Methods in Computational Chemistry

Volume 2
Relativistic Effects in Atoms and Molecules

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Volume 2 Relativistic Effects in Atoms and Molecules
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From the Preface to Volume 1

Today the digital computer is a major tool of research in chemistry and the chemical sciences. However, although computers have been employed in chemical research since their very inception, it is only in the past ten or fifteen years that computational chemistry has emerged as a field of research in its own right. The computer has become an increasingly valuable source of chemical information, one which can complement and sometimes replace more traditional laboratory experiments. The computational approach to chemical problems can not only provide a route to information which is not available from laboratory experiments but can also afford additional insight into the problems being studied, and, as it is often more efficient than the alternatives, the computational approach can be justified in terms of economics.

The applications of computers in chemistry are manifold. A broad overview of both the methods of computational chemistry and their applications in both the industrial research laboratory and the academic research environment is given in my book *Chemistry by Computer* (Plenum Press, 1986). Applications of the techniques of computational chemistry transcend the traditional divisions of chemistry—physical, inorganic and organic—and include many neighbouring areas in physics, biochemistry and biology. Numerous applications have been reported in fields as diverse as solid-state physics and pesticide research, catalysis and pharmaceuticals, nuclear physics and forestry, interstellar chemistry and molecular biology, surface physics and molecular electronics. The range of applications continues to increase as research workers in chemistry and allied fields identify problems to which the methods of computational chemistry can be applied.

The techniques employed by the computational chemist depend on the size of the system being investigated, the property or range of properties which are of interest, and the accuracy to which these properties must be measured. The methods of computational chemistry range from quantum mechanical studies of the electronic structure of small molecules to the

determination of bulk properties by means of Monte Carlo or molecular dynamics simulations, from the study of protein structures using the methods of molecular mechanics to the investigation of simple molecular collisions, from expert systems for the design of synthetic routes in organic chemistry to the use of computer graphic techniques to investigate interactions between biological molecules.

The computers employed in chemical calculations vary enormously, from small microcomputers used for data analysis to large state-of-the-art machines which are frequently necessary for contemporary *ab initio* calculations of molecular electronic structure. Increasingly, large mainframe computers are departing from the traditional von Neumann architecture with its emphasis on serial computation and a similar change is already underway in smaller machines. With the advent of vector processing and parallel processing computers, the need to match an algorithm closely to the target machine has been recognized. Whereas different implementations of a given algorithm on traditional serial computers may lead to programs which differ in speed by a factor of about two, factors of twenty were not uncommon with the first vector processors and larger factors can be expected in the future.

With the increasing use of computational techniques in chemistry, there is an obvious need to provide specialist reviews of methods and algorithms so as to enable the effective exploitation of the computing power available. This is the aim of the present series of volumes. Each volume will cover a particular area of research in computational chemistry and will provide a broad-ranging yet detailed analysis of contemporary theories, algorithms and computational techniques. The series will be of interest to those whose research is concerned with the development of computational methods in chemistry. More importantly, it will provide an up-to-date summary of computational techniques for the chemist, atomic and molecular physicist, biochemist, and molecular biologist who wishes to employ the methods to further their research programs. The series will also provide the graduate student with an easily accessible introduction to the field.

Preface

This volume is devoted to methods for the study of the effects of relativity on the electronic structure of atoms and molecules. The accurate description of relativistic effects in heavy atoms has long been recognized as one of the central problems of atomic physics. Contemporary relativistic atomic structure calculations can be performed almost routinely. Recent years have seen a growing interest in the study of the effects of relativity on the structure of molecules. Even for molecular systems containing atoms from the second row of the periodic table the energy associated with relativistic effects is often larger than that arising from electron correlation. For molecules containing heavier atoms relativistic effects become increasingly important, and for systems containing very heavy atoms relativity is known to dominate many chemical properties.

In this volume, one of the pioneers of relativistic atomic structure calculations, Ian P. Grant, provides a detailed survey of the computational techniques employed in contemporary studies of the effects of relativity on atomic structure. This is an area of research in which calculations can often lead to a particularly impressive degree of agreement between theory and experiment. Furthermore, these atomic studies have provided many of the foundations of a fully relativistic quantum chemistry. However, the spherical symmetry of atoms allows significant simplifications to be made in their quantum mechanical treatment, simplifications which are not possible in studies of molecules. In particular, as is well known from non-relativistic theories of molecular electronic structure, it is almost obligatory to invoke the algebraic approximation in molecular work and use finite basis set expansions. The problem of describing relativistic effects in molecules is addressed in Chapter 2 by Stephen Wilson. This chapter is devoted to *ab initio* relativistic molecular structure calculations in which all electrons are explicitly considered. The problem of including relativistic effects in molecular studies is also addressed in Chapters 3 and 4. In Chapter 3, Odd Gropen describes the use of relativistic effective core

potentials in calculations on molecular systems involving heavy atoms. This approach can lead to more tractable algorithms than the methods described in Chapter 2 and thus significantly extends the range of applications. The use of semiempirical methods has yielded a wealth of information about the influence of relativity on the chemistry of the heavier elements. This important area is reviewed in Chapter 4 by Pekka Pyykkö. Finally, in Chapter 5, Harry M. Quiney addresses the problem of describing electron correlation effects in relativistic electronic structure calculations. He concentrates on the very promising relativistic many-body perturbation theory. As was clearly demonstrated in Volume 1 of this series, the many-body perturbation theory is already recognized as a powerful approach to the nonrelativistic correlation problem.

It seems certain that relativistic quantum chemistry will become increasingly important over the next few years as quantum chemists continue to extend their horizons to include molecules containing heavier elements. Together the five chapters in this volume provide a broad-ranging, yet thorough, analysis of the most important aspects of contemporary research into the problem of describing relativistic effects in atomic and molecular systems.

