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DOCTORAL DISSERTATION

Title of doctoral dissertation: Relativistic Elastic Electron-Atom Scattering Near and At Zero Energy Threshold

Title of doctoral dissertation (in Polish): Relatywistyczne sprężyste rozpraszanie elektronów o niskiej i zerowej energii na atomach

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DESCRIPTION OF DOCTORAL DISSERTATION

The Author of the doctoral dissertation: Michał Piotr Piłat
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Summary of doctoral dissertation in Polish: Celem pracy jest przedstawienie teorii relatywistycznego sprężystego rozpraszania elektronów na atomów dla niskiej energii. Praca skupia się na teorii wyznaczania długości rozpraszania i jak ona może być sformułowana w relatywistycznej mechanice kwantowej. W pracy przedstawiono przybliżone rozwiązanie równania Diraca z potencjałem polaryzacyjnym zachowującym się w nieskończoności jak r^{-4} oraz sformułowano przybliżenie „zasięgu skutecznego" (effective range theory) dla równania Diraca. Te wzory zostały użyte do wyznaczania długości rozpraszania dla argonu, kryptonu, ksenonu, radonu i oganesonu. Wartości otrzymane dla argonu, krypton I ksenonu zgadzają się z wartościami otrzymanymi innymi metodami teoretycznymi i doświadczalnymi. Wyniki dla radonu i oganesonu zostały otrzymane po raz pierwszy. W tej pracy pakiet GRASP2018 został użyty do wyznaczenia stanów związanych atomów a zmodyfikowany program COWF do wyznaczania orbitali continuum.

Summary of doctoral dissertation in English: The aim of this dissertation is to present the theory of relativistic electron-atom scattering at low energies. This work focuses on the theory of calculation of scattering length and how it can be formulated in the relativistic quantum theory. An approximate solution to the Dirac equation with polarization potential behaving as r^{-4} is presented as well as the formulation of the effective range theory for Dirac's equation. Those formulas were later used to calculate the scattering lengths of argon, krypton, xenon, radon and oganesson. Values for argon, krypton and xenon coincide with the values obtained by different groups, both theoretically and experimentally. Values for radon and oganesson were obtained for the first time. In this work GRASP2018 computational package was used to calculate the bound states of an atom and the modified COWF code for obtaining the continuum states.

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Contents

Chapter 1

Introduction

One of the most important fields of quantum mechanics is atomic physics. The quantum theory is used to describe the parameters and behaviour of the atomic systems. The introduction of experimental methods, such as particle scattering, enables us to verify the mathematical calculations with the results obtained in laboratories. From the development of Bose-Einstein condensates, Rydberg atoms and ultra-cold gases, there is a need for theoretical investigation in the scattering of particles on atoms in the regime of low energies. One of the results of such investigations is the evaluation of the scattering length of the atoms.

The scattering theory is one of the most thoroughly inspected parts of quantum theory, starting from Rutherford's experiment with alpha particles and gold atoms. There are many books on elastic and inelastic scattering presented in non-relativistic (Schrödinger) formalism, such as Newton's "Scattering Theory of Waves and Particles" [1] and Joachain's "Quantum Collision Theory" [2], as the non-relativistic theory is easier to grasp and to implement and gives sufficiently good results that inclusion of relativistic effects, such as spin, is negligible. However, the further development of the experimental results and computational technology brings a necessity to use more refined theories, such as relativistic equations created by Paul A. M. Dirac. One of the main problems with using the Dirac equation is the lack of proper treatment of the scattering theory, and many results that are commonly used in non-relativistic theory are not properly converted to the relativistic theory, and there is no investigation of whether those two theories coincide with each other. It is known that in limit the results should be the same, but it is not known what the differences are between the two theories. Moreover, many books focus on the general theory of scattering, which does not describe the intricacies of the atomic structure. In the book "Theory of Electron–Atom Collisions" [3] Burke and Joachain try to connect the scattering theory with the theory of the atom by including for example the polarisation potentials and how scattering length is connected to other effects, such as Ramsauer minimum, but still without using Dirac nomenclature. Some authors started to create the basics of relativistic scattering like Mott and Massey in "The Theory of Atomic Collisions" [4], but they did not develop it enough to be useful in this dissertation. There are books on relativistic quantum mechanics such as in the book by Bjorken and Drell "Relativistic Quantum Mechanics" [5] and the book by Greiner "Relativistic Quantum Mechanics, Wave Equations" [6], but they mainly focus on the theory of the free particle and explain the scattering of particles by using Feynmann diagrams and introducing quantum electrodynamics rather than concentrating on Dirac equation. There are also books on relativistic atomic physics such as "Relativistic Quantum Theory of Atoms and Molecules" by Grant [7] which includes chapters on scattering, but there is no definition of

scattering length proven from the basics of relativistic quantum theory. In many articles that calculate the scattering length for various atoms, or measure it experimentally, mainly noble gases, (the articles are mentioned in Chapter 5) main definition of scattering length is used, which connects the momentum of the particle with the phase shift. However, it has not been proven that the definition of scattering length presented in non-relativistic theory could be used in relativistic theory. Scattering length can also be introduced by using effective range theory. This theory is well developed in Schrödinger's nomenclature, including polarisation potentials, but there is only one work that presents a notion similar to effective range theory for relativistic equations [8], but it is not developing further. Although there are also works by Szmytkowski [9, 10, 11] which develops the theory of scattering length for various potentials, they all start from non-relativistic formalism and cannot be fully used in relativistic case.

There is no proper introduction to scattering length in relativistic theory, which could be found in the literature. Moreover, the notion of effective range theory, which can be formulated in relativistic formalism, is not developed. There is also the long-standing question of the inclusion of polarisation potential and its effect on scattering length. There is also no computer programme that would be able to properly simulate the values of the scattering lengths for various atoms. Measuring the scattering length is hard, but the values are often needed in other applications, such as Rydberg atoms scattering and photo-association of two atoms [12]. Calculations were performed only for a few elements, mainly noble gases, but not all of them. The goal is to properly define the theory of scattering length for relativistic equations, including polarisation, and develop a programme that could evaluate this property for other atoms, not only noble gases.

The goal of my work is to present the basics of the scattering theory in the relativistic case and develop new formulas whose corresponding versions are present in the non-relativistic formulation. Moreover, it is used to evaluate the scattering length for noble gas atoms, where two results were not previously presented in the literature.

The structure of my dissertation is as follows. In Chapter 2, the theory of potential scattering is quickly summarised, starting from the general case of inelastic scattering in non-relativistic theory to further focus on the elastic scattering and the definition of scattering length. Later, I present the elements of relativistic scattering found in literature that are later used to develop further formulas. The dissertation aims to set the ground for the theory of relativistic particle-atom scattering.

In Chapter 3 the methods to obtain the potentials used in Dirac equations to calculate the scattering length are presented. The main potentials are the Coulomb and exchange potentials which come from the interaction of a scattered electron with an atom. To calculate them, a multiconfigurational self-consistent-field Dirac-Hartree-Fock method (MCSCF DHF) is used, which is briefly presented, together with its predecessor multiconfigurational Hartree-Fock method (MCHF). I also present the method of implementing a polarisation potential in the model of an atom. I also included a brief passage on solving the radial wavefunction of the scattered electron.

Chapter 4 consists of the calculation of the near-threshold solutions of the Dirac radial equation for various cases which are later used to develop the effective range theory for the Dirac equation (equation (4.2.33)) and to approximate the zero-energy solution of the Dirac equation with polarisation potential which behaves asymptotically as r^{-4} (equations (4.3.60) and (4.3.62)). Both the effective range and the zero-energy solutions were never presented in the literature and are a novelty in the relativistic scattering theory.

Chapter 5 consists of the results of the calculation of scattering lengths of noble gases (specifically

argon, krypton, xenon, radon and oganesson) by using two methods. In the first method, given a set of approximate scattering lengths for very low electron energies, the final results are obtained by extrapolating to the zero energy case to calculate the scattering length using a formula connecting it with the phase shift. This is done by fitting points to the least squares line and finding its intersection. Additionally, in my work, I prove that this formula can be used as a good approximation of the value of scattering length in a relativistic regime. The second method uses the zero-energy wavefunction of the scattered particle. When the particle energy is zero, the solution behaves like a straight line at a certain distance from the origin. To accurately approximate this straight line, the least squares method is used. This approximation can be corrected by using the proper solution of the scattered wavefunction, whose better approximation I have found, connecting it with the parameters describing polarisation potentials. Moreover, the new method gives better results closer to the origin. Results done by those methods were presented in the article [13], which I co-authored.

Chapter 6 is a conclusion section where I summarize all the information presented in the dissertation. There, I also present my plans regarding this topic. The dissertation ends with the index of used literature.

Chapter 2

Theory

2.1 Fundamentals of scattering theory in non-relativistic theory

In a simple scattering on the potential in non-relativistic theory, we have to solve Schrödinger equation in the form [14]

$$\left[-\frac{\hbar^2}{2\mu}\Delta + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{2.1.1}$$

where μ is a reduced mass of the scattered particle and $E = \hbar^2 k^2/(2\mu)$ is a connection between the momentum and the energy of the particle. Our boundary condition of this problem must consist of two parts: one, which is a wavefunction of the non-scattered electron as a plane wave, and the spherical wave, which is a wavefunction of the scattered particle. We seek the solution to this problem in the form:

$$\psi(\mathbf{r}) \underset{r\to\infty}{\sim} A\left[e^{\mathrm{i}kr\cos(\theta)} + f(\theta,\phi)\frac{e^{\mathrm{i}kr}}{r}\right]. \tag{2.1.2}$$

To define cross-sections, we have to begin with the continuity equation

$$\nabla\cdot\mathbf{j} + \frac{\partial\rho}{\partial t} = 0, \tag{2.1.3}$$

where (in atomic units) the probability flux and the probability density are defined as

$$\mathbf{j} = \frac{1}{2\mathrm{i}}(\psi^*\nabla\psi - \psi\nabla\psi^*), \tag{2.1.4}$$

$$\rho = \psi^*\psi. \tag{2.1.5}$$

In a stationary case, the equation (2.1.3) reduces to

$$\nabla\cdot\mathbf{j} = 0. \tag{2.1.6}$$

The gradient operator in spherical coordinates can be written as

$$\nabla = \frac{\partial}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{\phi}. \tag{2.1.7}$$

Using (2.1.2) to calculate the radial outgoing probability flux through a unit area perpendicular to the normal vector $\hat{\mathbf{r}}$ we get

$$\mathbf{j}\cdot\hat{\mathbf{r}} = \left(A^*A\frac{1}{2i}\left[e^{-\mathrm{i}kr\cos(\theta)} + f^*(\theta,\phi)\frac{e^{-\mathrm{i}kr}}{r}\right]\frac{\partial}{\partial r}\left[e^{\mathrm{i}kr\cos(\theta)} + f(\theta,\phi)\frac{e^{\mathrm{i}kr}}{r}\right]\right) + c.c, \tag{2.1.8}$$

where $c.c$ stands for complex conjugation. The flux of incoming wave Ae^{ikz} through a unit plane perpendicular to z direction is

$$\mathbf{j}_{in} \cdot \hat{\mathbf{z}} = A^* A k. \tag{2.1.9}$$

The outgoing flux of the spherical wave is given by

$$\mathbf{j}_{out} \cdot \hat{\mathbf{r}} = \left(A^* A \frac{1}{2i} f^*(\theta, \phi) \frac{e^{-\mathrm{i}kr}}{r} \frac{\partial}{\partial r} \left[f(\theta, \phi) \frac{e^{\mathrm{i}kr}}{r} \right] \right) + c.c. \tag{2.1.10}$$

It can be seen, that for large r it can be simplified to

$$\mathbf{j}_{out} \cdot \hat{\mathbf{r}} = A^* A \frac{k}{r^2} |f(\theta, \phi)|^2. \tag{2.1.11}$$

We are interested only in these parts of expansions with order r^{-2} because the definition of the differential cross section is given by the outgoing flux of particles scattered through the spherical surface $r^2 d\Omega$ per unit solid angle divided by the incident flux. From the definition, we get

$$\frac{\mathbf{j}_{out} \cdot \hat{\mathbf{r}}}{\mathbf{j}_{in} \cdot \hat{\mathbf{z}}} \cdot r^2 = \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta, \phi)|^2. \tag{2.1.12}$$

The total cross section is obtained by integrating over all scattering angles

$$\sigma_{tot} = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \sin\theta |f(\theta, \phi)|^2. \tag{2.1.13}$$

By obtaining the scattering amplitude $f(\theta, \phi)$ we get all the needed information about the scattering

Channel functions

Firstly, we focus on the scattering of electrons on atoms and ions using Schrödinger equation, because many parts of the theory are derived from this approach. From the start, we assume that the collision is inelastic, so the energy of the target is not conserved, but the energy of the whole system (scattered particle and target) is conserved. We then have to solve $N + 1$ particle Schrödinger's equation in the form of:

$$(H_{N+1} - E)\Psi = 0, \tag{2.1.14}$$

where N denotes the number of electrons in the target and a Hamiltonian operator written in atomic units is in the form:

$$H_{N+1} = -\frac{1}{2} \sum_{i=1}^{N+1} \left(\nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i>j=1}^{N+1} \frac{1}{r_{ij}}. \tag{2.1.15}$$

The Hamiltonian operator is diagonal when concerning: the total angular momentum operator L and its component on chosen axis L_z, total spin S and its chosen component S_z , and the total parity Π. We can rewrite the solution to the first equation (2.1.14) as [15]:

$$\Psi^{\Gamma}(X_{N+1}) = \mathcal{A} \sum_{i=1}^{n} \overline{\Phi}_i^{\Gamma}(x_1 \cdots x_N \hat{\mathbf{r}}_{N+1} \boldsymbol{\sigma}_{N+1}) r_{N+1}^{-1} F_i^{\Gamma}(r_{N+1}) + \sum_{i=1}^{m} \chi_i^{\Gamma}(x_1 \cdots x_{N+1}) a_i^{\Gamma}, \tag{2.1.16}$$

where $\Gamma \equiv LSM_L M_S \Pi$ and it will be omitted in later equations. X_{N+1} denotes all space and spin coordinates of $N + 1$ electrons, $\mathcal{A}$ is the operator anisymmetrisizing the first summation with respect to

the swapping of the coordinates between any two electrons, $x_i \equiv \mathbf{r}_i\sigma_i$ is the coordinates in spatial and spin space of the i-th electron, and $\overline{\Phi}_i$ is a channel function, which comes from coupling the wavefunction of the target $\Phi_i(x_1 \cdots x_N)$ with spin and angular parts of the scattered, $(N+1)$ electron, whose reduced radial wavefunction is written in form $F_i(r_{N+1})$. Additionally, by χ_i we will denote the set of antisymmetric functions, which are integrable over L^2. Given the sets of basis functions Φ_i and χ_i, we have to derive and solve the equations for the unknown functions F_i and for unknown coefficients a_i. In order to derive those equations for radial wavefunctions, it is helpful to introduce the notation

$$H_N = -\frac{1}{2}\sum_{i=1}^{N}\left(\nabla_i^2 + \frac{2Z}{r}\right) + \sum_{i>j=1}^{N}\frac{1}{r_{ij}}. \tag{2.1.17}$$

It is good to notice that there occurs the relation of orthogonality of Φ functions whilst operating on them the Hamiltonian operator H_N

$$\langle\Phi_i|\, H_N\, |\Phi_j\rangle = E_i\delta_{ij}, \tag{2.1.18}$$

where E_i is the energy of an atom in the state i. From the law of conservation of energy, we can write an equality

$$E = E_i + \frac{1}{2}k_i^2 = E_j + \frac{1}{2}k_j^2, \tag{2.1.19}$$

where k_i is a wavevector of the scattered electron. We can write the Hamiltonian operator H_{N+1} in an equivalent form:

$$H_{N+1} = H_N - \frac{1}{2}\nabla_{N+1}^2 - \frac{Z}{r_{N+1}} + \sum_{i=1}^{N}\frac{1}{r_{iN+1}}. \tag{2.1.20}$$

