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***MEAN-FIELD APPROACHES FOR THE
CHARACTERIZATION OF MANY-BODY SYSTEMS:
STUDY OF ELECTRON SCATTERING AND
NUCLEAR DECAY PROCESSES IN DIFFERENT
ENVIRONMENTS***

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Abstract

In this thesis, two theoretical-computational methods for the study and analysis of many-body systems are presented.

The protagonist of the first part of this writing will be the Dirac-Hartree-Fock (DHF) method, a relativistic quantum method that defines a mean-field (MF) approximation of the many-particle Dirac equation. This approach, implemented using Hermite Gaussian functions (HGFs) basis sets and radial mesh, will constitute the pivotal element of the first and second chapters.

In the first chapter, in particular, after having introduced the scattering theory and Gaussian functions, we will discuss the results obtained for electron elastic scattering in water.

In the second chapter, we will treat nuclear beta decays and describe the approach, based on the use of radial basis sets and Fermi-Dirac (FD) statistics, for the modeling and analysis of decay rates under terrestrial and stellar conditions.

Set aside the DHF method and its applications, in the third chapter, we will introduce the second and last approach, a non-relativistic variational method through which have been calculated the bound and scattering states, the energies, the photodetachment cross sections, the decay rates and the scattering phases of ions, atoms and molecules, such as the positronium negative ion (Ps^-) and hydrogen anion (H^-). The model adopts optimized multi-dimensional Gaussian basis functions (OMGBFs). An advantage of utilizing Gaussian basis functions consists in deriving analytically the one- and two-body integrals essential for the calculation of matrix elements.

The ultimate purpose of this thesis will be to show the efficiency and versatility of the two methods.

Key words

many-body; electron scattering; beta decay; photodetachment

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*To Professor Stefano Simonucci,
my family, my friends and my angels...*

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List of Abbreviations

AGB	Asymptotic Giant Branch
CC	Coupled Cluster
CI	Configuration Interaction
CPT	Charge-Parity-Time
DFT	Density Functional Theory
DHF	Dirac-Hartree-Fock
ELSEPA	ELastic Scattering of Electrons and Positrons by Atoms
FD	Fermi-Dirac
HF	Hartree-Fock
HGF	Hermite Gaussian Function
LDU	Lower-Diagonal-Upper
LEED	Low Energy Electron Diffraction
LS	Lippmann-Schwinger
MF	Mean-Field
ODE	Ordinary Differential Equation
OMGBF	Optimized Multi-dimensional Gaussian Basis Function
PANDORA	Plasmas for Astrophysics, Nuclear Decay Observation and Radiation for Archaeometry
PBE	Perdew-Burke-Ernzerhof
QED	Quantum Electrodynamics
RK	Runge-Kutta
SEA	Static-Exchange Approximation
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

Introduction

The many-body systems, systems consisting of N interacting particles, still represent an open problem in physics.

The many-body problem, indeed, defines the inability to solve exactly the Schrödinger equation for many-particle systems, that is, the inability to determine the physical properties of a system composed by many interacting particles [1].

For this reason, over the years, numerous theoretical approaches have been proposed and developed in an attempt to characterize these systems, among them the mean-field (MF) models [2].

The MF models are approximation models that allow to reduce a many-body problem to a one-body problem. The basic idea of these approaches consists in replacing the interactions acting on a particle with an average potential in which the same particle moves independently of the others. The field, in which the particle moves, determines the movement of the other constituents of the system, which in turn generates the effective potential. Such a condition by which the movement of particles, affected by the (mean) field produced by the other interacting particles, determines itself the field is known as self-consistency condition.

One of the first MF methods was formulated by D. R. Hartree, who, in the late twenties, introduced a method, the self-consistent field method, through which the English physicist tried to solve the many-body problem. This approach, based on ab initio methods¹, however, did not respect the Pauli exclusion principle. The fermionic wave function, described in the Hartree method, was

¹The ab initio ("from first principles") methods are quantum mechanical methods that assume, as calculation inputs, only physical constants [3]. These methods are "...*independent of any experiment other than the determination of fundamental observables...*" [4].

symmetric and not antisymmetric [5]. To overcome this problem, a rewriting of the many-particle wave function as a Slater determinant built on spin orbitals was proposed by J. C. Slater and V. A. Fock. The introduction of the determinant, antisymmetric product of single-particle wave functions, proved to be the correct ansatz and led to a reformulation of the method, now known as the Hartree-Fock (HF) method [6, 7, 8, 9].

"...The principles and general theory of a method for including exchange effects have already been given some years ago by Fock; they were suggested independently about the same time by Slater..." [10].

The HF method, as well as the iterative Hartree method, finds its roots in the self-consistency and variational principle, which states that the expectation value of the Hamiltonian, calculated with respect to a given normalized trial wave function, is always greater than or equal to the exact ground state energy. The better the choice of trial wave function will be, the more accurate the ground state energy estimation will be [11].

Both the methods, indeed, assume a Hamiltonian consisting of a MF potential, described, in the second approach, by the potential, called the Hartree potential, and in the HF method by the sum of the Hartree potential and the exchange potential (the HF potential). This MF potential, however, is not known a priori and, consequently, to determine the spin orbitals the variational method is applied.

"...so long as we do not know the Hartree-Fock potential, we, of course, cannot calculate the single-particle orbitals...To arrive at a way of determining these we make the ansatz of a Slater determinant of single-particle orbitals for the exact many-body wavefunction. By Ritz' variational theorem, there is a rational way to optimize this ansatz by minimizing the total energy of the system. Minimizing the total energy with respect to the single-particle orbitals will then yield the Hartree-Fock equation for these..." [12].

The MF models will form an integral part of this thesis, the aim of which

will be to introduce two theoretical-computational methods for the study and analysis of many-body systems. The first method that will be discussed will be the Dirac-Hartree-Fock (DHF) method, which defines a MF approximation of the many-particle Dirac equation. This self-consistent field approach, introduced for the first time by the British physicist B. Swirles in 1935 [13], has been implemented by us using Hermite Gaussian functions (HGFs) basis sets and radial mesh.

The first relativistic method, based on Gaussian functions, is the most suitable for the study of non-spherical polyatomic systems, such as clusters and molecules. The use of Gaussian basis functions, indeed, makes it possible to determine analytically integrals essential for molecular calculations. For this reason, through this approach, electron elastic scattering in liquid water has been analyzed. In particular, have been computed the total elastic scattering cross sections of electrons impinging on a single water molecule, two clusters of three water molecules and the Zundel cation (H_5O_2^+).

The second approach, built on radial basis sets, has been adopted for the study of nuclear β decay processes in terrestrial and stellar scenarios. This approach, differently from the first one, allows us to accurately analyze spherical symmetric systems. Assuming, in fact, a β -decaying system consists of a unique isolated nucleus surrounded by electrons, it is possible to approximate the latter to a spherical symmetric problem.

The second and last approach that will be treated will be a variational non-relativistic method based on the use of optimized multi-dimensional Gaussian basis functions (OMGBFs). With this approach have been calculated the bound and scattering states, the energies, the decay rates and the scattering phases of different systems, including the beryllium isotope (${}^7_4\text{Be}$), the helium atom (He), the positronium negative ion (Ps^-) and the hydrogen anion (H^-). As regards the hydrogen anion (H^-) and positronium negative ion (Ps^-), system composed of two electrons and a positron (the antiparticle of the electron), of these latter have also been analyzed the photodetachment processes.

Specifically, this thesis will be divided in four chapters.

In chapter 1, after introducing the scattering theory and MF methods, we will arrive at the treatment of the DHF method and its implementation. Defined

the HGFs, we will discuss the results obtained for elastic scattering of electrons in water and the implications of this study.

In chapter 2, we will describe nuclear decay processes, in particular, β decays, subject of analysis of this thesis. Later, after partly resumed what was discussed previously, we will describe the collocation method and treat the applications of the DHF approach, built on radial basis sets.

In chapter 3, introduced the variational method, we will present the second and last approach. Described the method, we will devote, once again, the last sections of this chapter to the results obtained and the applications of the latter.

In the last chapter, we shall summarize what was introduced in the previous chapters, starting point of future projects and developments.

The ultimate aim of this thesis, in fact, will be to show the efficiency and versatility of the two methods, protagonists of this writing and my research activity, whose goal was to develop and implement the methods previously introduced. Through the latter, many processes have been analyzed which, still today, represent a challenge in various research fields.

Concerning electron scattering processes in liquid water, their investigation is crucial to understand numerous phenomena, such as the physical-chemical mechanisms of radio-biological damage underlying cancer treatments [14, 15, 16].

With regard to nuclear decays, protagonists of chapter 2, an accurate assessment of these processes in astrophysical scenario will enable us to answer more and more questions about the chemical evolution of the Universe, the objective of the INFN project PANDORA (Plasmas for Astrophysics, Nuclear Decay Observation and Radiation for Archaeometry) [17, 18, 19, 20].

Last but not least, the study of few-body systems, such as the Ps^- system. The positronium, defined as the simplest atom, composed of an electron and its antiparticle, the positron, is the subject of numerous research activities some of which aim to test the quantum electrodynamics (QED) theory and the charge-parity-time (CPT) fundamental symmetry [21, 22].

The approaches described in this thesis were implemented using FORTRAN and Python code systems (single core).

Chapter 1

Relativistic mean-field approach and electron scattering

1.1 Scattering theory

A typical scattering experiment is characterized by an incident particle or a flux of incident particles (A) that, hitting a target (B), produces a series of fragments that are then collected by a detector.

Since the final sets (or channels) can be one or many, we distinguish a scattering process in single-channel scattering

$$A + B \rightarrow A + B \quad (1.1)$$

or multi-channel scattering

$$A + B \rightarrow \begin{cases} A + B \\ A + B^* \\ \dots \end{cases} \quad (1.2)$$

where B^* represents the excited state of B . These processes can be classified into elastic and inelastic processes [23]. In an inelastic scattering process, such as $A + B \rightarrow A + B^*$, the interaction between A and B results in an energy loss of the incident projectile. During this process, the total kinetic energy of the system is not conserved. On the contrary, during an elastic collision

$(A + B \rightarrow A + B)$, the kinetic energy as well as the momentum of the system are preserved.

A further subdivision regarding the scattering theory consists of the time-dependent and time-independent formalism. In the time-dependent formalism, the collision process is described by time-dependent wave functions. In the second approach, in contrast, the wave functions are expressed in terms of the stationary scattering states.

In the following sections, we will analyze and introduce some fundamental quantities at the base of the scattering theory, including the Møller wave operators $\Omega_{\pm}$, the S -matrix, the T operator and the differential cross section (for insights reference [24]).

1.1.1 Time-dependent scattering theory

A scattering process is a typical perturbative problem and in this picture it is essential to adopt an interaction representation [25]. The interaction representation, unlike the Heisenberg and Schrödinger representations, is characterized by the fact that both the state vectors and operators are time-dependent. In the interaction picture, also known as the Dirac picture, the full Hamiltonian H is expressed as

$$H = H_0 + V \quad (1.3)$$

with H_0 the free Hamiltonian and V the interaction term.

A scattering process, indeed, can be divided into three different stages: (1) the arrival of the projectile, (2) the interaction and (3) the departure of the fragments.

In the first and third parts, since the particles are placed at a great distance from the scattering center (the interaction tends to zero), we can consider the initial and final states as free particle states. Moreover, assuming that the orbit is almost straight except near the interaction region, we can define the orbit $\mathbf{x}(t) = \int d^3x' \mathbf{x}' |\psi(\mathbf{x}', t)|^2$ before the collision ($t \rightarrow -\infty$) as

$$\mathbf{x}(t) \xrightarrow[t \rightarrow -\infty]{} \mathbf{x}_{in}(t) \equiv \mathbf{a}_{in} + \mathbf{v}_{in}t \quad (1.4)$$

and after the collision ($t \rightarrow +\infty$) as

$$\mathbf{x}(t) \xrightarrow[t \rightarrow +\infty]{} \mathbf{x}_{out}(t) \equiv \mathbf{a}_{out} + \mathbf{v}_{out}t \quad (1.5)$$

where $\mathbf{x}_{in}(t)$ and $\mathbf{x}_{out}(t)$ are the incoming and outgoing asymptotes. Knowing the asymptotes means being able to fully characterize the scattering orbit. For this reason, it will be necessary to define, for a time-dependent quantum scattering process, two limits similar to equations (1.4) and (1.5), in addition to a direct relation between the in and out asymptotes.

To do this, let us first consider the time-dependent Schrödinger equation ($\hbar = 1$)

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle \quad (1.6)$$

with the vector $|\psi(t)\rangle = U(t) |\psi\rangle \equiv e^{-iHt} |\psi\rangle$ and $U(t)$ the unitary time evolution operator. Assuming that the orbit is now defined as $U(t) |\psi\rangle$, with $|\psi\rangle$ the state vector at $t = 0$, we impose, in a similar way to the classic case, that before the collision ($t \rightarrow -\infty$)

$$U(t) |\psi\rangle \xrightarrow[t \rightarrow -\infty]{} U_0(t) |\psi_{in}\rangle \quad (1.7)$$

and after the collision ($t \rightarrow +\infty$)

$$U(t) |\psi\rangle \xrightarrow[t \rightarrow +\infty]{} U_0(t) |\psi_{out}\rangle \quad (1.8)$$

with $U_0(t) \equiv e^{-iH_0t}$ the free evolution operator. The evolution of the system is regulated most of the time by the free Hamiltonian H_0 , while, during the collision, the interaction becomes important. At this point, having defined two limits analogous to (1.4) and (1.5), it remains only to determine the direct relation between the in and out asymptotes, in one word, the scattering operator S .

The Møller wave operators and the S -matrix

"...every vector in $\mathcal{H}$ (labelled $|\psi_{in}\rangle$ or $|\psi_{out}\rangle$ as appropriate) does represent the asymptote of some actual orbit; that is, for every vector $|\psi_{in}\rangle$ in $\mathcal{H}$ there is a solution $U(t) |\psi\rangle$ of the Schrödinger equation that is asymptotic to the free

orbit $U^0(t) |\psi_{in}\rangle$ as $t \rightarrow -\infty$; and likewise for every $|\psi_{out}\rangle$ as $t \rightarrow +\infty$. This result is known as the asymptotic condition...” [24].

The asymptotic condition allows us to assert that

$$|\psi\rangle = \lim_{t \rightarrow -\infty} U(t)^\dagger U_0(t) |\psi_{in}\rangle \quad (1.9)$$

and, similarly,

$$|\psi\rangle = \lim_{t \rightarrow +\infty} U(t)^\dagger U_0(t) |\psi_{out}\rangle \quad (1.10)$$

where the limits

$$\Omega_\pm = \lim_{t \rightarrow \mp\infty} U(t)^\dagger U_0(t) \quad (1.11)$$

are known as the Møller wave operators. The Møller operators $\Omega_\pm$ are operators that associate the eigenstates of the free Hamiltonian H_0 to those of H

$$\Omega_\pm H_0 = H \Omega_\pm. \quad (1.12)$$

Since the latter are isometric, we can invert the equation

$$|\psi\rangle = \Omega_- |\psi_{out}\rangle = \Omega_+ |\psi_{in}\rangle \quad (1.13)$$

obtaining

$$|\psi_{out}\rangle = \Omega_-^\dagger |\psi\rangle = \Omega_-^\dagger \Omega_+ |\psi_{in}\rangle \quad (1.14)$$

where $\Omega_-^\dagger \Omega_+$ is the scattering operator S .

The unitary scattering operator S , as announced, permits us to directly express the outgoing asymptote in terms of the incoming asymptote

$$|\psi_{out}\rangle = S |\psi_{in}\rangle \quad (1.15)$$

and to determine the probability amplitude. Considering a system and assuming that it evolves, we obtain that the probability of observing the system prepared in an initial state $|\alpha\rangle$ to emerge in a final state $|\beta\rangle$ is

$$\omega(\alpha \rightarrow \beta) = \left| \langle \beta | \Omega_-^\dagger \Omega_+ | \alpha \rangle \right|^2 = \left| \langle \beta | S | \alpha \rangle \right|^2 \quad (1.16)$$

with $\langle \beta | S | \alpha \rangle$ the scattering matrix element. The scattering matrix, or the S -matrix, will be the key element for the calculation of the differential cross section. Although the S operator “...contains all information of experimental interest...” [24], we have not yet defined a quantity that can be observed experimentally and this quantity is the differential cross section.

1.1.2 Time-independent scattering theory

At the beginning of this chapter, we distinguished the scattering theory in the time-dependent and time-independent formalism. In the time-dependent formalism, a scattering process is described by time-dependent wave functions, while, in the time-independent theory, the main characters are the stationary scattering states, the Green’s operators and the T operator. From the Green’s operators will begin our discussion on the time-independent scattering theory, which will lead us to the definition of the T operator and stationary scattering states.

Consider the following equation

$$|\psi_{\mathbf{k}}^{\pm}\rangle = \Omega_{\pm} |\phi_{\mathbf{k}}\rangle \quad (1.17)$$

where $\mathbf{k}$ is the momentum, $|\phi_{\mathbf{k}}\rangle$ is an eigenstate of the unperturbed Hamiltonian H_0

$$H_0 |\phi_{\mathbf{k}}\rangle = E |\phi_{\mathbf{k}}\rangle \quad (1.18)$$

and

$$\Omega_{\pm} = \lim_{t \rightarrow \mp\infty} U(t)^{\dagger} U_0(t) \quad (1.19)$$

are the Møller operators.

At this point, rewriting $U(t)^{\dagger} U_0(t)$ as the integral of the derivative

$$\frac{d}{dt} U(t)^{\dagger} U_0(t) = i e^{iHt} (H - H_0) e^{-iH_0 t} = i U(t)^{\dagger} V U_0(t), \quad (1.20)$$

we obtain that

$$\Omega_{-} = \mathbb{I} + i \lim_{\epsilon \rightarrow 0^{+}} \int_0^{\infty} d\tau e^{-\epsilon\tau} U(\tau)^{\dagger} V U_0(\tau) \quad (1.21)$$

and

$$\Omega_+ = \mathbb{I} - i \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^0 d\tau e^{\epsilon\tau} U(\tau)^\dagger V U_0(\tau) \quad (1.22)$$

with $e^{\pm\epsilon\tau}$ a damping factor. Replacing equation (1.21) in equation (1.17), it follows that

$$|\psi_{\mathbf{k}}^-\rangle = |\phi_{\mathbf{k}}\rangle + i \lim_{\epsilon \rightarrow 0^+} \int_0^\infty d\tau e^{-\epsilon\tau} U(\tau)^\dagger V U_0(\tau) |\phi_{\mathbf{k}}\rangle \quad (1.23)$$

and since

$$\int_0^\infty d\tau e^{-\epsilon\tau} U(\tau)^\dagger V U_0(\tau) |\phi_{\mathbf{k}}\rangle = [i(E - i\epsilon - H)]^{-1} V |\phi_{\mathbf{k}}\rangle = -iG(E - i\epsilon)V |\phi_{\mathbf{k}}\rangle, \quad (1.24)$$

we conclude that

$$|\psi_{\mathbf{k}}^-\rangle = |\phi_{\mathbf{k}}\rangle + G(E - i0^+)V |\phi_{\mathbf{k}}\rangle. \quad (1.25)$$

Similarly, substituting equation (1.22) in equation (1.17), we have that

$$|\psi_{\mathbf{k}}^+\rangle = |\phi_{\mathbf{k}}\rangle - i \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^0 d\tau e^{\epsilon\tau} U(\tau)^\dagger V U_0(\tau) |\phi_{\mathbf{k}}\rangle \quad (1.26)$$

from which

$$|\psi_{\mathbf{k}}^+\rangle = |\phi_{\mathbf{k}}\rangle + G(E + i0^+)V |\phi_{\mathbf{k}}\rangle \quad (1.27)$$

with $G(E \pm i0^+)$ the Green's operator. For further details refer to [24] (chapter 8) and [26] (appendices A.2 and A.3).

The Green's operator or resolvent

$$G(z) \equiv \frac{1}{z - H} = \begin{cases} -i \int_{-\infty}^0 dt \exp[-i(z - H)t] \\ +i \int_0^{+\infty} dt \exp[-i(z - H)t] \end{cases} \quad (1.28)$$

defines the T operator

$$T(z) = V + VG(z)V, \quad (1.29)$$

which in turn defines the stationary scattering states.

Keeping in mind, indeed, that

$$G_0(z)T(z) = G(z)V \quad (1.30)$$

with

$$G_0(z) \equiv \frac{1}{z - H_0} \quad (1.31)$$

the free Green's operator and

$$T(E \pm i0^+) |\phi_{\mathbf{k}}\rangle = V[1 + G(E \pm i0^+)V] |\phi_{\mathbf{k}}\rangle = V |\psi_{\mathbf{k}}^{\pm}\rangle, \quad (1.32)$$

we obtain that

$$|\psi_{\mathbf{k}}^{\pm}\rangle = |\phi_{\mathbf{k}}\rangle + G_0(E \pm i0^+)T(E \pm i0^+) |\phi_{\mathbf{k}}\rangle \quad (1.33)$$

from which

$$|\psi_{\mathbf{k}}^{\pm}\rangle = |\phi_{\mathbf{k}}\rangle + G_0(E \pm i0^+)V |\psi_{\mathbf{k}}^{\pm}\rangle \quad (1.34)$$

where equation (1.34) is known as the Lippmann-Schwinger (LS) equation for the stationary scattering states $|\psi_{\mathbf{k}}^{\pm}\rangle$. The stationary scattering states, solution of the time-independent Schrödinger equation, are eigenstates of the full Hamiltonian H .

Asymptotically, for $r \rightarrow \infty$, we can define the wave function $\psi_{\mathbf{k}}^+(\mathbf{r})$ as

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \langle \mathbf{r} | \psi_{\mathbf{k}}^+ \rangle \xrightarrow{r \rightarrow \infty} e^{i\mathbf{k} \cdot \mathbf{r}} + f(\theta, \varphi) \frac{e^{ikr}}{r} \quad (1.35)$$

with the first term an incoming plane wave and the second term an outgoing spherical wave. The term $f(\theta, \varphi)$ is the scattering amplitude with θ and φ two angles. Assuming that the interaction does not depend on the spin of the interacting particles², we express the scattering amplitude $f(\theta)$, independent of φ , in terms of partial waves [27]

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) f_l(k) P_l(\cos\theta) \quad (1.36)$$

with

$$f_l(k) = \frac{S_l(k) - 1}{2ik} = \frac{e^{2i\delta_l(k)} - 1}{2ik} \quad (1.37)$$

²The scattering process of electrons colliding with one or more water molecules, discussed in the following pages, represents a closed shell system (zero total electronic spin). In this case, the approximation introduced is good.

the partial wave scattering amplitude, $\delta_l(k)$ the phase shift, $P_l(\cos\theta)$ the Legendre polynomials and

$$S_l(k) = e^{2i\delta_l(k)} \quad (1.38)$$

the scattering matrix eigenvalues. Through the scattering amplitude, we will define the differential cross section, with which we will conclude the first part of this chapter.

The differential cross section

We consider, once again, a typical scattering process and presuming to repeat the experiment N times, we compute the total number of particles scattered into a given solid angle $d\Omega$ per unit time in direction (θ, φ)

$$N_{scat} = n_{inc}\sigma \quad (1.39)$$

with θ the scattering angle, φ the azimuthal angle, n_{inc} the incident flux (number of projectiles incident on the target per unit time per unit area) and σ the total scattering cross section [28]. The total cross section is proportional to the differential cross section $\frac{d\sigma}{d\Omega}$

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} \quad (1.40)$$

and since the latter can be expressed as

$$\sigma = \int d\Omega |f(\theta, \varphi)|^2, \quad (1.41)$$

we conclude that the differential cross section is

$$\frac{d\sigma}{d\Omega} = |f(\theta, \varphi)|^2 \quad (1.42)$$

with $f(\theta, \varphi)$ the scattering amplitude. The scattering amplitude, introduced in equation (1.35), can be expressed in terms of the transition matrix T . Considering, indeed, equation (1.34) and rewriting it as (position basis)

$$\langle \mathbf{r} | \psi_{\mathbf{k}}^{\pm} \rangle = \langle \mathbf{r} | \phi_{\mathbf{k}} \rangle + \int d^3r' \langle \mathbf{r} | G_0(E \pm i0^+) | \mathbf{r}' \rangle \langle \mathbf{r}' | V | \psi_{\mathbf{k}}^{\pm} \rangle, \quad (1.43)$$

we get the expression

$$\langle \mathbf{r} | \psi_{\mathbf{k}}^{\pm} \rangle = \langle \mathbf{r} | \phi_{\mathbf{k}} \rangle - \frac{m}{2\pi} \int d^3 r' \frac{e^{\pm i k |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \langle \mathbf{r}' | V | \psi_{\mathbf{k}}^{\pm} \rangle \quad (1.44)$$

with $(\hbar = 1)$

$$\langle \mathbf{r} | G_0(E \pm i0^+) | \mathbf{r}' \rangle = -\frac{m}{2\pi} \frac{e^{\pm i k |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.45)$$

At this point, assuming that the detector is placed at a great distance from the scatterer, we approximate for large r

$$\frac{e^{\pm i k |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \simeq \frac{e^{\pm i k r} e^{\mp i \mathbf{k}' \cdot \mathbf{r}'}}{r} \quad (1.46)$$

with $\mathbf{k}' \equiv k \hat{n}$, from which it follows that

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \langle \mathbf{r} | \psi_{\mathbf{k}}^+ \rangle \xrightarrow{r \rightarrow \infty} e^{i \mathbf{k} \cdot \mathbf{r}} - \frac{m}{2\pi} \frac{e^{i k r}}{r} \int d^3 r' e^{-i \mathbf{k}' \cdot \mathbf{r}'} \langle \mathbf{r}' | V | \psi_{\mathbf{k}}^+ \rangle \quad (1.47)$$

where $\langle \mathbf{r} | \phi_{\mathbf{k}} \rangle = e^{i \mathbf{k} \cdot \mathbf{r}}$ is the incident plane wave. Finally, comparing the previous result (1.47) with equation (1.35)

$$f(\theta, \varphi) = -\frac{m}{2\pi} \int d^3 r' e^{-i \mathbf{k}' \cdot \mathbf{r}'} \langle \mathbf{r}' | V | \psi_{\mathbf{k}}^+ \rangle = -\frac{m}{2\pi} \langle \phi_{\mathbf{k}'} | V | \psi_{\mathbf{k}}^+ \rangle \quad (1.48)$$

and using the identity (1.32), we conclude that

$$f(\theta, \varphi) = -\frac{m}{2\pi} \langle \phi_{\mathbf{k}'} | V | \psi_{\mathbf{k}}^+ \rangle = -\frac{m}{2\pi} \langle \phi_{\mathbf{k}'} | T(E + i0^+) | \phi_{\mathbf{k}} \rangle \quad (1.49)$$

where $\langle \phi_{\mathbf{k}'} | T(E + i0^+) | \phi_{\mathbf{k}} \rangle$ is the T -matrix element. References [24] (chapter 10), [25] (chapter 6) and [29] for further insights.

The cross sections as well as the T -matrix elements and phase shifts were the subject of our study on electron scattering in water. This study, protagonist of the last part of chapter 1, was carried out using the Dirac-Hartree-Fock (DHF) method implemented by introducing Hermite Gaussian functions (HGFs). The mean-field (MF) methods and, in particular, the DHF approach will be introduced in the following sections, the last pages of which, as anticipated, will be dedicated to the analysis of electron-water scattering.

1.2 Mean-field methods

The mean-field (MF) methods represent the starting point of many, if not all, many-body theories.

The basic idea of these approaches consists in replacing the interactions acting on a particle with an average potential in which the same particle moves independently of the others.

The latter are approximation models that allow to reduce a many-body problem to a one-body problem.

Applying a MF approximation, indeed, it is possible to translate a N -body system in a one-body system subject to a potential (the MF) generated by the remaining $N - 1$ constituents [2].

One of the best known MF methods is the Hartree-Fock (HF) method [7, 9, 30]. In this model, the Hamiltonian H of a system composed of N interacting particles

$$H = T + V = \sum_{i=1}^N t_i + \frac{1}{2} \sum_{i,j=1; i \neq j}^N v_{ij} \quad (1.50)$$

with the first term, the kinetic term, which acts on the i -th particle and v_{ij} the two-body interaction potential, is defined as

$$H = \left[T + \sum_{i=1}^N v_i^{HF} \right] + \left[V - \sum_{i=1}^N v_i^{HF} \right] \quad (1.51)$$

where v^{HF} is the single-particle HF potential.