Stephen Wilson

Wood End

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Relativistic Atomic Structure Calculations

IAN P. GRANT

1. Methods of Relativistic Atomic Structure Calculation

1.1. Introduction

This review surveys methods for computing the electronic structures of atoms based on the use of relativistic quantum mechanics. The main mathematical formulas are presented with some account of the underlying physical assumptions. The way in which these formulas are translated into practical computer codes is briefly discussed as well.

It is neither possible, nor really desirable, to give an exhaustive account of the field. It is now some 30 years since Hartree published his monograph *The calculation of atomic structures*[1] in which he was able to survey relativistic atomic structure calculations in just 7 pages. The author's review[2] in 1970, which in some ways is updated by this chapter, occupied 65 pages and gave 109 references. By 1986, Pyykkö had compiled a bibliography[3] listing 3119 references covering the period 1916–1985, and articles have continued to appear since then at an increasing rate. The need to restrict consideration to a manageable part of this material is obvious.

The central method of calculation is based on a model in which the electronic motions are described by Dirac's Hamiltonian[4,5] with the conventional minimal coupling to the electromagnetic field. The most useful

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point of departure in QED (quantum electrodynamics) to construct a rigorous theory of atomic structure is provided by Furry's bound interaction picture.[6,7] In practice, the full implications of this formulation are rarely considered in atomic structure calculations, which are usually based on the (so-called) Dirac–Coulomb Hamiltonian for an N-electron system; in Hartree's atomic units[1] this can be written

$$H_{\mathrm{DC}} = \sum_{i=1}^{N} H_{\mathrm{D}}(i) + \frac{1}{2} \sum_{i,j=1}^{N} \frac{1}{r_{ij}} \tag{1}$$

where

$$H_{\mathrm{D}}(i) = c\boldsymbol{\alpha}(i) \cdot \mathbf{p}_i + [\beta(i) - 1]\, c^2 - \frac{Z}{r_i} \tag{2}$$

is Dirac's Hamiltonian for the ith electron. The conventions of Ref. 2 will generally be followed in this chapter, so that c denotes the velocity of light (α^{-1} atomic units, where $\alpha \approx 1/137$ is the fine structure constant); $\boldsymbol{\alpha}(i)$, $\beta(i)$ are 4×4 Dirac matrices for the ith electron; Z is nuclear charge; and r_i and $\mathbf{p}_i$ are the radial coordinate of the ith electron and its (3-)momentum, respectively.

The controversy surrounding the Dirac–Coulomb Hamiltonian makes some mention of its status essential, though the details of the controversy have no place in this review. Brown and Ravenhall[8] asserted in 1951 that equation (1), if interpreted in the classical manner as an unquantized Hamiltonian, has no stable bound states: that is, that any initially bound state of a many-electron system whose motion is governed by H_{DC} will evolve into an unbound state by mixing with continuum states of the same total energy through the Coulomb interaction. Bethe and Salpeter[9] make a similar point in discussion of Breit's two-electron Hamiltonian for the helium atom. Sucher[10,11] has been particularly active in the recent controversy, advancing various proposals for dealing with this so-called "Brown–Ravenhall disease." Recent discussions[12–14] have emphasized that a properly formulated relativistic atomic structure theory based on Furry's[6] bound interaction picture is not threatened by this problem. Thus the ad hoc derivations of relativistic self-consistent field equations due to Swirles,[15] and later Grant,[16] which were based on the allegedly suspect H_{DC}, can be obtained also as a legitimate approximation within a properly quantized QED theory.[12]

Although methods and programs based on equations (1) and (2) are central to relativistic atomic structure theory, there are both more exact approaches within the Furry picture QED as well as "simplifications" which we shall examine below. Methods based on H_{DC} will be described in Section 1.2; the handling of corrections to the instantaneous Coulomb

interaction, the effect of the nuclear charge distribution and of its motion, radiative corrections predicted by QED, and electron correlation effects will be discussed in Section 1.3. Section 2 will present the main formulas of relativistic atomic structure theory. The algebraic methods of Racah play a central part in this exposition, which gives a systematic presentation of the main formulas needed in practical calculations with Dirac orbitals. This leads naturally on to the *jj* coupling seniority scheme in Section 2.3, to the exploitation of the angular momentum diagrams of Yutsis in Section 2.4, and the presentation of formulas for matrix elements between general open-shell many-electron states in Section 2.5. The special features involved in calculating radiative transition probabilities are dealt with in Section 2.6.

Section 3 deals with some aspects of the implementation of the theory, focusing primarily on the programs built by the author and his collaborators. These make use of numerical finite difference methods to construct the radial wave functions and radial integrals. Some account is taken at this stage of other approaches to relativistic atomic structure, particularly the well-known semirelativistic computer codes due to Cowan.

The final section briefly summarizes the author's view of the state of the art of relativistic atomic calculations.

1.2. Methods Based on H_{DC}

1.2.1. The Central Field Approximation

This section introduces some of the basic notions that will be needed throughout this review.

The independent particle central field approximation is the starting point for most calculations of the electronic structure of atoms and ions in nonrelativistic quantum mechanics. The same starting point has been adopted in relativistic atomic structure calculations. We begin by partitioning H_{DC} into two parts:

$$H_{DC} = H_0 + V \tag{3}$$

where

$$H_0 = \sum_{i=1}^{N} \{c\boldsymbol{\alpha}(i) \cdot \mathbf{p}_i + [\beta(i) - 1]c^2 + U(r_i)\} \tag{4}$$

and

$$V = \frac{1}{2} \sum_{i,j=1}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \left(U(r_i) + \frac{Z}{r_i} \right) \tag{5}$$