To make the calculation easier, we can rewrite it in the form

$$\Psi(X_{N+1}) = \sum_k \Phi_k(X_n)\overline{F_k}(x_{N+1}), \tag{2.1.21}$$

(here k in a subscript is a dummy index, not a wavenumber). It can be described as a product of the wavefunction of the target and the wavefunction of the scattered electron. I will introduce the notation, where bar over functions represents the function that describes the spin-angular part of the scattered electron wavefunction. Putting those equations (2.1.20) and (2.1.21) do (2.1.14) and multiplying from the left side with $\Phi_k^*(X_N)$ and integrating on all coordinates, we get as a result :

$$\left\langle \Phi_i \middle| H_N - \frac{1}{2}\nabla_{N+1}^2 - \frac{Z}{r_{N+1}} + \sum_{i=1}^{N}\frac{1}{r_{iN+1}} \middle| \sum_j \Phi_j\overline{F}_j \right\rangle = \left\langle \Phi_k \middle| E \middle| \sum_j \Phi_j\overline{F}_j \right\rangle. \tag{2.1.22}$$

Then, we calculate each part of the formula in the bra-ket bit by bit:

$$\langle\Phi_k|\, H_N\, |\sum_j \Phi_j\overline{F}_j\rangle = E_k\overline{F}_k \tag{2.1.23}$$

$$\langle\Phi_k|\, -\frac{1}{2}\nabla_{N+1}^2\, |\sum_j \Phi_j\overline{F}_j\rangle = -\frac{1}{2}\nabla_{N+1}^2\overline{F}_k \tag{2.1.24}$$

$$\langle\Phi_k|\sum_{i=1}^{N}\frac{1}{r_{iN+1}} - \frac{Z}{r_{N+1}}\, |\sum_j \Phi_j\overline{F}_j\rangle = \sum_j W_{kj}\overline{F}_k \tag{2.1.25}$$

$$\langle\Phi_k|\, E\, |\sum_j \Phi_j\overline{F}_j\rangle = E\overline{F}_k, \tag{2.1.26}$$

where

$$W_{kj} = \langle \Phi_k | \sum_{i=1}^{N} \frac{1}{r_{iN+1}} - \frac{Z}{r_{N+1}} | \Phi_j \rangle \,. \tag{2.1.27}$$

Applying those parts of the formula into (2.1.22) we get the result

$$E_k \overline{F}_k - \frac{1}{2}\nabla^2_{N+1}\overline{F}_k + \sum_j W_{kj}\overline{F}_k = (E_k + \frac{1}{2}k_k^2\overline{F}_k). \tag{2.1.28}$$

By modifying this equation, we get

$$(\nabla^2_{N+1} + k_k^2)\overline{F}_k = 2\sum_j W_{kj}\overline{F}_k. \tag{2.1.29}$$

If we rewrite the equation (2.1.21) in the antisymmetrisized form:

$$\Psi(X_{N+1}) = \mathcal{A}\sum_k \Phi_k \overline{F}_k(x_{N+1}), \tag{2.1.30}$$

we get

$$(\nabla^2_{N+1} + k_k^2)\overline{F}_k = 2\sum_j V_{kj}\overline{F}_k + 2\sum_j K_{kj}\overline{F}_k. \tag{2.1.31}$$

where the sum V_{kj} is called Coulomb interaction, and the part K_{kj} is named exchange interaction. From the nature of those potentials, Coulomb potential is long-raging and always existing, and exchange potential, which comes from Pauli's exclusion principle, happens only on short distances. A common practice in the approximation methods is neglecting the exchange potential when the scattered particle has high energy due to the fact that interaction is very short and this process does not occur.

Partial waves expansion. Asymptotic approximation.

From now on, we will focus on elastic scattering and assume that the potential generated by an atom is spherically symmetrical. We can now expand the scattered wavefunction as a sum [16]

$$\psi(r) = \sum_{l=0}^{\infty} C_l(k)\frac{F_l(r)}{r}P_l\cos(\theta), \tag{2.1.32}$$

where l is orbital angular momentum and $P_l\cos(\theta)$ are Legendre polynomials. Such treatment of a wavefunction is called partial wave analysis, and for different orbital angular momentum numbers, we have different partial waves. Partial waves are often named similarly to electron orbitals with the same orbital angular momentum i.e. for $l = 0$ partial wave is named "s-wave" and for $l = 1$ is named "p-wave" and so on. In order to have an intuition to form asymptotic behaviour of the radial wavefunction, let us start with the solution to the free particle in radial coordinates. The radial equation can be written as

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + k^2\right]F_l(r) = 0. \tag{2.1.33}$$

It has a close resemblance to the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}z^2} + \frac{2}{z}\frac{\mathrm{d}}{\mathrm{d}z} + 1 - \frac{l(l+1)}{z^2}\right]\mathcal{F}_l(z) = 0, \tag{2.1.34}$$

whose solutions are spherical Bessel functions of the first and second kind which have a strong correlation to the Bessel functions of the appropriate kind

$$j_l(z) = \sqrt{\frac{\pi}{2z}} J_{l+1/2}(z), \tag{2.1.35}$$

$$n_l(z) = \sqrt{\frac{\pi}{2z}} N_{l+1/2}(z) = (-1)^{l+1} \sqrt{\frac{\pi}{2z}} J_{-l-1/2}(z) \qquad (l \in \mathbb{Z}). \tag{2.1.36}$$

The solution to the equation (2.1.33) is in the form [2]

$$s_l(kr) = kr j_l(kr), \tag{2.1.37}$$

$$c_l(kr) = kr n_l(kr), \tag{2.1.38}$$

which has an asymptotic approximation form for $r \to \infty$

$$s_l(kr) \underset{r\to\infty}{\sim} \sin\left(kr - \frac{l\pi}{2}\right), \tag{2.1.39}$$

$$c_l(kr) \underset{r\to\infty}{\sim} \cos\left(kr - \frac{l\pi}{2}\right). \tag{2.1.40}$$

When we introduce the potential $U(r)$ to the equation,

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + k^2 - U(r)\right] F(r) = 0, \tag{2.1.41}$$

which we assume that vanishes asymptotically faster than r^{-1} away from the centre, we can represent the solutions of the equation as a linear combination of two free-particle radial wave solutions

$$F_l(r) = A s_l(kr) + B c_l(kr), \tag{2.1.42}$$

which for the large distance can be approximated by

$$F_l(r) = C \sin\left(kr - \frac{l\pi}{2} + \delta_l\right), \tag{2.1.43}$$

where we introduce the phase shift δ_l, which is connected with the previous equation as

$$\tan(\delta_l) = \frac{B}{A}. \tag{2.1.44}$$

In the special case of the hard sphere with radius R, the wavefunction must vanish for $r < R$ and behave as presented in (2.1.42) for $r > R$. The phase shift could be determined by the condition

$$A s_l(kr) + B c_l(kr) = 0, \tag{2.1.45}$$

which yields

$$\tan(\delta_l) = \frac{j_l(kR)}{y_l(kR)}, \quad \delta_l = \arctan\left(\frac{j_l(kR)}{y_l(kR)}\right), \tag{2.1.46}$$

which for low energy can be approximated as [17]

$$\delta_l \underset{k\to 0}{\sim} -\frac{\pi}{\Gamma\left(l+\frac{3}{2}\right)\Gamma\left(l+\frac{1}{2}\right)} \left(\frac{kR}{2}\right)^{2l+1} \left[1 - \left(\frac{kR}{2}\right)^2 \left(\frac{1}{l-\frac{1}{2}} + \frac{1}{l-\frac{3}{2}}\right)\right] \tag{2.1.47}$$

for $l > 0$ and it simplifies to

$$\delta_0 = -kR \tag{2.1.48}$$

for $l = 0$.

Scattering length and its application

At the distance where there is no potential, the wavefunction is a superposition of free-particle wavefunction as presented in (2.1.42). At the threshold, where $k \to 0$, by using small-argument expression, it can be written as

$$F_l(r) \underset{k\to 0}{\sim} \frac{\sqrt{\pi}k^{l+1}}{2^{l+1}\Gamma\left(l+\frac{3}{2}\right)}\left[r^{l+1} + \tan(\delta_l)\frac{2^{2l+1}\Gamma\left(l+\frac{1}{2}\right)\Gamma\left(l+\frac{3}{2}\right)}{\pi k^{2l+1}r^l}\right]. \tag{2.1.49}$$

At the threshold, the solution to the Schrödinger equation has a regularity defined by the boundary condition $F_l^{(0)}(0) = 0$, up to the multiplicational constant, and is the function only of the distance r. To ensure the k-independence for small k, the phase shift should behave as

$$\tan(\delta_l) \underset{k\to 0}{\sim} -\frac{\pi}{\Gamma\left(l+\frac{1}{2}\right)\Gamma\left(l+\frac{3}{2}\right)}\left(\frac{a_l k}{2}\right)^{2l+1}. \tag{2.1.50}$$

Here, the characteristic length a_l is introduced which is called the scattering length in the l-th partial wave. It was introduced by Fermi and Marshall [18] for nuclear physics, but it was later adopted for atomic and molecular physics. Since the contributions of higher partial waves diminish at low energies, it is defined mainly for the s-wave, but it could be defined for higher partial waves. Also, only for s-wave, the scattering length has a unit of length. For s-waves, this expression simplifies to

$$\tan(\delta_0) \underset{k\to 0}{\sim} -ak, \tag{2.1.51}$$

which brings the definition of the scattering length (the subscript 0 is commonly omitted for the s-wave) as

$$a = -\lim_{k\to 0}\frac{\tan(\delta_l)}{k}. \tag{2.1.52}$$

The scattering length is also connected with the total cross section because the only non-vanishing contribution to it, for very low energies, is the s-wave. The formula for the total cross-section at low energies is

$$\lim_{k\to 0}\sigma_{tot} = 4\pi a_0^2. \tag{2.1.53}$$

By comparing (2.1.48) and (2.1.51), we see that for hard-sphere scattering, the scattering length is equal to the radius of the sphere. However, the sign of the scattering length is connected to the character of the potential. If the potential is repulsive, the scattering length is positive. For attractive potential both signs are possible, however, the positive sign usually is a sign of a close bound state.

There is also a rather peculiar property of the s-wave scattering length. For s-wave and low energies, away from potential, the wavefunction has a form

$$F_0(r) = \sin(kr) + \tan(\delta_0)\cos(kr). \tag{2.1.54}$$

Additionally, when the energy is 0, the Schrödinger equation simplifies to

$$\frac{\mathrm{d}^2F_0(r)}{\mathrm{d}r^2} = 0 \to F_0(r) = Ar + B, \tag{2.1.55}$$

where its solution is a straight line. By using a small argument expression and the definition of scattering length, we can transform the equation (2.1.54) in the form (2.1.55) to write it as

$$F_0(r) = kr - ak = k(r-a), \tag{2.1.56}$$

which has a graphical interpretation. When we have the zero-energy wavefunction, the intersection of its asymptote with the r-axis is the scattering length.

Solutions with polarised potentials

One of the most important potentials used in calculations are infinite range potentials, which behave as $r^{-\tau}$ asymptotically, where τ is typically a natural number. For $\tau = 1$, we have Coulomb potential, $\tau = 3$ a resonant dipole-dipole interaction of two identical atoms in different states, $\tau = 4$ an interaction of a charged particle with neutral atom and $\tau = 6$ a van der Waals interaction. At zero energy, the radial Schrödinger equation with polarisation reads

$$\Big[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} \mp \frac{\beta^{\tau-2}}{r^\tau}\Big] F_l(r) = 0, \tag{2.1.57}$$

where β is a characteristic quantum length, which corresponds to the strength of the potential. The sign before the potential is negative if the potential is attractive and positive if the potential is repulsive. The solution to this equation is known and is written using Bessel functions [19]

$$F_l(r) = \sqrt{\frac{r}{\beta}}\big[A\mathcal{Z}^1_\nu(\zeta) + B\mathcal{Z}^2_\nu(\zeta)\big] \tag{2.1.58}$$

with

$$\nu = \frac{2l+1}{\tau-2}, \quad \zeta = \frac{2}{\tau-2}\left(\frac{\beta}{r}\right)^{(\tau-2)/2}, \tag{2.1.59}$$

and $\mathcal{Z}^1_\nu$ and $\mathcal{Z}^2_\nu$ are the ordinary Bessel functions J_ν and Y_ν for attractive potential and modified Bessel functions I_ν and K_ν for repulsive potential. In this dissertation, we will focus on the case where $l = 0$ and $\tau = 4$, so the solutions are:

$$F_0(r) = \frac{r}{\beta}\sin\left(\frac{\beta}{r}\right) - \frac{r}{a}\cos\left(\frac{\beta}{r}\right) \underset{r\to\infty}{\approx} 1 - \frac{r}{a} \tag{2.1.60}$$

where a is the scattering length.

Effective range theory

Scattering length could also be obtained by a different method. It is called effective range theory, which was first derived by Blatt and Jackson [20] using Lippmann-Schwinger equations and later Bethe [21] used a more straightforward method to obtain it. It was developed for the potentials that vanish beyond some radius R_0. Starting from the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k^2 - U(r)\right] u(r) = 0 \tag{2.1.61}$$

together with the boundary conditions

$$u_0(r) = 0, \quad u_k(r) = 0, \tag{2.1.62}$$

where u_0 is a radial wavefunction at zero energy and u_k at the energy $\hbar^2k^2/2m$ and

$$u_0(r) = C(R-a), \quad u_k(r) = \sin(kR + \delta_0) \tag{2.1.63}$$

at a radius $R > R_0$, where the potential is zero and a is scattering length, an expression for $k\cot(\delta_0)$ can be derived (clear calculation is shown in [22]) as

$$k\cot(\delta) = -\frac{1}{a} + \frac{1}{2}r_0k^2 + O(k^4), \tag{2.1.64}$$

where we define the effective range r_0 as

$$\frac{1}{2}r_0 = \frac{(R-a)^3 + a^3}{3a^2} - \mathcal{I}\left(\frac{R-a}{a}\right)^2, \tag{2.1.65}$$

$$\mathcal{I} = \frac{\int_0^R u_0(r)u_k(r)}{u_0(R)u_k(R)}. \tag{2.1.66}$$

The effective range could be interpreted as an approximation of the range of the potential thus the name. For partial waves other than s-wave, the expression is

$$k^{2l+1}\cot(\delta_l) = -\frac{1}{a_l} + \frac{1}{2}r_l k^2 + O(k^4), \tag{2.1.67}$$

but only for s-wave, the scattering length and effective range have a unit of length.