The sum, in particular,

$$H^{HF} = \sum_{i=1}^N h_i^{HF} = T + \sum_{i=1}^N v_i^{HF} = \sum_{i=1}^N (t_i + v_i^{HF}) \quad (1.52)$$

represents the HF Hamiltonian, while

$$V^{RES} = V - \sum_{i=1}^N v_i^{HF} = \frac{1}{2} \sum_{i,j=1; i \neq j}^N v_{ij} - \sum_{i=1}^N v_i^{HF} \quad (1.53)$$

the difference between the potential v_{ij} and the MF potential, defines the residual interaction.

The aim of this independent particle model is to *"...describe an interacting fermion system in terms of an effective single-particle problem. The starting point is the idea that each particle moves in a mean-field potential..."* [12], however, the effective potential v^{HF} is not known a priori and to solve the following Schrödinger equation

$$H^{HF}\Psi = E\Psi \quad (1.54)$$

with Ψ the many-particle wave function, a Slater determinant built on spin orbitals $\psi_i(x_j)$ with x_j the spatial-spin coordinates and $\frac{1}{\sqrt{N!}}$ the normalization constant (antisymmetric product of one-particle wave functions)

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \dots & \psi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & \dots & \psi_N(x_N) \end{vmatrix}, \quad (1.55)$$

is necessary to adopt a variational approach (the Rayleigh-Ritz variational method).

The variational principle states that the expectation value of the Hamiltonian H , calculated with respect to a given normalized trial wave function φ ($\langle\varphi|\varphi\rangle = 1$), is always greater than or equal to the exact ground state energy E_{gs}

$$E[\varphi] = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \langle\varphi|H|\varphi\rangle \geq E_{gs}. \quad (1.56)$$

The better the choice of trial wave function will be, the more accurate the ground state energy estimation will be

$$E_{gs} = \min \langle\varphi|H|\varphi\rangle. \quad (1.57)$$

Therefore, defined the normalized wave function Ψ , we minimize the energy with respect to the spin orbitals

$$\frac{\delta}{\delta\psi_\alpha^*(x)} \left[\langle\Psi|H|\Psi\rangle - \sum_{i=1}^N \epsilon_i \int dx' \psi_i^*(x') \psi_i(x') \right] = 0 \quad (1.58)$$

where ϵ_i are the Lagrangian multipliers.

Calculated the expectation value of H

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_{i=1}^N \int dx' \psi_i^*(x') h(x') \psi_i(x') + \frac{1}{2} \sum_{i,j=1, i \neq j}^N \int \int dx' dx'' \psi_i^*(x') \psi_j^*(x'') v(x', x'') \psi_i(x') \psi_j(x'') \\ &\quad - \frac{1}{2} \sum_{i,j=1, i \neq j}^N \int \int dx' dx'' \psi_i^*(x') \psi_j^*(x'') v(x', x'') \psi_j(x') \psi_i(x''), \end{aligned} \quad (1.59)$$

we replace equation (1.59) in equation (1.58)

$$\begin{aligned} &h(x) \psi_\alpha(x) + \frac{1}{2} \sum_{j=1}^N \int dx'' \psi_j^*(x'') v(x, x'') \psi_\alpha(x) \psi_j(x'') \\ &+ \frac{1}{2} \left[\sum_{i=1}^N \int dx' \psi_i^*(x') v(x', x) \psi_i(x') \psi_\alpha(x) - \sum_{j=1}^N \int dx'' \psi_j^*(x'') v(x, x'') \psi_j(x'') \psi_\alpha(x'') \right] \\ &- \frac{1}{2} \sum_{i=1}^N \int dx' \psi_i^*(x') v(x', x) \psi_\alpha(x') \psi_i(x) - \epsilon_\alpha \psi_\alpha(x) = 0 \end{aligned} \quad (1.60)$$

with $h(x)$ the single-particle Hamiltonian, sum of a kinetic term and a potential $v(x)$, from which we obtain the HF equation

$$\left[h(x) + \int dx' \rho(x') v(x, x') \right] \psi_\alpha(x) - \int dx' \rho(x, x') v(x, x') \psi_\alpha(x') = \epsilon_\alpha \psi_\alpha(x) \quad (1.61)$$

where

$$\rho(x') = \sum_{i=1}^N \psi_i^*(x') \psi_i(x') \quad (1.62)$$

and

$$\rho(x, x') = \sum_{i=1}^N \psi_i^*(x') \psi_i(x) \quad (1.63)$$

are, respectively, the density and density matrix.

From equation (1.61), we conclude that

$$v^{HF}[\psi_\alpha] = v(x) \psi_\alpha(x) + \int dx' \rho(x') v(x, x') \psi_\alpha(x) - \int dx' \rho(x, x') v(x, x') \psi_\alpha(x') \quad (1.64)$$

with the term

$$v^H(x) = \int dx' \rho(x') v(x, x') \quad (1.65)$$

the direct or Hartree potential and

$$v^{ex}(x, x') = \rho(x, x') v(x, x'), \quad (1.66)$$

consequence of the Pauli exclusion principle, the exchange term.

Both potentials, however, depend on the spin orbitals (unknowns of the problem) and, to solve the HF equation, an iterative method is applied.

This procedure, which consists of the following steps:

- (1) selection of a complete set of trial single-particle wave functions;
- (2) calculation of the HF potential;
- (3) resolution of equation (1.61),

is repeated N times *"...until 'self-consistency' is achieved, that is, the procedure converges..."* [12]. At the end of each cycle, N wave functions (the spin orbitals with the lowest eigenenergies ϵ_α) are selected from the solutions obtained in step (3) and, repeating step (1), a new HF potential is calculated. Fulfilled the convergence condition³, the iterations end and the computed MF potential is consistent with the spin orbitals, hence the name.

"...The process is iterated until (hopefully) the n -th set of solutions $\{\psi_i^n\}$ differs from the $(n - 1)$ -th one $\{\psi_i^{n-1}\}$ less than a reasonably small amount...When this occurs, the procedure is said to have converged and the solution orbitals are called self-consistent; also, a calculation of this kind is commonly termed self-consistent field..." [32].

With the self-consistent field method, we finish the second part of chapter 1, whose last sections, as repeatedly stated, will be devoted to the Dirac-Hartree-Fock (DHF) approach. The following will refer to [14].

³The convergence condition is not always guaranteed. To date, there are many methods and programs (e.g. [31]) that can overcome this problem.

1.3 The Dirac-Hartree-Fock method

In 1935 the British physicist B. Swirles proposed a reformulation of the Hartree-Fock (HF) method. Starting from the Dirac equation, she developed a new self-consistent field approach for the study of many-body systems. This relativistic extension, today known as the Dirac-Hartree-Fock (DHF) method, will be the subject of analysis of this section. Introduced the DHF equation, we will present an implementation of the method and discuss the results obtained for electron elastic scattering in water. The method, based on the use of Hermite Gaussian functions (HGFs), indeed, will prove the most suitable for the study of multi-centric systems, such as clusters and molecules.

1.3.1 The Dirac-Hartree-Fock equation

Consider the following Dirac equation, in atomic units, for a many-body system

$$\left\{ \sum_i (c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i mc^2 + V_i) + \sum_{i < j} [\beta_i \beta_j g_{S,ij} + (1 - \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j) g_{V,ij}] \right\} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (1.67)$$

where g_S and g_V represent, respectively, a scalar potential and a vector potential, c the speed of light, m the particle mass, $\mathbf{p}$ the momentum, while $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and β define the Hermitian matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad (1.68)$$

with I the (2×2) identity matrix and $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ the Pauli spin matrices. Applying the HF approximation to the Dirac Hamiltonian

$$\begin{aligned} H = \sum_{s_1 s_2} \int d^3 r \hat{\Psi}_{s_1}^+(\mathbf{r}) [-ic\boldsymbol{\alpha}_{s_1 s_2} \cdot \boldsymbol{\nabla} + \beta_{s_1 s_2} mc^2 + \delta_{s_1 s_2} V(\mathbf{r})] \hat{\Psi}_{s_2}(\mathbf{r}) \\ + \frac{1}{2} \sum_{s_1 s_2 s'_1 s'_2} \int d^3 r d^3 r' \hat{\Psi}_{s_1}^+(\mathbf{r}) \hat{\Psi}_{s'_1}^+(\mathbf{r}') \\ \times [\beta_{s_1 s_2} \beta_{s'_1 s'_2} g_S(\mathbf{r}, \mathbf{r}') + (\delta_{s_1 s_2} \delta_{s'_1 s'_2} - \boldsymbol{\alpha}_{s_1 s_2} \cdot \boldsymbol{\alpha}'_{s'_1 s'_2}) g_V(\mathbf{r}, \mathbf{r}')] \hat{\Psi}_{s'_2}(\mathbf{r}') \hat{\Psi}_{s_2}(\mathbf{r}) \end{aligned} \quad (1.69)$$

with $V(\mathbf{r})$ an external potential, we obtain, in second quantization,

$$\begin{aligned}
H_{DHF} = & \sum_{s_1 s_2} \int d^3 r \hat{\Psi}_{s_1}^+(\mathbf{r}) \{ -\boldsymbol{\alpha}_{s_1 s_2} \cdot [ic \boldsymbol{\nabla} + \mathbf{A}_H(\mathbf{r})] + \beta_{s_1 s_2} [mc^2 + V_{HS}(\mathbf{r})] \\
& + \delta_{s_1 s_2} [V(\mathbf{r}) + V_H(\mathbf{r})] \} \hat{\Psi}_{s_2}(\mathbf{r}) \\
& - \sum_{s'_1 s_2} \int d^3 r d^3 r' \hat{\Psi}_{s'_1}^+(\mathbf{r}') [V_{FS, s'_1 s_2}(\mathbf{r}', \mathbf{r}) - A_{F, s'_1 s_2}(\mathbf{r}', \mathbf{r}) + V_{F, s'_1 s_2}(\mathbf{r}', \mathbf{r})] \hat{\Psi}_{s_2}(\mathbf{r})
\end{aligned} \tag{1.70}$$

where

$$\mathbf{A}_H(\mathbf{r}) = \int d^3 r' \sum_{s'_1 s'_2} [\rho_{s'_2 s'_1}(\mathbf{r}', \mathbf{r}') \boldsymbol{\alpha}_{s'_1 s'_2}] g_V(\mathbf{r}, \mathbf{r}') \tag{1.71}$$

$$V_H(\mathbf{r}) = \int d^3 r' \sum_{s'_1 s'_2} [\rho_{s'_2 s'_1}(\mathbf{r}', \mathbf{r}') \delta_{s'_1 s'_2}] g_V(\mathbf{r}, \mathbf{r}') \tag{1.72}$$

$$V_{HS}(\mathbf{r}) = \int d^3 r' \sum_{s'_1 s'_2} [\rho_{s'_2 s'_1}(\mathbf{r}', \mathbf{r}') \beta_{s'_1 s'_2}] g_S(\mathbf{r}, \mathbf{r}') \tag{1.73}$$

$$A_{F, s'_1 s_2}(\mathbf{r}', \mathbf{r}) = \sum_{s_1 s'_2} \boldsymbol{\alpha}_{s_1 s_2} \cdot \boldsymbol{\alpha}_{s'_1 s'_2} \rho_{s'_2 s_1}(\mathbf{r}, \mathbf{r}') g_V(\mathbf{r}, \mathbf{r}') \tag{1.74}$$

$$V_{F, s'_1 s_2}(\mathbf{r}', \mathbf{r}) = \sum_{s_1 s'_2} \delta_{s_1 s_2} \delta_{s'_1 s'_2} \rho_{s'_2 s_1}(\mathbf{r}, \mathbf{r}') g_V(\mathbf{r}, \mathbf{r}') \tag{1.75}$$

and

$$V_{FS, s'_1 s_2}(\mathbf{r}', \mathbf{r}) = \sum_{s_1 s'_2} \beta_{s_1 s_2} \beta_{s'_1 s'_2} \rho_{s'_2 s_1}(\mathbf{r}, \mathbf{r}') g_S(\mathbf{r}, \mathbf{r}'). \tag{1.76}$$

The terms

$$\rho_{s'_2 s'_1}(\mathbf{r}', \mathbf{r}') = \langle \hat{\Psi}_{s'_1}^+(\mathbf{r}') \hat{\Psi}_{s'_2}(\mathbf{r}') \rangle, \quad \rho_{s'_2 s_1}(\mathbf{r}, \mathbf{r}') = \langle \hat{\Psi}_{s_1}^+(\mathbf{r}') \hat{\Psi}_{s'_2}(\mathbf{r}') \rangle \tag{1.77}$$

are two (4×4) density matrices for many-particle wave functions where s'_1, s'_2, s_1, s_2 label the Dirac bispinor lower and upper components.

Rewriting the density matrices as

$$\rho(\mathbf{r}', \mathbf{r}') = \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}') & \rho_{LS}(\mathbf{r}', \mathbf{r}') \\ \rho_{SL}(\mathbf{r}', \mathbf{r}') & \rho_{SS}(\mathbf{r}', \mathbf{r}') \end{pmatrix} \tag{1.78}$$

and

$$\rho(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \rho_{LL}(\mathbf{r}, \mathbf{r}') & \rho_{LS}(\mathbf{r}, \mathbf{r}') \\ \rho_{SL}(\mathbf{r}, \mathbf{r}') & \rho_{SS}(\mathbf{r}, \mathbf{r}') \end{pmatrix} \quad (1.79)$$

where L defines the large component and S the small component of bispinor, we conclude that

$$\begin{aligned} \mathbf{A}_H(\mathbf{r}) &= \int d^3r' Tr \left[\begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}') & \rho_{LS}(\mathbf{r}', \mathbf{r}') \\ \rho_{SL}(\mathbf{r}', \mathbf{r}') & \rho_{SS}(\mathbf{r}', \mathbf{r}') \end{pmatrix} \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \right] g_V(\mathbf{r}, \mathbf{r}') \\ &= \int d^3r' Tr \{ [\rho_{LS}(\mathbf{r}', \mathbf{r}') + \rho_{SL}(\mathbf{r}', \mathbf{r}')] \boldsymbol{\sigma} \} g_V(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (1.80)$$

$$\begin{aligned} V_H(\mathbf{r}) &= \int d^3r' Tr \left[\begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}') & \rho_{LS}(\mathbf{r}', \mathbf{r}') \\ \rho_{SL}(\mathbf{r}', \mathbf{r}') & \rho_{SS}(\mathbf{r}', \mathbf{r}') \end{pmatrix} \right] g_V(\mathbf{r}, \mathbf{r}') \\ &= \int d^3r' Tr [\rho_{LL}(\mathbf{r}', \mathbf{r}') + \rho_{SS}(\mathbf{r}', \mathbf{r}')] g_V(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (1.81)$$

$$\begin{aligned} V_{HS}(\mathbf{r}) &= \int d^3r' Tr \left[\begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}') & \rho_{LS}(\mathbf{r}', \mathbf{r}') \\ \rho_{SL}(\mathbf{r}', \mathbf{r}') & \rho_{SS}(\mathbf{r}', \mathbf{r}') \end{pmatrix} \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \right] g_S(\mathbf{r}, \mathbf{r}') \\ &= \int d^3r' Tr [\rho_{LL}(\mathbf{r}', \mathbf{r}') - \rho_{SS}(\mathbf{r}', \mathbf{r}')] g_S(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (1.82)$$

$$\begin{aligned} A_F(\mathbf{r}', \mathbf{r}) &= \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \cdot \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}) & \rho_{LS}(\mathbf{r}', \mathbf{r}) \\ \rho_{SL}(\mathbf{r}', \mathbf{r}) & \rho_{SS}(\mathbf{r}', \mathbf{r}) \end{pmatrix} \cdot \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} g_V(\mathbf{r}', \mathbf{r}) \\ &= \begin{pmatrix} \boldsymbol{\sigma} \cdot \rho_{SS}(\mathbf{r}', \mathbf{r}) \cdot \boldsymbol{\sigma} & \boldsymbol{\sigma} \cdot \rho_{LS}(\mathbf{r}', \mathbf{r}) \cdot \boldsymbol{\sigma} \\ \boldsymbol{\sigma} \cdot \rho_{SL}(\mathbf{r}', \mathbf{r}) \cdot \boldsymbol{\sigma} & \boldsymbol{\sigma} \cdot \rho_{LL}(\mathbf{r}', \mathbf{r}) \cdot \boldsymbol{\sigma} \end{pmatrix} g_V(\mathbf{r}', \mathbf{r}) \end{aligned} \quad (1.83)$$

$$V_F(\mathbf{r}', \mathbf{r}) = \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}) & \rho_{SL}(\mathbf{r}', \mathbf{r}) \\ \rho_{LS}(\mathbf{r}', \mathbf{r}) & \rho_{SS}(\mathbf{r}', \mathbf{r}) \end{pmatrix} g_V(\mathbf{r}', \mathbf{r}) \quad (1.84)$$

and

$$V_{FS}(\mathbf{r}', \mathbf{r}) = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \cdot \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}) & \rho_{LS}(\mathbf{r}', \mathbf{r}) \\ \rho_{SL}(\mathbf{r}', \mathbf{r}) & \rho_{SS}(\mathbf{r}', \mathbf{r}) \end{pmatrix} \cdot \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} g_S(\mathbf{r}', \mathbf{r})$$

$$= \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}) & -\rho_{SL}(\mathbf{r}', \mathbf{r}) \\ -\rho_{LS}(\mathbf{r}', \mathbf{r}) & \rho_{SS}(\mathbf{r}', \mathbf{r}) \end{pmatrix} g_S(\mathbf{r}', \mathbf{r}) \quad (1.85)$$

from which it follows that

$$\begin{pmatrix} mc^2 + W_V + W_S + \mathbf{A}_P \cdot \boldsymbol{\sigma} - E & -c\boldsymbol{\sigma} \cdot i\nabla - \boldsymbol{\sigma} \cdot \mathbf{A} + W_{PS} \\ -c\boldsymbol{\sigma} \cdot i\nabla - \boldsymbol{\sigma} \cdot \mathbf{A} + W_{PS} & -mc^2 + W_V + \mathbf{A}_P \cdot \boldsymbol{\sigma} - W_S - E \end{pmatrix} \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} = 0 \quad (1.86)$$

where $W_V, W_S, \mathbf{A}_P$ and W_{PS} are, respectively, a vector potential, a scalar potential, a pseudo-vector potential and a pseudo-scalar potential. Specifically, in our treatment, we define the potential W_V as

$$W_V = V_H(\mathbf{r}) + V_F(\mathbf{r}', \mathbf{r}), \quad (1.87)$$

the scalar potential W_S as

$$W_S = V_{HS}(\mathbf{r}) + V_{FS}(\mathbf{r}', \mathbf{r}) \quad (1.88)$$

and we neglect the potentials $\mathbf{A}_H(\mathbf{r}), A_F(\mathbf{r}', \mathbf{r}), \mathbf{A}_P$ and W_{PS} .

Ψ_L and Ψ_S constitute, in accordance with the above, the large and small components of the many-particle wave function and the difference $(W_V - W_S)$, which acts on the lower part of the spinor (the antiparticle), represents the spin-orbit interaction, while the sum $(W_V + W_S)$ acts on the upper component of the spinor (the particle). The vector potential $\mathbf{A}$ describes the electromagnetic field.

Equation (1.86), the DHF equation, will constitute the key element of the next subsection, in which, as previously announced, we will present an implementation of the Swirles relativistic method. This approach, in turn, will constitute the main ingredient of the last pages of this chapter, where the elastic scattering of electrons in water will be analyzed.

1.3.2 The semi-projected potential method

The Dirac-Hartree-Fock (DHF) method defines a mean-field (MF) approximation of the many-particle Dirac equation.

By taking up part of what has already been introduced in the previous pages and by applying the semi-projected potential method⁴, we rewrite the total Hamiltonian as the sum of an unperturbed Hamiltonian (kinetic term)

$$H_0 = \begin{pmatrix} mc^2 & -c\boldsymbol{\sigma} \cdot i\nabla \\ -c\boldsymbol{\sigma} \cdot i\nabla & -mc^2 \end{pmatrix} \quad (1.89)$$

and a potential term

$$V = \pi \begin{pmatrix} W_V + W_S & -\boldsymbol{\sigma} \cdot \mathbf{A} \\ -\boldsymbol{\sigma} \cdot \mathbf{A} & W_V - W_S \end{pmatrix} \pi, \quad (1.90)$$

obtained from equation (1.86), with π the projection operator.

The projector

$$\pi = \sum_{\lambda} |\lambda\rangle \langle \lambda| \quad (1.91)$$

is expressed in terms of λ , which constitute a composition of Hermite Gaussian functions (HGFs). The choice to use the semi-projected method and HGFs, square-integrable (L^2) functions, arises from the need to describe both the bound and scattering states.

"...The kinetic term...is not projected into the Hilbert subspace spanned by the projector in order to recover the continuum for dealing with scattering states..."
[14].

The projected potential, on the contrary, represents one key component for the bound state calculations, where wave functions are confined to a limited region. An advantage in using HGFs, indeed, is to derive analytically the mono- and bi-electronic integrals essential for molecular calculations. These integrals will be introduced in the next part.

⁴The semi-projected potential method consists in projecting the only potential term into a finite functional space. Using a projector, constructed in terms of square-integrable (L^2) functions, the physical space is divided into two regions. A finite internal region, containing all the bound states, and an external region (asymptotic region), where only the continuum states are relevant. Through this approach, the scattering quantities, such as the T -matrix element, the cross section and the (approximate) scattering states are calculated [33, 34, 35].

1.3.3 Hermite Gaussian functions

Consider, first of all, a Hermite Gaussian function (HGF)

$$g(\mathbf{r}) = N \frac{\partial^{u+v+w}}{\partial X^u \partial Y^v \partial Z^w} s(\alpha, \mathbf{R}) = N \frac{\partial^{u+v+w}}{\partial X^u \partial Y^v \partial Z^w} \left(\frac{2\alpha}{\pi} \right)^{3/4} \exp[-\alpha(\mathbf{r} - \mathbf{R})^2] \quad (1.92)$$

with α the function width coefficient, $R \equiv (X, Y, Z)$ the center of the function $s(\alpha, \mathbf{R})$, 1s-type Gaussian function, and N a normalization constant

$$N = [\alpha^l (2u-1)!! (2v-1)!! (2w-1)!!]^{-1/2} \quad (1.93)$$

where (u, v, w) , the order of derivation, defines the type of symmetry and $l = u + v + w$ [36].

At this point, wishing to treat a multi-fermion system, we compute the mono-electronic integral for a Coulomb potential, with $\mathbf{C}$ the position of a center, as

$$\left\langle g_1 \left| \frac{1}{|\mathbf{r} - \mathbf{C}|} \right| g_2 \right\rangle = \left(\frac{2\sqrt{\alpha_1 \alpha_2}}{\pi} \right)^{\frac{3}{2}} e^{-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} (\mathbf{R}_1 - \mathbf{R}_2)^2} \left(\frac{\pi}{\alpha_1 + \alpha_2} \right)^{\frac{3}{2}} \frac{\text{erf} \left(\sqrt{(\alpha_1 + \alpha_2) \left| \frac{\alpha_1 \mathbf{R}_1 + \alpha_2 \mathbf{R}_2}{\alpha_1 + \alpha_2} - \mathbf{C} \right|^2} \right)}{\left| \frac{\alpha_1 \mathbf{R}_1 + \alpha_2 \mathbf{R}_2}{\alpha_1 + \alpha_2} - \mathbf{C} \right|} \quad (1.94)$$

and the bi-electronic integrals for a screened Coulomb potential as

$$\begin{aligned} \left\langle s_1 s_3 \left| \frac{e^{-\frac{|\mathbf{r} - \mathbf{r}'|}{\xi}}}{|\mathbf{r} - \mathbf{r}'|} \right| s_2 s_4 \right\rangle &= \left(\frac{2\alpha_1}{\pi} \right)^{\frac{3}{4}} \left(\frac{2\alpha_2}{\pi} \right)^{\frac{3}{4}} \left(\frac{2\alpha_3}{\pi} \right)^{\frac{3}{4}} \left(\frac{2\alpha_4}{\pi} \right)^{\frac{3}{4}} \\ &\int d^3 r \int d^3 r' e^{-\alpha_1(\mathbf{r} - \mathbf{R}_1)^2} e^{-\alpha_2(\mathbf{r} - \mathbf{R}_2)^2} e^{-\alpha_3(\mathbf{r}' - \mathbf{R}_3)^2} e^{-\alpha_4(\mathbf{r}' - \mathbf{R}_4)^2} \\ &= \left[\frac{2(\alpha_1 \alpha_2 \alpha_3 \alpha_4)^{\frac{1}{4}}}{\pi} \right]^3 e^{-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} (\mathbf{R}_1 - \mathbf{R}_2)^2} e^{-\frac{\alpha_3 \alpha_4}{\alpha_3 + \alpha_4} (\mathbf{R}_3 - \mathbf{R}_4)^2} \\ &\int d^3 r \int d^3 r' e^{-(\alpha_1 + \alpha_2)(\mathbf{r} - \mathbf{P}_{12})^2} e^{-(\alpha_3 + \alpha_4)(\mathbf{r}' - \mathbf{P}_{34})^2} \frac{e^{-\frac{|\mathbf{r} - \mathbf{r}'|}{\xi}}}{|\mathbf{r} - \mathbf{r}'|} \quad (1.95) \end{aligned}$$

from which, putting $\mathbf{s} = \frac{\mathbf{r}+\mathbf{r}'}{2}$ and $\mathbf{q} = \mathbf{r} - \mathbf{r}'$, we obtain that

$$\begin{aligned}
& \int d^3r \int d^3r' e^{-(\alpha_1+\alpha_2)(\mathbf{r}-\mathbf{P}_{12})^2} e^{-(\alpha_3+\alpha_4)(\mathbf{r}'-\mathbf{P}_{34})^2} \frac{e^{-\frac{|\mathbf{r}-\mathbf{r}'|}{\xi}}}{|\mathbf{r}-\mathbf{r}'|} \\
&= \int d^3s \int d^3q e^{-(\alpha_1+\alpha_2)\left(\mathbf{s}+\frac{\mathbf{q}}{2}-\mathbf{P}_{12}\right)^2} e^{-(\alpha_3+\alpha_4)\left(\mathbf{s}-\frac{\mathbf{q}}{2}-\mathbf{P}_{34}\right)^2} \frac{e^{-\frac{q}{\xi}}}{q} \\
&= \left(\frac{\pi}{\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4} \right)^{\frac{3}{2}} \int d^3q e^{-\frac{(\alpha_1+\alpha_2)(\alpha_3+\alpha_4)}{\alpha_1+\alpha_2+\alpha_3+\alpha_4} [\mathbf{q}-(\mathbf{P}_{12}-\mathbf{P}_{34})]^2} \frac{e^{-\frac{q}{\xi}}}{q} \quad (1.96)
\end{aligned}$$

with $\mathbf{P}_{12} = \frac{\alpha_1\mathbf{R}_1+\alpha_2\mathbf{R}_2}{\alpha_1+\alpha_2}$ and $\mathbf{P}_{34} = \frac{\alpha_3\mathbf{R}_3+\alpha_4\mathbf{R}_4}{\alpha_3+\alpha_4}$.

The resolution of equations of type (1.94) and (1.95) is a mandatory step of the variational approach, described in section 1.2. The ultimate aim of the process is to determine the best set of basis functions through which to approximate, in the best possible way, the many-particle wave functions. A basis set, indeed, defines a set of basis functions, which determine the molecular spin orbitals [37]. The spin orbitals, linear combination of basis functions, define in turn the many-particle wave functions, solutions of the equation

$$(H_0 - E + \pi V \pi) \Psi = 0. \quad (1.97)$$

In order to show the accuracy and effectiveness of the method described, we discuss electron-water scattering. This study, an integral part of my research project, will be analyzed in this next section. What is reported, in particular, will refer to the article [38].

