nature of Dirac's equation, which consequently appeared to dominate the outcome.

This was more or less the status quo when the investigations described in this thesis where set up. A major source of inspiration to approach the problem by straightforward "Hartree-Fock-Dirac" theory to the extent possible came from the Nato Advanced Study Institute on "Relativistic Effects in Atoms, Molecules and Solids" that I attended. This Institute was held under the inspiring direction of Professor G.L. Malli in Vancouver B.C., Canada,1981 and the idea's of dr. F. Mark and Professor W.H.E. Schwarz, subject of chapter IV.4, were presented there by the latter.

The aim of this research is to incorporate relativistic effects in proper model calculations on molecules by using Dirac's equation from the outset. Several arguments are in favour of this approach. In addition to the aspects mentioned earlier the method described in this work can be considered as the relativistic version of what is commonly referred to as the *ab initio* LCAO-MO-SCF method. The term ab initio in this context means that given the hamiltonian of the system, the only approximations to its eigenfunctions and eigenvalues are due to the use of a truncated basis set expansion. No a priori adjustments in order to reproduce experimental data are employed in the model and of course one must make sure that the approximate solutions converge as a function of a truncation parameter. Whether or not molecular systems are modelled sufficiently well by the hamiltonians defined in the subsequent chapters is quite another though not unimportant subject.

Rigorous mathematical proofs and fundamental physical issues concerning relativistic many-particle systems are beyond the scope of this thesis which is primarily focussed on the ultimate applicability of the methods described in it. Given the initial state of development in this research area it was necessary to devote much time to the investigation of what sloppily became called the Dirac one-electron problem. The remainder of the thesis is devoted to a discussion of many electron systems and the first "kinetically balanced" all electron Hartree-Fock-Dirac calculations on non-linear molecular systems.