1
Introduction

This first chapter provides a short reader's guide, which may help to make the material presented in this book more easily accessible. Moreover, it serves to highlight the philosophy and intention of this book.

1.1
Philosophy of this Book

Relativistic quantum chemistry is the relativistic formulation of quantum mechanics applied to many-electron systems, i.e., to atoms, molecules and solids. It combines the principles of Einstein's theory of special relativity, which have to be obeyed by any fundamental physical theory, with the basic rules of quantum mechanics. By construction, it represents the most fundamental theory of all molecular sciences, which describes matter by the action, interaction, and motion of the elementary particles of the theory. In this sense it is important for physicists, chemists, material scientists, and biologists with a molecular view of the world. It is important to note that the energy range relevant to the molecular sciences allows us to operate with a reduced and idealized set of "elementary" particles. "Elementary" to chemistry are atomic nuclei and electrons. In most cases, neither the structure of the nuclei nor the *explicit* description of photons is required for the theory of molecular processes. Of course, this elementary level is not always the most appropriate one if it comes to the investigation of very large nanometer-sized molecular systems. Nevertheless it has two very convenient features:

(i) As a fundamental theory it does not require any experimental information (other than that needed to formulate the basic axioms of the theory) as input and is therefore a so-called *first-principles* or *ab initio* theory, which can be deduced completely from the postulates of relativistic quantum mechanics.

(ii) As the theory describes the motion of elementary particles solely on the basis of the laws of quantum mechanics and special relativity, it can be

used for the derivation of more approximate models for large molecules without falling back on experimental data. This can be achieved by integrating out those degrees of freedom that are deemed irrelevant, thus arriving at effective *ab initio* or even *classical* model theories which describe certain chemical processes sufficiently well.

For all issues relevant to the chemistry and physics of atoms, molecules, clusters, and solids only electromagnetic and — to a negligible extent — weak interactions, which are responsible for the radioactive β-decay and the non-conservation of parity, contribute. The internal structure of hadrons, i.e., protons and neutrons built up by quarks governed by strong interactions and also gravitational forces, do not play any role and are therefore not covered by this presentation.

A main purpose of this book is to provide a structured and self-contained presentation of relativistic quantum chemistry as a semi-classical theory. We deem this necessary as there hardly exists any such contiguous and detailed presentation. The main reason appears to be the fact that quantum electrodynamics was developed in the 1930s and 1940s shortly after the advent of the new quantum theory. It was already clear in those days that quantum electrodynamics represents the fundamental theory of light and electrons, and hence the semi-classical theory was almost instantaneously abandoned. However, this most elegant and sophisticated theory of quantum electrodynamics is too abstract to be grasped immediately. The connection to classical physics, which has always been a guiding principle in quantum theory and even for the development of quantum electrodynamics, is seldom made. Instead, especially modern accounts start directly with the field-quantized formulation although the semi-classical theory is sufficient for chemistry as countless numerical studies in quantum chemistry demonstrated. This issue had already been noted by Dirac in his famous lectures on quantum theory, but he nevertheless changed the presentation of the electromagnetic quantum field theory in one of the later editions and gave up the semi-classical theory. However, because of the paramount importance of the semi-classical theory to chemistry, we derive this theory from the very basis, i.e., from classical electrodynamics. Of course, the transition to quantum electrodynamics is also made in this book, but it plays a minor role. This transition can be much better understood once the problems with the classical and the semi-classical theory have been worked out. Only then can one fully appreciate the emergence of concepts such as *retarded electromagnetic interactions*, *magnetic spin–spin coupling* or *orbit–other-orbit interaction*.

Because of the limited space available and the vast number of relativistic studies on atoms and molecules, we chose to accompany the derivation of the theory with a multitude of references to the original research literature in

order to provide the reader with a topical overview of results for electronic systems.

Relativity adds a new dimension to quantum chemistry, which is the choice of the Hamiltonian operator. While the Hamiltonian of a molecule is exactly known in nonrelativistic quantum mechanics (if one focuses on the dominating electrostatic monopole interactions to be considered as being transmitted instantaneously), this is no longer the case for the relativistic formulation. Numerical results obtained by many researchers over the past decades have shown how Hamiltonians which capture most of the (numerical) effect of relativity on physical observables can be derived. Relativistic quantum chemistry therefore comes in various flavors, which are more or less well rooted in fundamental physical theory and whose relation to one another will be described in detail in this book. The new dimension of relativistic Hamiltonians makes the presentation of the relativistic many-electron theory very complicated, and the degree of complexity is far greater than for nonrelativistic quantum chemistry. However, the relativistic theory provides the consistent approach toward the description of nature: molecular structures containing heavy atoms can *only* be treated correctly within a relativistic framework. Prominent examples known to everyone are the color of gold and the liquid state of mercury at room temperature. Moreover, it must be understood that relativistic quantum chemistry provides universal theoretical means that are applicable to any element from the periodic table or to any molecule — not only to heavy-element compounds.