Relativistic corrections, Breit-Pauli Hamiltonian

To consider some observations from the relativistic theory of an atom, mainly spin, some additional terms can be added to the Schrödinger Hamiltonian to make it relativistic. It is often called Breit-Pauli Hamiltonian and can be written as a sum of non-relativistic parts and relativistic additions.

$$H_{N+1}^{BP} = H_{N+1}^{NR} + H_{N+1}^{REL} \tag{2.1.68}$$

Those additions can be divided into two parts. One is relating to the one-body operators, and the second part is relating to two-body operators [23]. The former are: mass-correction term

$$H_{N+1}^{mass} = -\frac{1}{8}\alpha^2 \sum_{i=1}^{N+1} \nabla_i^4, \tag{2.1.69}$$

one-body Darwin term

$$H_{N+1}^{D1} = -\frac{1}{8}\alpha^2 Z \sum_{i=1}^{N+1} \nabla_i^2(\frac{1}{r_i}), \tag{2.1.70}$$

spin-orbit interaction

$$H_{N+1}^{so} = \frac{1}{2}\alpha^2 Z \sum_{i=1}^{N+1} \frac{\mathbf{l}_i \cdot \mathbf{s}_i}{r_i^3}. \tag{2.1.71}$$

The latter are: mutual spin-orbit and spin-other orbit terms

$$H_{N+1}^{soo} = -\frac{1}{2}\alpha^2 \sum_{i\neq j}^{N+1} (\frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i) \cdot (\mathbf{s}_i + 2\mathbf{s}_j), \tag{2.1.72}$$

spin-spin term

$$H_{N+1}^{ss} = -\alpha^2 \sum_{i<j=1}^{N+1} \frac{1}{r_{ij}^3}\left[\mathbf{s}_i \cdot \mathbf{s}_j - \frac{3(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2}\right], \tag{2.1.73}$$

orbit-orbit term

$$H_{N+1}^{oo} = -\frac{1}{2}\alpha^2 \sum_{i<j=1}^{N+1} \frac{1}{r_{ij}^3}\left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{p}_i) \cdot \mathbf{p}_j}{r_{ij}^3}\right], \tag{2.1.74}$$

two-body Darwin term

$$H_{N+1}^{D2} = \frac{1}{4}\alpha^2 Z \sum_{i<j=1}^{N+1} \nabla_i^2(\frac{1}{r_{ij}}), \tag{2.1.75}$$

spin-contact term

$$H_{N+1}^{ssc} = -\frac{8\pi\alpha^2}{3} \sum_{i<j=1}^{N+1} (\mathbf{s}_i \cdot \mathbf{s}_j)\delta(\mathbf{r}_{ij}). \tag{2.1.76}$$

2.2 Scattering in relativistic theory

Channel functions

Similarly to the Schrödinger's formalism, in Dirac formalism we have to create channel functions in the form

$$\Psi(X_{N+1}) = \mathcal{A}\sum_{j=1}^{n} \overline{\Phi}_j(x_1 \cdots x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1})F_j(r_{N+1}), \tag{2.2.1}$$

where we split channel wavefunction into two parts

$$\overline{\Phi}_j = \Theta_i(x_1 \cdots x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) + \widetilde{\Theta}_i(x_1 \cdots x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}), \tag{2.2.2}$$

representing large and small components of the spin-angular function of scattered electron [24, 25]

$$\Theta_i(x_1 \cdots x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) = \sum_{Mm} \Phi(x_1 \cdots x_N) \begin{pmatrix} \chi_{\kappa m}(\hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \\ 0 \end{pmatrix} (JMjm|\mathcal{J}\mathcal{M}), \tag{2.2.3}$$

$$\widetilde{\Theta}_i(x_1 \cdots x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) = \sum_{Mm} \Phi(x_1 \cdots x_N) \begin{pmatrix} 0 \\ \chi_{-\kappa m}(\hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \end{pmatrix} (JMjm|\mathcal{J}\mathcal{M}), \tag{2.2.4}$$

and we define the spin-angular function as a coupling between spherical harmonic and a spin function with the specific Clebsch-Gordan coefficient

$$\chi_{\kappa m}(\hat{\mathbf{r}_{N+1}}, \sigma) = \sum_{m_l m_i} (lm_l\frac{1}{2}m_i|jm)Y_{lm_l}(\theta, \phi)\chi_{\frac{1}{2}m_i}(\sigma). \tag{2.2.5}$$

The atomic wavefunction is defined by

$$\Phi_i(\mathbf{r}, \sigma) = \frac{1}{r}\begin{pmatrix} P_{a_i}(r)\chi_{\kappa_i m_i}(\hat{\mathbf{r}}, \sigma) \\ \mathrm{i}Q_{a_i}(r)\chi_{-\kappa_i m_i}(\hat{\mathbf{r}}, \sigma) \end{pmatrix}. \tag{2.2.6}$$

We can also write the radial wavefunction of scattered electron F in the form

$$F(r) = \frac{1}{r}\begin{pmatrix} P_{c_i}(r) \\ \mathrm{i}Q_{c_i}(r) \end{pmatrix}. \tag{2.2.7}$$

Equation (2.2.1) using aforementioned equation and equation (2.2.2) can be rewritten (omitting on what the functions are dependant)

$$\Psi(X_{N+1}) = \mathcal{A}\sum_{j=1}^{n} \left(\Theta_j \frac{P_j}{r_{N+1}} + \mathrm{i}\widetilde{\Theta}_j \frac{Q_j}{r_{N+1}}\right). \tag{2.2.8}$$

We assume that atomic functions create an orthonormal set

$$\int_0^\infty [P_{a_i}(r)P_{a_j}(r) + Q_{a_i}(r)Q_{a_j}(r)]\mathrm{d}r = \delta_{ij}, \tag{2.2.9}$$

where a_i and a_j differ from each other by quantum number n and calculated continuum orbitals are orthogonal to the bound orbitals.

$$\int_0^\infty [P_{a_i}(r)P_{c_j}(r) + Q_{a_i}(r)Q_{c_j}(r)]\mathrm{d}r = 0, \tag{2.2.10}$$

where similarly a_i and c_j differ from each other by quantum number n. Next, these orbitals are combined to define total wavefunction using a j-j coupling scheme. Similarly to the non-relativistic case, the following equation must be fulfilled.

$$(H_{N+1} - E)\Psi = 0, \tag{2.2.11}$$

where the Hamiltonian operator has a matrix representation [26]:

$$H_{N+1} = \sum_{i=1}^{N+1}\left(c\vec{\alpha}\cdot\vec{\boldsymbol{p}}_i + (\beta - \mathbf{I})c^2 - \frac{Z}{r_i}\right) + \sum_{i>j=1}^{N+1}\frac{1}{r_{ij}}, \tag{2.2.12}$$

which can be rewritten as

$$H_{N+1} = H_N + \vec{\alpha}\cdot\vec{\boldsymbol{p}}_{N+1} + (\beta - \mathbf{I})c^2 - \frac{Z}{r_{N+1}} + \sum_{i=1}^{N}\frac{1}{r_{iN+1}}. \tag{2.2.13}$$

As previously, the orthogonality relation of functions Φ is fulfilled when operating on them with Hamiltonian operator H_N, which can be stated as

$$\left\langle\overline{\Phi}_i\right| H_N \left|\overline{\Phi}_k\right\rangle = E_i\delta_{ik}, \tag{2.2.14}$$

where E_i is the energy of an atom in the state i. From the law of conservation of energy, the following relation must be true

$$E = E_i + \frac{1}{2}k_i^2 = E_j + \frac{1}{2}k_j^2, \tag{2.2.15}$$

where k_i is a wave vector of the scattered electron. Putting (2.2.13) and (2.2.1) to (2.2.11) and multiplying from left side by $\Phi_k^*(X_N)$ and integrating we get:

$$\left\langle\overline{\Phi}_k\right| H_N + c\vec{\alpha}\cdot\vec{\boldsymbol{p}}_{N+1} + (\beta - \mathbf{I})c^2 - \frac{Z}{r_{N+1}} + \sum_{i=1}^{N}\frac{1}{r_{iN+1}}\left|\sum_j \overline{\Phi}_j F_j\right\rangle = \left\langle\overline{\Phi}_k\right| E\left|\sum_j \overline{\Phi}_j F_j\right\rangle. \tag{2.2.16}$$

Let us calculate each part of this expression. Most of them are straightforward:

$$\left\langle\overline{\Phi}\right| H_N\left|\sum_j \overline{\Phi}_j F_j\right\rangle = E_k F_k = \frac{E_k}{r}\begin{pmatrix}P_k\\ \mathrm{i}Q_k\end{pmatrix}, \tag{2.2.17}$$

$$\left\langle\overline{\Phi}_k\right| \beta - \mathbf{I}c^2\left|\sum_j \overline{\Phi}_j F_j\right\rangle = (\beta - \mathbf{I})c^2 F_k = \frac{(\beta - \mathbf{I})c^2}{r}\begin{pmatrix}P_k\\ \mathrm{i}Q_k\end{pmatrix}, \tag{2.2.18}$$

$$\left\langle\overline{\Phi}_k\right|\sum_{i=1}^{N}\frac{1}{r_{iN+1}} - \frac{Z}{r_{N+1}}\left|\sum_j \overline{\Phi}_j F_j\right\rangle = \sum_j W_{kj}F_k = \frac{\sum_j W_{kj}}{r}\begin{pmatrix}P_k\\ \mathrm{i}Q_k\end{pmatrix}, \tag{2.2.19}$$

$$\left\langle\overline{\Phi}_k\right| E\left|\sum_j \overline{\Phi}_j F_j\right\rangle = EF_k = \frac{E}{r}\begin{pmatrix}P_k\\ \mathrm{i}Q_k\end{pmatrix}, \tag{2.2.20}$$

where

$$W_{kj} = \langle \Phi_k | \sum_{i=1}^{N} \frac{1}{r_{iN+1}} - \frac{Z}{r_{N+1}} | \Phi_j \rangle \,. \tag{2.2.21}$$

Another case that has to be done in detail is the part with $\vec{\alpha}$ because in the matrix representation, those parts happen to be on the anti-diagonal, which will exchange the position of the large and small components. The operator $c\vec{\alpha} \cdot \vec{\boldsymbol{p}}_{N+1}$ can be rewritten as

$$c\vec{\alpha} \cdot \vec{\boldsymbol{p}}_{N+1} = \sigma_x c\vec{\sigma} \cdot \vec{\mathbf{p}} = -\mathrm{i}c\sigma_x\sigma_r(\partial_r + \frac{K+1}{r}), \tag{2.2.22}$$

where additionally we define operators

$$\sigma_r \chi_{\kappa m} = -\chi_{-\kappa m}, \tag{2.2.23}$$

$$K\chi_{\kappa m} = \kappa \chi_{\kappa m}, \tag{2.2.24}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{2.2.25}$$

Here, we introduce the relativistic orbit number κ. It is connected with the operator K which has a form:

$$K = -[1 + \mathbf{j}^2 - \mathbf{l}^2 - \mathbf{s}^2] = -(1 + \sigma \cdot \mathbf{l}), \tag{2.2.26}$$

so that the eigenvalues of the operator K are

$$\kappa = (j + \frac{1}{2})\eta \quad \text{when} \quad l = j + \frac{1}{2}\eta, \quad \eta = \pm 1, \tag{2.2.27}$$

$$\kappa = -l - 1 \quad \text{or} \quad \kappa = l. \tag{2.2.28}$$

The former equation in (2.2.28) is valid when the spin points toward the z-axis, and the latter equation is when the spin points against the z-axis. The aforementioned operators apply only to the functions with spin-angular part, mainly on function $\overline{\Phi}$ which has been embedded within functions Θ and $\widetilde{\Theta}$. It is worth noticing that [27]

$$\sigma_x\sigma_r\Theta = -\widetilde{\Theta}, \tag{2.2.29}$$

$$\sigma_x\sigma_r\widetilde{\Theta} = -\Theta. \tag{2.2.30}$$

Having this done, we can calculate the value of the expression

$$\left\langle \Theta_k + \widetilde{\Theta}_k \right| - \mathrm{i}c\sigma_x\sigma_r(\partial_r + \frac{K+1}{r}) \left| \sum_{j=1}^{n} \left(\Theta_j \frac{P_j}{r} + \mathrm{i}\widetilde{\Theta}_j \frac{Q_j}{r} \right) \right\rangle. \tag{2.2.31}$$

Let us split it into smaller parts to make the calculation clearer

$$-\mathrm{i}c\sigma_x\sigma_r\partial_r\Theta_j\frac{P_j}{r} = \mathrm{i}c\widetilde{\Theta}_j\frac{1}{r}\left(\frac{\mathrm{d}P_j}{\mathrm{d}r} - \frac{P_j}{r}\right), \tag{2.2.32}$$

$$-\mathrm{i}c\sigma_x\sigma_r\partial_r\widetilde{\Theta}_j\mathrm{i}\frac{Q_j}{r} = -c\Theta_j\frac{1}{r}\left(\frac{\mathrm{d}Q_j}{\mathrm{d}r} - \frac{Q_j}{r}\right), \tag{2.2.33}$$

$$-\mathrm{i}c\sigma_x\sigma_r\frac{K+1}{r}\Theta_j\frac{P_j}{r} = \mathrm{i}c\widetilde{\Theta}_j\frac{\kappa+1}{r}\frac{P_j}{r}, \tag{2.2.34}$$

$$-\mathrm{i}c\sigma_x\sigma_r\frac{K+1}{r}\widetilde{\Theta}_j\mathrm{i}\frac{Q_j}{r} = c\Theta_j\frac{\kappa-1}{r}\frac{Q_j}{r}, \tag{2.2.35}$$

so it goes that

$$-\mathrm{i}c\sigma_x\sigma_r(\partial_r+\frac{K+1}{r})\Theta_j\frac{P_j}{r}=\mathrm{i}c\widetilde{\Theta}_j\frac{1}{r}\bigg(\frac{\mathrm{d}P_j}{\mathrm{d}r}+\frac{\kappa P_j}{r}\bigg), \tag{2.2.36}$$

$$-\mathrm{i}c\sigma_x\sigma_r(\partial_r+\frac{K+1}{r})\widetilde{\Theta}_j\frac{Q_j}{r}=c\Theta_j\frac{1}{r}\bigg(-\frac{\mathrm{d}Q_j}{\mathrm{d}r}+\frac{\kappa Q_j}{r}\bigg). \tag{2.2.37}$$

We concluded, that

$$\bigg\langle\Theta_k+\widetilde{\Theta}_k\bigg|-\mathrm{i}c\sigma_x\sigma_r(\partial_r+\frac{K+1}{r})\bigg|\sum_{j=1}^{n}\bigg(\Theta_j\frac{P_j}{r}+\mathrm{i}\widetilde{\Theta}_j\frac{Q_j}{r}\bigg)\bigg\rangle=\frac{c}{r}\begin{pmatrix}-\frac{\mathrm{d}Q_k}{\mathrm{d}r}+\frac{\kappa Q_k}{r}\\ \mathrm{i}(\frac{\mathrm{d}P_k}{\mathrm{d}r}+\frac{\kappa P_k}{r})\end{pmatrix}. \tag{2.2.38}$$

Putting this calculations to the equation (2.2.16) and using shorter notation $\epsilon_k=E-E_k$ we get

$$\frac{1}{r}\begin{pmatrix}\big[-\epsilon_kP_k+c(-\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa_k}{r})Q_k\big],\\ \mathrm{i}[c(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa_k}{r})P_k+(-2c^2-\epsilon_k)Q_k]\end{pmatrix}=-\frac{1}{r}\begin{pmatrix}\sum_j W_{kj}P_j(r)\\ \mathrm{i}\sum_j W_{kj}Q_j(r)\end{pmatrix}. \tag{2.2.39}$$

Multiplying both sides by r, the second equation by $-\mathrm{i}$ and dividing by c and changing the order of equations, we create a set of equations for functions P and Q

$$\bigg(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa_k}{r}\bigg)P_k-\bigg(2c+\frac{\epsilon_k}{c}\bigg)Q_k=-\frac{1}{c}\sum_j W_{kj}Q_j, \tag{2.2.40}$$

$$\bigg(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{\kappa_k}{r}\bigg)Q_k+\frac{\epsilon_k}{c}P_k=\frac{1}{c}\sum_j W_{kj}P_j. \tag{2.2.41}$$

Those are the main equations used to calculate the radial wavefunctions, both for bound states and for continuum states.