1.4 Applications

1.4.1 Electron elastic scattering in water

The scattering of charged particles by molecules, atoms and solids defines a key element in various research fields from physics to medicine. Their accurate evaluation, indeed, is the focal point for the analysis of numerous processes, such as the charge transport processes in stellar and interstellar plasma [39] or radiation-induced DNA damage mechanisms [40]. These collision processes represent an investigative tool, for example, electron beams are used in tech-

niques such as the low energy electron diffraction (LEED) to characterize the surface structure of materials [41]. In hadrontherapy [15, 16, 42], cancer treatment based on the use of ion beams, the interaction between ionizing radiation and biological matter induces the emission of a vast number of secondary electrons. These low energy electrons (below 1 keV) cause 75-90 % of biodamage. Therefore, the study of electron interaction processes with water, the main constituent of the human body and not only, is of fundamental importance in order to determine the radio-biological effects, for the development of new treatments and radio-protection mechanisms. However, although electron-water collisions represent one of the most studied processes, the theoretical and experimental research in this field is now incomplete, given the many difficulties in carrying out scattering experiments in vacuum with liquid water or, at the theoretical level, in developing methods that can take into account all the physical properties of water, including the permanent dipole moment, the electronic excited and rotational-vibrational states, the electron-electron exchange-correlation interaction between the projectile and the target, the inter- and intra-molecular multi-scattering effects. These mechanisms, especially at low energy [43], range in which quantum effects dominate and elastic scattering events are the most probable, were the subject of our study on scattering processes of electrons impinging on a single water molecule, clusters of water molecules and the Zundel cation (H_5O_2^+). This study, based on the Dirac-Hartree-Fock (DHF) method, has some substantial differences from the known Mott theory [44] and R-matrix approach [45, 46]. The ab initio R-matrix approach, for example, consists of dividing the system into a scattering zone and an asymptotic region. In the asymptotic region, the non-interacting wave function is obtained analytically, while, in the scattering region, the electron-molecule interaction is determined by quantum methods, such as coupled cluster (CC) and configuration interaction (CI). The matching of both solutions (inner and outer at the boundary) in turn defines the transmission probability and phase shift. However, this method is limited to the study of electron scattering with one water molecule, where the kinetic energy of the projectile is larger than 10 eV. Moreover, the use of partial wave expansion implies that this expansion converges slowly in the presence of large dipole moments.

As regards the relativistic Mott theory, in this case, the differential elastic scattering cross section of electrons colliding with a single water molecule is described by the following equation [47]

$$\frac{d\sigma_{el}(T, \theta)}{d\Omega} = N \sum_{m,n} e^{i\mathbf{q}\cdot\mathbf{r}_{mn}} [f_m(\theta)f_n^*(\theta) + g_m(\theta)g_n^*(\theta)] \quad (1.98)$$

with $d\Omega = \sin\theta d\theta d\phi$ the differential solid angle, N the atomic number density of the target, $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$ the distance between the atoms m and n , θ the scattering angle, $\mathbf{q}$ the momentum transfer, $f_{m,n}(\theta)$ and $g_{m,n}(\theta)$, respectively, the direct and spin-flip amplitudes that can be derived from the relativistic Dirac equation in a central atomic potential. The continuum wave function and molecular potential are treated as a superposition of independent atomic centers, neglecting, in this way, the multi-scattering effects and the overlapping tails of potentials. In these approaches based on the Mott theory, effects, such as the permanent dipole moment of water, are included semi-empirically and the presence of molecules, randomly oriented, in liquid water is introduced by the relation

$$\frac{d\sigma_{el}}{d\Omega} = \sum_{m,n} \frac{\sin(kr_{m,n})}{kr_{m,n}} [f_m^*(\theta)f_n(\theta) + g_m^*(\theta)g_n(\theta)], \quad (1.99)$$

average over all possible orientations of equation (1.98).

Bearing in mind what we have just discussed, our main objective was to develop an accurate model capable of overcoming these limitations. This method, totally ab initio, consists of three steps. First, we solve self-consistently the DHF equation for one water molecule and clusters of water molecules. Second, we expand the Coulomb potential and the electronic wave functions using optimized Hermite Gaussian functions (HGFs) (subsection 1.3.3). Third, we determine the electron elastic cross sections by solving the Lippmann-Schwinger (LS) equations for the scattering states, including multiple scattering and correlation effects, with the non-spherical molecular potential term projected on a functional space spanned by Gaussian functions. It should be stressed, however, that electron-water scattering, protagonist of the next section, is only a test case. Our theoretical-computational method, indeed, can be extended

to the study and analysis of inelastic processes, such as excitation and ionization. Inelastic collisions, in the same way as elastic ones, represent a tool to expand our knowledge. In analytical techniques such as transmission (TEM) and scanning (SEM) electron microscopy, the primary beam, hitting the specimen, releases energy and the loss pattern is used to characterize materials [48].

Through this approach, we were able to describe the phase shifts, the T -matrix elements and, consequently, the total elastic scattering cross section in a range from 0.001 to 1000 eV. In the following pages, introduced once again the method, we will discuss the results obtained for electron-water scattering. The above, as reiterated, will refer to the article [38].

The method

A scattering process in the time-independent formalism is described by two fundamental quantities, such as the Green's operator and T -matrix (subsection 1.1.2). The T -matrix in turn allows to calculate the differential cross section, replacing equation (1.49) in equation (1.42), we get

$$\frac{d\sigma_{el}}{d\Omega} = \frac{m^2}{4\pi^2} |\langle \phi_{k\hat{n}} | T(E + i0^+) | \phi_{\mathbf{k}} \rangle|^2 = \frac{m^2}{4\pi^2} |\langle \phi_{k\hat{n}} | V | \psi_{\mathbf{k}}^+ \rangle|^2 \quad (1.100)$$

with m the mass of the projectile, $\phi_{k\hat{n}}$ the impinging particle wave function with momentum (modulus) k ($E = k^2/2m$) in the direction $\hat{n}$ (unit vector), T the transition operator, $\phi_{\mathbf{k}}$ the outgoing electron wave function along the incident direction $\mathbf{k}$, V the potential and $\psi_{\mathbf{k}}^+$ the scattering wave function. The wave function $\psi_{\mathbf{k}}^+(\mathbf{r})$ can be determined directly by solving the many-body Hamiltonian

$$H\psi_{\mathbf{k}}^+(\mathbf{r}) = (H_0 + V)\psi_{\mathbf{k}}^+(\mathbf{r}) = E\psi_{\mathbf{k}}^+(\mathbf{r}) \quad (1.101)$$

where H_0 is the free Hamiltonian (kinetic energy) and V the electron-electron Coulomb repulsion term. Given the difficulty in solving a many-body problem exactly, the latter, applying appropriate approximations, can be reduced to a single-body problem, where the stationary scattering states are obtained from

the LS equation

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + G_0(E + i0^+)V\psi_{\mathbf{k}}^+(\mathbf{r}), \quad (1.102)$$

equation (1.34), with $G_0(E + i0^+)$ the free Green's operator and $\phi_{\mathbf{k}}(\mathbf{r})$ the eigenvector of H_0 . Starting from the latter approach and employing a semi-projected potential method (subsection 1.3.2), we computed the elastic scattering cross sections of electrons impinging on one water molecule, water clusters and the Zundel cation. Introduced the DHF equation, we have rewritten the full Hamiltonian as the sum of a kinetic term and a Coulomb potential, which, applying the Hartree-Fock (HF) approximation, is expressed as the sum of the Hartree potential and an exchange term. At this point, using HGFs, we reformulated equation (1.102) as

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + G_0(E + i0^+)V^t\psi_{\mathbf{k}}^+(\mathbf{r}) \quad (1.103)$$

(LS equation for the continuum orbital) where the term $\phi_{\mathbf{k}}(\mathbf{r})$ is approximated by a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and

$$V^t = \sum_{\lambda\mu\nu\tau} |\lambda\rangle S_{\lambda\mu}^{-1} \langle\mu|V|\nu\rangle S_{\nu\tau}^{-1} \langle\tau| \quad (1.104)$$

is the DHF self-consistent projected potential with $|\lambda\rangle$, $|\mu\rangle$ two vectors of a non-orthogonal basis and $S_{\lambda\mu} = \langle\lambda|\mu\rangle$ the overlap matrix (similarly $|\nu\rangle$, $|\tau\rangle$ and $S_{\nu\tau}$). The preceding equation (1.103), employing the identity (1.32), can be further rewritten as

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + G_0(E + i0^+)Te^{i\mathbf{k}\cdot\mathbf{r}} \quad (1.105)$$

where $T = V^t + V^tG_0(E + i0^+)T$ represents the T operator and E the energy. To determine the orbital wave function and the projected scattering potential, we used the self-consistent procedure described in section 1.2 (the elements of the basis set are selected to minimize the difference $(V - V^t)\psi_{\mathbf{k}}^+(\mathbf{r})$ in the zone of interest). Obtained the best orbital wave function, expression built on spin orbitals which minimize the energy [9], we computed the differential elastic

scattering cross section, from which, integrating, we calculated the total cross section

$$\sigma_{el}(T) = \int_{\Omega} d\Omega \frac{d\sigma_{el}(T, \Omega)}{d\Omega} \quad (1.106)$$

with T the kinetic energy of the electron beam. To neglect the effects of the continuum orbital on bound ones, we have employed the static-exchange approximation (SEA) [46, 49, 50, 51, 52] and to take into account molecular orientations, we have chosen to span various directions θ, ϕ of the incident electron by stopping rotations. Moreover, because of the difficulties in describing the scattering wave function in energy range from 0.001 to 1000 eV, we decided to adopt two basis sets. The first, centered on the hydrogen and oxygen atoms, independent of the number of molecules, and the second (s -symmetry Gaussian basis set), uniformly distributed inside a sphere of variable radius $R = 1.25/\sqrt{a}$ with a the exponential coefficient of the HGF, centered on the center of mass of the molecule. The use of two basis sets allowed us to accurately reproduce the properties of the continuum orbital in different electron energy regions. The narrower Gaussian functions, characterized by large exponents a , indeed, are the most suitable for the study of oscillating behavior of the wave function in the high energy regime. On the contrary, wider HGFs, namely with smaller a , better describe the slowly changing behavior of the scattering wave function in a low energy range. This is further confirmed by the toy model potential calculations, where the accuracy of the solutions strongly depends on the type and number of basis functions used. These calculations for the T -matrix elements and phase shifts were carried out with the purpose of testing the validity of the method. For this reason, before discussing the results of the total elastic cross sections, we analyze, in the next pages, the toy model potential calculations.

The toy model potential problem

We consider a two-channels problem, in which the physical system (an electron, for example) can be represented by a couple of wave functions, namely the Hilbert space is formed by square-integrable functions

$$\psi : \mathbb{R}^3 \rightarrow \mathbb{C}^2. \quad (1.107)$$

Assuming a central symmetric potential dependent on the channel, we obtain the non-relativistic time-independent Schrödinger equation ($\hbar = 1$)

$$-\frac{1}{2m}\nabla^2\psi_j(\mathbf{r}) + \sum_k V_{jk}(\mathbf{r})\psi_k(\mathbf{r}) = E\psi_j(\mathbf{r}) \quad (1.108)$$

where j, k are the indices of the s -orbitals channels. Expressing the wave function in polar coordinates

$$\psi_j(\mathbf{r}) = \mathcal{R}_{j,l}(r)Y_{l,m}(\vartheta, \varphi), \quad (1.109)$$

which for the s -channels case is $\psi_j(\mathbf{r}) = \mathcal{R}_{j,0}/\sqrt{4\pi}$, we write the following system of coupled differential equations

$$-\frac{1}{2m}\frac{d^2}{dr^2}u_1(r) + V_{11}(r)u_1(r) + V_{12}(r)u_2(r) = Eu_1(r) \quad (1.110)$$

$$-\frac{1}{2m}\frac{d^2}{dr^2}u_2(r) + V_{21}(r)u_1(r) + V_{22}(r)u_2(r) = Eu_2(r) \quad (1.111)$$

where $u_j(r) = r\mathcal{R}_j(r)$ and $u : \mathbb{R}_+ \rightarrow \mathbb{C}^2$ satisfies the condition $u_j(0) = 0$. Problem (1.108), restricted to spherical or totally symmetric wave functions, is equivalent to the system, therefore, assuming the mass of the particle $m = 1$ and selected the Yukawa-type potentials

$$V_{11}(r) = -V_{22}(r) = -14\frac{e^{-0.5r}}{r} + 7\frac{e^{-0.2r}}{r} \quad (1.112)$$

$$V_{12}(r) = V_{21}(r) = 2\frac{e^{-0.3r}}{r}, \quad (1.113)$$

we solve the problem through two different approaches. The first, integrating equations (1.110) and (1.111) by means of a fourth-order Runge-Kutta (RK) method and the second resolving problem (1.108) by applying the LS approach, where the potential term is projected using 40 well-tempered s -Gaussian functions [53]. The results for the phase shifts and T -matrix elements are reported in Figure 1.1, where the colored continuous lines represent the numerical solution of the radial problem (ODE = Ordinary differential equation) obtained by the RK method and the points describe the results of problem (1.108) solved by the semi-projected method (LS = Lippmann-Schwinger). The phase shifts

computed in the auto-channels, channels where the incoming and outgoing wave functions are in the same one, converge except in the region around 10 Hartree where the LS calculations deviate from the ODE calculations. This behavior is also reflected in the calculations of the T -matrix elements, in which the LS resonance (auto-channel 2 to 2) around 10 Hartree is shifted.

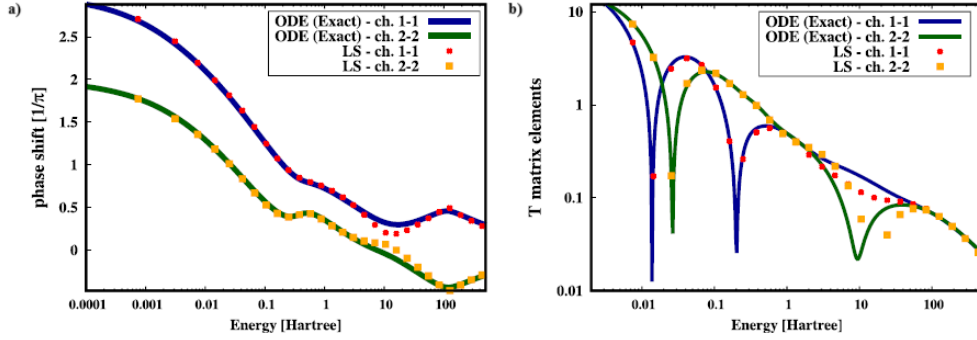


Figure 1.1: Results of the toy model potential problem. Phase shifts for the auto-channels obtained through the LS and ODE approaches (left). T -matrix elements for the auto-channels obtained through the LS and ODE approaches (right).

This can be explained by the fact that, as pointed out above, the use of a single basis set is not sufficient to accurately describe the entire energy region; however, narrowing the area of analysis, we observe that the ODE calculations and LS data, below 4 Hartree, are in good agreement.

Noted that the resolution of the calculations depends on the number of basis functions used, in Figure 1.2, Figure 1.4 and Figure 1.5 are shown the results for electron elastic scattering cross sections in water obtained with two HGFs basis sets.

Total elastic scattering cross sections

In Figure 1.2, in particular, we compared our ab initio calculations for the single water molecule (continuous multi-colored line) with the theoretical and experimental data (points) reported in [54]. Our total elastic scattering cross section was computed using the fixed-nuclei approximation (i.e. not considering the vibrational and rotational degrees of freedom) and different Gaussian functions. Each color of the continuous line, indeed, characterizes a different width a (bohr⁻²), which depends on the energy range, optimized by comparison with the experimental data. Above 4 eV our data are in excellent agreement

with the results of M. A. Khakoo et al. [55] (full blue squares with error bars) and at energies larger than 10 eV our LS results fit well the recommended total cross section [54] (green triangles). However, if we compare our elastic data, above 4 eV, with the results obtained with the ELSEPA (ELastic Scattering of Electrons and Positrons by Atoms) code [52] (cyan points) and below 4 eV with M. A. Khakoo et al. data, we observe some discrepancies. This can be attributed to the different models adopted. As regards the M. A. Khakoo et al. data, the latter were obtained by using the Schwinger multi-channel method [56], while for the ELSEPA code, this last one, based on the Mott theory, includes the permanent dipole moment semi-empirically and accounts for the atomic interaction potential. Our fully relativistic multi-channel method, on the contrary, considers a molecular potential as well the polarization and dipole-scattering effects. To test the accuracy and robustness of our model, we also determined the statistical error for different impact kinetic electron energies using seven HGFs basis sets.

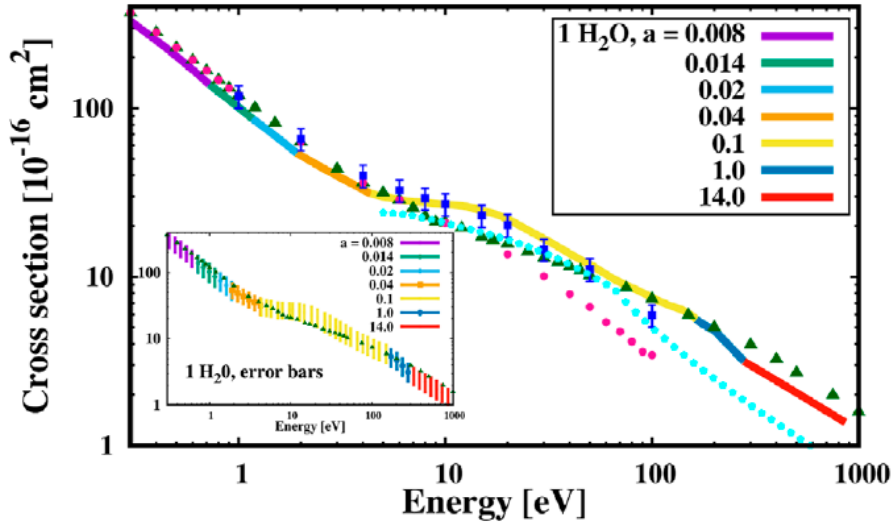


Figure 1.2: Total scattering cross section of electrons impinging on a single water molecule. Our elastic scattering cross section (continuous multi-colored line) compared with the values obtained through the ELSEPA code [52] (cyan points), the theoretical/experimental data from [55] (full blue squares with error bars), the recommended elastic (full magenta circles) and total (green triangles) scattering cross sections from [54]. The recommended total cross section of [54] at 0.1-7 eV is based on the R-matrix calculations [57, 58], at 7-50 eV on experiments of [59, 60, 61] and above 50 eV on measurements of [62]. In the inset the recommended total scattering cross section compared with the statistical error bar of our elastic cross section for different kinetic energies. The error is overestimated since the different values were equally weighted across the entire spectrum.

Figure 1.4 shows the total elastic scattering cross sections of electrons impinging on the water clusters 1 and 2 (upper multi-colored points) compared with the ELSEPA results for the water cluster 1 (cyan points) and the data for a single water molecule (Figure 1.2). The two clusters of three water molecules, in Figure 1.3, were determined by trimming a large cubic liquid water cell of density 1 g/cm^3 , whose configuration was optimized using density functional theory (DFT) implemented by introducing a Perdew-Burke-Ernzerhof (PBE) functional [63]. The two clusters 1 and 2, whose dipole moments were pointed in different directions, are intended to mimic liquid water. The aim of this study, indeed, is to determine the effect of multi-scattering on the total elastic cross section simulating the presence of the surrounding molecular environment.

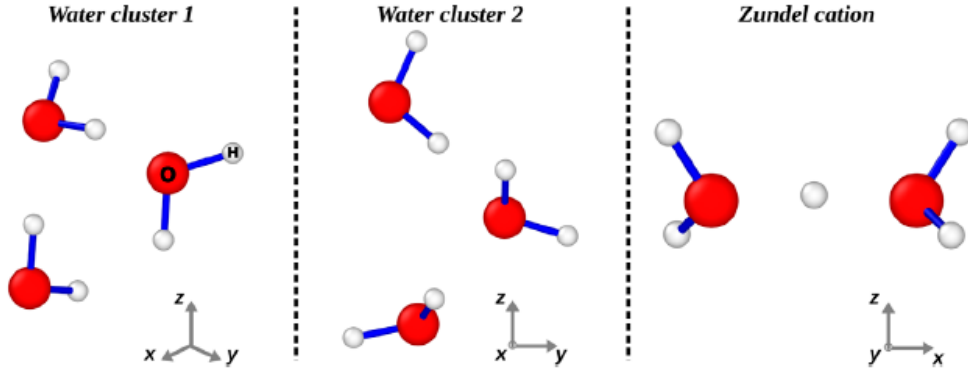


Figure 1.3: Two different configurations of water molecules in the liquid phase and the Zundel cation (H_5O_2^+) configuration from [64].

The LS calculations obtained for the two clusters are represented by the multi-colored points, where the colors, once again, describe a different a (bohr^{-2}). The results for the water clusters 1 and 2, normalized by three, are in good agreement with the single molecule data, except in the intermediate energy range ($1 < E < 30 \text{ eV}$) where the cross sections diverge. This discrepancy can be attributed to the accurate treatment of the inter- and intra-molecular potential, in addition to multiple scattering effects. Moreover, it should be underlined that our calculations were carried out in liquid water-like conditions, while the experimental measurements were performed on water vapor, where

molecules are distant and consequently more similar to the single molecule behavior.

The experimental data and the results obtained with the ELSEPA code, based on the use of an atomic interaction potential, indeed, follow the same trend of the single water molecule simulations.

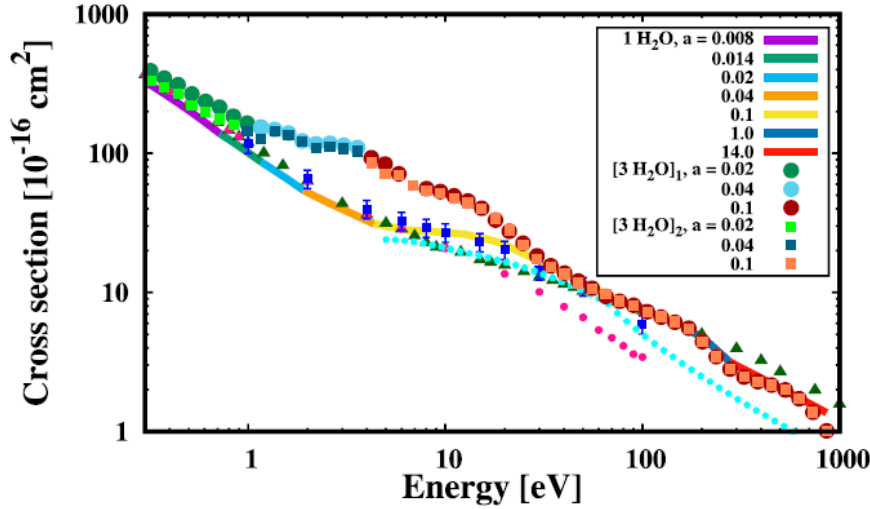


Figure 1.4: Elastic scattering cross sections of electrons impinging on the two clusters of three water molecules shown in Figure 1.3 ($[3 \text{ H}_2\text{O}]_{1,2}$, multi-colored points) compared with the data reported in Figure 1.2 for a single water molecule ($1 \text{ H}_2\text{O}$, continuous multi-colored line represents our ab initio calculations) and the results obtained through the ELSEPA code [52] on the water cluster 1 of Figure 1.3 (cyan points). The cross sections of the water clusters have been normalized by the number of molecules.

Concerning Figure 1.5, the latter shows the total elastic cross section of electrons colliding with the Zundel cation (Figure 1.3). Our ab initio data (upper multi-colored empty squares) and the ELSEPA simulations (cyan points) for protonated water (hydrogen ions bind to water molecules forming weakly bound structures) were compared with the total cross sections of the water clusters 1 and 2 (multi-colored points), where each color defines three different widths ($a = 0.02, 0.04$ and 0.1 bohr^{-2}). In the low and intermediate energy regimes (below 100 eV), the Zundel LS data diverge from the others, while at high energy the results, normalized by the number of molecules, converge. This trend can be explained, once again, by multi-scattering effects and different environment represented by the Zundel cation (H_5O_2^+) and water clusters. Concerning the ELSEPA results for the Zundel cation and the total elastic cross sections of the water clusters 1 and 2, the latter, above 4 eV, are in

good agreement. The ELSEPA total molecular cross sections, in fact, are obtained by using a single-scattering independent-atom approximation, where the electron density of a bound atom is approximated by the electron density of neutral free atom.

As regards our calculations, although the LS equations are usually characterized by a convergence problem for long range potentials, the cross sections obtained through this approach are in good agreement with the theoretical/experimental data reported (the cross sections computed converge).

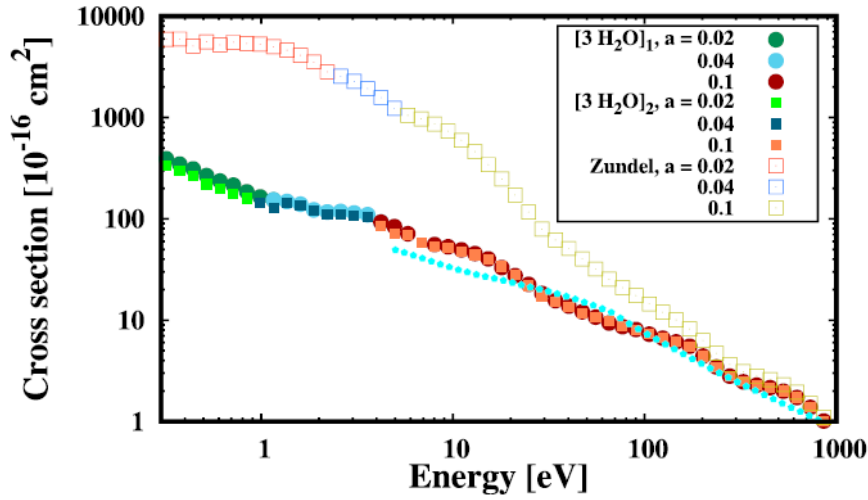


Figure 1.5: Elastic scattering cross sections of electrons impinging on the Zundel cation of Figure 1.3 (multi-colored empty squares) compared with our results for the water clusters 1 and 2 of Figure 1.3 ($[3 \text{ H}_2\text{O}]_{1,2}$, multi-colored points) and the data obtained through the ELSEPA code [52] on the Zundel cation (cyan points), in which the charge of the shared proton is compensated by an extra electron to get neutrality. The cross sections have been divided by three for the water clusters and by two for the Zundel molecule.

Conclusions

The last pages of this chapter have been entirely devoted to the study of electron-water scattering. Purpose and objective of this last section was to show the robustness and efficiency of our ab initio method that differs from the well-known Mott theory and R-matrix method for different factors. The Mott theory, otherwise from our mean-field (MF) approach, describes the scattering potential as a mere superposition of atomic contributions, neglecting multi-scattering effects. The latter and dipole moment, in our model, derive from the treatment of the inter- and intra-molecular potential, an accurate

description of which is crucial to the calculation of the total elastic cross sections. Concerning *ab initio* approaches, including the R-matrix approach, the latter are usually limited to the study of scattering processes for a single water molecule. Moreover, these last ones, unlike our method, do not take into account the relativistic effects. The Mott theory and the R-matrix method have always been the main models for electron-molecule scattering analysis. For this reason, we decided to compare our results for a single water molecule with the R-matrix calculations [57, 58] and the data reported in Figures 1.2, 1.4 and 1.5 with the ELSEPA simulations [52]. ELSEPA (ELastic Scattering of Electrons and Positrons by Atoms) is one of the most widely used programs for electron elastic scattering studies. This FORTRAN 77 code system allows relativistic Dirac partial wave calculations of electron and positron elastic scattering by (positive) ions, atoms and molecules. For the ELSEPA simulations reported in Figures 1.2, 1.4 and 1.5, in particular, we employed the program ELSCATM, through which we determined the Mott elastic scattering cross sections of electrons colliding with a single water molecule, a water cluster and the Zundel cation. These analyses represented one of the possible applications of the implementation of the Dirac-Hartree-Fock (DHF) method based on the use of Hermite Gaussian functions (HGFs). This model, once again protagonist of the next chapter, was developed by introducing radial basis sets. Through the latter approach, we have analyzed numerous nuclear processes, such as β^- decays and electron captures. This implementation, unlike the previous one, is most suitable for the study of spherical symmetric systems. Assuming a β^- -decaying system like a system consisting of a unique isolated nucleus surrounded by electrons, it is possible to approximate the latter to a spherical symmetric problem.

In the next chapter, described β decays and Fermi's theory, we will analyze the results obtained for these nuclear reactions in terrestrial and stellar scenarios. Nuclear decay processes, essential for the investigation of the chemical evolution of the Universe and not only, will constitute the main topic of chapter 2, in which, as anticipated, we will introduce a second implementation of the DHF method based on the use of radial mesh.