It is the nature of the subject that makes its presentation rather formal and requires some basic, mainly conceptual knowledge in mathematics and physics. However, only standard mathematical techniques (such as differential and integral calculus, matrix algebra) are required. More advanced subjects such as complex analysis and tensor calculus are occasionally also used. Furthermore, also basic knowledge of classical Newtonian mechanics and electrodynamics will be helpful to more quickly understand the concise but short review of these matters in the second chapter of this book.

Many (pseudo-)relativistic quantum chemical approaches provide methods which can be implemented in computer programs in a very efficient manner — an aspect which may be called a boundary condition of computational chemistry imposed on theoretical chemistry. Most of these approaches demand only as much computing time as their nonrelativistic analogs (or are more expensive by a constant but small factor). The quantum chemistry community has developed a certain working knowledge of the reliability of these relativistic methods, but their relation to one another sometimes remains unclear. In the light of the importance of relativistic methods, we therefore derive all methods from first principles and highlight their development to sophisticated computational tools in chemistry. In doing so, we shall understand

which aspects of the rigorous theory of relativistic quantum *mechanics* survive in relativistic quantum *chemistry*; we learn and have to accept that relativistic effects in extended molecules are about the art of efficiently correcting numerical results such as energies for many-electron systems in an essentially nonrelativistic framework.

1.2
Short Reader's Guide

A book on a theoretical topic, which is based on fundamental physical theory but extends to the realm of experimental chemistry — such as the present one does — always faces difficulties, as it might be too formal for chemists while it could be too technical and specialized for non-experts and even physicists. Our main goal is the presentation of an almost complete derivation of the relativistic theory for many-electron systems as the fundamental theory of the molecular sciences. For this purpose, we have tried to introduce all essential concepts and ideas and derive all basic equations explicitly. As a consequence, parts of the book — such as the solution of the Dirac hydrogen atom — seem to be lengthy. However, many derivations cannot be easily found in such detail elsewhere in the literature (if at all). Also, the number of misconceptions can be rather large regarding issues of relativistic quantum chemistry, which is the reason why we try to provide a self-contained presentation of the theory. The resulting equations for many-particle systems cannot be solved analytically, and the derivation of working equations is strongly driven by the need to be able to solve them on modern computer hardware. Although it is not possible to delve deeply into how this is achieved in every detail, the reader will be given sufficient hints and information so that the equations derived do not appear like mathematical deadwood but are designed to be actually solvable, the essential boundary condition for quantum chemistry. Often, however, only one way for solving these equations is chosen in our presentation, but references to other possibilities are included.

In order to grasp all the essential ideas of the book the reader is strongly advised to go through it from the very beginning. However, each chapter is designed to represent a single unit which may be read with little knowledge of the contents of other chapters. This will help readers to use the book also as a quick reference (in combination with the index). However, especially the later chapters make frequent reference to results derived in previous parts of the book.

Our guiding principles for the preparation of this book were the goals to make all derivations comprehensible and to elaborate on all basic principles relevant for each topic. Each chapter is headed by a brief summary of the essential ideas. Of course, it is hardly possible to present all steps of a derivation,

but we aim at a reasonable number of steps, which should allow for a quick re-derivation of the equations given. Needless to say, the more understanding of physical theories and quantum chemical methods the reader already possesses, the easier it will be to understand the presentation. If the reader finds the extensive mathematical formalism of relativistic quantum chemistry too involved and complicated, we ask for patience: it should still be possible to access the basic ideas. Furthermore, all equations are in general presented in a way such that it is possible to easily verify intermediate derivation steps not explicitly given. If such steps are particularly easy, the reader will find comments like "it can be easily verified" or "it follows immediately" with additional references to equations. The purpose of these comments is to let the reader know that the derivation is indeed easy so that he or she can instantly realize that the ansatz is wrong from the start if a re-derivation turns out to be too complicated.