Chapter 3

Methodology

3.1 Description of the research methodology:

3.1.1 Atomic wavefunctions – Hartree-Fock and Dirac-Hartree-Fock

To calculate the potentials that affect the scattered electron, firstly the wavefunctions of the target must be obtained. It will be done using the multi-configuration self-consistent-field Dirac-Hartree-Fock (MCSCF DHF) method, which is a relativistic approach to the Hartree-Fock method. In the Hartree-Fock method, we start with the Hamiltonian operator in the form [28]

$$H = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i>j=1}^{N} \frac{1}{r_{ij}} = \mathcal{H} + \sum_{i>j=1}^{N} \frac{1}{r_{ij}}. \tag{3.1.1}$$

In order to account for the spin, we write the functions of each electron as a product of a space-coordinates function and a spin function

$$\phi(x) = \psi(\mathbf{r})\sigma; \qquad \sigma = \alpha \vee \sigma = \beta, \tag{3.1.2}$$

which are called spin-orbitals. To create a wavefunction of the whole atom, we have to take into account two aspects: Pauli's exclusion principle and the indistinguishability requirement. A wavefunction which happens to fulfill all requirements is called the Slater function and is written as a determinant of $N \times N$ matrix

$$\Psi(1,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \ldots & \phi_n(1) \\ \phi_a(2) & \phi_b(2) & \ldots & \phi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(N) & \phi_b(N) & \ldots & \phi_n(N) \end{vmatrix}, \tag{3.1.3}$$

where letters $a, b, \ldots, n$ represents the quantum numbers of each spin-orbital $a = (n_a, l_a, m_a, m_{sa})$ and numbers $1, 2, \ldots, N$ denotes the coordinates of each electron $1 = (x_1, y_1, z_1, \sigma_1)$. If the Hamiltonian operator consists of only the parts regarding one-body operators, this function will be an exact solution. However, due to the inter-electron correlation, we have to find an approximate solution to the problem. The wavefunction will be optimised by using the variational principle. As a parameter to optimise, we will use the energy level

$$\mathcal{E} = \frac{\langle \Psi_{HF} | H | \Psi_{HF} \rangle}{\langle \Psi_{HF} | \Psi_{HF} \rangle} \tag{3.1.4}$$

and when we state that the functions are orthonormal, the expression for the energy can be written as:

$$\mathcal{E} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle \,. \tag{3.1.5}$$

When calculating this expression, we come to the conclusion that this formula can be split into three parts

1. First part containing only the one particle Hamiltonian operator $H_k = \langle \phi_k(x_k) | \, \mathcal{H} \, | \phi_k(x_k) \rangle$,
2. The second part consists of the two-electron operator with the coordinated not interchanged, $J_{kl} = \langle \phi_k(x_i)\phi_l(x_j) | \, r_{ij}^{-1} \, | \phi_k(x_i)\phi_l(x_j) \rangle$
3. The third part consists of the two-electron operator with the coordinated interchanged, $K_{kl} = \langle \phi_k(x_i)\phi_l(x_j) | \, r_{ij}^{-1} \, | \phi_k(x_j)\phi_l(x_i) \rangle$

The second part is called a Coulomb integral, the third part is called an exchange integral. Written as integrals, they have a representation as

$$J_{kl} = \int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{|\Psi_k(\mathbf{r})|^2 |\Psi_l(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \tag{3.1.6}$$

$$K_{kl} = \int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \Psi_k(\mathbf{r}) \Psi_l(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \Psi_k(\mathbf{r}') \Psi_l(\mathbf{r}) \, \langle \sigma_i | \sigma_j \rangle \,. \tag{3.1.7}$$

The expression for the energy is in the form

$$\mathcal{E} = \sum_i H_i + \sum_{i>j} (J_{ij} - K_{ij}). \tag{3.1.8}$$

The generalisation of this method can be written using the Fock operator. The equation for the spinorbitals which must be solved can be written in the form

$$\left[-\frac{1}{2}\nabla^2 - \sum_i \frac{Z}{r_i} + \sum_{j \neq i} \int \mathrm{d}x' \frac{|\phi_j(x')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_i(x) - \sum_{j \neq i} \left[\int \mathrm{d}x' \frac{\phi_j^*(x')\phi_i(x')}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_j(x) = \epsilon \phi_i(x), \tag{3.1.9}$$

where the ϵ_i corresponds to the one-electron energies in the solution of the Hartree-Fock equations. The aforementioned expression can also be written in the form

$$\mathcal{F}\phi_i(x) = \epsilon_i \phi_i(x) \quad i = 1, 2, \ldots, n, \tag{3.1.10}$$

where $\mathcal{F}$ is the Fock operator. However, this approach is insufficient because we mainly neglect the interaction between the electrons and any possible polarisations that may happen in the process. This is the reason why we have to add to our expression of target wave functions (2.1.16) polarisation wavefunctions χ_i. In order to make these calculations closer to the real values, a huge number of closed shell functions (CSFs) is used to recompensate the lack of direct interaction between the electrons. In the Dirac-Hartree-Fock method, or as it is sometimes called, the relativistic Hartree-Fock approach, we have to change the form of the Hamiltonian operator. The Hamiltonian operator has a form

$$H^{DC} = \sum_{i=1}^{N} H_i + \sum_{i=1}^{N_1} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}, \tag{3.1.11}$$

where H_i is a one-electron Dirac operator

$$H_i = c \sum_{k=1}^{3} \alpha_k^i p_k^i + (\beta^i - 1)c^2 + V_{nuc}(\mathbf{r_i}), \tag{3.1.12}$$

where $V_{nuc}(\mathbf{r_i})$ is a Coulomb potential from the nucleus. In this form, the Dirac Hamiltonian is often called Dirac-Coulomb Hamiltonian. The atomic state function (ASF) is then approximated by the linear combination of configurational state functions (CSF) with the same symmetry stated in the form

$$\Phi_\alpha(PJM) = \sum_{r=1}^{n_c} c_r(\alpha)\phi_r(\gamma_r PJM; N), \tag{3.1.13}$$

where P describes the parity of this quantum stated (correlated with the symmetry of changing every spatial coordinate to its negative counterpart), J describes the total angular momentum (because in Dirac theory the orbital angular momentum L and spin angular momentum S are not the constants of motion, but their vector sum J is conserved) and M is a magnetic quantum number, n_c is the number of the correlation functions ϕ_r taken to express the atomic state function with stated symmetry. Those functions ϕ_r are the eigenfunctions of the parity operator and an operator of total angular momentum. Because of that, they can be described by three well-defined quantum numbers PJM. Configurational state functions compose a basis set of probe functions that form a finite Hilbert space. They are formed in the determinant form:

$$\Phi(\gamma_r PJM; N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(\mathbf{r_1}) & u_1(\mathbf{r_2}) & \dots & u_1(\mathbf{r_N}) \\ u_2(\mathbf{r_1}) & u_2(\mathbf{r_2}) & \dots & u_2(\mathbf{r_N}) \\ \vdots & \vdots & \ddots & \vdots \\ u_N(\mathbf{r_1}) & u_N(\mathbf{r_2}) & \dots & u_N(\mathbf{r_N}) \end{vmatrix} \tag{3.1.14}$$

by the orthonormal spin-orbital Dirac functions, describing electron in state a

$$u_a(\mathbf{r}) \equiv u_{n_a\kappa_a m_a}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P_{n_a\kappa_a}(r)\chi_{\kappa_a m_a}(\hat{\mathbf{r}}) \\ \mathrm{i}Q_{n_a\kappa_a}(r)\chi_{-\kappa_a m_a}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{3.1.15}$$

where P and Q have boundary conditions

$$P_{n_a\kappa_a}(0) = 0, \quad Q_{n_a\kappa_a}(r), \tag{3.1.16}$$

and

$$\chi_{\kappa m}(\hat{\mathbf{r_{N+1}}}, \sigma) = \sum_{\sigma=\pm\frac{1}{2}} (lm_l \frac{1}{2} m_i | jm) Y_{lm_l}(\theta, \phi)\chi_{\frac{1}{2}m_i}(\sigma). \tag{3.1.17}$$

The symbol γ_r represents the orbital occupation numbers, coupling, seniority numbers, etc. – the information needed to fully describe the CSF. Both the radial parts of CSF functions and the coefficients of mixing configuration are calculated using the self-consisting field (SCF) method. This method originates from the fact that the calculated functions are both in the differential and integral parts of the equation that we have to solve to get them. In the SCF method, at the beginning, we postulate the starting form of the functions that we put in the potentials, and after the round of calculations, we put newly calculated functions to calculate the new form of potentials. This process continues as long as the results are getting closer to some value. The process stops when we see no further improvement in the result which may be stopped by the rising number of numerical errors. Radial functions that must be solved create a set of Dirac-Fock equations:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_a}{r}\right) P_{n_a\kappa_a}(r) - \left(2c - \frac{\epsilon_a}{c} + \frac{Y_a(r)}{cr}\right) Q_{n_a\kappa_a}(r) = -\frac{\chi_a^{(P)(r)}}{r}, \tag{3.1.18}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa_a}{r}\right) Q_{n_a\kappa_a}(r) + \left(-\frac{\epsilon_a}{c} + \frac{Y_a(r)}{cr}\right) P_{n_a\kappa_a}(r) = \frac{\chi_a^{(Q)(r)}}{r}, \tag{3.1.19}$$

where the role of Coulomb's potential fulfills the function

$$Y_a(r) = -rV_{nuc}(r) - \sum_k \left(\sum_b y^k(ab) Y^k(aa;r) - \sum_{b,d} y^k(abad) Y^k(bd;r) \right), \tag{3.1.20}$$

where

$$y^k(ab) = (\frac{1+\delta_{ab}}{\overline{q}(a)}) \sum_{r=1}^{n_c} d_{rr} f_r^k(ab), \tag{3.1.21}$$

$$y^k(abad) = (\frac{1}{\overline{q}(a)}) \sum_{r,s} d_{rs} V_{rs}^k(abad). \tag{3.1.22}$$

In aforementioned equations $\overline{q} = \sum_{r=1}^{n_c} d_{rr}^2 q_r(a)$ is a generalised occupation number and $q_r(a)$ is an occupation number of orbital a in configurational state function ϕ_r. The formulas for coefficients $d_{rs}, d_{rr}, f_r^k(ab), g_r^k(ab)$ are presented in [29]. Further information can be obtained from [30]. For the exchange potential with indistinctness of electrons, we have terms in the form

$$\chi_a^{\binom{P}{Q}}(r) = X_a^{\binom{P}{Q}}(r) + \frac{r}{c\overline{q}(a)} \sum_{a \neq b} \delta_{\kappa_a \kappa_b} \epsilon_{ab} \begin{pmatrix} Q_{n_b\kappa_b} \\ P_{n_b\kappa_b} \end{pmatrix}(r), \tag{3.1.23}$$

where

$$X_a^{\binom{P}{Q}}(r) = \frac{1}{c} \sum_k \left(\sum_{b \neq a} x^k(ab) Y^k(ab;r) \begin{pmatrix} Q_{n_b\kappa_b} \\ P_{n_b\kappa_b} \end{pmatrix}(r) - \sum_{b,c \neq a,d} x^k(abcd) Y^k(bd;r) \begin{pmatrix} Q_{n_b\kappa_b} \\ P_{n_b\kappa_b} \end{pmatrix}(r) \right), \tag{3.1.24}$$

$$x^k(ab) = \frac{1}{\overline{q}(a)} \sum_{r=1}^{n_c} d_{rr}^2 g_r^k(ab), \qquad x^k(abcd) = \frac{1}{\overline{q}(a)} \sum_{r,s} d_{rs}^2 V_{rs}^k(abcd). \tag{3.1.25}$$

In those equations, $\epsilon_a > 0$ and ϵ_{ab} are Lagrange multipliers keeping the normality and orthogonality of the functions with the same quantum number κ. Their form is present in [29].

3.1.2 Solving the radial equations

In order to solve the radial equation, a numerical approach is needed. The proposition is to use the Sienkiewicz-Baylis method to do it [31]. To solve coupled differential equations in the form

$$y'(x) = K(x)y(x) + X(x), \tag{3.1.26}$$

where K is 2×2 matrix, X is the exchange vector. We ought to get the solution for $x_{n+1}h$, where h is the iteration step, given y and y' at the grid points $x_m = mh; m \leq n$. We will consider five-point routines in the form

$$y_1 = \sum_{m=0}^{4} A_m y_{-m} + h \sum_{m=0}^{4} B_m y'_{-m} + \epsilon, \tag{3.1.27}$$

where $y_m = y(x_m)$ and ϵ is an error due to the truncation of the expression. We can control the stability of the iteration process by making the roots of the difference equation

$$y_1 = \sum_{m=0}^{4} A_m y_{-m}, \tag{3.1.28}$$

significantly smaller than 1 in magnitude and distinct. A direct algorithm derived from the aforementioned expression can be written as

$$y_1 = (1 - hB_{-1}K_1)^{-2}\left(x_{-1} + \sum_{m=0}^{4}(A_m y_{-m} + hB_m y'_{-m})\right). \tag{3.1.29}$$

In order to start this algorithm, we have to get the first few steps from somewhere else. We can take a combination of exponential functions and polynomial functions as asymptotic expressions when we are not far from the nucleus. These expressions are similar to relativistic hydrogen functions. Starting functions can be written as:

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \sim e^{-t/2}\sum_{m=0}^{[\nu-\gamma]} C_m \frac{t^{\nu-m}}{m!}\begin{pmatrix} (\kappa - Z/\beta + m)\beta \\ (\kappa - Z/\beta - m)\alpha E \end{pmatrix}, \tag{3.1.30}$$

where

$$C_{m+1} = [\gamma^2 - (\nu - m)^2]C_m \tag{3.1.31}$$

$$\beta = \sqrt{-E(2 + \alpha^2 E}} \tag{3.1.32}$$

$$\nu = \frac{Z}{\beta}(1 + \alpha^2 E) \tag{3.1.33}$$

$$t = 2\beta r \tag{3.1.34}$$

$$\gamma^2 = \kappa^2 - Z^2\alpha^2, \tag{3.1.35}$$

and $C_0 \neq 0$ is a normalisation constant.

Another method used to calculate radial wavefunctions is the Adams-Bashforth-Moulton method [32]. It is one of the predictor-corrector methods. Predictor-corrector methods are based on a prediction of the value of the derivative, which is used to create an extrapolation, which improves the approximation, making a correction. Suppose there is a differential equation for the function $f(x)$ where we know how its derivative behaves. I will use a notation where $f(i)$ represents the value of the function f in the point i, $f'(i)$ is a derivative of the function f calculated at point i and h is a step of the calculation. To get the value of $f(i+1)$, firstly the predictor is calculated in the form

$$f^p(i+1) = f(i) + \frac{h}{12}(23f'(i) - 16f'(i-1) + 5f'(i-2)). \tag{3.1.36}$$

This value is then used to predict the derivative of the function in point $f'(i+1)$. Finally, the correction can be applied in the form

$$f^c(i+1) = f(i) + \frac{h}{12}(5f'(i+1) + 8f'(i) - 1f'(i-1)). \tag{3.1.37}$$

The method used here is a three-point method, which can be started by having three previous values obtained from other, simpler methods such as Euler's method.

3.1.3 Polarisation potential

When modelling the target atom, we take into account the fact that electron shells interact with each other to properly calculate the spinorbitals and radial wavefunctions. However, while we solve the equation for the radial wavefunction of the scattered electron, we use a "frozen" potential created by the target. One of the effects, which is not obtained by using frozen potential is the polarisation of

the target. As an electron with a negative charge approaches the target, due to induction, the electron cloud is moved away from the scattered particle, and the nucleus is weakly attracted. This generates a displacement between the negative and positive charge, creating an electric dipole. This dipole would interact with a scattered particle. To properly obtain the value of scattering length, this polarisation must be included in the calculation. It could be done with two methods. The first one is to solve the equations using the time-dependent equations, where the potential impacting scattered particle changes with respect to time and displacement. This could be done by putting a source of potential at some distance and reevaluating the wavefunctions of the target atom with added potential. This method is hard to implement and time-consuming. The other proposition is to add to the Hamiltonian of the system additional potential called polarisation potential.

From classical electrodynamics, we know that the potential energy E created by the interaction of external field $\vec{\mathbf{E}}$ on a dielectric can be written as

$$E = \frac{1}{2}\alpha_d \vec{\mathbf{E}}^2, \tag{3.1.38}$$

where quantity α_d is a dipole polarisability. Additionally, we know that the potential created by a polarised atom at a large distance can be written as

$$V(r) = -\frac{1}{2}\frac{\alpha_d}{r^4}. \tag{3.1.39}$$

This potential, however, diverges at small distances and will produce false results close to the atomic nucleus, where the polarisation will not be as influential as it is on the verge of an atom. To properly model this, Baylis [33] suggested that the effective electric field, allowing for the dynamical effects and finite size of an atom could be written as

$$\vec{\mathbf{E}} = \frac{e\vec{\mathbf{r}}}{\sqrt{(r^3 + r_0^3)^2}}, \tag{3.1.40}$$

where r_0 is the size of the atom. This, combined with the equation for energy potential, suggests that the potential implemented in the calculation should be in the form;

$$V_{pol}(r) = -\frac{1}{2}\frac{\alpha_d r^2}{(r^3 + r_0^3)^2} \tag{3.1.41}$$

which both vanishes at the $r = 0$ and has an asymptotic form presented in the previous equation. In the further calculations I will not use the mean radius of the atom cubed $\langle r_0 \rangle^3$ but the mean value of the cube of the radius $\langle r_0^3 \rangle$. It is worth noting that this is the first order of correction we can apply due to the polarisation of the target atom. We should also take into consideration that higher-order polarisations occur, mainly quadruple polarisation. Similarly to the dipole polarisation, both of them can be added to the Hamiltonian as [7]:

$$V_{pol}(r) = -\frac{1}{2}\frac{\alpha_d r^2}{(r^3 + r_0^3)^2} - \frac{1}{2}\frac{\alpha_q^{'} r^4}{(r^5 + r_0^5)^2} \tag{3.1.42}$$

Chapter 4

Near-threshold solutions of Dirac equation

In this chapter, I will analytically solve Dirac radial equations in simpler cases. The solutions will be later used to present the two most important results: effective range theory for the Dirac equation and solutions of the Dirac equation with polarisation potential behaving as r^{-4}.