Chapter 2

Relativistic mean-field approach and nuclear decays

Following the discovery of X-rays in 1895 by W. C. Röntgen, A. H. Becquerel, in 1896, conducted a series of studies on uranium salts to demonstrate that the phosphorescent materials emitted rays similar to X-rays [65]. However, and to his own surprise, he understood that the emission was not due to sunlight. The *Becquerel rays* were different from X-rays. The former were deflected in the presence of a magnetic field. The radiation emitted by uranium was a new type of radiation named by M. Curie radioactivity [66].

Radioactive decays, in particular, β decays, will be the subject of analysis of this chapter, in which we will present a second implementation of the Dirac-Hartree-Fock (DHF) method. Through this approach, based on the use of radial basis sets, various nuclear processes were analyzed. After nuclear beta decays have been introduced, we will come to the treatment of the implementation of the DHF method and, in the final pages, we will discuss the results obtained in terrestrial and astrophysical scenarios.

2.1 Nuclear beta decays

A radioactive decay is a spontaneous process in which a parent radionuclide (unstable nucleus) turns into one or more daughter nuclides with the consequent emission of particles. This transformation can be direct: the parent radionuclide decays directly in a stable nuclide, or the parent is transformed

until a radioactive daughter decays in a stable one (radioactive decay chain). Nuclear beta decays (β^- decay, β^+ decay and electron capture) are some of the most common radioactive decays.

β^- decay (negative beta decay) is a nuclear process in which a neutron n of an unstable nucleus (${}^A_Z\text{X}$) is transformed into a proton p . During this process, an electron e^- (β^- particle) and an electron antineutrino $\bar{\nu}_e$ are emitted

$${}^A_Z\text{X} \longrightarrow {}^A_{Z+1}\text{Y} + e^- + \bar{\nu}_e. \quad (2.1)$$

Consequently, the atomic number (proton number) Z increases by one unit, while the mass number A , the sum of the number of neutrons and protons, remains unchanged. For the decay to occur, assuming that the antineutrino is massless, the parent nuclear binding energy must be greater than or equal to the sum of the daughter nuclear binding energy and electron rest mass

$$E(A, Z) \geq E(A, Z + 1) + m_e \cdot c^2. \quad (2.2)$$

Expressing equation (2.2) in terms of nuclear masses, we obtain that

$$Q_{\beta^-} = \{m_N(A, Z) - [m_N(A, Z + 1) + m_e]\} \cdot c^2 \geq 0 \quad (2.3)$$

while, in terms of atomic masses

$$m_A(A, Z) \cdot c^2 = [m_N(A, Z) + Z \cdot m_e] \cdot c^2 - \sum_{i=1}^Z B_i \quad (2.4)$$

with B_i the binding energy of the i -th electron, we have

$$Q_{\beta^-} = \{m_A(A, Z) - Z \cdot m_e - [m_A(A, Z + 1) - (Z + 1) \cdot m_e] - m_e\} \cdot c^2 \geq 0$$

$$Q_{\beta^-} = [m_A(A, Z) - m_A(A, Z + 1)] \cdot c^2 \geq 0 \quad (2.5)$$

where Q_{β^-} defines the Q -value of the nuclear reaction⁵.

⁵If the Q -value, the energy released or absorbed in a nuclear process, is positive the process is said exothermic (exoergic); on the contrary, if the Q -value is negative the process is said endothermic (endoergic).

Concerning β^+ decay (positive beta decay), the latter, unlike the previous one, is a nuclear process where a proton p of an unstable nucleus (${}^A_Z\text{X}$) decays into a neutron n . During this process, a positron e^+ (β^+ particle) and an electron neutrino ν_e are emitted

$${}^A_Z\text{X} \longrightarrow {}^A_{Z-1}\text{Y} + e^+ + \nu_e. \quad (2.6)$$

Accordingly, the mass number A , once again, remains unchanged, while the atomic number Z decreases by one unit.

For this process to take place, similarly to β^- decay, the parent nuclear binding energy must be greater than or equal to the sum of the daughter nuclear binding energy and positron rest mass (neutrino massless)

$$E(A, Z) \geq E(A, Z - 1) + m_e \cdot c^2 \quad (2.7)$$

from which, we obtain, in terms of nuclear masses

$$Q_{\beta^+} = \{m_N(A, Z) - [m_N(A, Z - 1) + m_e]\} \cdot c^2 \geq 0 \quad (2.8)$$

and in terms of atomic masses⁶

$$Q_{\beta^+} = [m_A(A, Z) - m_A(A, Z - 1) - 2m_e] \cdot c^2 \geq 0. \quad (2.9)$$

As last, electron capture [67]. Electron capture is a process in which an orbital electron e^- is borrowed from an atomic shell (usually from the inner shells). The captured electron and a nuclear proton p are converted into a neutron n and an electron neutrino ν_e is emitted

$${}^A_Z\text{X} + e^- \longrightarrow {}^A_{Z-1}\text{Y} + \nu_e. \quad (2.10)$$

The atomic number Z is, therefore, reduced by one unit, whereas the number A does not change.

⁶The Q -values, in terms of atomic masses, were determined neglecting differences in atomic electron binding energies.

The energy condition for an electron capture to occur is

$$E(A, Z) + E_e \geq E(A, Z - 1) \quad (2.11)$$

where, once more, $E(A, Z)$ and $E(A, Z - 1)$ define, respectively, the nuclear binding energy of parent and daughter, while E_e represents the electron energy. Determining the Q -value, in terms of nuclear masses, we obtain

$$Q_{EC} = [m_N(A, Z) + m_e - m_N(A, Z - 1)] \cdot c^2 \geq 0 \quad (2.12)$$

from which, in terms of atomic masses, we conclude that

$$Q_{EC} = [m_A(A, Z) - m_A(A, Z - 1)] \cdot c^2 - B_n \geq 0. \quad (2.13)$$

"...the calculation of the Q value must take into account that the atom X' is in an atomic excited state immediately after the capture. That is, if the capture takes place from an inner shell, the K shell for instance, an electronic vacancy in that shell results. The vacancy is quickly filled as electrons from higher shells make downward transitions and emit characteristic X rays. Whether one X ray is emitted or several, the total X -ray energy is equal to the binding energy of the captured electron. Thus the atomic mass of X' immediately after the decay is greater than the mass of X' in its atomic ground state by B_n , the binding energy of the captured n -shell electron ($n = K, L, \dots$)..." [68].

2.1.1 Conservation laws and selection rules

Nuclear transmutations, including beta decays, must fulfill numerous conservation laws [69], namely some quantities such as the total energy (mass), the momentum, the charge, the baryon number and the lepton number, before and after the process, must be the same.

- Conservation of mass-energy: in accordance with the principle of mass-energy equivalence, the total energy in a nuclear process is conserved. If, for example, the mass of the parent is greater than the total mass of decay products, the missing mass (energy) appears in the form of particle kinetic energy.

- Conservation of momentum: the sum of momenta, before and after a nuclear process, is the same.
- Conservation of charge: the sum of charges, before and after a nuclear process, is the same.
- Conservation of lepton number: the total number of leptons, before and after a nuclear process, must be the same. Leptons, such as the electron and neutrino, are characterized by a lepton number $+1$, while antileptons, such as the positron and antineutrino, are characterized by a lepton number -1 . Particles that are not leptons, including the proton and neutron, are characterized by a lepton number 0 .
- Conservation of baryon number: the total number of baryons, before and after a nuclear process, must be the same. Baryons, such as the proton and neutron, are characterized by a baryon number $+1$, while antibaryons, such as the antiproton and antineutron, are characterized by a baryon number -1 . Particles that are not baryons, including leptons, are characterized by a baryon number 0 .

In the previous section, starting from the principle of energy conservation, we determined the Q -value of β^- decay, β^+ decay and electron capture. These three isobaric transitions⁷, analyzing the angular momentum and parity change between the initial and final nuclear states, can be classified into allowed and forbidden decays.

The allowed decays do not present a parity change

$$\Delta\pi = no \iff \pi_i = \pi_f, \quad (2.14)$$

while the angular momentum difference can be

$$\Delta I = |I_i - I_f| = 0, 1. \quad (2.15)$$

The forbidden decays, less probable than the allowed transitions, may, in turn, be classified into first-forbidden decays, second-forbidden decays and so on.

⁷Decay processes in which the mass number A (nucleon number) remains unchanged are defined isobaric transitions.

The first-forbidden decays are featured by a change of parity

$$\Delta\pi = yes \iff \pi_i = -\pi_f \quad (2.16)$$

and the angular momentum difference can be

$$\Delta I = |I_i - I_f| = 0, 1, 2. \quad (2.17)$$

For the second-forbidden transitions

$$\Delta\pi = no \iff \pi_i = \pi_f \quad (2.18)$$

and

$$\Delta I = |I_i - I_f| = 2, 3. \quad (2.19)$$

"...Transitions with $\Delta I \geq 2$, but with no change in parity, are permitted by neither the allowed nor the first-forbidden selection rules...these are known as second-forbidden decays...The $\Delta I = 0$ and 1 cases fall within the selection rules for allowed decays, and we expect that the contribution of the second-forbidden terms to those decays will be negligible...Continuing this process, we would find third-forbidden decays...in which the selection rules not also satisfied by first-forbidden processes are $\Delta I = 3$ or 4 and $\Delta\pi = yes$...even fourth-forbidden decays...with $\Delta I = 4$ or 5 and $\Delta\pi = no$..." [68].

Transitions	Angular momentum	Parity
Super-allowed ($0^+ \rightarrow 0^+$)	$\Delta I = 0$	$\Delta\pi = no$
Allowed	$\Delta I = 0, 1$	$\Delta\pi = no$
First-forbidden	$\Delta I = 0, 1, 2$	$\Delta\pi = yes$
Second-forbidden	$\Delta I = 2, 3$	$\Delta\pi = no$
Third-forbidden	$\Delta I = 3, 4$	$\Delta\pi = yes$
Fourth-forbidden	$\Delta I = 4, 5$	$\Delta\pi = no$

Table 2.1: Selection rules nuclear beta decays.

2.1.2 The radioactive decay law

On 28 March 1901, a meeting, "*The Existence of Bodies Smaller than an Atom*", was held at McGill Physical Society in Montreal, which E. Rutherford and F. Soddy attended [70]. Some days after the meeting, Rutherford proposed to Soddy a collaboration with the aim of investigating the thorium emanation.

"...The present researches had as their starting-point the facts that had come to light with regard to thorium radioactivity...Besides being radioactive in the same sense as the uranium compounds, the compounds of thorium continuously emit into the surrounding atmosphere a gas which possesses the property of temporary radioactivity. This 'emanation', as it has been named, is the source of rays..." [71].

In 1901, thus, they began a series of experiments leading to the discovery of $^{224}_{88}\text{Ra}$, originally named thorium X (ThX), and the formulation of the radioactive decay law.

After the Christmas holidays, in 1902, comparing the activity of thorium hydroxide and ThX, they concluded that the activity of thorium X decreased according to the equation (geometrical progression)

$$I_t/I_0 = e^{-\lambda t} \quad (2.20)$$

with I_0 the initial activity, I_t the activity after a certain time t and λ a constant, while the activity of thorium hydroxide was expressed by the equation

$$I_t/I_0 = 1 - e^{-\lambda t} \quad (2.21)$$

where I_0 represents the activity recovered at the time the maximum is reached and I_t the activity restored after time t .

"...I am sending you a manuscript by Mr Soddy and myself on the radioactivity of thorium. We know that thorium-X like uranium-X, loses its activity in a ge-

ometrical progression with time, yet the deactivated thorium regains its activity with time. I think we have conclusively proved that most of the radioactivity is due to the production of thorium-X by the thorium at a (practically) constant rate and that this thorium-X decays with time. The equilibrium point is reached when the rate of production is balanced by the rate of decay. We have strong evidence that uranium and radium behave similarly, only that the time rate of change is different. All these processes are independent of chemical and physical conditions and we are driven to the conclusion that the whole process is subatomic. I believe that in the radioactive elements we have a process of disintegration or transformation going on which is the source of the energy dissipated in radioactivity...” [72].

Radioactivity, a spontaneous transformation of an element into another with the emission of radiation, is a statistical process [68, 73, 74]. It is impossible to predict when a radioactive decay will occur, but it is possible to provide the probability that a decay occurs in a given time interval, the average number of nuclei decayed in a given time interval.

Considering the equation

$$\frac{dN_P(t)}{dt} = -\lambda \cdot N_P(t) \quad (2.22)$$

with $N_P(t)$ the number of nuclei (parents) at time t and λ the decay constant (the probability of decay of an unstable nucleus per unit time).

Integrating the differential equation (2.22), we obtain (radioactive decay law)

$$N_P(t) = N_P(0) \cdot e^{-\lambda t} \quad (2.23)$$

where $N_P(0)$ represents the number of nuclei at $t = 0$. Expressing the previous equation (2.23) in terms of mean life, $\tau = \frac{1}{\lambda}$, we have

$$N_P(t) = N_P(0) \cdot e^{-\frac{t}{\tau}} \quad (2.24)$$

where τ defines the average lifetime of unstable nuclei (before they decay). Introducing the half-life $T_{1/2}$, the time required for one-half of the unstable

nuclei to decay, with

$$T_{1/2} = \frac{\ln(2)}{\lambda} = \tau \ln(2), \quad (2.25)$$

we conclude that

$$N_P(t) = N_P(0) \cdot \left(\frac{1}{2}\right)^{t/T_{1/2}}. \quad (2.26)$$

At this point, differentiating between a direct radioactive decay and a radioactive decay chain, we define, for a direct process

$$dN_D(t) = -dN_P(t) = \lambda \cdot N_P(t) \cdot dt \quad (2.27)$$

from which, assuming that $N_D(0) = 0$, the number of nuclei (daughters) at time $t = 0$ is zero, we obtain

$$N_D(t) - N_D(0) = N_P(0) \cdot (1 - e^{-\lambda t}) \iff N_D(t) = N_P(0) \cdot (1 - e^{-\lambda t}). \quad (2.28)$$

On the contrary, for a decay chain (cascade), we define the system [75]

$$\begin{cases} dN_1(t) = -\lambda_1 \cdot N_1(t) \cdot dt \\ dN_2(t) = \lambda_1 \cdot N_1(t) \cdot dt - \lambda_2 \cdot N_2(t) \cdot dt \\ \vdots \\ dN_N(t) = \lambda_{N-1} \cdot N_{N-1}(t) \cdot dt \end{cases} \quad (2.29)$$

from which we conclude that⁸

$$N_N(t) = N_1(0) \cdot \left(\prod_{n=1}^{N-1} \lambda_n\right) \cdot \sum_{m=1}^N \frac{e^{-\lambda_m t}}{\prod_{n=1, n \neq m}^N (\lambda_n - \lambda_m)} \quad (2.30)$$

and $a_N(t) = 0$. Being the n -th daughter the stable one, the activity $a_N(t)$ and the decay constant λ_N are equal to zero.

The activity $a(t)$, the rate of decay, defined as

$$a(t) = \lambda \cdot N(t) = \lambda \cdot N(0) \cdot e^{-\lambda t} \quad (2.31)$$

⁸Secular equilibrium: the half-life of the parent is much greater than the half-life of the daughter. Transient equilibrium: the half-life of the parent is greater than the half-life of the daughter. No equilibrium: the half-life of the parent is shorter than the half-life of the daughter.

describes the number of transformations (decays) per unit time.

The first theory of beta decay was formulated by E. Fermi in 1933. Starting from Fermi's theory and introduced its generalization, we will describe the second implementation of the Dirac-Hartree-Fock (DHF) method and the results obtained by applying the latter approach.

2.1.3 Fermi's theory of beta decay

In October 1933, E. Fermi attended the seventh Solvay conference in which the neutrino hypothesis and neutron discovery were discussed [76]. The existence of this neutral particle, the neutron, renamed by Fermi neutrino and postulated by W. Pauli in 1930, was able to decipher the open problem of the continuous beta spectrum.

"...I have hit upon a desperate remedy to save the "exchange theorem" of statistics and the law of conservation of energy. Namely, the possibility that there could exist in the nuclei electrically neutral particles, that I wish to call neutrons, which have spin 1/2 and obey the exclusion principle and which further differ from light quanta in that they do not travel with the velocity of light. The mass of the neutrons should be of the same order of magnitude as the electron mass and in any event not larger than 0.01 proton masses. The continuous beta spectrum would then become understandable by the assumption that in beta decay a neutron is emitted in addition to the electron such that the sum of the energies of the neutron and the electron is constant..." [77, 78].

Moreover, the discovery of the neutron of 1932 by J. Chadwick made it possible to develop a new nuclear model, the neutron-proton model, which supplanted the proton-electron model.

"...In 1932 the neutron, a heavy particle with the mass practically equal to the mass of the proton, was discovered by J. Chadwick...Soon after this discovery Heisenberg...,Majorana...and Ivanenko...put forward a hypothesis that nuclei are bound states of protons and neutrons. This hypothesis could successfully describe all nuclear data. The problem of the spin of $^{14}\text{N}_7$ and other

nuclei disappeared...” [79].

Both hypotheses led Fermi to the formulation of the first theory of beta decay. In 1934, Fermi sent his *attempt* to *Il Nuovo Cimento* and *Zeitschrift für Physik*, which published it in January and March of the same year [80, 81].

The Italian physicist, according to the Pauli hypothesis, described nuclear beta decay as a process during which an electron and a neutrino are emitted simultaneously; furthermore, he assumed that the nuclei were composed of protons and neutrons.

”...One admits, furthermore, that in every β process are simultaneously emitted an electron, observed as a β ray, and a neutrino escaping observation and carrying away part of the energy...it seems more appropriate to admit with HEISENBERG...that all nuclei only consist of heavy particles, protons and neutrons. Nevertheless to understand the possibility of β rays emission, we shall attempt the construction of a theory for the emission of light particles from a nucleus in analogy with the emission theory of a light quantum by an excited atom in the ordinary radiation process...” [82].

Relying on radiation theory and the Dirac-Jordan-Klein’s method, the second quantization method, Fermi determined the Hamiltonian and the transition probability for beta decay, from which he deduced the formulae for the mean life and continuous spectrum shape.

Specifically, he expressed the energy of the system as the sum of:

- the energy of heavy particles

$$H_h = \frac{1 + \rho}{2} N + \frac{1 - \rho}{2} P \quad (2.32)$$

where the operators P and N represent the energy of the proton and neutron (for heavy particles Fermi used the configuration space representation and introduced the internal coordinate $\rho = -1$ for the proton and $\rho = +1$ for the neutron);

- the energy of light particles

$$H_l = \sum_s H_s N_s + \sum_\sigma K_\sigma M_\sigma \quad (2.33)$$

with $H_1...H_s$ ($K_1...K_\sigma$) and $N_1...N_s$ ($M_1...M_\sigma$) the energies of the stationary states and the functions of the occupation numbers of quantum states of electrons (neutrinos). For the Pauli exclusion principle, each N_s and M_σ can only assume values 0 or 1 (for electrons the eigenfunctions in the screened Coulomb field of the nucleus, while for neutrinos the plane waves);

- the generalized interaction term⁹

$$H_{int} = g[Q\tilde{\psi}^*\delta\varphi + Q^*\tilde{\psi}\delta\varphi^*] \quad (2.34)$$

where g represents a constant, Q and Q^* two operators

$$Q = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad Q^* = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (2.35)$$

that determine the transition from proton to neutron (Q) or from neutron to proton (Q^*), ψ and φ the probability amplitudes of electrons and neutrinos (ψ^* and φ^* their complex conjugates)

$$\psi = \sum_s \psi_s a_s, \quad \psi^* = \sum_s \psi_s^* a_s^* \iff \varphi = \sum_\sigma \varphi_\sigma b_\sigma, \quad \varphi^* = \sum_\sigma \varphi_\sigma^* b_\sigma^* \quad (2.36)$$

with a_s (b_σ) and a_s^* (b_σ^*) the electron (neutrino) creation and annihilation operators (an electron or a neutrino is created or destroyed in the quantum state s or σ), defined as (field) operators, represented by matrices ($\tilde{\psi}^*$ and $\tilde{\psi}$ the conjugate transpose matrices) and

$$\delta = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \quad (2.37)$$

⁹The energy between proton and electrons was neglected, in the same way some terms of the order v/c were not included as the speed of heavy particles in the nucleus is small compared to the speed of light. The interaction term was generalized so that light particles could be treated relativistically.

"...With the just established Hamiltonian it is possible to develop the β decay theory in complete analogy with radiation theory. In the latter, the HAMILTON function consists, as is known, of the sum: atom Energy + Radiation field Energy + Interaction between atom and radiation; the last term is considered as a perturbation of the other two..." [82].

Described the Hamiltonian function as the sum of an unperturbed Hamiltonian ($H_h + H_l$) and a perturbation (H_{int}), Fermi defined the matrix element and the transition probability, the probability that a β disintegration will take place over time in which the β particle is emitted in the quantum state s

$$P = \frac{8\pi^3 g^2}{c^3 h^4} \left| \int d\tau v_m^* u_n \right|^2 \tilde{\psi}_s \psi_s (W - H_s)^2 \quad (2.38)$$

with v_m and u_n the eigenfunctions of the proton and neutron in the nucleus, ψ_s the electron eigenfunction and W the energy difference between the heavy particle states, from which, as mentioned, he deduced the formulae for the mean life and continuous spectrum shape.

"...the Fermi model, an "effective transition operator" for nucleons is actually the unit matrix and thereby a nucleon spin flip is not possible...One may thus conclude that the original Fermi model, though conceptually correct (and applicable at least in a limited sense), is certainly incomplete and must therefore be generalized if one wants to get a realistic effective theory of weak nuclear force..." [83].

2.1.4 Generalization of Fermi's theory

The generalization of Fermi's theory describes an extension of the original model of 1933, in order to determine not only the spin-conserving transitions, named Fermi transitions¹⁰, but also the spin-changing processes, called

¹⁰Nuclear beta decay processes can be further classified in the Fermi transitions, the Gamow-Teller transitions and the mixed (Fermi+Gamow-Teller) transitions.

Gamow-Teller transitions [84].

The generalization of Fermi's theory, rewriting of the model based on the use of scalar (S), vector (V), axial vector (A), tensor (T) and pseudo-scalar (P) bilinear forms, was proposed, for the first time, by G. Gamow and E. Teller. Considering the interaction Hamiltonian density

$$\mathcal{H}_{int} = G(\bar{\psi}_p \gamma^\mu \psi_n)(\bar{\psi}_e \gamma_\mu \psi_\nu) + h.c. \quad (2.39)$$

with ψ_f ($f = p, n, e, \nu$) the spinor (fermion) fields, γ^μ ($\mu = 0, 1, 2, 3$) the Dirac contravariant gamma matrices

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

$$\gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}, \quad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix},$$

$\gamma_\mu = \eta_{\mu\nu} \gamma^\nu = \{\gamma^0, -\gamma^1, -\gamma^2, -\gamma^3\}$ the covariant matrices and G the coupling constant, we obtain in terms of matrices Γ , combinations of Dirac matrices,

$$\mathcal{H}_{int} = \sum_{k=S,V,A,T,P} C_k (\bar{\psi}_p \Gamma^k \psi_n) [\bar{\psi}_e (1 + \alpha_k \gamma^5) \Gamma_k \psi_\nu] + h.c. \quad (2.40)$$

with C_k the (real) parameters of dimension M^{-2} , in analogy with the constant G ($[G] = M^{-2}$ with M an arbitrary mass scale), Γ^k the contravariant matrices

$$\Gamma^S = I \quad (2.41)$$

$$\Gamma^V = \gamma^\mu \quad (2.42)$$

$$\Gamma^A = \gamma^5 \gamma^\mu \quad (2.43)$$

$$\Gamma^T = \sigma^{\mu\nu} = \frac{i}{2} [\gamma^\mu, \gamma^\nu] \quad (2.44)$$

$$\Gamma^P = \gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3, \quad (2.45)$$

Γ_k the covariant matrices and α_k the (real) dimensionless parameters that supply a measurement of parity violation [85, 86]. The term involving the unity is parity-even (parity-conserving Hamiltonian), while the term corresponding to $\alpha_k\gamma^5$ is parity-odd (parity-violating Hamiltonian).

Reformulating the previous equation as

$$\begin{aligned} \mathcal{H}_{int} = & C_S(\bar{\psi}_p\psi_n)[\bar{\psi}_e(1 + \alpha_S\gamma^5)\psi_\nu] + C_V(\bar{\psi}_p\gamma^\mu\psi_n)[\bar{\psi}_e(1 + \alpha_V\gamma^5)\gamma_\mu\psi_\nu] + \\ & C_A(\bar{\psi}_p\gamma^5\gamma^\mu\psi_n)[\bar{\psi}_e(1 + \alpha_A\gamma^5)\gamma^5\gamma_\mu\psi_\nu] + C_T(\bar{\psi}_p\sigma^{\mu\nu}\psi_n)[\bar{\psi}_e(1 + \alpha_T\gamma^5)\sigma_{\mu\nu}\psi_\nu] \end{aligned} \quad (2.46)$$

where the processes due to S, V couplings, mediated by the unit matrix, define the Fermi transitions, while the processes due to A, T couplings define the Gamow-Teller decays and the pseudo-scalar term does not contribute (in non-relativistic approximation),

"...the S and V couplings are effectively represented by the 2×2 unit matrix (i.e. a spin-zero transition operator), while the A and T couplings both lead to Pauli matrices and constitute thereby an effective transition operator carrying spin 1; these can therefore account for spin-changing Gamow-Teller processes..."[83]

we obtain, taking in mind that

$$C_S C_V (1 - \alpha_S \alpha_V) = 0 \quad (2.47)$$

and

$$a_F = \frac{C_V^2(1 + \alpha_V^2) - C_S^2(1 + \alpha_S^2)}{C_V^2(1 + \alpha_V^2) + C_S^2(1 + \alpha_S^2)} = 1 \quad (2.48)$$

that $C_S = 0$, similarly, for

$$C_A C_T (1 - \alpha_A \alpha_T) = 0 \quad (2.49)$$

and

$$a_{GT} = -\frac{1}{3} \frac{C_A^2(1 + \alpha_A^2) - 4C_T^2(1 + \alpha_T^2)}{C_A^2(1 + \alpha_A^2) + 4C_T^2(1 + \alpha_T^2)} = -\frac{1}{3} \quad (2.50)$$

we have $C_T = 0$. Conditions (2.47) and (2.49) are due to the absence of the Fierz interference term, the term proportional to $\frac{m_e}{E_e}$ (ratio of electron mass to energy) in the equation

$$\frac{d\lambda_F}{dE_e} = \frac{1}{2\pi^3} \left[C_S^2(1+\alpha_S^2) + C_V^2(1+\alpha_V^2) + 2C_S C_V(1-\alpha_S\alpha_V) \frac{m_e}{E_e} \right] |\mathbf{k}_e| E_e (E_e^{max} - E_e)^2 \quad (2.51)$$

that describes the electron energy spectrum (differential decay rate) for Fermi transitions with E_e^{max} the endpoint of the spectrum and $\mathbf{k}_e$ the electron momentum. The Fierz term is consistent with zero for both the spin-conserving (Fermi) and spin-changing (Gamow-Teller) transitions, consequently

$$C_S C_V(1 - \alpha_S \alpha_V) = 0 \quad (2.52)$$

from which $C_S = 0, C_V = 0$ or $1 - \alpha_S \alpha_V = 0$ and

$$C_A C_T(1 - \alpha_A \alpha_T) = 0 \quad (2.53)$$

(from the analogous equation (2.51) for Gamow-Teller decays) from which it follows that $C_A = 0, C_T = 0$ or $1 - \alpha_A \alpha_T = 0$. As regards expressions (2.48) and (2.50), the latter are derived from the calculation of lepton angular distribution. Analyzing the angular correlations

$$\frac{d\lambda_F}{d\Omega} = const. \times (1 + a_F \beta_e \cos\theta_l) \quad (2.54)$$

for Fermi transitions and

$$\frac{d\lambda_{GT}}{d\Omega} = const. \times (1 + a_{GT} \beta_e \cos\theta_l) \quad (2.55)$$

for Gamow-Teller transitions with $d\Omega$ an element of solid angle, β_e the electron velocity and θ_l the angle between the directions of lepton (electron and antineutrino) momenta, we have that

$$a_F = \frac{C_V^2(1 + \alpha_V^2) - C_S^2(1 + \alpha_S^2)}{C_V^2(1 + \alpha_V^2) + C_S^2(1 + \alpha_S^2)} \quad (2.56)$$

and

$$a_{GT} = -\frac{1}{3} \frac{C_A^2(1 + \alpha_A^2) - 4C_T^2(1 + \alpha_T^2)}{C_A^2(1 + \alpha_A^2) + 4C_T^2(1 + \alpha_T^2)} \quad (2.57)$$

where a_F and a_{GT} are the respective correlation coefficients. These coefficients, as demonstrated experimentally, are equal to $a_F = 1$ and $a_{GT} = -\frac{1}{3}$, consequently

$$2C_S^2(1 + \alpha_S^2) = 0 \quad (2.58)$$

and

$$8C_T^2(1 + \alpha_T^2) = 0. \quad (2.59)$$

From the measurement of the degree of longitudinal polarization (helicity), we obtain

$$\alpha_A = \alpha_V = 1 \quad (2.60)$$

from which, defining

$$x = \frac{C_A}{C_V}, \quad C_V = \frac{G_F}{\sqrt{2}} \quad (2.61)$$

with G_F the Fermi constant, we conclude that

$$\mathcal{H}_{int} = \frac{G_F}{\sqrt{2}} [\bar{\psi}_p \gamma^\mu (1 - x\gamma^5) \psi_n] [\bar{\psi}_e \gamma_\mu (1 - \gamma^5) \psi_\nu] + h.c. \quad (2.62)$$

with $[\bar{\psi}_p \gamma^\mu (1 - x\gamma^5) \psi_n]$ the hadronic current and $[\bar{\psi}_e \gamma_\mu (1 - \gamma^5) \psi_\nu]$ the leptonic current (combinations of Lorentz vectors and axial vectors)¹¹.