The topics of the individual chapters are well separated and the division of the book into five major parts emphasizes this structure. Part I contains all material, which is essential for understanding the physical ideas behind the merging of classical mechanics, principles of special relativity, and quantum mechanics to the complex field of relativistic quantum chemistry. However, one or all of these three chapters may be skipped by the experienced reader. As is good practice in theoretical physics (and even in textbooks on physical chemistry), *exact* treatments of the relativistic theory of the electron as well as analytically solvable problems such as the Dirac electron in a central field (i.e., the Dirac hydrogen atom) are contained in part II.

Chemistry and the molecular sciences start with the many-particle theories of physics; part III of the book deals with these many-electron extensions of the theoretical framwork, which have their foundations in the one-electron framework presented in part II. The first chapter in part III is on the most general many-electron theory known in physics: quantum electrodynamics (QED). From the point of view of physics this is the fundamental theory of chemistry, although far too complicated to be used for calculations on systems with more than a few electrons. Standard chemistry does not require all features covered by QED (such as pair creation), and so neither does a basic and at the same time practical theory of chemistry. Three subsequent chapters describe the suitable approximations, which provide a first-quantized theory for many-electron systems with a, basically, fixed number of particles. A major result from this discussion is the fact that this successful model is still plagued by practical as well as by conceptual difficulties. As a consequence further 'simplifications' are introduced, which eliminate the conceptual difficulties; these 'simplifications' are discussed in part IV.

The reader who proceeds stepwise will realize at this point that the theories of relativistic quantum chemistry are approximate anyhow and do not obey

the basic formal principles of relativity, although they capture most of the effect on the numerical values of physical observables relevant to chemistry. After this stringent development of relativistic quantum chemical methods for many-electron systems, we are in a position to finally discuss molecular properties and relativistic effects in chemistry in part V.

1.3
Notational Conventions and Choice of Units

Several conventions are used throughout this book. We may summarize some basic principles of notation here.

Cartesian vectors with three components, so-called 3-vectors, are indicated by boldface type, e.g., the position vector $\boldsymbol{r}$. Relativistic four-component vectors, so-called 4-vectors, are denoted by normal type. If not otherwise stated, all vectors irrespective of their dimension are assumed to be column vectors. The corresponding row vector is given by the transposed quantity, e.g., $\boldsymbol{r}^T = (x, y, z)$. For the sake of brevity, however, the transposition is not explicitly denoted in ubiquitous scalar products like $\boldsymbol{\sigma} \cdot \boldsymbol{p}$ or $\boldsymbol{\alpha} \cdot \boldsymbol{p}$, for example.

A dot on top of a symbol for a physical quantity denotes the *total* time derivative of that quantity, e.g., $\dot{\boldsymbol{r}} = \mathrm{d}\boldsymbol{r}/\mathrm{d}t$. Partial time derivatives are symbolized by $\partial/\partial t$. The spatial derivatives in one- or three-dimensional space are symbolized by $A'(x)$ or $\nabla\phi$ and $\nabla \cdot \boldsymbol{A}(\boldsymbol{r})$, respectively.

The same symbols will be used for classical quantities and also for the corresponding operators of the quantized formulation. Consequently, $\boldsymbol{p}$ might symbolize classical momentum as well as the quantum mechanical momentum operator $\boldsymbol{p} = -\mathrm{i}\hbar\nabla$ for example. The detailed meaning of symbols will become obvious from the context. Occasionally one might encounter a hat on top of a symbol chosen in order to emphasize that this symbol denotes an operator. However, a hat on top of a vector may also denote the corresponding unit vector pointing in the direction of the vector, e.g., the position vector may therefore be expressed as $\boldsymbol{r} = r\,\hat{\boldsymbol{r}}$.

Most quantities require extensive use of indices. In principle, we may distinguish the following sets of indices:

(i) General coordinates: In relativistic or covariant equations lower-case Latin indices $i, j, k, \ldots$ generally run over the three spatial coordinates, usually denoted x, y, z or x_1, x_2, x_3. Greek indices $\alpha, \beta, \gamma, \delta, \ldots$ and also $\mu, \nu, \varrho, \tau, \ldots$ run over the four space-time coordinates ranging from 0 to 3, where $x^0 = ct$ represents the time-like coordinate and x^i the space-like coordinates.