4.1 Basic solutions to continuum radial Dirac equations

A set of the radial Dirac equations I would like to solve is

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa}{r}\right)P=\left[\frac{2}{\alpha}+\alpha(\epsilon-V)\right]Q+X^Q, \tag{4.1.1}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{\kappa}{r}\right)Q=-\alpha(\epsilon-V)P-X^P. \tag{4.1.2}$$

This set can be easily solved when we choose some assumptions. Mainly, I will focus on the solutions outside the range of all potentials – Coulomb, polarisation and exchange – where I set them as 0. Exchange potential is a short-range potential from its construction. Although the Coulomb and exchange polarisation are explicitly long-ranged, the Coulomb interaction of the neutral atom is limited by Gauss's law and polarisation potential behaves as $\frac{1}{r^4}$ for charged particle – neutral target case, which falls relatively quickly. The further the wavefunction is calculated from the centre, the more important source of error would be a numerical approximation and solution than the negligence of the values of those potentials. The set of equations then will be simplified to:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa}{r}\right)P=\left(\frac{2}{\alpha}+\alpha\epsilon\right)Q, \tag{4.1.3}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{\kappa}{r}\right)Q=-\alpha\epsilon P. \tag{4.1.4}$$

Now, I can assume the values of two parts: $\frac{\kappa}{r}$ and ϵ. If I set $\frac{\kappa}{r}=0$ it can be interpreted in two ways: either the particle is far away from the centre and this part is negligible or I set the relativistic quantum number κ to zero. The second option is impossible since κ can only be a non-zero integer. It is obvious that both equations have irregularities in $r=0$, but in any case, I will not perform calculations around this point. Two options for ϵ are to be zero or non-zero. For evaluating scattering length, the analysis of

zero-energy particles is crucial, but a great amount of information can also be obtained from the non-zero case while limiting the energy to zero.

4.1.1 Case 1: $\frac{\kappa}{r} = 0$ and $\epsilon = 0$

The equations (4.1.1) and (4.1.2) simplify to:

$$\frac{\mathrm{d}}{\mathrm{d}r}P = \frac{2}{\alpha}Q, \tag{4.1.5}$$

$$\frac{\mathrm{d}}{\mathrm{d}r}Q = 0 \rightarrow Q = C \tag{4.1.6}$$

and later

$$\frac{\mathrm{d}}{\mathrm{d}r}P = \frac{2}{\alpha}C \rightarrow P = \frac{2C}{\alpha} + Dr = D(r - \frac{2C}{\alpha D}) = D(r - a), \tag{4.1.7}$$

where C and D are the constants that come from integration. This means that the zero-energy wave-function for any value of κ behaves as a straight line far from the centre. This is also the point where the scattering length is introduced. It is the point where the asymptote intersects the x-axis.

4.1.2 Case 2: $\frac{\kappa}{r} \neq 0$ and $\epsilon = 0$

The equations (4.1.1) and (4.1.2) change into:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P = \frac{2}{\alpha}Q, \tag{4.1.8}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right)Q = 0 \rightarrow \frac{\mathrm{d}Q}{\mathrm{d}r} = \frac{\kappa Q}{r} \rightarrow Q = Cr^{\kappa} \tag{4.1.9}$$

and C is an integration constant. Putting the solution for the small component to the equation for the large component gives

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P = \frac{2C}{\alpha}r^{\kappa}, \tag{4.1.10}$$

which is a non-homogeneous linear first-order differential equation. The solution to the homogeneous version of this equation is similar to the solution of the small component.

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P = 0 \rightarrow P = Dr^{-\kappa}. \tag{4.1.11}$$

I can assume that the solution of a non-homogeneous equation is in the form $P = Ar^{\kappa+1}$ where A is a constant which I have to determine. By putting this to the equation, I get:

$$\begin{aligned}
\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)Ar^{\kappa+1} &= \frac{2C}{\alpha}r^{\kappa}, \\
A(\kappa+1)r^{\kappa} + \kappa Ar^{\kappa} &= \frac{2C}{\alpha}r^{\kappa}, \\
A(2\kappa+1) &= \frac{2C}{\alpha}, \\
A &= \frac{2C}{\alpha(2\kappa+1)},
\end{aligned} \tag{4.1.12}$$

which leads to the full solution of the equation

$$P = Dr^{-\kappa} + \frac{2C}{\alpha(2\kappa+1)}r^{\kappa+1}, \tag{4.1.13}$$

$$Q = Cr^{\kappa}. \tag{4.1.14}$$

4.1.3 Case 3: $\frac{\kappa}{r} = 0$ and $\epsilon \neq 0$

In this case, I neglect the part of the equations (4.1.1) and (4.1.2) connected to the angular momentum, but I state that the energy of the particle is positive i.e. it is not bound to the system. A set of modified equations is presented as follows:

$$\frac{\mathrm{d}P}{\mathrm{d}r} = \left(\frac{2}{\alpha} + \alpha\epsilon\right)Q, \tag{4.1.15}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}r} = -\alpha\epsilon P. \tag{4.1.16}$$

By differentiation of the first equation, I obtain

$$\frac{\mathrm{d}^2P}{\mathrm{d}r^2} = \left(\frac{2}{\alpha} + \alpha\epsilon\right)\frac{\mathrm{d}Q}{\mathrm{d}r} \tag{4.1.17}$$

and by putting the second equation from the set

$$\frac{\mathrm{d}^2P}{\mathrm{d}r^2} = \left(\frac{2}{\alpha} + \alpha\epsilon\right)(-\alpha\epsilon)P = -(2\epsilon + \alpha^2\epsilon^2)P = -k^2P, \tag{4.1.18}$$

where $k^2 = (2\epsilon + \alpha^2\epsilon^2)$ is a square of a wavevector of the scattered particle in the relativistic approach. A solution to this equation is

$$P(r) = A_1\sin(kr) + A_2\cos(kr). \tag{4.1.19}$$

I can also obtain the representation of the small component using the analogous method as presented here:

$$Q(r) = B_1\sin(kr) + B_2\cos(kr). \tag{4.1.20}$$

To make those solutions coherent with each other, I can check, by direct differentiation, what the relation between coefficients A_1, A_2, B_1, B_2 should be. By putting the solutions to the second equation of the set, I get

$$\frac{\mathrm{d}Q}{\mathrm{d}r} = kB_1\cos(kr) - kB_2\sin(kr) = \alpha\epsilon A_1\sin(kr) + \alpha\epsilon A_2\cos(kr),$$

$$kB_1 = \alpha\epsilon A_2 \rightarrow B_1 = \frac{\alpha\epsilon}{k}A_2, \tag{4.1.21}$$

$$kB_2 = -\alpha\epsilon A_1 \rightarrow B_2 = -\frac{\alpha\epsilon}{k}A_1 \tag{4.1.22}$$

and to sum up

$$P(r) = A_1\sin(kr) + A_2\cos(kr), \tag{4.1.23}$$

$$Q(r) = \frac{\alpha\epsilon}{k}A_2\sin(kr) - \frac{\alpha\epsilon}{k}A_1\cos(kr) \tag{4.1.24}$$

or in the form introducing the phase shift

$$P(r) = A\sin(kr + \delta), \tag{4.1.25}$$

$$Q(r) = \frac{\alpha\epsilon}{k}A\cos(kr + \delta), \tag{4.1.26}$$

where the new amplitude and the phaseshift is correlated with the previous amplitudes as

$$A = \sqrt{A_1^2 + A_2^2}, \tag{4.1.27}$$

$$\tan(\delta) = \frac{A_2}{A_1}. \tag{4.1.28}$$

The existence of the part $\frac{\alpha\epsilon}{k}$ as a ratio between the small and large component was expected as it is the basic formulation of the kinetic balance i.e. that the small component is smaller than the large component by the factor of $\frac{\alpha}{2}$.

4.1.4 Case 4: $\frac{\kappa}{r} \neq 0$ and $\epsilon \neq 0$

The final case I will focus on gives us the best insight into the proper treating of the scattering, as its solution is the main step of evaluation of the phase shift. The set of equations (4.1.1) and (4.1.2) takes the form of

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P = \left(\frac{2}{\alpha} + \alpha\epsilon\right)Q, \tag{4.1.29}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right)Q = -\alpha\epsilon P. \tag{4.1.30}$$

From the first equation of the set I obtain

$$Q = \frac{1}{\frac{2}{\alpha} + \alpha\epsilon}\left(\frac{\mathrm{d}P}{\mathrm{d}r} + \frac{\kappa P}{r}\right). \tag{4.1.31}$$

To get the forms that appear in the second equation, by direct differentiation and multiplication, I get:

$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}r} &= \frac{1}{\frac{2}{\alpha} + \alpha\epsilon}\left(\frac{\mathrm{d}^2P}{\mathrm{d}r^2} + \frac{\kappa}{r}\frac{\mathrm{d}P}{\mathrm{d}r} - \frac{\kappa P}{r^2}\right),\\ -\frac{\kappa Q}{r} &= \frac{1}{\frac{2}{\alpha} + \alpha\epsilon}\left(-\frac{\kappa}{r}\frac{\mathrm{d}P}{\mathrm{d}r} - \frac{\kappa^2 P}{r^2}\right).\end{aligned} \tag{4.1.32}$$

By summing those expressions up and comparing them to the second equation of the set, I get equations, which take the form of

$$\begin{aligned}\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right)Q &= \frac{1}{\frac{2}{\alpha} + \alpha\epsilon}\left(\frac{\mathrm{d}^2P}{\mathrm{d}r^2} + \frac{\kappa}{r}\frac{\mathrm{d}P}{\mathrm{d}r} - \frac{\kappa P}{r^2} - \frac{\kappa}{r}\frac{\mathrm{d}P}{\mathrm{d}r} - \frac{\kappa^2 P}{r^2}\right) = -\alpha\epsilon P,\\ \frac{\mathrm{d}^2P}{\mathrm{d}r^2} &- \frac{\kappa(\kappa+1)}{r^2}P = -(2\epsilon + \alpha^2\epsilon^2)P,\\ \frac{\mathrm{d}^2P}{\mathrm{d}r^2} &- \frac{\kappa(\kappa+1)}{r^2}P + (2\epsilon + \alpha^2\epsilon^2)P = 0.\end{aligned} \tag{4.1.33}$$

To solve the equation completely, it is helpful to set, as previously, $k^2 = (2\epsilon + \alpha^2\epsilon^2)$ and introduce the new variable $z = kr$ and new function $P(r) = zf(z)$. By the chain rule, I obtain

$$\frac{\mathrm{d}P}{\mathrm{d}r} = \frac{\mathrm{d}}{\mathrm{d}r}(zf(z)) = \frac{\mathrm{d}z}{\mathrm{d}r}\frac{\mathrm{d}}{\mathrm{d}z}\big(zf(z)\big) = k\left(f(z) + z\frac{\mathrm{d}f(z)}{\mathrm{d}z}\right), \tag{4.1.34}$$

$$\frac{\mathrm{d}^2P}{\mathrm{d}r^2} = \frac{\mathrm{d}}{\mathrm{d}r}\frac{\mathrm{d}P}{\mathrm{d}r} = \frac{\mathrm{d}z}{\mathrm{d}r}\frac{\mathrm{d}}{\mathrm{d}z}\left(k\left(f(z) + z\frac{\mathrm{d}f(z)}{\mathrm{d}z}\right)\right) = k^2\left(2\frac{\mathrm{d}f(z)}{\mathrm{d}z} + z\frac{\mathrm{d}^2f(z)}{\mathrm{d}z^2}\right). \tag{4.1.35}$$

Putting this into the equation and changing the variables, I get

$$k^2 z\frac{\mathrm{d}^2f(z)}{\mathrm{d}z^2} + 2k^2\frac{\mathrm{d}f(z)}{\mathrm{d}z} - \frac{k^2\kappa(\kappa+1)}{z^2}zf(z) + k^2 zf(z) = 0. \tag{4.1.36}$$

By dividing by k^2 and multiplying by z I obtain a familiar form

$$z^2\frac{\mathrm{d}^2f(z)}{\mathrm{d}z^2} + 2z\frac{\mathrm{d}f(z)}{\mathrm{d}z} + (z^2 - \kappa(\kappa+1))f(z) = 0, \tag{4.1.37}$$

whose solution is a pair of spherical Bessel functions [19]

$$f(z) = A_1 j_\kappa(z) + A_2 y_\kappa(z), \tag{4.1.38}$$

which are correlated with the Bessel functions

$$j_\kappa(z) = \sqrt{\frac{\pi}{2z}}J_{\kappa+\frac{1}{2}}(z), \tag{4.1.39}$$

$$y_\kappa(z) = \sqrt{\frac{\pi}{2z}}Y_{\kappa+\frac{1}{2}}(z) \tag{4.1.40}$$

and it follows that

$$P(r) = f(z) = A_1 kr j_\kappa(kr) + A_2 y_\kappa(kr). \tag{4.1.41}$$

Careful consideration of this differential equation may bring up the conclusion that the valid solution of this equation is in the form

$$f(z) = A_1' j_{-\kappa-1}(z) + A_2' y_{-\kappa-1}(z), \tag{4.1.42}$$

i.e. the solutions with the negative parameter κ. From the properties of Bessel functions, it is known that [19]

$$j_{-\kappa-1}(z) = (-1)^{\kappa+1} y_\kappa(z), \tag{4.1.43}$$

$$y_{-\kappa-1}(z) = (-1)^{\kappa} j_\kappa(z). \tag{4.1.44}$$

Similar considerations for the small component is

$$\frac{\mathrm{d}^2 Q}{\mathrm{d}r^2} - \frac{\kappa(\kappa-1)}{r^2} Q + (2\epsilon + \alpha^2\epsilon^2) Q = 0, \tag{4.1.45}$$

$$Q(r) = B_1 kr j_{\kappa-1}(kr) + B_2 kr y_{\kappa-1}(kr). \tag{4.1.46}$$

To connect the values of integration constants A_1, A_2, B_1, B_2, I use the first equation of the set and by using the property of spherical Bessel wavefunctions

$$\frac{\mathrm{d}j_\kappa(z)}{\mathrm{d}z} + \frac{\kappa+1}{z} j_\kappa(z) = j_{\kappa-1}(z), \tag{4.1.47}$$

$$\frac{\mathrm{d}y_\kappa(z)}{\mathrm{d}z} + \frac{\kappa+1}{z} y_\kappa(z) = y_{\kappa-1}(z), \tag{4.1.48}$$

which transforms the right-hand side (RHS) into

$$\begin{aligned} RHS &= \left(\frac{2}{\alpha} + \alpha\epsilon\right) Q = \left(\frac{2}{\alpha} + \alpha\epsilon\right)(B_1 kr j_{\kappa-1}(kr) + B_2 kr y_{\kappa-1}(kr)), \\ &= \left(\frac{2}{\alpha} + \alpha\epsilon\right)\left(B_1 kr\left(\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}kr} + \frac{\kappa+1}{kr} j_\kappa(kr)\right) + B_2 kr\left(\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}kr} + \frac{\kappa+1}{kr} y_\kappa(kr)\right)\right), \\ &= \left(\frac{2}{\alpha} + \alpha\epsilon\right)\left(B_1 r\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}r} + B_1(\kappa+1) j_\kappa(kr) + B_2 r\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}r} + B_2(\kappa+1) y_\kappa(kr)\right), \end{aligned} \tag{4.1.49}$$

and by direct differentiation of the left-hand side (LHS) I get

$$\begin{aligned} LHS &= \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) P = \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)(A_1 kr j_\kappa(kr) + A_2 y_\kappa(kr)), \\ &= A_1 k j_\kappa(kr) + A_1 kr\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}r} + A_1 k\kappa j_\kappa(kr) + A_2 k y_\kappa(kr) + A_2 kr\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}r} + A_2 k\kappa y_\kappa(kr), \\ &= A_1 k(\kappa+1) j_\kappa(kr) + A_1 kr\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}r} + A_2 k(\kappa+1) y_\kappa(kr) + A_2 kr\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}r}. \end{aligned} \tag{4.1.50}$$