Constraints (2.60) represent a consequence of parity violation in electroweak interactions. Consider the degree of longitudinal lepton polarization

$$P_l = \frac{N_R - N_L}{N_R + N_L} \quad (2.63)$$

with N_R the number of right-handed (positive helicity) electrons and N_L the number of left-handed (negative helicity) electrons, we obtain, computing equation (2.63) for only the vector (V) and axial vector (A) terms, that

$$P_l^V = -\frac{2\alpha_V}{1 + \alpha_V^2} \beta_e \quad (2.64)$$

¹¹In the original Fermi's theory the four-fermion interaction was described as a contact coupling (zero range) of two currents, bilinear combinations of four-component spinor fields (Lorentz four-vectors), in analogy with electromagnetic current. Today, we know that the weak force is mediated by bosons ($W_\pm$ and Z_0) [87].

and

$$P_l^A = -\frac{2\alpha_A}{1 + \alpha_A^2}\beta_e \quad (2.65)$$

from which, comparing the results (2.64) and (2.65) with the experimental data

$$P_l^{exp} = -\beta_e, \quad (2.66)$$

we conclude that

$$\alpha_A = \alpha_V = 1. \quad (2.67)$$

”...If an asymmetry between N_R and N_L appears in the case of unpolarized initial nucleons, it can only be accounted for by an intrinsic parity violation...”[83].

From equation (2.62) will begin our discussion concerning the Dirac-Hartree-Fock (DHF) method implemented, in this last case, using radial basis sets. The radial mesh approach, differently from the first one (Hermite Gaussian functions approach), is the most suitable for the study of spherical symmetric systems. Assuming a β -decaying system like as a unique isolated nucleus surrounded by electrons, it is possible to approximate the latter to a spherical symmetric problem. The relativistic radial mesh approach, indeed, was employed for the analysis of weak interaction processes, nuclear β decays, protagonists of the last pages of this chapter. What is reported, in particular, will refer to [14, 18]. With regard to this last subsection, for further details reference [83] (chapter 1).

2.2 The radial mesh approach

The Dirac-Hartree-Fock (DHF) equation (1.70) for spherical symmetric problems can be expressed as

$$\frac{d\Psi}{dr} = F_E(\Psi, r) \quad (2.68)$$

with Ψ a two-component vector,

$$F_E(\Psi, r) = A(r)\Psi \quad (2.69)$$

a linear function of the energy E and vector Ψ and finally $A(r)$ a (2×2) linear operator.

Specifically, the solutions of the DHF equation in spherical symmetry

$$H\Psi_{\alpha,\kappa,m}(\mathbf{r}) = E_{\alpha,\kappa}\Psi_{\alpha,\kappa,m}(\mathbf{r}), \quad (2.70)$$

in accordance with

$$\Psi_{\alpha,\kappa,m}(\mathbf{r}) = \begin{pmatrix} \Psi_{\alpha,\kappa,L}(r)\chi_{\kappa,m}(\theta, \phi) \\ \Psi_{\alpha,\kappa,S}(r)\chi_{-\kappa,m}(\theta, \phi) \end{pmatrix}, \quad (2.71)$$

can be defined as the product of radial and angular functions

$$\Psi_{\kappa,m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} u_{\kappa}(r)\chi_{\kappa,m}(\Omega) \\ iv_{\kappa}(r)\chi_{-\kappa,m}(\Omega) \end{pmatrix} \quad (2.72)$$

with $u_{\kappa}(r)$ and $v_{\kappa}(r)$ the radial functions and $\chi_{\kappa,m}$ the tensor product of orbital and spin spherical harmonics featured by the quantum numbers κ and m . For further details reference [88] (chapter 6).

The Hartree potential (1.81)

$$V_H(\mathbf{r}) = \int d^3r' Tr[\rho_{LL}(\mathbf{r}', \mathbf{r}') + \rho_{SS}(\mathbf{r}', \mathbf{r}')]g_V(\mathbf{r}, \mathbf{r}'), \quad (2.73)$$

consequently, can be rewritten as

$$V_H(\mathbf{r}) = \int dr' r'^2 g_{V,l}(r_{<}, r_{>}) \sum_{\alpha,\kappa} n(E_{\alpha,\kappa}) [|\Psi_{\alpha,\kappa,L}(r')|^2 + |\Psi_{\alpha,\kappa,S}(r')|^2] \quad (2.74)$$

and similarly equation (1.82)

$$V_{HS}(\mathbf{r}) = \int d^3r' Tr[\rho_{LL}(\mathbf{r}', \mathbf{r}') - \rho_{SS}(\mathbf{r}', \mathbf{r}')]g_S(\mathbf{r}, \mathbf{r}') \quad (2.75)$$

can be expressed as

$$= \int dr' r'^2 g_{S,l}(r_{<}, r_{>}) \sum_{\alpha,\kappa} n(E_{\alpha,\kappa}) [|\Psi_{\alpha,\kappa,L}(r')|^2 - |\Psi_{\alpha,\kappa,S}(r')|^2] \quad (2.76)$$

where

$$g_{V,S}(\mathbf{r}, \mathbf{r}') = g_{V,S}(|\mathbf{r} - \mathbf{r}'|) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} g_{V,S,l}(r_{<}, r_{>}) \sum_{m=-l}^l Y_{l,m}^*(\theta, \phi) Y_{l,m}(\theta', \phi') \quad (2.77)$$

with $Y_{l,m}$ the spherical harmonics, $r_{<} = \min(r, r')$, $r_{>} = \max(r, r')$ and the function

$$n(E_{\alpha,\kappa}) = \frac{1}{e^{(E_{\alpha,\kappa}-\mu)/(K_B T)} + 1} \quad (2.78)$$

the Fermi-Dirac (FD) distribution (grand canonical ensemble) in terms of the eigenvalues $E_{\alpha,\kappa}$, the chemical potential μ , the Boltzmann constant K_B and the temperature T .

As regards equation (1.84), the Fock potential, the latter becomes

$$V_F(\mathbf{r}', \mathbf{r}) = \begin{pmatrix} \rho_{LL}(\mathbf{r}', \mathbf{r}) & \rho_{LS}(\mathbf{r}', \mathbf{r}) \\ \rho_{SL}(\mathbf{r}', \mathbf{r}) & \rho_{SS}(\mathbf{r}', \mathbf{r}) \end{pmatrix} g_V(\mathbf{r}, \mathbf{r}') \quad (2.79)$$

with

$$\rho(\mathbf{r}', \mathbf{r}) = \sum_{\alpha,\kappa,m} n(E_{\alpha,\kappa}) \begin{pmatrix} \Psi_{\alpha,\kappa,L}(r') \chi_{\kappa,m}(\theta', \phi') \\ \Psi_{\alpha,\kappa,S}(r') \chi_{-\kappa,m}(\theta', \phi') \end{pmatrix} \begin{pmatrix} \Psi_{\alpha,\kappa,L}^*(r) \chi_{\kappa,m}^+(\theta, \phi) & \Psi_{\alpha,\kappa,S}^*(r) \chi_{-\kappa,m}^+(\theta, \phi) \end{pmatrix} \quad (2.80)$$

from which, writing the diagonal term as

$$\begin{aligned} & \int d^3r \rho_{LL}(\mathbf{r}', \mathbf{r}) g_V(\mathbf{r}, \mathbf{r}') \Psi(r) \chi_{\kappa,m}(\theta, \phi) \\ &= \sum_{\alpha,\kappa',m'} n(E_{\alpha,\kappa'}) \Psi_{\alpha,\kappa',L}(r') \chi_{\kappa',m'}(\theta', \phi') \int d\Omega dr r^2 \Psi_{\alpha,\kappa',L}^*(r) \Psi(r) \chi_{\kappa',m'}^+(\theta, \phi) \chi_{\kappa,m}(\theta, \phi) \\ & \quad \times \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} f_{V,S,l}(r_{<}) h_{V,S,l}(r_{>}) Y_{l,m-m'}^*(\theta, \phi) Y_{l,m-m'}(\theta', \phi') \end{aligned} \quad (2.81)$$

and defining

$$\int d\Omega \chi_{\kappa_1,m_1}^+(\Omega) \chi_{\kappa_2,m_2}(\Omega) Y_{l,m}^*(\Omega)$$

$$= \sqrt{\frac{(2l+1)(2j_1+1)(2j_2+1)}{4\pi}} \delta_{m,m_2-m_1} (-1)^{m_2+1/2} \begin{pmatrix} j_2 & l & j_1 \\ -m_2 & m & m_1 \end{pmatrix} \begin{pmatrix} j_2 & l & j_1 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}, \quad (2.82)$$

we obtain, projecting on $\chi_{k',m'}$

$$\begin{aligned} & \int d\Omega' \chi_{\kappa',m'}^+(\theta', \phi') \int d^3r \rho_{LL}(\mathbf{r}', \mathbf{r}) g_V(\mathbf{r}, \mathbf{r}') \Psi(r) \chi_{\kappa,m}(\theta, \phi) \\ &= \sum_{\alpha, \kappa''} n(E_{\alpha, \kappa''}) \Psi_{\alpha, \kappa'', L}(r') \int dr r^2 \Psi_{\alpha, \kappa'', L}^*(r) \Psi(r) \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} f_{V,S,l}(r_{<}) h_{V,S,l}(r_{>}) \\ & \sum_{m''}^{\infty} F_{m'',m,m-m''}^{\kappa'',\kappa,l} F_{m'',m',m-m''}^{\kappa'',\kappa',l} = \sum_{\alpha, \kappa''} n(E_{\alpha, \kappa''}) \Psi_{\alpha, \kappa'', L}(r') \int dr r^2 \Psi_{\alpha, \kappa'', L}^*(r) \Psi(r) \\ & \sum_{l=0}^{\infty} f_{V,S,l}(r_{<}) h_{V,S,l}(r_{>}) \frac{|\kappa''|}{2l+1} \delta_{\kappa', \kappa} \end{aligned} \quad (2.83)$$

where the angular eigenfunctions satisfy the completeness relation

$$\sum_m \frac{4\pi}{2l+1} \int d\Omega' \chi_{\kappa,m}^+(\theta', \phi') \chi_{\kappa,m}(\theta', \phi') Y_{l,0}^*(\theta', \phi') = 2 |\kappa| \sqrt{4\pi} \delta_{l0}. \quad (2.84)$$

Applying the same procedure, we compute expressions for ρ_{SS} , ρ_{SL} and ρ_{LS} in order to determine the potential terms of the DHF equation.

At this point, considering a many-body system (fermions) interacting via a mean-field (MF), we redefine equation (2.68) replacing the non-local Fock term (2.79) of the function F_E with

$$V^{ex} = \frac{9}{4} \left[\frac{3}{\pi} \rho(r) \right]^{1/3} \quad (2.85)$$

(local density approximation) where $\rho(r)$ represents the electronic density and taking into account expression (2.72), we rewrite the DHF equation as

$$\frac{\partial}{\partial r} \begin{pmatrix} u_{\kappa}(r) \\ v_{\kappa}(r) \end{pmatrix} = \begin{pmatrix} -\frac{\kappa}{r} & \frac{E}{c} - \frac{V(r)}{c} + c \\ -\frac{E}{c} + \frac{V(r)}{c} + c & \frac{\kappa}{r} \end{pmatrix} \begin{pmatrix} u_{\kappa}(r) \\ v_{\kappa}(r) \end{pmatrix} \quad (2.86)$$

with

$$V(r) = -\frac{Z}{r} + \int d^3r' \frac{\rho(r')}{r_{>}} - V^{ex}(r) \quad (2.87)$$

the total potential dependent only on the radial coordinate modulus r and rotational invariant (Z is the proton number). To solve (self-consistently) equation (2.86), where the eigenvalues constitute the electron binding energies, we employ a radial basis function collocation method (modified Runge-Kutta method), which consists of spatial discretization using a grid of points, called collocation points [89]. The method can be schematized as follows:

- we divide the interval $[0, R]$, in which we look for the solution, into a certain number of points $[0 = r_0, \dots, r_N = R]$;
- we discretize each subinterval $[r_{j-1}, r_j]$ using s_j points $\{x_{j,l}\}$, in which the derivative $\frac{d\Psi}{dr}$ is approximated by

$$\frac{d\Psi}{dr} \simeq \sum_{l=1}^{s_j} q_{j,l} \varphi'_{j,l}(r); \quad (2.88)$$

- we determine, integrating the previous equation, the wave function, $\varphi'_{j,l}(x_{j,m}) = \delta_{lm}$,

$$\begin{aligned} \Psi(r) &= \Psi(r_{j-1}) + \int_{r_{j-1}}^r dx \sum_{l=1}^{s_j} q_{j,l} \varphi'_{j,l}(x) \\ &= \sum_{i=1}^{j-1} \sum_{l=1}^{s_i} q_{i,l} \int_{r_{i-1}}^{r_i} dx \varphi'_{i,l}(x) + \sum_{l=1}^{s_j} q_{j,l} \int_{r_{j-1}}^r dx \varphi'_{j,l}(x) \end{aligned} \quad (2.89)$$

from which, setting

$$\varphi_{j,l}(r) = \int_{r_{j-1}}^r dx \varphi'_{j,l}(x), \quad a_{j,lm} = \int_{r_{j-1}}^{x_{j,l}} dx \varphi'_{j,m}(x), \quad b_{j,l} = \int_{r_{j-1}}^{r_j} dx \varphi'_{j,l}(x), \quad (2.90)$$

we conclude that

$$\frac{d\Psi}{dr}(x_{j,l}) = q_{j,l} = F_E \left(\sum_{i=1}^{j-1} \sum_{l=1}^{s_i} b_{i,m} q_{i,m} + \sum_{l=1}^{s_j} a_{j,lm} q_{j,m}, x_{j,l} \right). \quad (2.91)$$

The DHF equation (2.86) can be, in turn, defined as an eigenvalue problem

$$[c\gamma Q + (V + \beta mc^2)AQ - EAQ]q' = 0 \quad (2.92)$$

where

$$A = \begin{pmatrix} a_1 & 0 & 0 & \cdots & 0 \\ b_1 & a_2 & 0 & \cdots & 0 \\ b_1 & b_2 & a_3 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ b_1 & b_2 & b_3 & \cdots & a_N \end{pmatrix} \quad (2.93)$$

was rewritten as a lower bi-diagonal matrix,

$$Q = \begin{pmatrix} 1 & 0 & \cdots & 0 & 0 & 0 \\ -b_2^{-1}b_1 & 1 & \cdots & 0 & 0 & 0 \\ 0 & -b_3^{-1}b_2 & \cdots & 1 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & -b_{N-1}^{-1}b_{N-2} & 1 & 0 \\ 0 & 0 & \cdots & 0 & 0 & 1 \end{pmatrix}, \quad (2.94)$$

γ and β two (2×2) matrices, $q' = Q^{-1}q$ and $\Psi = Aq = AQq'$, from which, applying a lower-diagonal-upper (LDU) decomposition [90], we determine the eigenvalues E .

The main advantages of the radial mesh approach lie in versatility and calculation accuracy, which can be systematically improved by infusing the grid (the error, indeed, is proportional to the step size, the distance between neighboring collocation points of the mesh). In the next section, we will describe the model, based on the newly introduced method, through which we analyzed β decays in terrestrial and astrophysical scenarios.

2.3 Applications

2.3.1 Nuclear decays in terrestrial and stellar scenarios

The method

We write the total Hamiltonian of the system as

$$H = H_{nucl} + H_e + H_{weak} \quad (2.95)$$

where H_{nucl} defines the nucleon-nucleon interaction, H_e the electron-electron Coulomb interaction and finally

$$H_{weak} = \int d^3r \mathcal{H}_{int}(\mathbf{r}) \int d^3r \frac{G_F}{\sqrt{2}} H^\mu(\mathbf{r}) L_\mu(\mathbf{r}) \quad (2.96)$$

the weak interaction (Lorentz invariant), which is, in turn, expressed as the product of the hadronic current

$$H^\mu(\mathbf{r}) = \bar{\Psi}_p(\mathbf{r}) \gamma^\mu (1 - x \gamma^5) \Psi_n(\mathbf{r}) \quad (2.97)$$

and leptonic current

$$L_\mu(\mathbf{r}) = \bar{\Psi}_e(\mathbf{r}) \gamma_\mu (1 - \gamma^5) \Psi_\nu(\mathbf{r}) \quad (2.98)$$

with $G_F = 1.16637 \times 10^{-5} \text{ GeV}^{-2}$, $x = 1.26 \pm 0.02$ (ratio between the coupling constants C_A and C_V) and $\Psi_f(\mathbf{r})$ ($f = p, n, e, \nu$) the fermionic field operators. Applying the Fermi golden rule

$$\Lambda_{i \rightarrow f} = 2\pi \frac{|\langle i | H_{weak} | f \rangle|^2}{\langle i | i \rangle \langle f | f \rangle} \delta(E_i - E_f) \quad (2.99)$$

($\langle i | H_{weak} | f \rangle$ is called the transition matrix element [68]) and, in particular, the equation

$$\Lambda_{i \rightarrow f} = 2\pi Tr(\hat{\rho}_i H_{weak} P_f H_{weak}) \delta(E_i - E_f) + h.c., \quad (2.100)$$

we compute the transition probability per unit time (transition rate) from a statistical mixture of initial states ($\hat{\rho}_i = p_i |i\rangle \langle i|$) to a mixture of final states ($\hat{\rho}_f = p_f |f\rangle \langle f|$), in which the initial $|i\rangle$ and final $|f\rangle$ states are defined respectively as

$$|i\rangle = |h_i\rangle \otimes |e_i\rangle \quad (2.101)$$

and

$$|f\rangle = |h_f\rangle \otimes |e_f\rangle \otimes |\bar{\nu}_f\rangle. \quad (2.102)$$

Specifically, $P_f = \sum_f |f\rangle \langle f|$ represents the projector onto the final states, $|h_{i,f}\rangle$ the initial and final multi-nucleon states featured by the quantum numbers $|J_{i,f}, M_{i,f}, T_{i,f}\rangle_{nucl}$ with $J_{i,f}$ the total angular momentum, $M_{i,f}$ the pro-

jection of $J_{i,f}$ on a fixed axis of the states and $T_{i,f}$ the isospin. As regards $|e_i\rangle$, the initial multi-electron state, the latter is defined as

$$|e_i\rangle = |j_i, m_i; [n_1^b \cdots n_k^b]_i\rangle_e \quad (2.103)$$

with $[n_1^b \cdots n_k^b]_{i,f}$ the bound orbitals, while $|\bar{\nu}_f\rangle$ represents the final antineutrino state. The $|h_{i,f}\rangle$ and $|e_i\rangle$ states are characterized by a discrete spectrum, on the contrary, the final multi-electron state

$$|e_f\rangle = \sum_j I_{j,f} \wedge |\eta_{j,f}\rangle \quad (2.104)$$

is a continuum state with $|\eta_{j,f}\rangle$ the β continuum wave function and $I_{j,f}$ the final bound state.

Within this framework, assuming that electrons and neutrinos are uncoupled, we factorize the leptonic current in the product of the electron and neutrino field operators (wave functions). For the hadronic current, similarly, we factorize the latter in the product of the proton and neutron field operators. In the model, in fact, it is assumed that a single nucleon of the parent nucleus is involved in the decay process and that the decaying nucleon acts as an independent particle correlated only geometrically to the core of remaining nucleons to recover the total angular momentum of the parent and daughter (the core is approximated by a linear combination of angular momentum wave functions). Analyzing the leptonic current $L_\mu(\mathbf{r})$, we define, bearing in mind equation (2.72), the neutrino wave function as

$$\Psi_\nu(\mathbf{r}) \equiv \Psi_{\kappa_\nu, m_\nu}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} k_\nu \sqrt{\frac{1}{\pi c}} j_{l_{\kappa_\nu}}(k_\nu r) \chi_{\kappa_\nu, m_\nu}(\Omega) \\ -i S_{\kappa_\nu} k_\nu \sqrt{\frac{1}{\pi c}} j_{l_{-\kappa_\nu}}(k_\nu r) \chi_{-\kappa_\nu, m_\nu}(\Omega) \end{pmatrix} \quad (2.105)$$

where

$$u_\kappa(r) = k_\nu \sqrt{\frac{1}{\pi c}} j_{l_{\kappa_\nu}}(k_\nu r) \quad (2.106)$$

and

$$v_\kappa(r) = -S_{\kappa_\nu} k_\nu \sqrt{\frac{1}{\pi c}} j_{l_{-\kappa_\nu}}(k_\nu r) \quad (2.107)$$

represent the energy-normalized wave functions, solution of the Dirac-Hartree-Fock (DHF) equation (2.86) for free particle. In the model, the massless antineutrino is treated as a free particle and the potential is set zero.

Concerning the electron wave function $\Psi_e(\mathbf{r})$, the latter is obtained by self-consistently solving the DHF equation (2.86) for electrons interacting through a central mean-field potential (2.87) where the non-local Fock exchange term is replaced by equation (2.85) for the electron gas. Keeping in mind, once again, equation (2.72) and considering that, asymptotically, when $V(r)$ is negligible, electrons can be dealt with as free particles, we write

$$u_\kappa(r) \simeq c_u \frac{\sin(kr - l_\kappa \frac{\pi}{2} + \phi)}{k} \quad (2.108)$$

and

$$v_\kappa(r) \simeq c_v \frac{\sin(x - l_{-\kappa} \frac{\pi}{2} + \phi)}{k} \quad (2.109)$$

with

$$c_u = k \sqrt{\frac{E + mc^2}{\pi E}} A, \quad c_v = k S_\kappa \sqrt{\frac{E - mc^2}{\pi E}} A \quad (2.110)$$

and

$$\frac{\pi}{2k^2} (|c_u|^2 + |c_v|^2) \delta(k - k') \quad (2.111)$$

the normalization condition.

In detail, to account for the atomic exchange (the Pauli exclusion principle), we define the continuum electron wave function, computed in the field produced by the nucleus and surrounding electrons, as the Slater determinant

$$\Psi_e(\mathbf{r}) = \begin{vmatrix} \langle n_{f,1}^b | n_{i,1}^b \rangle & \langle n_{f,1}^b | n_{i,2}^b \rangle & \dots & \langle n_{f,1}^b | n_{i,N}^b \rangle & n_{f,1}^b(r) \\ \langle n_{f,2}^b | n_{i,1}^b \rangle & \langle n_{f,2}^b | n_{i,2}^b \rangle & \dots & \langle n_{f,2}^b | n_{i,N}^b \rangle & n_{f,2}^b(r) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \langle n_{f,N}^b | n_{i,1}^b \rangle & \langle n_{f,N}^b | n_{i,2}^b \rangle & \dots & \langle n_{f,N}^b | n_{i,N}^b \rangle & n_{f,N}^b(r) \\ \langle \Psi_f^c | n_{i,1}^b \rangle & \langle \Psi_f^c | n_{i,2}^b \rangle & \dots & \langle \Psi_f^c | n_{i,N}^b \rangle & \Psi_f^c(r) \end{vmatrix}. \quad (2.112)$$

In this way, the non-orthogonality between the initial n_i^b and final n_f^b orbitals, obtained by resolving the DHF equation (2.86) for different atomic numbers (the parent and daughter nuclei are characterized by different atomic numbers), as well as the possible shake-up (excitation) and shake-off (ejection)

states are included in the model (Ψ_f^c represents the bare Coulomb wave function corrected for the non-orthogonality). The emitted particle can decay in a bound state of the daughter nuclide, causing the ejection of a secondary bound electron and final state excitations. These atomic effects can affect the decay rate, in particular, at low energy range, where the overlap between the discrete and continuum wave functions is maximum.

Concerning the hadronic current $H^\mu(\mathbf{r})$, the latter is determined by the numerical solution of the DHF equation (2.86), in which the nucleon-nucleon interaction is modeled by a semi-empirical scalar and vector relativistic Wood-Saxon potential. The central (spherically symmetric) potential is defined as

$$V_C(r) = -V_C \left[1 + \exp\left(\frac{r-R}{a}\right) \right]^{-1} \quad (2.113)$$

with

$$V_C = V_0 \left(1 \pm \sigma \frac{N-Z}{A} \right) \quad (2.114)$$

the total strength (isospin-dependent), $R = R_0 A^{1/3}$ the nuclear radius (range of nuclear potential), A the mass number, N the neutron number, Z the proton number, a a constant, which represents the nuclear surface diffuseness, and σ a parameter. To reproduce the nuclear force, we introduce the spin-orbit term

$$\tilde{V}_{SO}(r) = \tilde{V}_{SO} \left[1 + \exp\left(\frac{r-R_{SO}}{a_{SO}}\right) \right]^{-1} \quad (2.115)$$

where $\tilde{V}_{SO} = \lambda V_C$ is the interaction strength, λ a constant of proportionality, $R_{SO} = R_{0,SO} A^{1/3}$ the radius and finally a_{SO} a constant, which defines the diffuseness of the spin-orbit term.

The ab initio calculation of the leptonic and hadronic currents through the real-space grid method (section 2.2) is essential in order to determine the transition probability, described by equation (2.100). The results obtained in terrestrial and stellar scenarios are discussed in the next section, in which the electron capture of ${}^7_4\text{Be}$, the β^+ decay of ${}^{18}_9\text{F}$ and the β^- decays of ${}^{14}_6\text{C}$, ${}^{63}_{28}\text{Ni}$, ${}^{79}_{34}\text{Se}$, ${}^{85}_{36}\text{Kr}$, ${}^{87}_{37}\text{Rb}$, ${}^{93}_{40}\text{Zr}$, ${}^{94}_{41}\text{Nb}$ and ${}^{176}_{71}\text{Lu}$ will be analyzed.

In the approach, based on the nuclear shell model, we assume that the electron energy levels are populated in accordance with the Fermi-Dirac (FD) distribu-

tion

$$n_e = \frac{1}{e^{(\epsilon_i - \mu_e)/(K_B T)} + 1} = F(T, \mu_e) \quad (2.116)$$

where ϵ_i represent the eigenvalues (the energies of the levels i) derived from the self-consistent solution of the DHF equation for electrons and μ_e the chemical potential computed assuming that leptons behave as an ideal Fermi gas in a box with the relativistic dispersion relation $E^2 = c^2 p^2 + m_e^2 c^4$, from which

$$n_e = \int_0^\infty dp \frac{p^2}{\pi^2} \times \left\{ F \left[\frac{(c \times \sqrt{p^2 + m_e^2 c^2}) - \mu_e}{(K_B T)} \right] - F \left[\frac{(c \times \sqrt{p^2 + m_e^2 c^2}) + \mu_e}{(K_B T)} \right] \right\}. \quad (2.117)$$

Beta decays in terrestrial scenario

In the following pages, as stated, we will analyze the results for β decays obtained by means of the radial mesh approach, introduced in the previous section. In particular, in the first part, we will describe the results obtained in terrestrial scenario; in the second part, we will discuss the results obtained in stellar scenario. The nuclear decay data reported refer to [91], moreover, all terrestrial spectra are compared with the experimental data of [92].