(ii) Particle coordinates in molecular systems: For molecular systems nuclear coordinates are denoted by capital letter indices $I, J, K, \ldots$, while electronic coordinates are labeled by lower-case Latin indices $i, j, k, \ldots$.

(iii) Basis functions: One-electron functions (i.e., orbitals and spinors) are distinguished via Latin indices. We use $i, j, k, \ldots$ for occupied orbitals and $a, b, c, \ldots$ for virtuals. Basis functions used for the representation of the one-electron functions are labeled by Greek indices $\mu, \nu, \kappa, \lambda, \ldots$.

(iv) One-electron quantities are distinguished from those of the total system by lower-case versus capital letters. Examples are the one-electron Hamiltonian h and the many-particle Hamiltonian H or the orbital ψ and the total wave function Ψ. Of course, if a system contains only one electron, this distinction becomes meaningless. Only in these cases may the lower- and upper-case symbols be used interchangeably.

In relativistic equations, the position of indices (subscripts or superscripts) is determined by the transformation property of the corresponding quantity under Lorentz transformations. In nonrelativistic equations, indices will always be chosen as subscripts.

Almost all equations in this book are given in so-called *Gaussian units*, i.e., the dielectric constant of the vacuum is dimensionless with $4\pi\varepsilon_0 = 1$. The whole existence of Gaussian units is based on the (trivial) fact that we are free to choose the proportionality constant in Coulomb's force law to be 1 (Gaussian units) instead of $1/4\pi\epsilon_0$ (SI units). The positive elementary charge e, the electron (rest) mass m_e, and the reduced Planck constant $\hbar = h/2\pi$ are explicitly taken into account. For the sake of convenience, however, a few equations are given in *Hartree atomic units*, where these fundamental physical constants all adopt a numerical value of one, since in most accounts on quantum chemistry these units are employed. In Hartree atomic units (often abbreviated as 'a.u.'), a charge is then measured in multiples of the elementary charge e and a mass is given in terms of multiples of the electron's rest mass m_e. The speed of light, however, is approximately 137.036 a.u. and depends on experimental measurements (the most accurate current value is 137.035999074(44) [37]; by contrast, in the SI unit system, the value of c is fixed at 299792458 m/s). The fine-structure constant, which is $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ in SI units or $\alpha = e^2/(\hbar c)$ in Gaussian units, takes the simple form $\alpha = 1/c$ in Hartree atomic units, so that expansions in terms of the fine-structure constant become equivalent to expansions in $1/c$. It is important to emphasize that the choice of $1/(4\pi\epsilon_0) = 1$ in Hartree atomic units automatically implies that Gaussian units are the basis of this atomic-units system. In the literature, one encounters a third choice of units — often called *natural units* and applied in quantum field theory — where the speed of light c and the reduced Planck constant $\hbar$ are set equal to unity, while the electron's rest mass m_e and the elementary charge e differ

from unity. Hence, only those fundamental physical constants which are independent of specific elementary particles are chosen to be unity in this system of units.

The use of SI units bears a catch. This is the fact that the dielectric constant of the vacuum ϵ_0 is connected with the speed of light c via the permittivity μ_0, $\epsilon_0\mu_0 = c^{-2}$. As a consequence, equations containing electromagnetic potentials may carry a c or not depending on the system of units chosen [38]. The important point to understand is that magnetic fields $\boldsymbol{B}$ are suppressed by a factor of $1/c$ when compared to electric fields $\boldsymbol{E}$ in *any* system of units. This fact is most easily seen in Gaussian units rather than SI units, which is the reason why we abandon the latter. Furthermore, in contrast to the SI system of units, only in Gaussian units electric ($\boldsymbol{E}$) and magnetic ($\boldsymbol{B}$) fields, or analogously, scalar (ϕ) and vector ($\boldsymbol{A}$) potentials feature the same units, clearly exhibiting their physical nature and indicating their transformation properties into one another.

Relativistic theories often employ series expansions in powers of $1/c$ in order to study cases of small velocities or the nonrelativistic limit. The physics, however, must not change by the choice of units and we recall that all quantities in, for example, a force law need to be expressed in the same units (e.g., the electrical charges also take different values in different systems of units).

Finally, the logical symbols $\forall$ ('for all') and $\exists$ ('there exists') are employed as abbreviations rather than as precise logical quantors. For truncated series expansions, we use the Landau notation $O(...)$ to denote the leading order in the expansion parameter of the truncated terms.