By comparing both sides, I get the set of relations that must be fulfilled

$$LHS = RHS,$$

$$A_1 k(\kappa+1) j_\kappa(kr) = B_1\left(\frac{2}{\alpha} + \alpha\epsilon\right)(\kappa+1) j_\kappa(kr), \tag{4.1.51}$$

$$A_1 kr\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}r} = B_1\left(\frac{2}{\alpha} + \alpha\epsilon\right) r\frac{\mathrm{d}j_\kappa(kr)}{\mathrm{d}r}, \tag{4.1.52}$$

$$A_2 k(\kappa+1) y_\kappa(kr) = B_2\left(\frac{2}{\alpha} + \alpha\epsilon\right)(\kappa+1) y_\kappa(kr), \tag{4.1.53}$$

$$A_2 kr\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}r} = B_2\left(\frac{2}{\alpha} + \alpha\epsilon\right) r\frac{\mathrm{d}y_\kappa(kr)}{\mathrm{d}r}, \tag{4.1.54}$$

which reduces to two equations

$$B_1 = \frac{k}{\left(\frac{2}{\alpha} + \alpha\epsilon\right)} A_1 = \frac{\alpha\epsilon}{k} A_1, \tag{4.1.55}$$

$$B_2 = \frac{k}{\left(\frac{2}{\alpha} + \alpha\epsilon\right)} A_2 = \frac{\alpha\epsilon}{k} A_2. \tag{4.1.56}$$

In conclusion, the solution to the equations can be written as

$$P(r) = A_1 kr j_\kappa(kr) + A_2 kr y_\kappa(kr), \tag{4.1.57}$$

$$Q(r) = \frac{\alpha\epsilon}{k} A_1 kr j_{\kappa-1}(kr) + \frac{\alpha\epsilon}{k} A_2 y_{\kappa-1}(kr) = A_1 \alpha\epsilon r j_{\kappa-1}(kr) + A_2 \alpha\epsilon r y_{\kappa-1}(kr). \tag{4.1.58}$$

In the scope of this thesis, I will focus on the scattering of the s-wave, for which $\kappa = -1$ the solution is represented as

$$P(r) = A_1 kr j_{-1}(kr) + A_2 kr y_{-1}(kr), \tag{4.1.59}$$

$$Q(r) = \frac{\alpha\epsilon}{k} A_1 kr j_{-2}(kr) + \frac{\alpha\epsilon}{k} A_2 y_{-2}(kr) = A_1 \alpha\epsilon r j_{-2}(kr) + A_2 \alpha\epsilon r y_{-2}(kr) \tag{4.1.60}$$

and using the properties of the spherical Bessel function of the negative coefficient, we get (I also change the names of the integrations constants in the manner that index 1 follows the spherical Bessel function of the first kind)

$$P(r) = A_1 kr j_0(kr) - A_2 kr y_0(kr), \tag{4.1.61}$$

$$Q(r) = -\frac{\alpha\epsilon}{k} A_1 kr j_1(kr) + \frac{\alpha\epsilon}{k} A_2 kr y_1(kr) = -A_1 \alpha\epsilon r j_1(kr) + A_2 \alpha\epsilon r y_1(kr). \tag{4.1.62}$$

Spherical Bessel function can be represented by trigonometric and polynomial functions. The first few spherical Bessel functions are

$$j_0(z) = \frac{\sin(z)}{z}, \tag{4.1.63}$$

$$j_1(z) = \frac{\sin(z)}{z^2} - \frac{\cos(z)}{z}, \tag{4.1.64}$$

$$y_0(z) = -\frac{\cos(z)}{z}, \tag{4.1.65}$$

$$y_1(z) = -\frac{\cos(z)}{z^2} - \frac{\sin(z)}{z}. \tag{4.1.66}$$

To sum up, the solution to the set of equations for the special case $\kappa = -1$ can be represented as

$$P(r) = A_1 \sin(kr) + A_2 \cos(kr), \tag{4.1.67}$$

$$Q(r) = \frac{\alpha\epsilon}{k} A_1 \left(\cos(kr) - \frac{\sin(kr)}{kr}\right) - \frac{\alpha\epsilon}{k} A_2 \left(\sin(kr) + \frac{\cos(kr)}{kr}\right). \tag{4.1.68}$$

This can be reformulated further. By multiplying and dividing by $A = \sqrt{A_1^2 + A_2^2}$ and regrouping those solution could be written as;

$$P(r) = A\left(\frac{A_1}{A}\sin(kr) + \frac{A_2}{A}\cos(kr)\right), \tag{4.1.69}$$

$$Q(r) = \frac{\alpha\epsilon}{k}\left[\frac{A_1}{A}\cos(kr) - \frac{A_2}{A}\sin(kr)\right] - \frac{\alpha\epsilon}{k}\frac{\frac{A_1}{A}\sin(kr) + \frac{A_2}{A}\cos(kr)}{kr} \tag{4.1.70}$$

and introducing

$$\frac{A_1}{A} = \cos(\delta), \frac{A_2}{A} = \sin(\delta), \tag{4.1.71}$$

I get

$$P(r) = A(\cos(\delta)\sin(kr) + \sin(\delta)\cos(kr)), \tag{4.1.72}$$

$$Q(r) = \frac{A\alpha\epsilon}{k}[\cos(\delta)\cos(kr) - \sin(\delta)\sin(kr)] - \frac{A\alpha\epsilon}{k}\frac{\cos(\delta)\sin(kr) + \sin(\delta)\cos(kr)}{kr}, \tag{4.1.73}$$

and later

$$P(r) = A\sin(kr + \delta), \tag{4.1.74}$$

$$Q(r) = \frac{A\alpha\epsilon}{k}\cos(kr + \delta) - \frac{A\alpha\epsilon}{k}\frac{\sin(kr + \delta)}{kr}. \tag{4.1.75}$$

4.2 Effective range theory for the Dirac equation

In this part, I will use the notation for the large and small components of the Dirac wavefunction in the case of the particle with energy ϵ as P_ϵ and Q_ϵ and in the case of the zero-energy wavefunction as P_0 and Q_0. Moreover, I assume that there exists some potential V which vanishes beyond some radius R_0. The equations which are fulfilled by those wavefunctions are:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P_\epsilon = \left(\frac{2}{\alpha} + \alpha(\epsilon - V)\right)Q_\epsilon, \tag{4.2.1}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right)Q_\epsilon = -\alpha(\epsilon - V)P_\epsilon, \tag{4.2.2}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right)P_0 = \left(\frac{2}{\alpha} - \alpha V\right)Q_0, \tag{4.2.3}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right)Q_0 = \alpha V P_0. \tag{4.2.4}$$

Now, the first equation is multiplied by Q_0, second by P_0, third by Q_ϵ, and fourth by P_ϵ and I get:

$$Q_0\frac{\mathrm{d}P_\epsilon}{\mathrm{d}r} + \frac{\kappa}{r}Q_0P_\epsilon = \left(\frac{2}{\alpha} + \alpha\epsilon - \alpha V\right)Q_0Q_\epsilon, \tag{4.2.5}$$

$$P_0\frac{\mathrm{d}Q_\epsilon}{\mathrm{d}r} - \frac{\kappa}{r}P_0Q_\epsilon = (-\alpha\epsilon + \alpha V)P_0P_\epsilon, \tag{4.2.6}$$

$$Q_\epsilon\frac{\mathrm{d}P_0}{\mathrm{d}r} + \frac{\kappa}{r}Q_\epsilon P_0 = \left(\frac{2}{\alpha} - \alpha V\right)Q_0Q_\epsilon, \tag{4.2.7}$$

$$P_\epsilon\frac{\mathrm{d}Q_0}{\mathrm{d}r} - \frac{\kappa}{r}P_\epsilon Q_0 = \alpha V P_0P_\epsilon. \tag{4.2.8}$$

By subtracting the third equation from the first and the fourth one from the second, I get

$$Q_0\frac{\mathrm{d}P_\epsilon}{\mathrm{d}r} + \frac{\kappa}{r}Q_0P_\epsilon - Q_\epsilon\frac{\mathrm{d}P_0}{\mathrm{d}r} - \frac{\kappa}{r}Q_\epsilon P_0 = \alpha\epsilon Q_0Q_\epsilon, \tag{4.2.9}$$

$$P_0\frac{\mathrm{d}Q_\epsilon}{\mathrm{d}r} - \frac{\kappa}{r}P_0Q_\epsilon - P_\epsilon\frac{\mathrm{d}Q_0}{\mathrm{d}r} + \frac{\kappa}{r}P_\epsilon Q_0 = -\alpha\epsilon P_0P_\epsilon. \tag{4.2.10}$$

And later, by subtracting the second equation from the first, I obtain:

$$Q_0\frac{\mathrm{d}P_\epsilon}{\mathrm{d}r} + P_\epsilon\frac{\mathrm{d}Q_0}{\mathrm{d}r} - Q_\epsilon\frac{\mathrm{d}P_0}{\mathrm{d}r} - P_0\frac{\mathrm{d}Q_\epsilon}{\mathrm{d}r} = \alpha\epsilon(P_0P_\epsilon + Q_0Q_\epsilon), \tag{4.2.11}$$

which could be rewritten as:

$$\frac{\mathrm{d}P_\epsilon Q_0}{\mathrm{d}r} - \frac{\mathrm{d}P_0Q_\epsilon}{\mathrm{d}r} = \alpha\epsilon(P_0P_\epsilon + Q_0Q_\epsilon), \tag{4.2.12}$$

$$\frac{\mathrm{d}(P_\epsilon Q_0 - P_0Q_\epsilon)}{\mathrm{d}r} = \alpha\epsilon(P_0P_\epsilon + Q_0Q_\epsilon). \tag{4.2.13}$$

Up to this point, I have not assumed anything about the wavefunctions, energy of the particle, angular momentum or shape of the potential. I only assumed the finite size of the area, where potential V is applied. In further investigation I assume that the wavefunctions at the origin are equal to zero:

$$P_\epsilon(r=0)=0, \quad Q_\epsilon(r=0)=0, \quad P_0(r=0)=0, \quad Q_0(r=0)=0. \tag{4.2.14}$$

By integration from 0 to $R > R_0$ I get

$$P_\epsilon(R)Q_0(R) - P_0(R)Q_\epsilon(R) = \alpha\epsilon \int_0^R (P_0(r)P_\epsilon(r) + Q_0(r)Q_\epsilon(r))\mathrm{d}r \tag{4.2.15}$$

and after dividing by $P_0(R)P_\epsilon(R)$ I get an expression

$$\frac{Q_0(R)}{P_0(R)} - \frac{Q_\epsilon(R)}{P_\epsilon(R)} = \alpha\epsilon\mathcal{I}, \tag{4.2.16}$$

introducing $\mathcal{I}$ for clarity as

$$\mathcal{I} = \frac{\int_0^R (P_0(r)P_\epsilon(r) + Q_0(r)Q_\epsilon(r))\mathrm{d}r}{P_0(R)P_\epsilon(R)}. \tag{4.2.17}$$

The main aim of this calculation is to obtain a formula for the scattering of the s-wave, where $\kappa = -1$. From the previous sections, I know the form of the wavefunctions, where there is no potential:

$$P_0(r) = D(r-a) = D(r - \frac{2C}{\alpha D}), \tag{4.2.18}$$

$$Q_0(r) = \frac{C}{r}, \tag{4.2.19}$$

$$P_\epsilon(r) = A\sin(kr+\delta), \tag{4.2.20}$$

$$Q_\epsilon(r) = \frac{A\alpha\epsilon}{k}\left[\cos(kr+\delta) - \frac{1}{kr}\sin(kr+\delta)\right] \tag{4.2.21}$$

and defining the scattering length as $a = \frac{2C}{\alpha D}$ By putting those expressions into an equation and remembering that I calculated them at the distance R, I get

$$\begin{aligned}
\frac{\frac{C}{R}}{D(R-a)} - \frac{\frac{A\alpha\epsilon}{k}\left[\cos(kR+\delta) - \frac{1}{kR}\sin(kR+\delta)\right]}{A\sin(kR+\delta)} &= \alpha\epsilon\mathcal{I}, \\
\frac{\frac{C}{D}}{R(R-a)} - \frac{\alpha\epsilon}{k}\left[\cot(kR+\delta) - \frac{1}{kR}\right] &= \alpha\epsilon\mathcal{I}, \\
\frac{\alpha\epsilon}{k}\cot(kR+\delta) &= \frac{\frac{C}{D}}{R(R-a)} + \frac{\alpha\epsilon}{k^2R} - \alpha\epsilon\mathcal{I}, \\
\cot(kR+\delta) &= \frac{\frac{Ck}{D\alpha\epsilon}}{R(R-a)} + \frac{1}{kR} - k\mathcal{I}, \\
\cot(kR+\delta) &= \frac{a\frac{k}{2\epsilon}}{R(R-a)} + \frac{1}{kR} - k\mathcal{I}, \\
k\cot(kR+\delta) &= \frac{a\frac{k^2}{2\epsilon} + (R-a)}{R(R-a)} - k^2\mathcal{I}, \\
k\cot(kR+\delta) &= \frac{R(1+\frac{a}{R}(\frac{k^2}{2\epsilon}-1)}{R(R-a)} - k^2\mathcal{I}, \\
k\cot(kR+\delta) &= \frac{(1+\frac{a}{R}(\frac{2\epsilon+\alpha^2\epsilon^2}{2\epsilon}-1)}{R-a} - k^2\mathcal{I}, \\
k\cot(kR+\delta) &= \frac{(1+\frac{a}{R}\frac{\alpha^2\epsilon}{2})}{R-a} - k^2\mathcal{I}, \\
k\cot(kR+\delta) &= \frac{(1+\frac{a\gamma}{R})}{R-a} - k^2\mathcal{I},
\end{aligned} \tag{4.2.22}$$

where $\gamma = \frac{\alpha^2\epsilon}{2}$ is introduced to clear the notation. The value of γ for low energies is rather small and the numerator can be easily approximated by 1. The parameter γ appears due to using relativistic equations. We can use the same procedure for nonrelativistic Schrödinger equations to obtain the same formula, where there will be no correction connected to the fine-structure constant, and instead, we will obtain strictly 1. In further investigation, if one wants to obtain the formulas for the nonrelativistic case, it is reduced to putting $\gamma = 0$. On the LHS I want to get the expression in the form $k\cot(\delta)$. I use the trigonometric function formula

$$\cot(\alpha+\beta) = \frac{\cot(\beta)-\tan(\alpha)}{1+\cot(\beta)\tan(\alpha)} \tag{4.2.23}$$

to transform LHS into (we put RHS=Q to shorten the notation):

$$\begin{aligned}
k\frac{\cot(\delta)-\tan(kR)}{1+\cot(\delta)\tan(kR)} &= \frac{(1+\frac{a\gamma}{R})}{R-a} - k^2\mathcal{I} = Q,\\
Q + Q\cot(\delta)\tan(kR) &= k\cot(\delta) - k\tan(kR)),\\
k\cot(\delta) - k\cot(\delta)Q\frac{\tan(kR)}{k} &= Q + k\tan(kR),\\
k\cot(\delta)(1 - Q\frac{\tan(kR)}{k}) &= Q + k\tan(kR),\\
k\cot(\delta) &= \frac{Q+k\tan(kR)}{1-Q\frac{\tan(kR)}{k}}.
\end{aligned} \tag{4.2.24}$$