In Figure 2.1 the β^- decay spectrum of $^{14}_6\text{C}$ is shown.

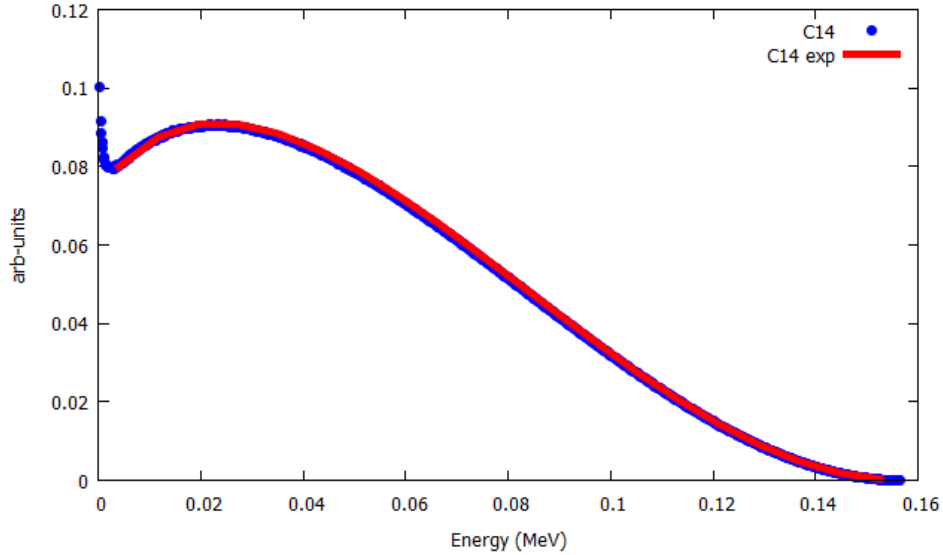


Figure 2.1: β decay spectrum of $^{14}_6\text{C}$. Experimental data (red line) from [92].

The $^{14}_6\text{C}$ (ground state), in configuration $0+$ (the total angular momentum is 0 and the parity is $\pi_i = +$), β^- decays to the ground state of $^{14}_7\text{N}$, in

configuration 1+ (the total angular momentum is 1 and the parity is $\pi_f = +$), with a probability of 100%



The allowed transition, analyzed in terrestrial scenario, is characterized by a Q -value of 156.475 keV and a half-life equal to 5700 years. Our theoretical simulation (blue dots) is in good agreement with the experimental data of [92] represented by the red line.

Concerning the β^+ decay (probability of 100%) of ${}^{18}_9\text{F}$ (ground state to ground state Q -value equal to 1655.50 keV and half-life equal to 109.77 minutes)



we determined the transition rate assuming that the parent nuclide ground state was in configuration 1+ (the total angular momentum is 1 and the parity is $\pi_i = +$) and the ground state of ${}^{18}_8\text{O}$ was in configuration 0+ (the total angular momentum is 0 and the parity is $\pi_f = +$). The results, obtained under Earth conditions, are reported in Figure 2.2, where our ab initio calculations (blue dots) are compared with the experimental measurements of [92] (red line).

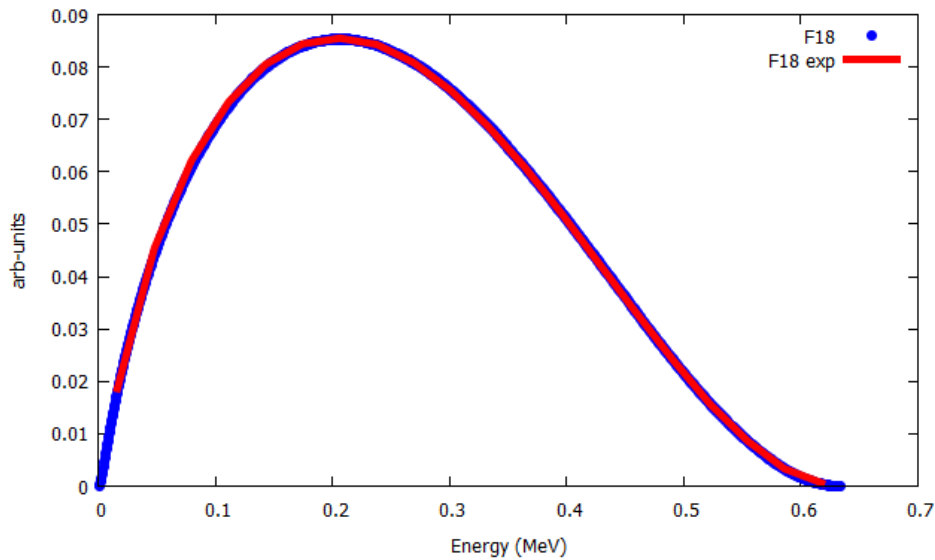
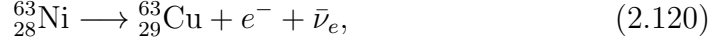


Figure 2.2: β decay spectrum of ${}^{18}_9\text{F}$. Experimental data (red line) from [92].

Once again, our allowed β spectrum is in good agreement with the experimental data.

For the calculation of the β^- decay rate of $^{63}_{28}\text{Ni}$



we considered the parent nuclide (ground state) in configuration $1/2^-$ (the total angular momentum is equal to $1/2$ and the parity is $\pi_i = -$) and the ground state of $^{63}_{29}\text{Cu}$ in configuration $3/2^-$ (the total angular momentum is equal to $3/2$ and the parity is $\pi_f = -$). The allowed transition (probability of 100%), at room conditions, is featured by a Q -value of 66.977 keV and a half-life of 100.8 years. The spectrum obtained, in agreement with the experimental data [92], is shown in Figure 2.3. The blue dots report the theoretical results, while the red line represents the experimental results.

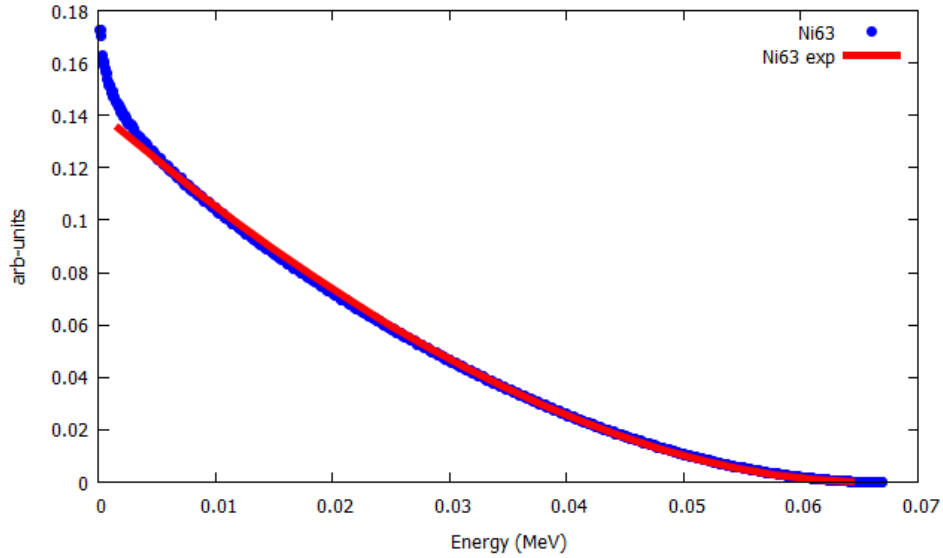


Figure 2.3: β decay spectrum of $^{63}_{28}\text{Ni}$. Experimental data (red line) from [92].

As regards the negative beta decay of $^{79}_{34}\text{Se}$



the latter (ground state), in configuration $7/2+$ (total angular momentum $7/2$ and parity $\pi_i = +$), decays to the ground state of $^{79}_{35}\text{Br}$, featured by the quantum number $3/2^-$ (total angular momentum $3/2$ and parity $\pi_f = -$),

with a probability of 100%. The forbidden transition (Q -value equal to 150.6 keV and half-life of 3.26×10^5 years) was analyzed in terrestrial scenario. In Figure 2.4 the theoretical (blue dots) and experimental [92] (red line) results are reported.

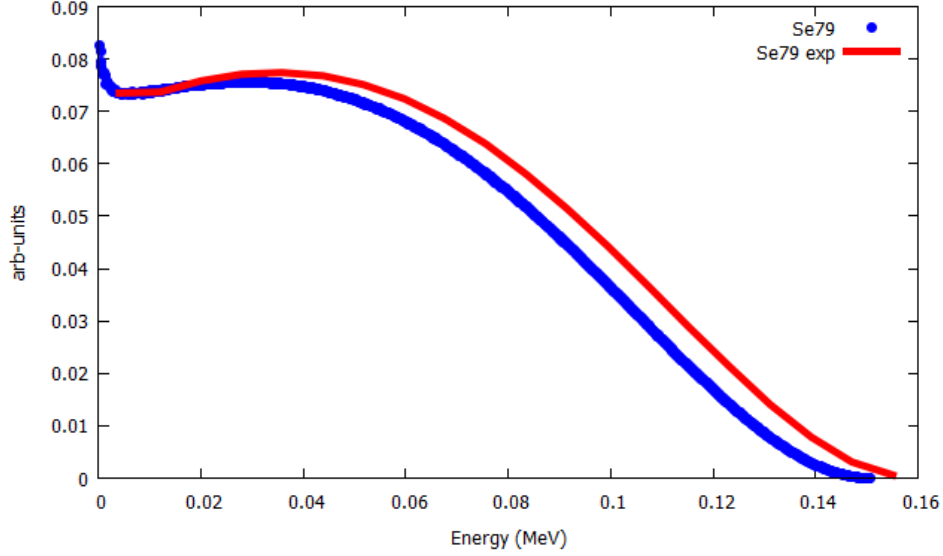


Figure 2.4: β decay spectrum of $^{79}_{34}\text{Se}$. Experimental data (red line) from [92].

Figures 2.5a and 2.5b show the decay spectra of $^{85}_{36}\text{Kr}$.

The $^{85}_{36}\text{Kr}$ β^- decays to $^{85}_{37}\text{Rb}$

$$^{85}_{36}\text{Kr} \longrightarrow ^{85}_{37}\text{Rb} + e^- + \bar{\nu}_e. \quad (2.122)$$

In particular, we determined the ground-to-ground beta decay spectrum at room conditions (Figure 2.5a) assuming that the parent nuclide (ground state) was in configuration $9/2+$ (total angular momentum equal to $9/2$ and parity $\pi_i = +$) and the daughter nuclide (ground state) was in configuration $5/2-$ (total angular momentum $5/2$ and parity $\pi_f = -$). The forbidden transition (probability of 99.563%) is characterized by a ground state to a ground state Q -value of 687.0 keV and a half-life equal to 10.739 years.

Concerning the calculation of the excited-to-excited beta spectrum (Figure 2.5b), we considered the first excited state of $^{85}_{36}\text{Kr}$, at 304.87 keV, in configuration $1/2-$ (total angular momentum equal to $1/2$ and parity $\pi_i = -$) and the first excited state of $^{85}_{37}\text{Rb}$, at 151.19 keV, in configuration $3/2-$ (total angular momentum equal to $3/2$ and parity $\pi_f = -$). The allowed transition (proba-

bility of 78.5% and half-life of 4.480 hours) was analyzed in terrestrial scenario. Both simulations (blue dots) were compared with the data (red lines) reported in [92]. Our results are in good agreement with the experimental measurements.

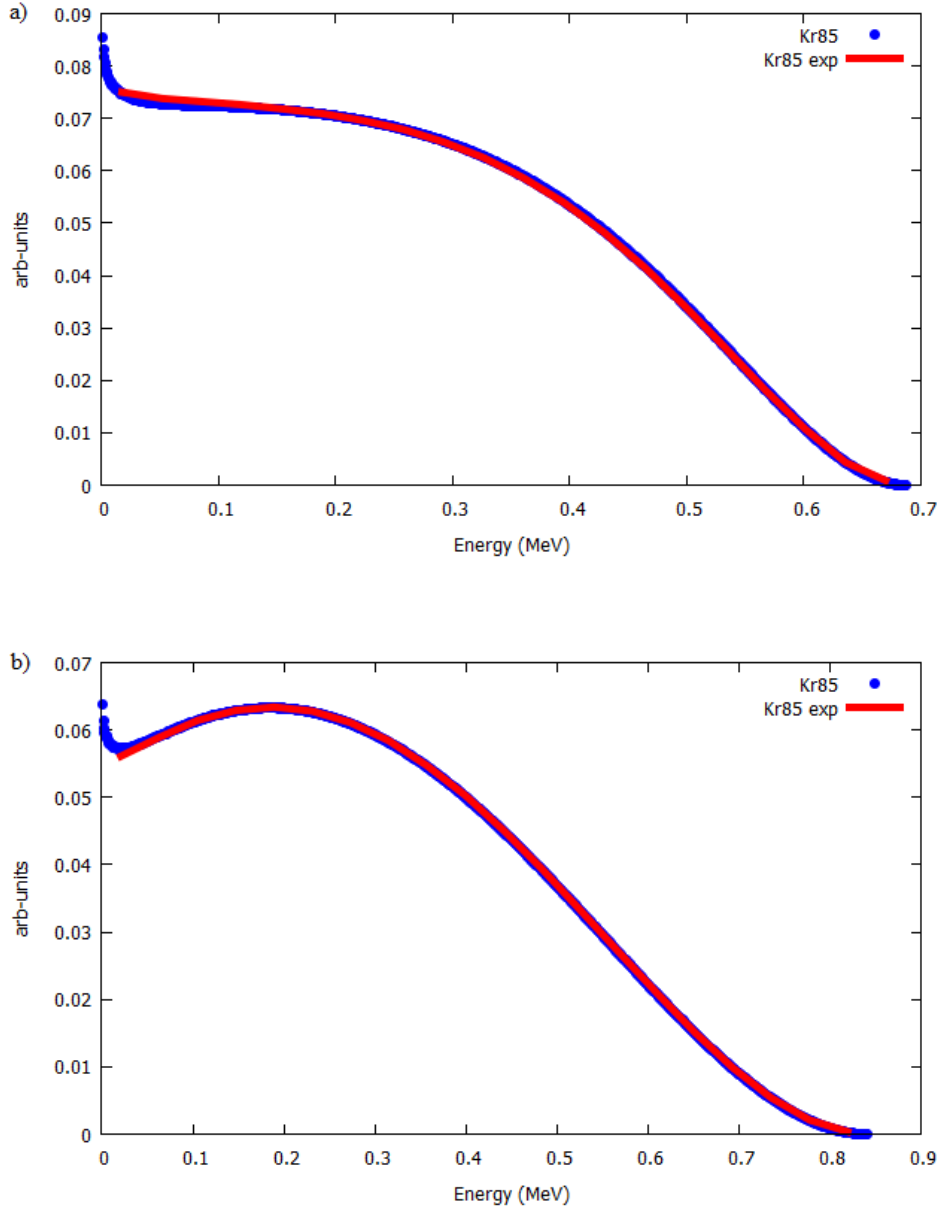
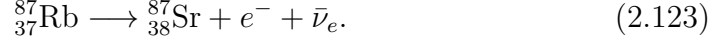


Figure 2.5: β decay spectra of ^{85}Kr . Experimental data (red lines) from [92].

For the β^- decay spectrum of ^{87}Rb , Figure 2.6, the calculations were performed under Earth conditions. The parent nuclide (ground state), which decays to ground state of ^{87}Sr with a probability of 100%, is characterized by the quantum number $3/2^-$ (the total angular momentum is equal to $3/2$ and the

parity is $\pi_i = -$), while the ground state of the daughter is in configuration $9/2+$ (total angular momentum equal to $9/2$ and parity $\pi_f = +$)



The transition is a forbidden transition with a Q -value of 282.2 keV and a half-life equal to 4.97×10^{10} years. In Figure 2.6, we compared our theoretical results (blue dots) with the experimental data [92] (red line).

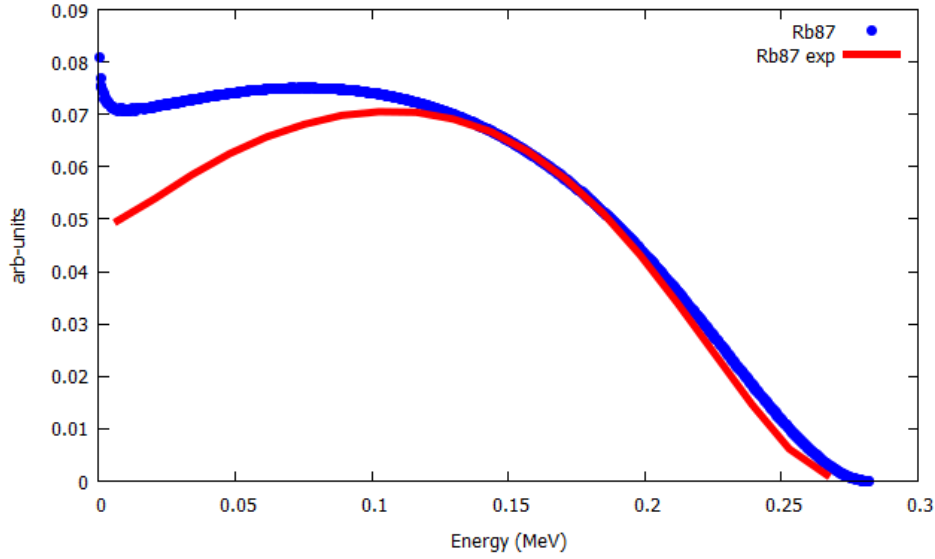
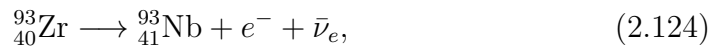


Figure 2.6: β decay spectrum of ${}^{87}_{37}\text{Rb}$. Experimental data (red line) from [92].

Concerning the β^- decay of ${}^{93}_{40}\text{Zr}$



we calculated the ground-to-excited decay spectrum (at room conditions) assuming that the parent nuclide was in configuration $5/2+$ (total angular momentum $5/2$ and parity $\pi_i = +$) and the daughter nuclide (first excited state at 30.8 keV) was in configuration $1/2-$ (total angular momentum $1/2$ and parity $\pi_f = -$). The forbidden transition, with probability of 73%, is featured by a ground state to a ground state Q -value equal to 90.8 keV and a half-life of 1.61×10^6 years.

In Figure 2.7 the comparison between our theoretical (blue dots) and experimental [92] (red line) spectra.

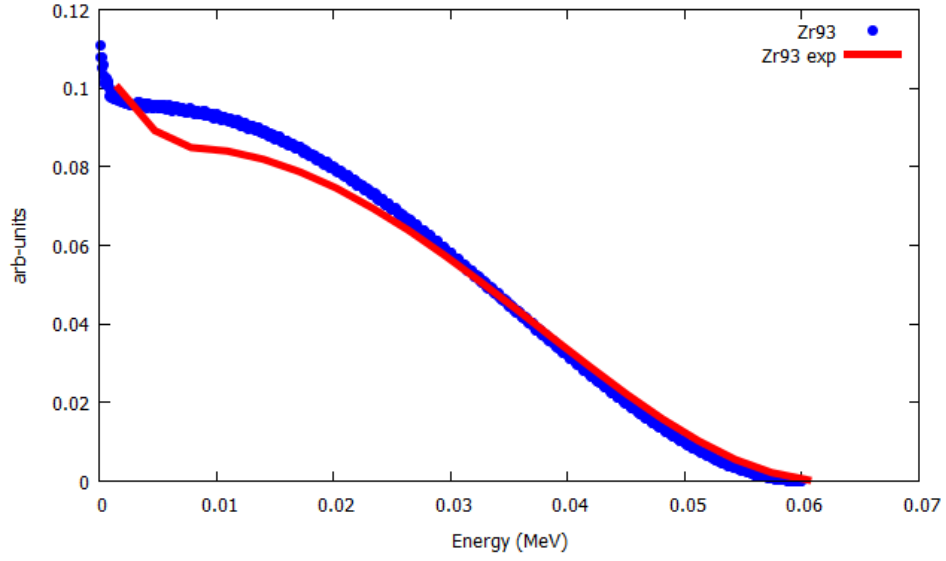


Figure 2.7: β decay spectrum of $^{93}_{40}\text{Zr}$. Experimental data (red line) from [92].

As regards the $^{94}_{41}\text{Nb}$, the latter β^- decays to $^{94}_{42}\text{Mo}$

$$^{94}_{41}\text{Nb} \longrightarrow ^{94}_{42}\text{Mo} + e^- + \bar{\nu}_e. \quad (2.125)$$

Specifically, we analyzed, in terrestrial scenario, the decay process from the ground state of $^{94}_{41}\text{Nb}$, in configuration $6+$ (total angular momentum equal to 6 and parity $\pi_i = +$), to the second excited state of $^{94}_{42}\text{Mo}$, at 1573.7 keV, in configuration $4+$ (total angular momentum 4 and parity $\pi_f = +$).

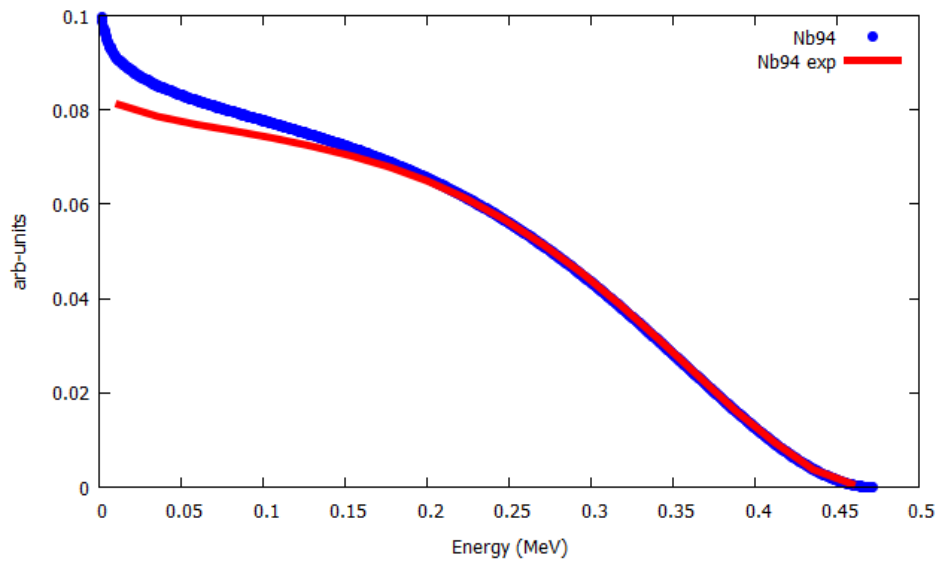


Figure 2.8: β decay spectrum of $^{94}_{41}\text{Nb}$. Experimental data (red line) from [92].

The forbidden transition (probability of 100%) is characterized by a ground state to a ground state Q -value of 2045.2 keV and a half-life of 2.03×10^4 years. The computed spectrum (blue dots), compared with the experimental data [92] (red line), is reported in Figure 2.8.

At least the decay spectra of $^{176}_{71}\text{Lu}$ (Figures 2.9a and 2.9b).

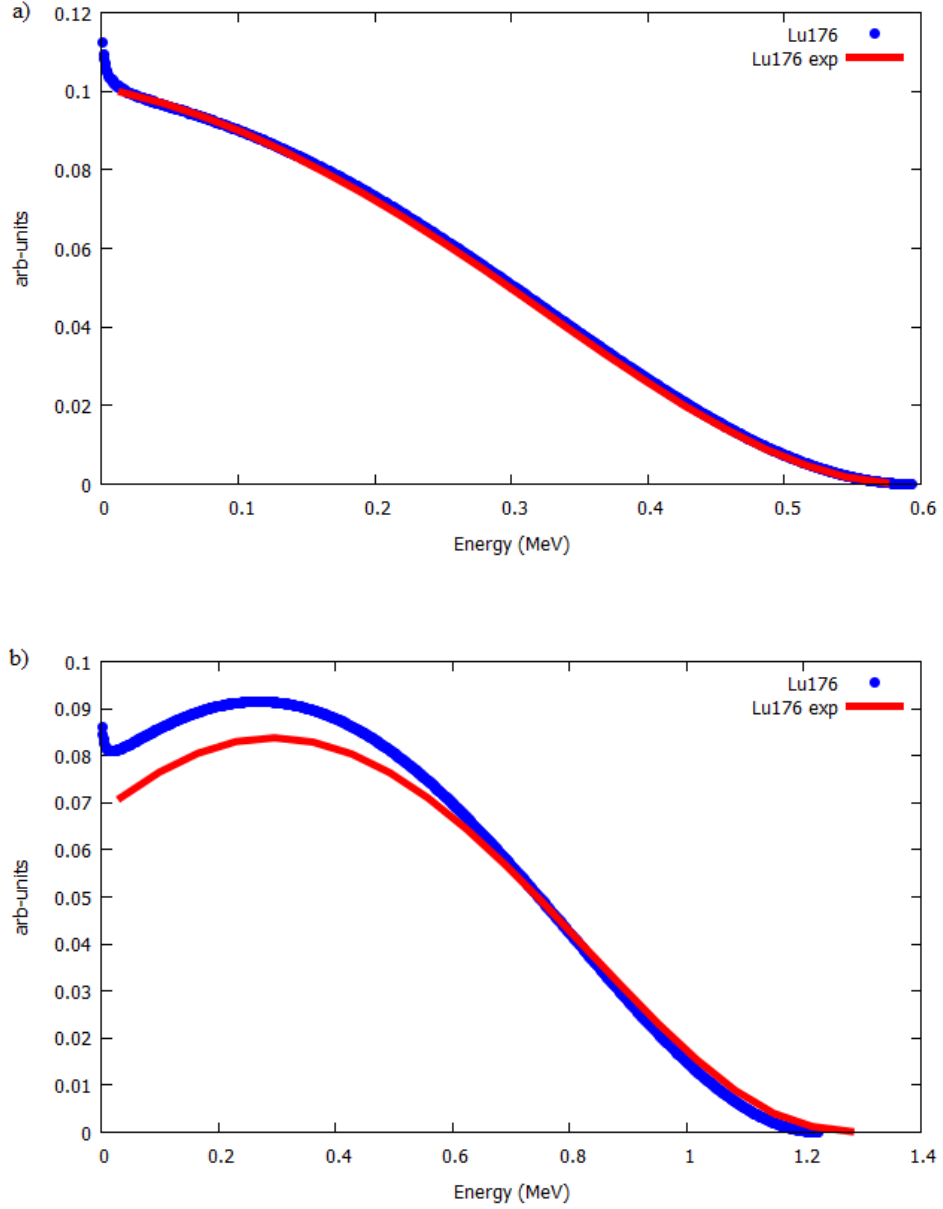


Figure 2.9: β decay spectra of $^{176}_{71}\text{Lu}$. Experimental data (red lines) from [92].

The $^{176}_{71}\text{Lu}$ β^- decays to $^{176}_{72}\text{Hf}$

$$^{176}_{71}\text{Lu} \longrightarrow ^{176}_{72}\text{Hf} + e^- + \bar{\nu}_e. \quad (2.126)$$

The parent nuclide ground state, in configuration $7-$ (total angular momentum equal to 7 and parity $\pi_i = -$), can decay to the third excited state of $^{176}_{72}\text{Hf}$, at 596.82 keV, with a probability of 99.61%. The excited state of $^{176}_{72}\text{Hf}$ is in configuration $6+$ (total angular momentum equal to 6 and parity $\pi_f = +$) and the transition, which is a forbidden transition, is characterized by a ground state to a ground state Q -value equal to 1190.2 keV and a half-life of 3.76×10^{10} years. On the contrary, the excited-to-excited decay is featured by a half-life of 3.664 hours and a probability of 61% (forbidden transition). In this case, we assumed the first excited state of $^{176}_{71}\text{Lu}$, at 122.845 keV, in configuration $1-$ (total angular momentum equal to 1 and parity $\pi_i = -$) and the first excited state of $^{176}_{72}\text{Hf}$, at 88.4 keV, in configuration $2+$ (total angular momentum equal to 2 and parity $\pi_f = +$). Both simulations (blue dots), analyzed in terrestrial scenario, were compared with the experimental results (red lines) reported in [92].

All processes discussed so far have been studied, as repeatedly stated, under Earth conditions. In the next section, as mentioned, we will describe the beta decays of ^7_4Be , $^{63}_{28}\text{Ni}$, $^{85}_{36}\text{Kr}$, $^{93}_{40}\text{Zr}$ and $^{176}_{71}\text{Lu}$ in stellar environment.