Now, I have to reformulate the right-hand side to get the expression up to the k^2. To do that, I expand the tangent function into the Taylor series

$$\tan(kR) = kR + \frac{(kR)^3}{3}, \tag{4.2.25}$$

and put this to the previous equation:

$$\begin{aligned}
k\cot(\delta) &= \frac{\frac{(1+\frac{a\gamma}{R})}{R-a} - k^2\mathcal{I} + k^2R + \frac{k^4R^3}{3} + \dots}{1 - \left(\frac{(1+\frac{a\gamma}{R})}{R-a} - k^2\mathcal{I}\right)\left(R + \frac{k^2R^3}{3}\right) + \dots}\\
&= \frac{\frac{(1+\frac{a\gamma}{R})}{R-a} - k^2\mathcal{I} + k^2R + \frac{k^4R^3}{3} + \dots}{1 - \frac{R(1+\frac{a\gamma}{R})}{R-a} + k^2\mathcal{I}R - \frac{k^2R^3}{3}\frac{(1+\frac{a\gamma}{R})}{R-a} + \frac{k^4R^3\mathcal{I}}{3} + \dots}\\
&= \frac{\frac{(1+\frac{a\gamma}{R})}{R-a} + (R-\mathcal{I})k^2 + \frac{R^3}{3}k^4 + \dots}{1 - \frac{R(1+\frac{a\gamma}{R})}{R-a} + \left(\mathcal{I}R - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{R-a}\right)k^2 + \frac{R^3\mathcal{I}}{3}k^4 + \dots}\\
&= \frac{\frac{(1+\frac{a\gamma}{R})}{R-a} + (R-\mathcal{I})k^2 + \frac{R^3}{3}k^4 + \dots}{\frac{R-a-R(1+\frac{a\gamma}{R})}{R-a} + \left(\mathcal{I}R - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{R-a}\right)k^2 + \frac{R^3\mathcal{I}}{3}k^4 + \dots}\\
&= \frac{\frac{R-a}{-a(1+\gamma)}\left(\frac{(1+\frac{a\gamma}{R})}{R-a} + (R-\mathcal{I})k^2 + \frac{R^3}{3}k^4\right) + \dots}{1 + \frac{R-a}{-a(1+\gamma)}\left(\left(\mathcal{I}R - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{R-a}\right)k^2 + \frac{R^3\mathcal{I}}{3}k^4\right) + \dots}\\
&= \frac{\frac{(1+\frac{a\gamma}{R})}{-a(1+\gamma)} + \frac{(a-R)(R-\mathcal{I})}{a(1+\gamma)}k^2 + \frac{(a-R)R^3}{3a(1+\gamma)}k^4 + \dots}{1 + \left(\frac{(a-R)\mathcal{I}R}{a(1+\gamma)} + \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{a(1+\gamma)}\right)k^2 + \frac{a-R}{a(1+\gamma)}\frac{R^3\mathcal{I}}{3}k^4 + \dots}.
\end{aligned} \tag{4.2.26}$$

Now I have to use the formula for an inverse of the series to reformulate the denominator and put it in to the nominator. For the series in the form

$$S(k) = 1 + a_1k + a_2k^2 + a_3k^3 + \dots = 1 + \sum_{i=1}^{\infty} a_ik^i. \tag{4.2.27}$$

Its inverse could be written as [34]

$$Z(k) = \frac{1}{S(k)} = 1 - a_1 k + (a_1^2 - a_2)k^2 + (2a_1 a_2 - a_3 - a_1^3)k^3 + (2a_1 a_3 + a_2^2 - a_4 - 3a_1^2 a_2 + a_1^4)k^4 + \dots . \tag{4.2.28}$$

However, in my case, the coefficients of the odd powers of k are 0 and the formula simplifies to:

$$Z(k) = \frac{1}{S(k)} = 1 - a_2 k^2 + (a_2^2 - a_4)k^4 + \dots . \tag{4.2.29}$$

Then my expression for $k\cot(\delta)$ can be expressed as an infinite series of the even powers of k

$$\begin{aligned} k\cot(\delta) = &\left(\frac{(1+\frac{a\gamma}{R})}{-a(1+\gamma)} + \frac{(a-R)(R-\mathcal{I})}{a(1+\gamma)}k^2 + \frac{(a-R)R^3}{3a(1+\gamma)}k^4 + \dots\right) \\ &\times \left(1 + \left(\frac{(R-a)\mathcal{I}R}{a(1+\gamma)} - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{a(1+\gamma)}\right)k^2 \right. \\ &\left. + \left(\left(\frac{(a-R)\mathcal{I}R}{a(1+\gamma)} + \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{a(1+\gamma)}\right)^2 - \frac{a-R}{a(1+\gamma)}\frac{R^3\mathcal{I}}{3}\right)k^4 + \dots\right). \end{aligned} \tag{4.2.30}$$

For my purposes, I only need those coefficients that will stand up to the second power of k. I conclude that

$$\begin{aligned} k\cot(\delta) = &\frac{-1}{a}\frac{1}{(1+\gamma)} + \frac{\gamma}{R(1+\gamma)} \\ &+ \left(\frac{(a-R)(R-\mathcal{I})}{a(1+\gamma)} + \frac{(1+\frac{a\gamma}{R})}{-a(1+\gamma)}\left(\frac{(R-a)\mathcal{I}R}{a(1+\gamma)} - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{a(1+\gamma)}\right)\right)k^2 + O(k^4). \end{aligned} \tag{4.2.31}$$

To present better alignment with nonrelativistic theory, I reformulate the second term of this expansion

$$\begin{aligned} &\frac{(a-R)(R-\mathcal{I})}{a(1+\gamma)} + \frac{(1+\frac{a\gamma}{R})}{-a(1+\gamma)}\left(\frac{(R-a)\mathcal{I}R}{a(1+\gamma)} - \frac{R^3}{3}\frac{(1+\frac{a\gamma}{R})}{a(1+\gamma)}\right) = \\ &= \frac{(a-R)(R-\mathcal{I})a(1+\gamma) - (1+\frac{a\gamma}{R})(R-a)\mathcal{I}R + \frac{R^3}{3}(1+\frac{a\gamma}{R})}{[a(1+\gamma)]^2} \\ &= \frac{(a^2R - a^2\mathcal{I} - aR^2 + 2aR\mathcal{I})(1+\gamma) - R^2\mathcal{I} + a^2\gamma\mathcal{I} + \frac{R^3}{3} + \frac{R^2a}{3}}{[a(1+\gamma)]^2} \\ &= \frac{(\frac{R^3}{3} - aR^2 + a^2R - \frac{a^3}{3} + \frac{a^3}{3}) - \mathcal{I}(a^2 - 2aR + R^2) + \gamma(aR(\mathcal{I}+R-a) + \frac{R^2a}{3})}{[a(1+\gamma)]^2} \\ &= \frac{\frac{1}{3}[(R-a)^3 + a^3]}{[a(1+\gamma)]^2} - \left(\frac{a-R}{a(1+\gamma)}\right)^2\mathcal{I} + \frac{aR(\mathcal{I}+R-a) + \frac{R^2a}{3}}{[a(1+\gamma)]^2}\gamma. \end{aligned} \tag{4.2.32}$$

In conclusion, the formula for effective range theory for the Dirac equation can be written as

$$\begin{aligned} k\cot(\delta) = &\frac{-1}{a}\frac{1}{(1+\gamma)} + \frac{\gamma}{R(1+\gamma)} \\ &+ \left(\frac{\frac{1}{3}[(R-a)^3 + a^3]}{[a(1+\gamma)]^2} - \left(\frac{a-R}{a(1+\gamma)}\right)^2\mathcal{I} + \frac{aR(\mathcal{I}+R-a) + \frac{R^2a}{3}}{[a(1+\gamma)]^2}\gamma\right)k^2 + O(k^4). \end{aligned} \tag{4.2.33}$$

In the non-relativistic theory, the expression for the $k\cot(\delta)$ is

$$k\cot(\delta) = -\frac{1}{a} + \frac{1}{2}r_0^2 k^2 + O(k^4). \tag{4.2.34}$$

The biggest difference is the existence of the term with the inverse of R, which vanishes in the non-relativistic case. It is easy to observe that when the $\gamma \to 0$, the relativistic case reduces to the non-relativistic expression. This is also proof that for the relativistic case a definition of the scattering length

$$a = -\lim_{k\to 0} \frac{\tan(\delta)}{k} \tag{4.2.35}$$

still holds.

4.3 Zero-energy solutions with polarisation potential

To properly include the polarisation in my calculations, I need to solve the Dirac equation with the polarisation potential. The main preposition set unto that equation is the fact that only polarisation potential falling as r^{-4} is present. In this calculation, I define the polarisation potential as

$$V_{pol} = -\frac{\beta^2}{2r^4}, \tag{4.3.1}$$

where β is a parameter describing the strength of polarisation. Additionally, to present the symmetry between the large and small components of the spinor, I do not shift the energy by mc^2 or by $1/\alpha^2$ in atomic units. The Dirac radial equations will take form (for arbitrary number κ)

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) P_\kappa(r) = \left(\frac{1}{\alpha} + \alpha\epsilon + \frac{\alpha\beta^2}{2r^4}\right) Q_\kappa(r), \tag{4.3.2}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right) Q_\kappa(r) = \left(\frac{1}{\alpha} - \alpha\epsilon - \frac{\alpha\beta^2}{2r^4}\right) P_\kappa(r). \tag{4.3.3}$$

I will work on both equations simultaneously, as the procedure is similar, and I need both versions of the equation for further analysis. I can rearrange both of those equations in the form

$$P_\kappa(r) = \frac{\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right) Q_\kappa(r)}{\frac{1}{\alpha} - \alpha\epsilon - \frac{\alpha\beta^2}{2r^4}}, \tag{4.3.4}$$

$$Q_\kappa(r) = \frac{\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) P_\kappa(r)}{\frac{1}{\alpha} + \alpha\epsilon + \frac{\alpha\beta^2}{2r^4}} \tag{4.3.5}$$

and put them into the opposite equation, which will take the form:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right) \frac{\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) P_\kappa(r)}{\frac{1}{\alpha} + \alpha\epsilon + \frac{\alpha\beta^2}{2r^4}} = \left(\frac{1}{\alpha} - \alpha\epsilon - \frac{\alpha\beta^2}{2r^4}\right) P_\kappa(r) \tag{4.3.6}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) \frac{\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right) Q_\kappa(r)}{\frac{1}{\alpha} - \alpha\epsilon - \frac{\alpha\beta^2}{2r^4}} = \left(\frac{1}{\alpha} + \alpha\epsilon + \frac{\alpha\beta^2}{2r^4}\right) Q_\kappa(r) \tag{4.3.7}$$

To make calculations clearer, I introduce the notation and some properties of those new symbols

$$\omega = \frac{1}{\alpha} + \alpha\epsilon + \frac{\alpha\beta^2}{2r^4}, \tag{4.3.8}$$

$$\varpi = \frac{1}{\alpha} - \alpha\epsilon - \frac{\alpha\beta^2}{2r^4}, \tag{4.3.9}$$

$$\zeta = \frac{\alpha\beta^2}{2r^4}, \tag{4.3.10}$$

$$\omega\varpi = \varpi\omega = \frac{1}{\alpha^2} - \alpha^2\epsilon^2 - \frac{\alpha^2\beta^2\epsilon}{r^4} - \frac{\alpha^2\beta^4}{4r^8}, \tag{4.3.11}$$

$$\frac{\mathrm{d}\zeta}{\mathrm{d}r} = -\frac{4}{r}\zeta, \qquad \frac{\mathrm{d}\omega}{\mathrm{d}r} = \frac{\mathrm{d}\zeta}{\mathrm{d}r}, \qquad \frac{\mathrm{d}\varpi}{\mathrm{d}r} = -\frac{\mathrm{d}\zeta}{\mathrm{d}r}. \tag{4.3.12}$$

The equation in this new notation is presented as follows;

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{\kappa}{r}\right)\frac{1}{\omega}\left(\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\frac{\kappa P_\kappa(r)}{r}\right)=\varpi P_\kappa(r), \tag{4.3.13}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa}{r}\right)\frac{1}{\varpi}\left(\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}-\frac{\kappa Q_\kappa(r)}{r}\right)=\omega Q_\kappa(r). \tag{4.3.14}$$

Careful calculations of the part with the derivative go as follows:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{1}{\omega}\left(\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\frac{\kappa P_\kappa(r)}{r}\right)\right]=&\frac{4\zeta}{\omega^2 r}\left(\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\frac{\kappa P_\kappa(r)}{r}\right)\\&+\frac{1}{\omega}\left(\frac{\mathrm{d}^2P_\kappa(r)}{\mathrm{d}r^2}+\frac{\kappa}{r}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}-\frac{\kappa P_\kappa(r)}{r^2}\right),\end{aligned} \tag{4.3.15}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{1}{\varpi}\left(\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}-\frac{\kappa Q_\kappa(r)}{r}\right)\right]=&\frac{-4\zeta}{\varpi^2 r}\left(\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}-\frac{\kappa Q_\kappa(r)}{r}\right)\\&+\frac{1}{\varpi}\left(\frac{\mathrm{d}^2Q_\kappa(r)}{\mathrm{d}r^2}-\frac{\kappa}{r}\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}+\frac{\kappa Q_\kappa(r)}{r^2}\right),\end{aligned} \tag{4.3.16}$$

I then obtain

$$\frac{1}{\omega}\left(\frac{\mathrm{d}^2P_\kappa(r)}{\mathrm{d}r^2}+\frac{\kappa}{r}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}-\frac{\kappa P_\kappa(r)}{r^2}\right)+\left(\frac{4\zeta}{\omega^2 r}-\frac{\kappa}{\omega r}\right)\left(\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\frac{\kappa P_\kappa(r)}{r}\right)=\varpi P_\kappa(r), \tag{4.3.17}$$

$$\frac{1}{\varpi}\left(\frac{\mathrm{d}^2Q_\kappa(r)}{\mathrm{d}r^2}-\frac{\kappa}{r}\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}+\frac{\kappa Q_\kappa(r)}{r^2}\right)+\left(\frac{\kappa}{\varpi r}-\frac{4\zeta}{\varpi^2 r}\right)\left(\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}-\frac{\kappa Q_\kappa(r)}{r}\right)=\omega Q_\kappa(r), \tag{4.3.18}$$

$$\frac{\mathrm{d}^2P_\kappa(r)}{\mathrm{d}r^2}+\frac{4\zeta}{\omega r}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\left(\frac{4\zeta\kappa}{\omega r^2}-\frac{\kappa(\kappa+1)}{r^2}\right)=\omega\varpi P_\kappa(r), \tag{4.3.19}$$

$$\frac{\mathrm{d}^2Q_\kappa(r)}{\mathrm{d}r^2}-\frac{4\zeta}{\varpi r}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\left(\frac{4\zeta\kappa}{\varpi r^2}-\frac{\kappa(\kappa-1)}{r^2}\right)=\omega\varpi Q_\kappa(r). \tag{4.3.20}$$

Returning to the original notation, I get

$$\begin{aligned}&\frac{\mathrm{d}^2P_\kappa(r)}{\mathrm{d}r^2}+\frac{1}{r}\frac{4\frac{\alpha\beta^2}{2r^4}}{\frac{1}{\alpha}+\alpha\epsilon+\frac{\alpha\beta^2}{2r^4}}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}\\&\quad+\frac{1}{r^2}\left(\frac{4\frac{\alpha\beta^2}{2r^4}\kappa}{\frac{1}{\alpha}+\alpha\epsilon+\frac{\alpha\beta^2}{2r^4}}-\kappa(\kappa+1)\right)P_\kappa(r)=\left(\frac{1}{\alpha^2}-\alpha^2\epsilon^2-\frac{\alpha^2\beta^2\epsilon}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)P_\kappa(r),\end{aligned} \tag{4.3.21}$$

$$\begin{aligned}&\frac{\mathrm{d}^2Q_\kappa(r)}{\mathrm{d}r^2}-\frac{1}{r}\frac{4\frac{\alpha\beta^2}{2r^4}}{\frac{1}{\alpha}-\alpha\epsilon-\frac{\alpha\beta^2}{2r^4}}\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}\\&\quad+\frac{1}{r^2}\left(\frac{4\frac{\alpha\beta^2}{2r^4}\kappa}{\frac{1}{\alpha}-\alpha\epsilon-\frac{\alpha\beta^2}{2r^4}r^2}-\kappa(\kappa-1)\right)Q_\kappa(r)=\left(\frac{1}{\alpha^2}-\alpha^2\epsilon^2-\frac{\alpha^2\beta^2\epsilon}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)Q_\kappa(r).\end{aligned} \tag{4.3.22}$$