Beta decays in stellar scenario

An accurate assessment of nuclear decay rates in terrestrial and astrophysical scenarios is crucial for the development of diagnostic techniques such as positron emission tomography (PET) [93], for the implementation of radioactive dating methods [94] and to understand the nucleosynthesis in stars as well as the chemical evolution of the Universe, the objective of the INFN-PANDORA experiment, whose purpose is to measure beta decay rates in stellar-like conditions through the use of magnetized plasmas [95, 96, 97, 98]. Considering, first of all, the electron capture of ^7_4Be

$$^7_4\text{Be} + e^- \longrightarrow ^7_3\text{Li} + \nu_e, \quad (2.127)$$

the latter process (ground state to ground state Q -value equal to 861.815 keV and a half-life of 53.22 days) was analyzed assuming the parent nuclide (ground state) in configuration $3/2-$ (the total angular momentum is $3/2$ and

the parity is $\pi_i = -$) and the daughter nuclide in configuration $3/2-$ and $1/2-$. The ground state of ${}^7_3\text{Li}$ is characterized by a total angular momentum $3/2$ and parity $\pi_f = -$, while the first excited state of ${}^7_3\text{Li}$, at 477.6 keV, is characterized by a total angular momentum $1/2$ and parity $\pi_f = -$. The allowed transitions (the ground-to-ground decay with probability 89.56% and the ground-to-excited decay with probability 10.44%) were examined in stellar environment. The cumulative decay rate, as a function of temperature and electron density, is shown in Figure 2.10.

The electron temperature was varied in the range from 0.00001 to 1000 keV and the density in the range from 1×10^{24} to 1×10^{28} particles/cm³. The plasma is considered overall charge-neutral ($n_p = n_e - n_{e+}$, with n_p the proton density, n_e the electron density and n_{e+} the positron density) and protons are treated as non-relativistic particles¹².

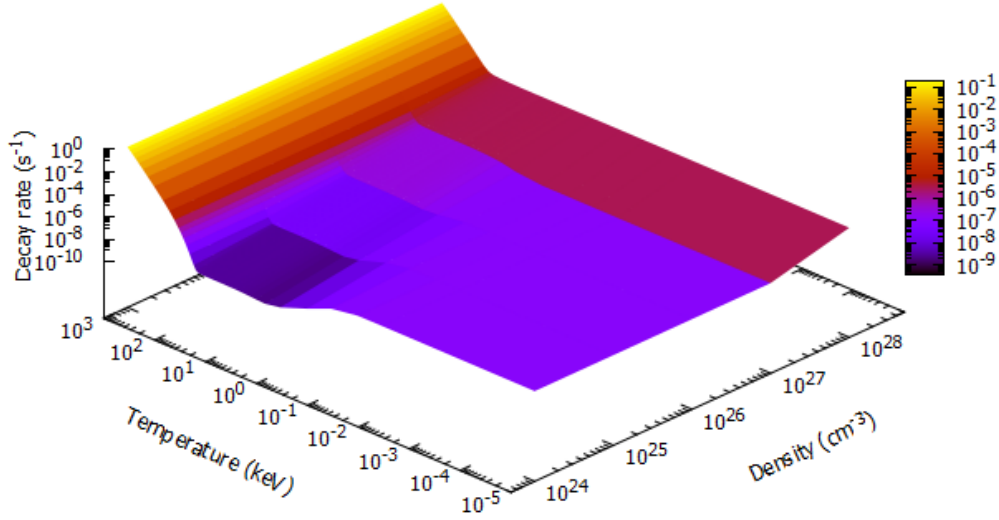


Figure 2.10: Decay rate of ${}^7_4\text{Be}$ as a function of temperature and density.

For the ground-to-ground β^- decay of ${}^{63}_{28}\text{Ni}$, assuming the same configurations introduced in the previous section, we calculate the transition rate, as a function of temperature and density, varying the temperature, once again, from 0.00001 to 1000 keV and the density from 1×10^{24} to 1×10^{28} particles/cm³.

¹²The conditions set out make it possible to characterize all stellar scenarios and processes, including a hydrogen burning stellar scenario or an Asymptotic Giant Branch (AGB) stellar environment [99].

The results obtained are reported in Figure 2.11.

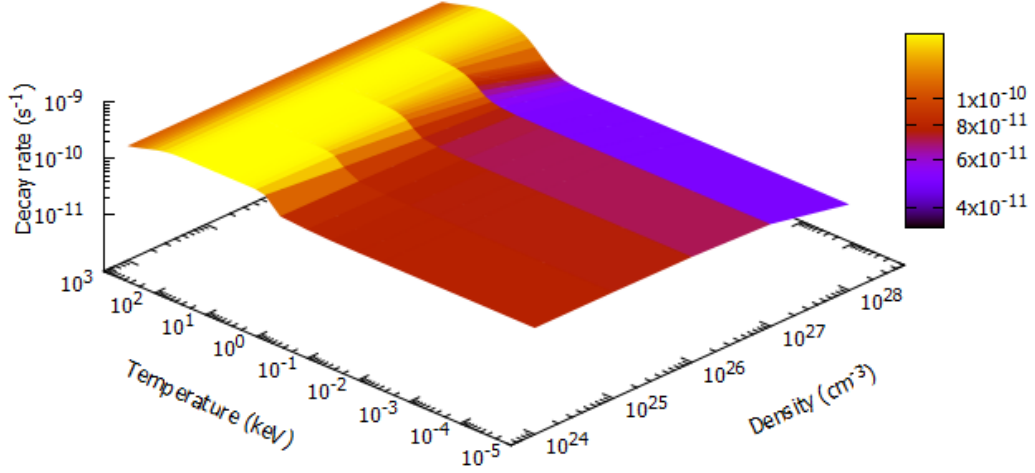
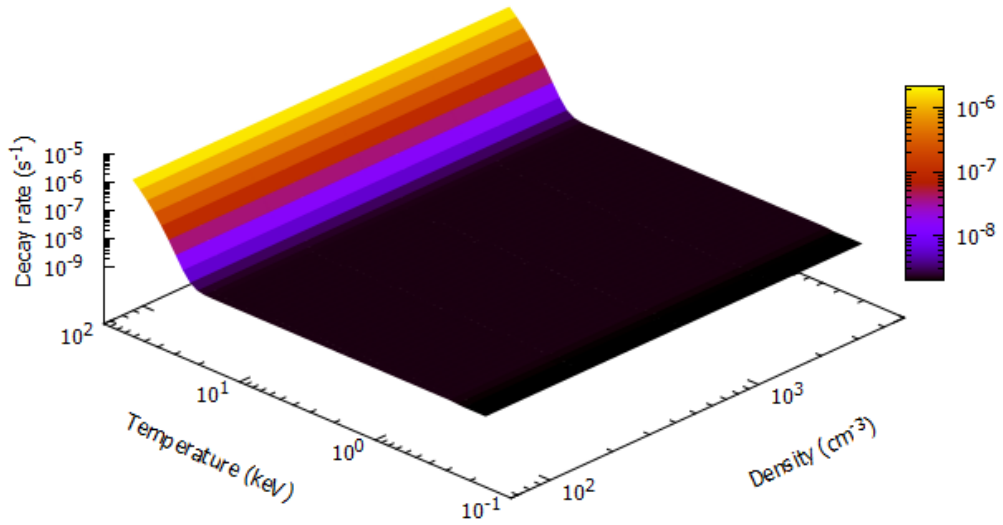


Figure 2.11: Decay rate of ^{63}Ni as a function of temperature and density.

Concerning the β^- decay of $^{85}_{36}\text{Kr}$, we have included two decay paths. The forbidden transition from the ground state of $^{85}_{36}\text{Kr}$ to the ground state of $^{85}_{37}\text{Rb}$ and the allowed transition from the excited state of $^{85}_{36}\text{Kr}$ to the excited state of $^{85}_{37}\text{Rb}$. The two nuclear processes, described in the previous section, were analyzed in astrophysical scenario, assuming the same configurations.

a)



b)

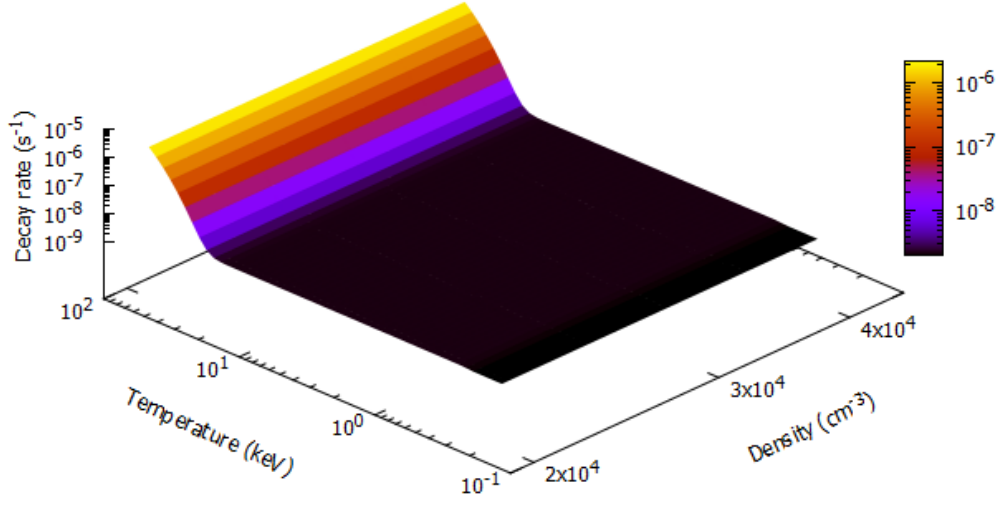


Figure 2.12: Decay rates of ^{85}Kr as a function of temperature and density.

In Figure 2.12a the density was varied from 70 to 4500 particles/ cm^3 and in Figure 2.12b the density was varied from 2×10^4 to 4×10^4 particles/ cm^3 . The temperature for both simulations is between 0.17 and 68.94 keV.

Regarding the negative beta decay of ^{93}Zr , as a function of temperature and electron density (Figure 2.13), we included, once more, two decay paths;

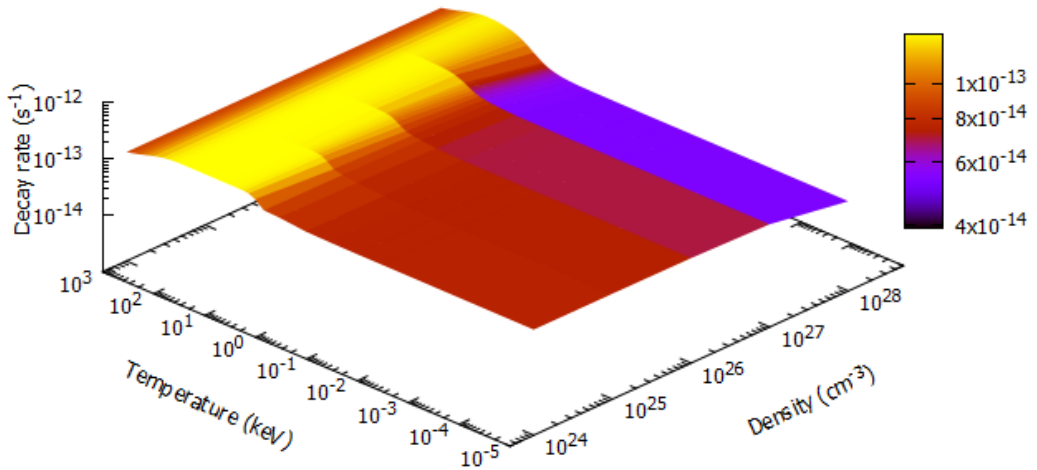


Figure 2.13: Decay rate of ^{93}Zr as a function of temperature and density.

the forbidden transition (probability of 27%) from the ground state of $^{93}_{40}\text{Zr}$ to the ground state of $^{93}_{41}\text{Nb}$ in configuration $9/2+$ (the total angular momentum is equal to $9/2$ and the parity is $\pi_f = +$) and the transition from the ground state of $^{93}_{40}\text{Zr}$ to the excited state of $^{93}_{41}\text{Nb}$, described previously. The temperature was varied in the range from 0.00001 to 1000 keV and the density from 1×10^{24} to 1×10^{28} particles/ cm^3 .

For the β^- decay of $^{176}_{71}\text{Lu}$, we included the transition from the ground state of $^{176}_{71}\text{Lu}$ to the excited state $6+$ of $^{176}_{72}\text{Hf}$ and the transition from the excited state $1-$ of $^{176}_{71}\text{Lu}$ to the excited state $2+$ of $^{176}_{72}\text{Hf}$. The cumulative rate obtained as a function of temperature and density is reported in Figure 2.14, where the temperature range is between 0.00001 and 1000 keV and the electron density range is between 1×10^{24} and 1×10^{28} particles/ cm^3 .

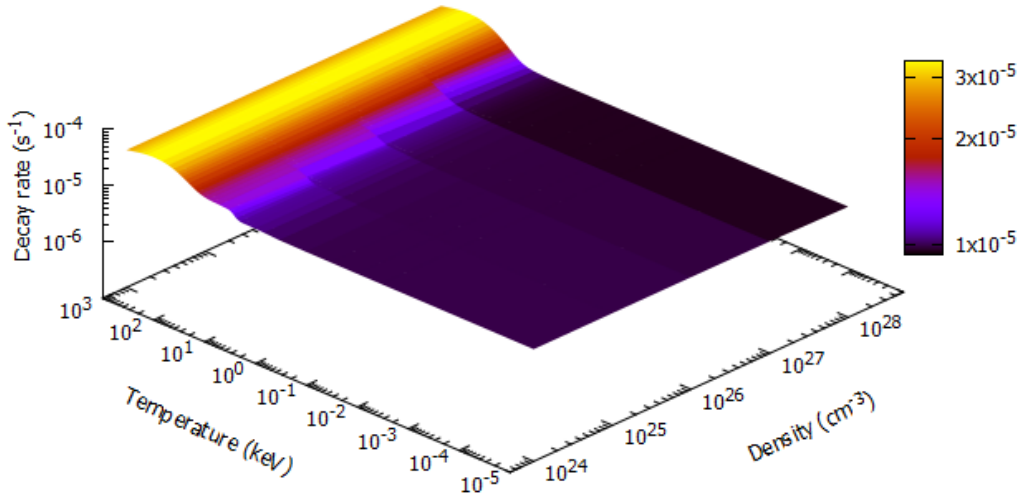


Figure 2.14: Decay rate of $^{176}_{71}\text{Lu}$ as a function of temperature and density.

Conclusions

As noted in previous pages, many of our simulations in terrestrial scenario are in good agreement with the experimental data [92], except for the decay spectra such as the ground-to-ground decay spectrum of $^{87}_{37}\text{Rb}$ or the excited-to-excited decay spectrum of $^{176}_{71}\text{Lu}$. The discrepancies that we observe between our ab initio calculations and experimental results can be attributed and explained by

the non-separability of the hadronic current, assumed in our relativistic model, namely by the presence of correlative effects due to the interaction among the final decay channels. In Figures 2.1, 2.2, 2.3, 2.4, 2.5a, 2.5b, 2.6, 2.7, 2.8, 2.9a and 2.9b, which describe the continuous energy distributions of beta particles, we observe an increase or decrease of the spectrum towards zero energy. This behavior, for β^- decay processes, is due to the exchange between the β particle and an orbital electron. The emitted β^- particle may, in fact, move away directly from the nucleus or the particle, hitting an electron, can occupy the vacancy left by it [100]. In contrast, with regard to a β^+ decay, Figure 2.2, we do not observe an increase of the spectrum towards zero energy as this process of exchange between the emitted positron and an orbital electron cannot occur. The asymmetric shape, typical of beta spectra, indeed, is determined by the (statistical) sharing of the decay energy between the electron (positron) and antineutrino (neutrino). Considering, for a β^- decay, the equation

$$E_f = E_e + E_{\bar{\nu}} \quad (2.128)$$

with E_f the final energy, E_e the electron energy and $E_{\bar{\nu}}$ the antineutrino energy (we neglect the recoil energy of the daughter nucleus, as the heaviest component, and the antineutrino mass), we have the energy distribution

$$\frac{d\lambda}{dE_{ek}} = C(Q_{\beta^-} - E_{ek})^2(E_{ek} + m_e c^2) \sqrt{E_{ek}^2 + 2E_{ek}m_e c^2} \quad (2.129)$$

where C is a constant,

$$E_{ek} = \sqrt{m_e^2 c^4 + (p_e c)^2} - m_e c^2 = E_e - m_e c^2 \quad (2.130)$$

is the electron kinetic energy, m_e and p_e the mass and momentum (modulus) of the particle, respectively, Q_{β^-} ($Q_{\beta^-} = E_{ek} + p_{\bar{\nu}} c$) the Q -value (2.5) and $p_{\bar{\nu}}$ the antineutrino momentum (modulus). The spectrum vanishes when $E_{ek} = 0$ and $E_{ek} = Q_{\beta^-}$ (endpoint) and the maximum represents the maximum distribution (probability). The probability of emitting a beta particle with a kinetic energy between E_{ek} and $E_{ek} + dE_{ek}$ is determined by the density of final states (phase space). For further details refer to [68] (chapter 9).

As regards the electron capture of ${}^7_4\text{Be}$, Figure 2.10, this nuclide decays more rapidly (larger decay constant) as the electron density on the nucleus increases. In fact, we observe that increasing the density (x axis) the decay rate (z axis) increases, while, increasing the temperature (y axis) the rate decreases. Increasing the temperature means increasing the kinetic energy (the nucleus attracts more electrons at low energy) and decreasing the electron density on the nucleus. In the range of approximately 1 to 100 keV, the decay rate decreases. However, at high temperatures (temperature above about 100 keV), the rate increases again. In this range, where the formation of electron-positron pairs is favored, the electron density on the nucleus increases and, according to what has been stated above, also the decay rate increases. Analyzing, instead, the β^- decays as a function of temperature and density of ${}^{63}_{28}\text{Ni}$, ${}^{93}_{40}\text{Zr}$ and ${}^{176}_{71}\text{Lu}$, we note that boosting the electron density (x axis) the rate (z axis) decreases. Unlike electron capture, in this nuclear process the parent radionuclide decays more slowly with increasing the electron density. The quantum states, if the energy exceeds the Fermi energy, are all occupied and consequently the nuclide decays more slowly. Nevertheless, boosting the temperature, the outer states will be occupied, whereas the inner states will be free. Boosting the temperature (y axis) the decay rate increases (maximum). In Figures 2.11, 2.13 and 2.14, however, at about 1000 keV (high temperature) the rate decreases again. This can be explained by the fact that at high temperatures lepton pairs are produced and this leads to an increase of the electron density and a consequent decrease in rate. This phenomenon, in fact, is not described in Figures 2.12a and 2.12b, which show the decay rates (z axis) as a function of temperature (y axis) and density (x axis) of ${}^{85}_{36}\text{Kr}$. In both simulations the temperature was varied from 0.17 to 68.94 keV, temperatures too low to observe the process of pair production. In these analyses, in accordance with the above, the rate increases with the temperature and decreases with the density. For the calculations reported in the previous subsection, which underline how the temperature and density (2.117) as well as the presence of electronic and nuclear excited states can affect the decay rates and ionization degree of the system, we decided to consider two different temperature and density ranges. Specifically, we decided to extend the ranges, adopted in ${}^{85}_{36}\text{Kr}$ β^- decay simu-

lations (electron density from 70 to 4500 particles/ cm^3 or from 2×10^4 to 4×10^4 particles/ cm^3 and temperature from 0.17 to 68.94 keV), in order to test the accuracy of the Dirac-Hartree-Fock (DHF) method and investigate nuclear β decay processes in different stellar conditions characterized by different temperatures and densities, such as Asymptotic Giant Branch (AGB) stars, whose temperature in the H-shell exceeds 10^7 K [101] and with an electron density (intershell) of the order of $10^{27} cm^{-3}$ [102], or the Sun with a core temperature of the order of 10^7 K and an electron density of the order of $10^{24} - 10^{25} cm^{-3}$. As regards chapter 3, as mentioned, we introduce a second approach, a variational method by which the bound and scattering states, the energies, the photodetachment cross sections, the decay rates and the scattering phases of many-body systems, including the positronium negative ion (Ps^-) and hydrogen anion (H^-), were computed. The aim of this last chapter will be to demonstrate the efficiency and versatility of the approach, based, in this case, on the use of optimized multi-dimensional Gaussian basis functions (OMGBFs). An advantage of utilizing Gaussian basis functions, as repeatedly stated, consists in deriving analytical expressions of the one- and two-body integrals essential for the calculation of the Hamiltonian matrix elements.

Chapter 3

Variational approach and many-body systems

In the initial pages of this writing we have defined the many-body problem as the inability to solve exactly the Schrödinger equation for many-particle systems, namely the inability to determine the physical properties of a system composed of N interacting particles. That is why, as underlined, over the years numerous approaches have been developed in an attempt to characterize these systems, for example, to test the fundamental symmetries, such as the charge-parity-time (CPT) symmetry, and conservation laws [103]. Among the well-known methods, the variational method [104], an approximation approach based on the variational principle (section 1.2), through which we are able to determine the best trial function and, consequently, describe the exact wave function of the system using analytic basis functions, whose parameters are optimized to obtain the minimum of the Hamiltonian expanded in the set.

In this chapter, in particular, we present a variational method implemented by introducing optimized multi-dimensional Gaussian basis functions (OMGBFs). The approach, which will be described in the next section, was employed for the study of many-body systems, protagonists of the last pages of this chapter.

3.1 The variational method

We write the non-relativistic Hamiltonian as

$$H = - \sum_j \frac{\nabla_j^2}{2m_j} + \sum_{j < k} V_{jk}(|\mathbf{r}_j - \mathbf{r}_k|) \quad (3.1)$$

with

$$V_{jk}(|\mathbf{r}_j - \mathbf{r}_k|) = \sum_l c_{jk,l} \frac{\exp(-\alpha_{jk,l} |\mathbf{r}_j - \mathbf{r}_k|)}{|\mathbf{r}_j - \mathbf{r}_k|} \quad (3.2)$$

the Yukawa-like potential¹³ between the particles characterized by the position vectors $\mathbf{r}_j, \mathbf{r}_k$ and define the interaction term as

$$H_I = - \sum_j \frac{q_j}{m_j} \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j \quad (3.3)$$

where $\mathbf{p}_j$ represents the momentum, m_j the mass and q_j the charge of the constituents to the external electromagnetic field represented by the vector potential $\mathbf{A}$.

Considering, at this point, the Gaussian function $(N \times N_d)$ - dimensional

$$g(B, \mathbf{b}; \mathbf{r}) = \exp [-(\mathbf{r} - \mathbf{b})^t B (\mathbf{r} - \mathbf{b})] \quad (3.4)$$

with N the number of particles and N_d the space dimensionality of each particle, centered in $\mathbf{b} \in \mathbb{R}^{N \times N_d}$ with B a $(N \times N)$ symmetric and positive-definite matrix, we obtain the derivative

$$d(B, \mathbf{b}; \mathbf{x}) = \nabla_{\mathbf{x}} g(B, \mathbf{b}; \mathbf{x}) = -\nabla_{\mathbf{b}} g(B, \mathbf{b}; \mathbf{x}) \quad (3.5)$$

with $d : \mathbb{R}^{N \times N_d} \rightarrow \mathbb{R}^{N \times N_d}$ and ∇ the gradient in the $(N \times N_d)$ - dimensional space, we expand the many-body wave function

$$\Psi = \sum_{i=1}^N \gamma_i \varphi_i \quad (3.6)$$

¹³The Yukawa potential is a short range potential that allows to describe interactions mediated by massive particles (nuclei and atoms). This potential, Fourier transform of a screened Coulomb potential, and the Gaussian functions permit one- and two-body integrals to be computed analytically required for the calculation of matrix elements. Different potentials, such as the Wood-Saxon potential, can be modeled by Yukawa-like potentials.

with φ_i a set of multi-dimensional Gaussian basis functions spanning the space of the states and γ_i a set of parameters.

Applying the Rayleigh-Ritz variational method, we reduce the latter, defined by the chosen trial function, to a generalized eigenvalue problem [103] (projection)

$$\sum_{i=1}^N \gamma_i \langle \varphi_k | H | \varphi_i \rangle = \lambda \sum_{i=1}^N \gamma_i \langle \varphi_k | \varphi_i \rangle \quad (3.7)$$

where $\mathcal{H}_{ki}$ represents the Hamiltonian matrix, $\mathcal{N}_{ki}$ the overlap matrix and λ the eigenvalues

$$\mathcal{H}_{ki} = \langle \varphi_k | H | \varphi_i \rangle, \quad \mathcal{N}_{ki} = \langle \varphi_k | \varphi_i \rangle \quad (i, k = 1, \dots, N). \quad (3.8)$$

The energy is minimized by using the coefficients characterizing Gaussian functions (3.4), such as the variable $\mathbf{r}$ and the parameters $\mathbf{b}$ and B , which define the centering and width of the function, respectively.

Transforming the coordinates to the center-of-mass coordinates

$$\mathbf{R} = \frac{\sum_{j=1}^N m_j \mathbf{r}_j}{\sum_{j=1}^N m_j} \quad (3.9)$$

and relative coordinates

$$\mathbf{s}_j = \mathbf{r}_j - \mathbf{r}_N \quad (j = 1, \dots, N-1), \quad (3.10)$$

we rewrite the separable wave function

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Phi \left(\frac{\sum_{j=1}^N m_j \mathbf{r}_j}{\sum_{j=1}^N m_j} \right) \psi(\mathbf{r}_1 - \mathbf{r}_N, \dots, \mathbf{r}_{N-1} - \mathbf{r}_N) \quad (3.11)$$

and the Hamiltonian as

$$H = -\frac{\nabla_R^2}{2M} - \frac{1}{2} \sum_{i,j=1}^{N-1} \nabla_{\mathbf{s}_i} \mathcal{M}_{ij}^{-1} \nabla_{\mathbf{s}_j} + \sum_{i < j=2}^{N-1} V_{ij}(\mathbf{s}_i - \mathbf{s}_j) + \sum_{i=1}^{N-1} V_{in}(\mathbf{s}_i) \quad (3.12)$$

where

$$M = m_1 + \dots + m_N \quad (3.13)$$

and

$$\mathcal{M}_{ij}^{-1} = \begin{pmatrix} \frac{m_1+m_N}{m_1 m_N} & \frac{1}{m_N} & \dots & \dots & \frac{1}{m_N} \\ \frac{1}{m_N} & \frac{m_2+m_N}{m_2 m_N} & \frac{1}{m_N} & \dots & \frac{1}{m_N} \\ \dots & \frac{1}{m_N} & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \frac{1}{m_N} \\ \dots & \dots & \dots & \frac{1}{m_N} & \frac{m_{N-1}+m_N}{m_{N-1} m_N} \end{pmatrix} \quad (3.14)$$

is the inverse mass matrix with

$$\mu_{ii}^{-1} = \frac{m_i + m_N}{m_i m_N} \quad (i = 1, \dots, N-1) \quad (3.15)$$

the inverse reduced masses and

$$\mu_{ij}^{-1} = \frac{1}{m_N} \quad (i \neq j). \quad (3.16)$$

This transformation is necessary to decouple the center-of-mass from the proper motion of interacting particles, consequently, restricting the problem to the relative coordinates alone, we compute the Hamiltonian matrix elements of the kinetic term

$$T_{12} = -\frac{1}{2} \nabla_{\mathbf{b}_2}^t \mathcal{M}^{-1} \nabla_{\mathbf{b}_2} \mathcal{N}_{12} \quad (3.17)$$

of the potential term

$$V_{12} = \int d^3 r g(B_1, \mathbf{b}_1; \mathbf{r}) g(B_2, \mathbf{b}_2; \mathbf{r}) V(\mathbf{s}) \quad (3.18)$$

and the overlap integral (integral of the product of two Gaussian functions)

$$\mathcal{N}_{12} = \int d^3 r g(B_1, \mathbf{b}_1; \mathbf{r}) g(B_2, \mathbf{b}_2; \mathbf{r}) \quad (3.19)$$

from which, being the product of two Gaussian functions proportional to a Gaussian function

$$g(B_1, \mathbf{b}_1; \mathbf{r}) g(B_2, \mathbf{b}_2; \mathbf{r}) = g(B, \mathbf{b}; \mathbf{r}) \exp[-(\mathbf{b}_2 - \mathbf{b}_1) C_{12} (\mathbf{b}_2 - \mathbf{b}_1)] \quad (3.20)$$

and

$$I = \int d^3r g(B, \mathbf{b}; \mathbf{r}) = \int d^3r \exp[-(\mathbf{r} - \mathbf{b})^t B (\mathbf{r} - \mathbf{b})] = \left[\sqrt{\frac{\pi^N}{\det(B)}} \right]^{N_d}, \quad (3.21)$$

we conclude that

$$\mathcal{N}_{12} = \left[\sqrt{\frac{\pi^N}{\det(B)}} \right]^{N_d} \exp[-(\mathbf{b}_2 - \mathbf{b}_1) C_{12} (\mathbf{b}_2 - \mathbf{b}_1)] \quad (3.22)$$

$$T_{12} = [N_d \text{Tr}(\mathcal{M}^{-1} C_{12}) - 2(\mathbf{b}_2 - \mathbf{b}_1)^t C_{12} \mathcal{M}^{-1} C_{12} (\mathbf{b}_2 - \mathbf{b}_1)] \mathcal{N}_{12} \quad (3.23)$$

and

$$V_{12} = \exp[-(\mathbf{b}_2 - \mathbf{b}_1) C_{12} (\mathbf{b}_2 - \mathbf{b}_1)] \int d^3r g(B, \mathbf{b}; \mathbf{r}) V(\mathbf{s}) \quad (3.24)$$

with

$$B = B_1 + B_2 \quad (3.25)$$

$$\mathbf{b} = (B_1 + B_2)^{-1} (B_1 \mathbf{b}_1 + B_2 \mathbf{b}_2) \quad (3.26)$$

and

$$C_{12} = \frac{1}{2} \left(B_1 \frac{1}{B_1 + B_2} B_2 + B_2 \frac{1}{B_1 + B_2} B_1 \right). \quad (3.27)$$

3.2 Applications

3.2.1 Many-body systems

The ground and excited states energies

Once we have calculated the previous equations, we solve the eigenvalue problem (3.7) and determine the ground and excited states energies, whose results are shown in Tables 3.1 and 3.2.

In Table 3.1, in particular, we report our calculations for the ground state energies of different systems¹⁴.

¹⁴The energy* reported was calculated by the data from [105].

System	Method	Ground state (a.u.)
Ps ⁻	This work [106]	-0.26200503 -0.262005070232980107770375
H ⁻	This work [107]	-0.52744444 -0.52744588111418
H ₂	This work [105]	-1.16349287 -1.1640*
He	This work [108]	-2.90329914 -2.90329969
H ₂ ⁺	This work [109]	-0.59713723 -0.597139063123405074
Ps ₂	This work [103]	-0.51595821 -0.515989
Li	This work [110]	-7.477916669 -7.478058

Table 3.1: Energies of the ground state of different systems.

In Table 3.2, we report our calculations for the ground and first excited states energies of the dihydrogen cation (H₂⁺), the helium (He) and the lithium¹⁵ (Li) atoms.

System	State	Energies (a.u.)
H ₂ ⁺	1 ¹ S	-0.59713723
H ₂ ⁺	2 ¹ S	-0.57734289
H ₂ ⁺	2 ³ S	-0.58705383
H ₂ ⁺	3 ¹ S	-0.55391673
H ₂ ⁺	3 ³ S	-0.56659641
He	1 ¹ S	-2.90329914
He	2 ¹ S	-2.14567478
He	2 ³ S	-2.17492639
He	3 ¹ S	-2.06096734
He	3 ³ S	-2.06839823
Li	1 ¹ S	-7.4731554
Li	2 ¹ S	-7.27744661
Li	2 ³ S	-7.43601453
Li	3 ¹ S	-7.05604666
Li	3 ³ S	-7.23965195

Table 3.2: Energies of the ground and excited states of different systems.

Our results are in good agreement with the theoretical and experimental data.

¹⁵In Table 3.1 is shown the variational ground state energy of the lithium atom (Li) with infinite nuclear mass, while in Table 3.2 the variational energies of the lithium atom (Li) with finite nuclear mass are reported.

The scattering phases

Regarding electron scattering by neutral hydrogen (H) and positronium (Ps) atoms, the calculations of the scattering phases were performed employing, once again, the semi-projected method (subsection 1.3.2). Projected the perturbation term, using the multi-dimensional Gaussian functions described previously, we determined the scattering matrix

$$S_{ij}\delta(E - E') = \delta(E - E')\delta_{ij} - 2\pi i t_{ij}\delta(E - E') \quad (3.28)$$

with E' the energy of the incoming state, E the energy of the outgoing state and t_{ij} the T -matrix element, from which we obtain the scattering phases (section 1.1) of H^- and Ps^- .

In Figures 3.1 and 3.2, the singlet and triplet scattering phases of H^- , calculated using a basis set of 1000 Gaussian functions, are shown.

The sharp peaks correspond to the first-excitation edge of hydrogen (excitation $1s \rightarrow 2s$).

Similarly, in Figures 3.3 and 3.4, the singlet and triplet scattering phases of Ps^- , computed using a basis set of 1000 Gaussian functions, are reported.

The sharp peaks, once again, are due to excitation $1s \rightarrow 2s$ in the scattering process.

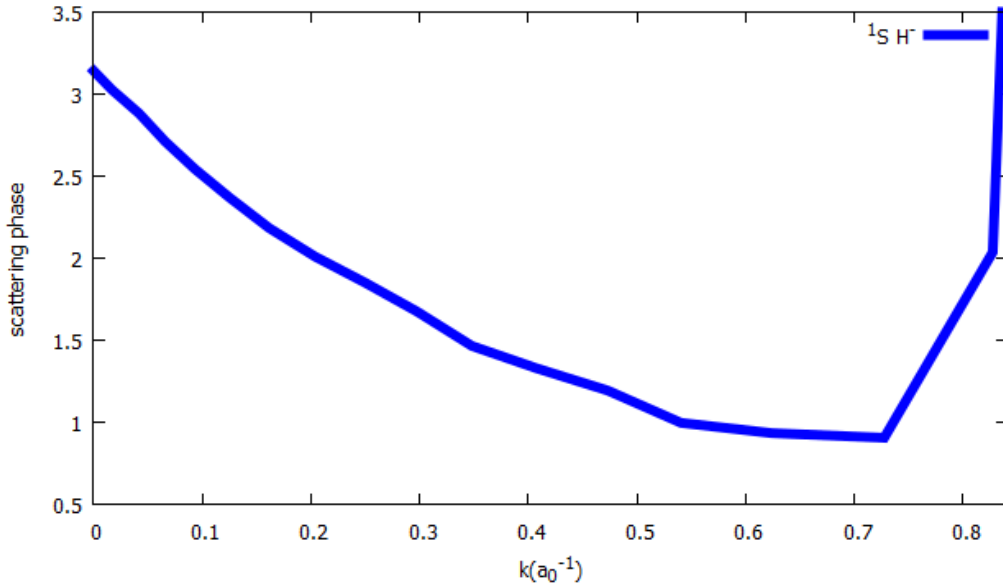


Figure 3.1: The singlet scattering phase of H^- .

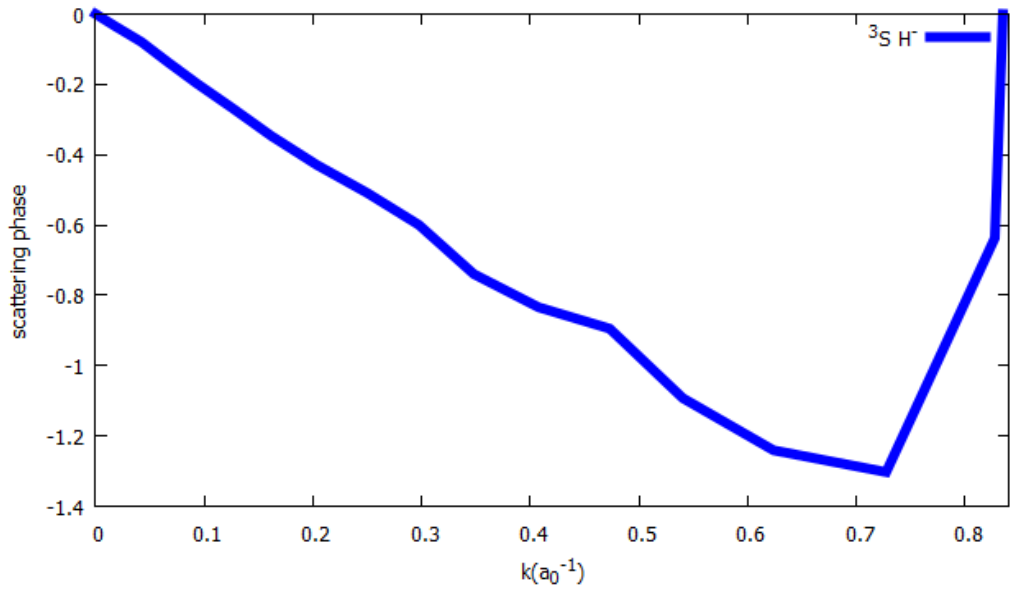


Figure 3.2: The triplet scattering phase of H^- .

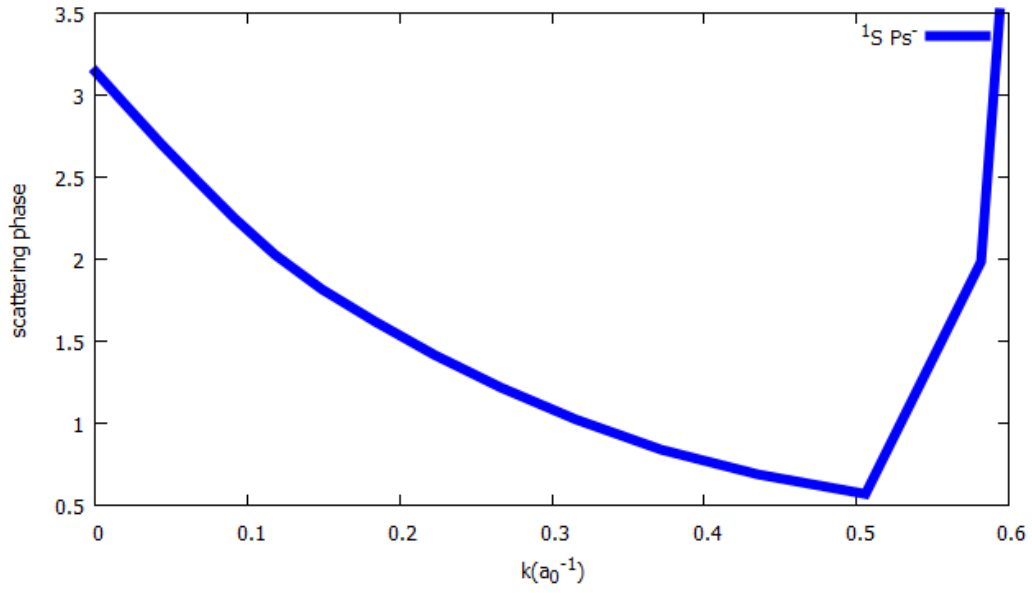


Figure 3.3: The singlet scattering phase of Ps^-

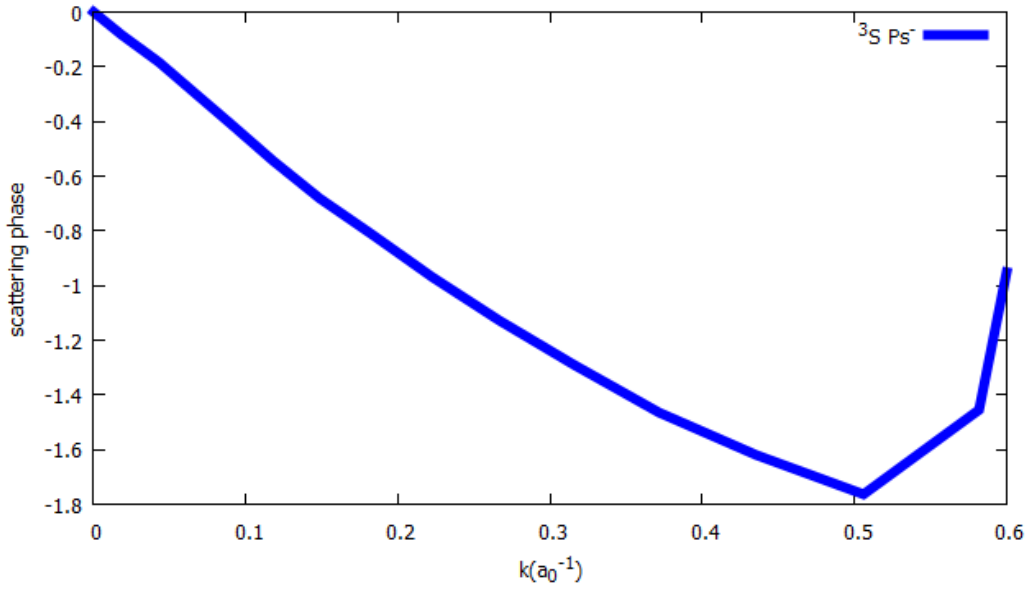


Figure 3.4: The triplet scattering phase of Ps^-

The photodetachment cross sections

To verify the accuracy of the method, we used the latter to calculate the H^- and Ps^- photodetachment cross sections. Taking up what has already been introduced in chapter 2, we determine the transition probability per unit time (photodetachment rate) by applying the Fermi golden rule [68]

$$\Lambda_{i \rightarrow f} = 2\pi \sum_f |\langle f | H_I | i \rangle|^2 \rho_f(E_i + \omega) \quad (3.29)$$

where $\rho_f(E_f)$ represents the density of final states at the energy $E_f = E_i + \omega$ with E_i the initial state energy, ω the frequency at which $\mathbf{A}$ oscillates and H_I the interaction term (3.3). The initial state $|i\rangle$ of our system, in particular, is the bound state corresponding to the positronium negative ion (Ps^-) or hydrogen anion (H^-). The final states $|f\rangle$, on the contrary, are continuum states consisting of the atom and an outgoing electron. For this reason, we can define the initial state as a linear combination of optimized multi-dimensional Gaussian basis functions (OMGBFs) and

$$\langle t | f \rangle = \sum_{j=1}^{\infty} \gamma_{f,j} \langle t | \varphi_j \rangle \quad (3.30)$$

where $\sum_{j=1}^{\infty} \gamma_{f,j} \varphi_j$ represents a infinite linear combination of the basis. The final states can be characterized by a scalar product for a dense subset of states $|t\rangle$ in the Hilbert space.

In Figure 3.5, we compared our data of Ps^- total photodetachment cross sections (continuous colored lines) with the theoretical results of A. Igarashi et al. [111] (red symbols) and Y. Nagashima [21] (green dots and line). Our calculations were obtained with different basis sets, each represented by a different color. Specifically, the purple line reports the results obtained with 2000 Gaussian functions, the dark green line the results obtained with 3200 Gaussian functions, the cyan line the results obtained with 4000 Gaussian functions and finally the orange line the results obtained with 6000 Gaussian functions. Similarly, in Figure 3.6, we compare our simulations of H^- total photodetachment cross sections (continuous colored lines) with the experimental data (red symbols) from [112]. Also in this case, the colored lines represent the results obtained with 2000, 3200, 4800 and 6000 Gaussian functions. For both systems, our cross sections are in good agreement with the theoretical and experimental data.

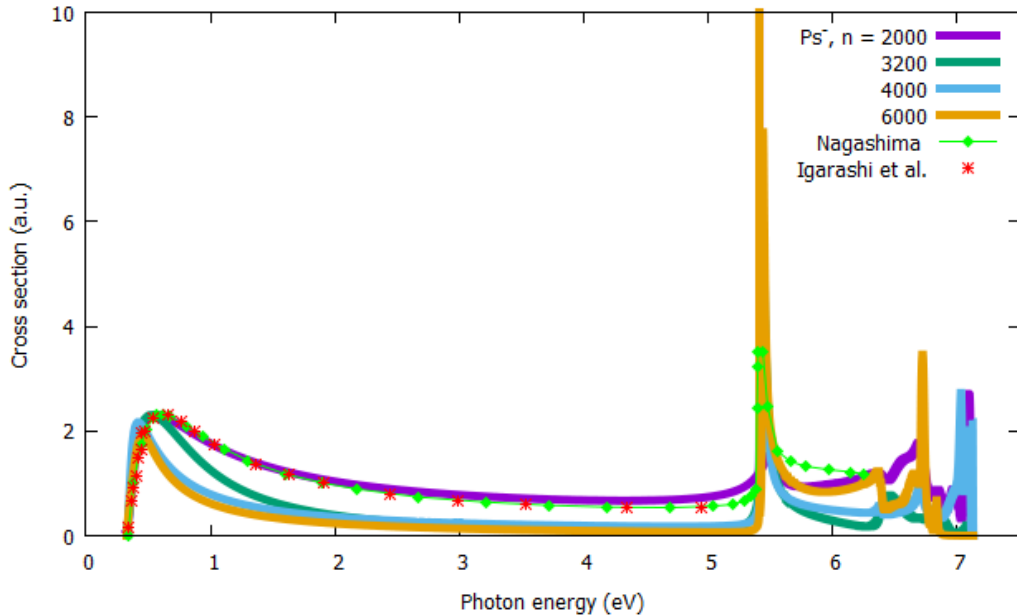


Figure 3.5: Ps^- total photodetachment cross sections. Theoretical results of A. Igarashi et al. [111] (red symbols) and Y. Nagashima [21] (green dots and line).

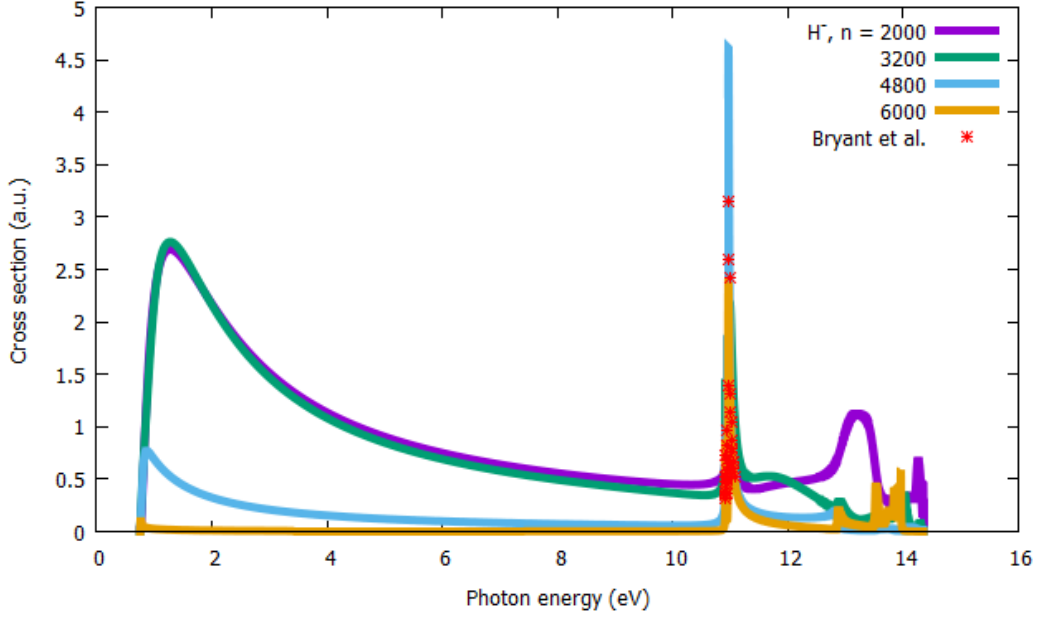


Figure 3.6: H^- total photodetachment cross sections. Experimental data (red symbols) from H. C. Bryant et al. [112].

The nuclear decay rates

As regards the calculations of the decay rates, by applying the semi-projected method and the Fermi golden rule, where the interaction term is defined as the product of the hadronic and leptonic currents (2.96), we determine the transition probability per unit time of ${}^7_4\text{Be}$ both for different electronic configurations (Table 3.3) and as a function of temperature and density (Table 3.4). The results, compared with the relativistic Dirac-Hartree-Fock (DHF) calculations, are obtained assuming ${}^7_4\text{Be}$ as an isolated physical system (fixed nucleus) in which the hadronic current is defined as a delta function, the leptonic current is approximated by the electron density and the average population of each state is described by the equation

$$n_j = \frac{e^{-(E_j - \mu N_j)/(K_B T)}}{\sum_j e^{-(E_j - \mu N_j)/(K_B T)}} \quad (3.31)$$

where E_j and N_j represent the energies of the j states and the corresponding number of electrons in the atom, respectively.

Specifically, the results of the transition rates, the sum of partial rates

$$\Lambda = \sum_j n_j \Lambda_j, \quad (3.32)$$

reported in Table 3.3, are calculated from the bound states (the latter depend only on the electronic configuration), while the calculations in Table 3.4 are obtained by means of the variational approach from the bound states and via the DHF method from both the bound and continuum states (total).

All the simulations were calculated using 500 optimized multi-dimensional Gaussian basis functions (OMGBFs).

Conf.	DHF (bound)	Variational (bound)	
	Rate (s^{-1})	Energy (a.u.)	Rate (s^{-1})
$1s^2 2s^2$	1.4804×10^{-7}	-14.6651	1.4817×10^{-7}
$1s^2 2s 3s \ ^3S$	1.4478×10^{-7}	-14.2803	1.3928×10^{-7}
$1s^2 2s 3s \ ^1S$		-14.2681	1.3406×10^{-7}
$1s 2s^2 3s$	0.7788×10^{-7}	/	/
$1s^2 2s$	1.4648×10^{-7}	-14.3232	1.4730×10^{-7}
$1s^2 3s$	1.4258×10^{-7}	-13.8272	1.3601×10^{-7}
$1s 2s^2$	0.8014×10^{-7}	/	/
$1s^2$	1.4284×10^{-7}	-13.6544	1.4552×10^{-7}
$1s 2s \ ^3S$	0.7706×10^{-7}	-9.1263	0.7598×10^{-7}
$1s 3s \ ^1S$	0.7252×10^{-7}	-8.4352	0.6449×10^{-7}
$1s$	0.7140×10^{-7}	-8.0	0.8617×10^{-7}
$2s$	0.0893×10^{-7}	-2.0	0.1077×10^{-7}

Table 3.3: Decay rates of ${}^7_4\text{Be}$ for different electronic configurations.

T (eV)	n_{el} (cm^{-3})	Variational rate (s^{-1}) (bound)	DHF rate (s^{-1}) (total)
2	1×10^{10}	1.455157×10^{-7}	1.409283×10^{-7}
12	1×10^{10}	5.193027×10^{-13}	6.101676×10^{-16}
22	1×10^{10}	5.490840×10^{-17}	1.263426×10^{-18}
32	1×10^{10}	1.422436×10^{-18}	9.994987×10^{-20}
42	1×10^{10}	1.876488×10^{-19}	2.370322×10^{-20}
2	1×10^{11}	1.455157×10^{-7}	1.409283×10^{-7}
12	1×10^{11}	5.192746×10^{-12}	6.101676×10^{-15}
22	1×10^{11}	5.490840×10^{-16}	1.263442×10^{-17}
32	1×10^{11}	1.422436×10^{-17}	9.994677×10^{-19}
42	1×10^{11}	1.876488×10^{-18}	2.369779×10^{-19}
2	1×10^{12}	1.455157×10^{-7}	1.409283×10^{-7}
12	1×10^{12}	5.189941×10^{-11}	6.101674×10^{-14}
22	1×10^{12}	5.490839×10^{-15}	1.263442×10^{-16}
32	1×10^{12}	1.422436×10^{-16}	9.994651×10^{-18}
42	1×10^{12}	1.876488×10^{-17}	2.369700×10^{-18}

Table 3.4: Decay rates of ${}^7_4\text{Be}$ as a function of temperature and density.

Conclusions

In this chapter we have presented a non-relativistic variational method based on the use of optimized multi-dimensional Gaussian basis functions (OMG-BFs). These functions allow not only to make calculations on different centers (the product of Gaussian functions is itself a Gaussian function) but, and in particular, they allow the analytical computation of matrix elements needed to solve the eigenvalue problem (3.7). The latter are not the only choice, but different functions can be adopted, such as exponential functions [106, 109] (Table 3.1). Through this approach, we have determined the bound and scattering states, the energies of the ground and excited states, the photodetachment cross sections, the decay rates and the scattering phases of many-body systems, such as ions, atoms and molecules. In subsection 3.2.1, we reported our calculations for the energies of different systems, including the positronium negative ion (Ps^-) and lithium atom (Li). Our results have been found to be in good agreement with the theoretical and experimental data cited. As regards electron scattering by neutral hydrogen (H) and positronium (Ps) atoms, we calculated the singlet and triplet scattering phases of H^- and Ps^- employing the semi-projected method (subsection 1.3.2). Data obtained with a basis set of 1000 Gaussian functions are shown in Figures 3.1, 3.2, 3.3 and 3.4. Analyzing, once again, the H^- and Ps^- systems, of the latter we have also determined the total photodetachment cross sections, Figures 3.5 and 3.6. The cross sections, obtained with 2000, 3200, 4000, 4800 and 6000 Gaussian functions, decrease as this number increases. This behavior is dictated by some overlapping problems (numerical problems). To overcome these problems, which arise as the basis increases, some states of sufficiently high kinetic energy are consequently removed, which results in a reduced of the cross section. The simulations obtained, once again, are in good agreement with the theoretical and experimental data [21, 111, 112]. Finally, the decay rates of ${}^7_4\text{Be}$. For the calculations in Table 3.4, we analyzed the electron capture of ${}^7_4\text{Be}$ in the nominal PANDORA (temperature and density) ranges [97, 98]. These studies were carried out using two different methods. The relativistic Dirac-Hartree-Fock (DHF) method and the variational method, the protagonist of this chapter. The results obtained by the two approaches are consistent with

each other at low temperature, however, increasing the temperature, the results differ. Such discrepancies can be attributed to the different number of excited states considered in the two different models. Concerning the DHF method, in the latter case all excited states are considered. On the contrary, in the non-relativistic variational method only the excited states reported in Table 3.3 are introduced (Boltzmann distribution). The presence of electronic and nuclear excited states, as stated in the previous chapter and underlined in Table 3.3, can affect the rates. The presence of more excited states, in particular, leads to a decrease in the decay probability. An additional factor is the single-particle correlations, characterizing the DHF model. For the temperature and density analyses, Table 3.4, we have again varied the ranges introduced in section 2.3 in order to investigate different astrophysical scenarios. Theoretical and experimental analyses of weak nuclear processes in terrestrial plasmas, subject of study in the INFN-PANDORA experiment, are essential for defining, for example, an agreement between nucleosynthesis models and observations [18]. With the electron capture of ${}^7_4\text{Be}$, we conclude the third chapter of this thesis, in whose last pages we will summarize what has been introduced in the previous sections, placing emphasis on future projects and developments.

Conclusions

The ultimate aim of this thesis was to introduce two theoretical-computational methods for the characterization of many-body systems. Specifically, in the first and second chapters, we described the relativistic Dirac-Hartree-Fock (DHF) method, which defines a mean-field (MF) approximation of the many-particle Dirac equation. The method, implemented using Hermite Gaussian functions (HGFs) and radial basis sets, was employed for the analysis of electron elastic scattering in water and for the study of nuclear β decays in terrestrial and stellar scenarios. The results obtained, presented and discussed in the last pages of chapters 1 and 2, demonstrated the efficiency and accuracy of both approaches, which left room, in chapter 3, for the treatment of a non-relativistic variational method developed by introducing optimized multi-dimensional Gaussian basis functions (OMGBFs). The variational method was used for the calculation of the bound and scattering states, the energies (ground and excited states), the photodetachment cross sections and the scattering phases of many-body systems such as ions, atoms and molecules. Through this approach, furthermore, the transition rate of ${}^7_4\text{Be}$ was determined. The decay rates, in particular, were analyzed for different electronic configurations and as a function of temperature and density.

This thesis, which summarizes my research activity carried out during the PhD, is intended to be the starting point of future projects and possible developments.

The many-body problems, fil rouge of this writing, still represent an open problem in various research fields. To test the validity and versatility of two approaches, indeed, we decided to investigate some many-body problems, such as the electron scattering in liquid water, the nuclear decays in astrophysical scenario or the Ps^- photodetachment, which constitute not only some of the

possible applications of the two mean-field methods, but themselves the bases of new implementations and studies.

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