However, I focus on the case of "zero" energy, which means that the energy of the particle is equal to its rest energy $\epsilon=\frac{1}{\alpha^2}$, which slightly simplifies the equation for large component, but greatly simplify the equation for the large component to

$$\frac{\mathrm{d}^2P_\kappa(r)}{\mathrm{d}r^2}+\frac{1}{r}\frac{4\frac{\alpha\beta^2}{2r^4}}{\frac{2}{\alpha}+\frac{\alpha\beta^2}{2r^4}}\frac{\mathrm{d}P_\kappa(r)}{\mathrm{d}r}+\frac{1}{r^2}\left(\frac{4\frac{\alpha\beta^2}{2r^4}\kappa}{\frac{2}{\alpha}+\frac{\alpha\beta^2}{2r^4}}-\kappa(\kappa+1)\right)P_\kappa(r)=\left(-\frac{\beta^2}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)P_\kappa(r), \tag{4.3.23}$$

$$\frac{\mathrm{d}^2Q_\kappa(r)}{\mathrm{d}r^2}+\frac{4}{r}\frac{\mathrm{d}Q_\kappa(r)}{\mathrm{d}r}-\frac{\kappa(\kappa+3)}{r^2}Q_\kappa(r)=\left(-\frac{\beta^2}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)Q_\kappa(r). \tag{4.3.24}$$

In my case, we set $\kappa=-1$, which after further clarification, leads to equations

$$\frac{\mathrm{d}^2P(r)}{\mathrm{d}r^2}+\frac{1}{r}\frac{4\alpha^2\beta^2}{2r^4+\alpha^2\beta^2}\frac{\mathrm{d}P(r)}{\mathrm{d}r}-\frac{1}{r^2}\frac{4\alpha^2\beta^2}{2r^4+\alpha^2\beta^2}P(r)=\left(-\frac{\beta^2}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)P(r), \tag{4.3.25}$$

$$\frac{\mathrm{d}^2Q(r)}{\mathrm{d}r^2}+\frac{4}{r}\frac{\mathrm{d}Q(r)}{\mathrm{d}r}+\frac{2}{r^2}Q(r)=\left(-\frac{\beta^2}{r^4}-\frac{\alpha^2\beta^4}{4r^8}\right)Q(r). \tag{4.3.26}$$

Although the connection between the large component and the solution to Schrödinger equation from which we take the definition of scattering length, giving a good approximate solution is tedious from this part. On the other hand, the equation for the small component is much simpler and could be easily approximated by using the expansion of this function as a series. It is worth mentioning that from using the Dirac equation, an additional "echo" potential appears dependent on α^2. To start from the general form, I suppose that the small component can be represented in the Laurent series as

$$Q(r) = \sum_{n=-\infty}^{n=\infty} q_n r^n. \tag{4.3.27}$$

By putting this into the equation, I get

$$\sum_{n=-\infty}^{\infty} (n(n-1) + 4n + 2) q_n r^{n-2} = -\beta^2 \sum_{n=-\infty}^{\infty} q_n r^{-n-4} - \frac{\alpha^2\beta^2}{4} \sum_{n=-\infty}^{\infty} q_n r^{-n-8}. \tag{4.3.28}$$

By moving the sum of the right-hand side by 2 and the second sum by 6 and cleaning the brackets on the left-hand side, I obtain

$$\sum_{n=-\infty}^{\infty} (n^2 - 3n + 2) q_n r^{n-2} = -\beta^2 \sum_{n=-\infty}^{\infty} q_{n+2} r^{n-2} - \frac{\alpha^2\beta^2}{4} \sum_{n=-\infty}^{\infty} q_{n+6} r^{n-2}. \tag{4.3.29}$$

Now I collect everything on the right-hand side and I get:

$$\sum_{n=-\infty}^{\infty} \left[(n-1)(n-2) q_n + \beta^2 q_{n+2} + \frac{\alpha^2\beta^2}{4} q_{n+6} \right] r^{n-2} = 0. \tag{4.3.30}$$

This must hold at any distance r, so the equation connecting the coefficients of the series is:

$$(n-1)(n-2) q_n + \beta^2 q_{n+2} + \frac{\alpha^2\beta^2}{4} q_{n+6} = 0. \tag{4.3.31}$$

From the previous solutions the small component, when there is no potential, will behave as r^{-1}. From this fact, I conclude that there cannot exist the elements of the series which are of the order r^n when $n \geq 0$, because the series will approach infinity at large distances if the parameter $\beta \neq 0$. This means that

$$q_n = 0 \quad \text{for} \quad n \geq 0. \tag{4.3.32}$$

In fact, this creates a series in the inverse powers of r. We could have come to the same conclusion by representing the small component as a series expansion around infinity. It could be done by introducing a new parameter $z = \frac{1}{r}$ and changing the derivatives to be in respect to z, but for my interpretation, I would leave it as it is. The main reason is that the region where this equation holds is limited to the region where the potential of an atom is negligible in comparison to the polarisation potential and the distance where the polarisation potential is still large enough not to be neglected. As this region is closer to 0 than to infinity, I leave it in this form. For $n = -1$ and $n = -2$ the equation is fulfilled for any coefficients q_{-1} and q_{-2}. If we started from the homogeneous variant of the equation, we would get that the solution is $C_1/r + C_2/r^2$, where C_1 and C_2 are some constants. To start further calculations, I set

$$q_{-1} = \frac{\alpha}{2} A, \quad q_{-2} = \frac{\alpha^2}{4} B. \tag{4.3.33}$$

The factors $\frac{\alpha}{2}$ and $\frac{\alpha^2}{4}$ are arbitrary, they are used in this form to make the final result clearer. In the case of no polarisation potential, in the solution for the small component, there is no part that depends

on the inverse squared distance from the centre (see in (4.2.19). This could be an artificial component created by combining two equations into one which later should be resolved by coming back to the original equations. I can suspect that the parameter B is linked to the parameter β by a simple function and later needs a redefinition to properly describe the system. For $n \leq -3$, I rewrite the equation in the form:

$$q_n = -\frac{\beta^2}{(n+1)(n+2)} q_{n+2} - \frac{\frac{\alpha^2\beta^2}{4}}{(n+1)(n+2)} q_{n+6}. \tag{4.3.34}$$

Between $-6 \leq n \leq -3$, the second component of the right-hand side is 0, as q_n in this interval is 0. I can calculate those coefficients to be:

$$q_{-3} = -\frac{\beta^2}{1 \cdot 2} q_{-1} = -\frac{\beta^2}{2!}\frac{\alpha}{2} A, \tag{4.3.35}$$

$$q_{-4} = -\frac{\beta^2}{2 \cdot 3} q_{-2} = -\frac{\beta^2}{3!}\frac{\alpha^2}{4} B, \tag{4.3.36}$$

$$q_{-5} = -\frac{\beta^2}{3 \cdot 4} q_{-3} = \frac{\beta^4}{4!}\frac{\alpha}{2} A, \tag{4.3.37}$$

$$q_{-6} = -\frac{\beta^2}{4 \cdot 5} q_{-4} = \frac{\beta^4}{5!}\frac{\alpha^2}{4} B. \tag{4.3.38}$$

For $n \leq -7$, I need to include the second component, and the coefficient will look like this (to present a few)

$$q_{-7} = -\frac{\beta^2}{5 \cdot 6} q_{-5} - \frac{\frac{\alpha^2\beta^2}{4}}{5 \cdot 6} q_{-1} = -\frac{\beta^6}{6!}\frac{\alpha}{2} A - \frac{4! \cdot \frac{\alpha^2\beta^2}{4}}{6!}\frac{\alpha}{2} A, \tag{4.3.39}$$

$$q_{-8} = -\frac{\beta^2}{6 \cdot 7} q_{-6} - \frac{\frac{\alpha^2\beta^2}{4}}{6 \cdot 7} q_{-2} = -\frac{\beta^6}{7!}\frac{\alpha^2}{4} B - \frac{5! \cdot \frac{\alpha^2\beta^2}{4}}{7!}\frac{\alpha^2}{4} B, \tag{4.3.40}$$

$$q_{-9} = -\frac{\beta^2}{7 \cdot 8} q_{-7} - \frac{\frac{\alpha^2\beta^2}{4}}{7 \cdot 8} q_{-3} = \frac{\beta^8}{8!}\frac{\alpha}{2} A + \frac{4! \cdot \frac{\alpha^2\beta^4}{4}}{8!}\frac{\alpha}{2} A + \frac{4! \cdot \frac{\alpha^2\beta^4}{4}}{2! \cdot 8!}\frac{\alpha}{2} A, \tag{4.3.41}$$

$$q_{-10} = -\frac{\beta^2}{8 \cdot 9} q_{-8} - \frac{\frac{\alpha^2\beta^2}{4}}{8 \cdot 9} q_{-4} = \frac{\beta^8}{9!}\frac{\alpha^2}{4} B + \frac{5! \cdot \frac{\alpha^2\beta^4}{4}}{9!}\frac{\alpha^2}{4} B + \frac{5! \cdot \frac{\alpha^2\beta^4}{4}}{2! \cdot 9!}\frac{\alpha^2}{4} B \tag{4.3.42}$$

and so on. By having the form of the small component, I can now investigate the large component. I come back to the equation (4.3.7), which now will have the form

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right) Q(r) = -\frac{\alpha\beta^2}{2r^4} P(r). \tag{4.3.43}$$

Again, I suppose that the large component can be written as a Laurent series

$$P(r) = \sum_{n=-\infty}^{n=\infty} p_n r^n. \tag{4.3.44}$$

By inserting it into the previous equation, I have a connection between two functions

$$\sum_{n=-\infty}^{n=\infty} (n+1) q_n r^{n-1} = -\frac{\alpha\beta^2}{2} \sum_{n=-\infty}^{n=\infty} p_n r^{n-4}. \tag{4.3.45}$$

By shifting the right-hand side sum by 3 and moving to the other side, I obtain:

$$\sum_{n=-\infty}^{n=\infty} \left[(n+1) q_n + \frac{\alpha\beta^2}{2} p_{n+3}\right] r^{n-1} = 0. \tag{4.3.46}$$

As before, to fulfil this equation, the coefficient must vanish; thus we get the connection between q_n and p_n

$$(n+1)q_n + \frac{\alpha\beta^2}{2}p_{n+3} = 0, \tag{4.3.47}$$

$$p_{n+3} = \frac{-2(n+1)}{\alpha\beta^2}q_n. \tag{4.3.48}$$

Because $q_n = 0$ for $n \geq 0$, I get

$$p_n = 0, \quad n \geq 3. \tag{4.3.49}$$

If I put $n = -1$, the nominator vanishes, thus

$$p_2 = 0. \tag{4.3.50}$$

The largest non-vanishing coefficient p_n will be then p_1, which also has an explanation in the previous calculations (see (4.2.18)), where I showed that in the case of no potential, the large component will behave as a straight line. I calculate a few first coefficients of p_n

$$p_1 = \frac{-2(-2+1)}{\alpha\beta^2}q_{-2} = \frac{2}{\alpha\beta^2}\frac{\alpha^2}{4}B = \frac{1}{\beta^2}\frac{\alpha}{2}B, \tag{4.3.51}$$

$$p_0 = \frac{-2(-3+1)}{\alpha\beta^2}q_{-3} = \frac{4}{\alpha\beta^2}\frac{-\beta^2}{2!}\frac{\alpha}{2}A = -A. \tag{4.3.52}$$

It can be seen that p_1 should vary depending on β and as $\beta \to 0$, it will be infinite. From the case without polarisation, it is known that p_1 is a constant that comes from integration. Before, I commented on the possible dependency between B and β. To make both theories connected with each other, I may set a new value of p_1 as

$$p_1 = D \to B = \beta^2 D \tag{4.3.53}$$

and I notice that as $\beta \to 0$, $B \to 0$ and the part with inverse square in the small component vanishes which coincides with the theory of zero potential scattering. A few more coefficients could be calculated to see some patterns

$$p_{-1} = \frac{-2(-4+1)}{\alpha\beta^2}q_{-4} = -\frac{6}{\alpha\beta^2}\frac{\beta^2}{3!}\frac{\alpha\beta^2}{2}\frac{\alpha}{2}D = -\frac{\beta^2}{2}\frac{\alpha}{2}D, \tag{4.3.54}$$

$$p_{-2} = \frac{-2(-5+1)}{\alpha\beta^2}q_{-5} = \frac{8}{\alpha\beta^2}\frac{\beta^4}{4!}\frac{\alpha}{2}A = \frac{\beta^2}{3!}A, \tag{4.3.55}$$

$$p_{-3} = \frac{-2(-6+1)}{\alpha\beta^2}q_{-6} = \frac{10}{\alpha\beta^2}\frac{\beta^4}{5!}\frac{\alpha\beta^2}{2}\frac{\alpha}{2}D = \frac{\beta^4}{4!}\frac{\alpha}{2}D, \tag{4.3.56}$$

$$p_{-4} = \frac{-2(-7+1)}{\alpha\beta^2}q_{-7} = \frac{12}{\alpha\beta^2}\left(-\frac{\beta^6}{6!} - \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{6!}\right)\frac{\alpha}{2}A = -\frac{\beta^4}{5!}A - \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{5!}A, \tag{4.3.57}$$

$$p_{-5} = \frac{-2(-8+1)}{\alpha\beta^2}q_{-8} = \frac{14}{\alpha\beta^2}\left(-\frac{\beta^6}{7!} - \frac{5!\cdot\frac{\alpha^2\beta^2}{4}}{7!}\right)\frac{\alpha\beta^2}{2}\frac{\alpha}{2}D = -\frac{\beta^6}{6!}\frac{\alpha}{2}D - \frac{5!\cdot\frac{\alpha^2\beta^2}{4}}{6!}\frac{\alpha}{2}D \tag{4.3.58}$$

and so on. If I now write the large component in explicit form

$$\begin{aligned} P(r) &= \frac{\alpha}{2}Dr - A - \frac{\beta^2}{2}\frac{\alpha}{2}D\frac{1}{r} + \frac{\beta^2}{3!}A\frac{1}{r^2} + \frac{\beta^4}{4!}\frac{\alpha}{2}D\frac{1}{r^3} - \left(\frac{\beta^4}{5!} + \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{5!}\right)A\frac{1}{r^4} + \dots \\ &= \frac{\alpha}{2}Dr\left(1 - \frac{\beta^2}{2}\frac{1}{r^2} + \frac{\beta^4}{4!}\frac{1}{r^4} - \dots\right) - \frac{r}{\beta}A\left(\frac{\beta}{r} - \frac{\beta^3}{3!}\frac{1}{r^3} + \frac{\beta^5}{5!}\frac{1}{r^5} - \dots\right) - \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{5!}A\frac{1}{r^4} + \dots \\ &= \frac{\alpha Dr}{2}\cos\left(\frac{\beta}{r}\right) - \frac{r}{\beta}A\sin\left(\frac{\beta}{r}\right) + O\left(\frac{1}{r^4}\right), \end{aligned} \tag{4.3.59}$$

where the last part is dependent on α^2. By extracting a common factor of A it could be rewritten as

$$P(r) = A\left[\frac{\alpha D r}{2A}\cos\left(\frac{\beta}{r}\right) - \frac{r}{\beta}\sin\left(\frac{\beta}{r}\right) + O\left(\frac{1}{r^4}\right)\right]. \tag{4.3.60}$$

However, I defined the scattering length as $a = \frac{2C'}{\alpha D'}$, where D' was a coefficient standing with the first power of r in the large component when there was no potential and C' was a coefficient standing with the first inverse power of r in the small component. In my case $A = C'$ and $D = D'$ so I can rewrite the first fraction as

$$P(r) \sim \frac{r}{a}\cos\left(\frac{\beta}{r}\right) - \frac{r}{\beta}\sin\left(\frac{\beta}{r}\right) + \alpha^2 O\left(\frac{1}{r^4}\right). \tag{4.3.61}$$

If one wants a non-relativistic result, it is as simple as setting $\alpha \to 0$, which means that the last part vanishes. I get the same result as it is presented in [35]. I can also get the explicit form of small component

$$\begin{aligned}
Q(r) &= \frac{\alpha}{2}\frac{A}{r} + \frac{\alpha^2}{4}\frac{B}{r^2} - \frac{\alpha}{2}\frac{\beta^2}{2!}\frac{A}{r^3} - \frac{\beta^2}{3!}\frac{\alpha^2}{4}\frac{B}{r^4} + \frac{\alpha}{2}\frac{\beta^4}{4!}\frac{A}{r^5} + \frac{\beta^4}{6!}\frac{\alpha^2}{4}\frac{B}{r^6} - \frac{\beta^6}{6!}\frac{1}{r^7} - \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{6!}\frac{\alpha}{2}\frac{A}{r^7} + \dots \\
&= \frac{\alpha}{2}\frac{A}{r}\left(1 - \frac{\beta^2}{2!}\frac{1}{r^2} + \frac{\beta^4}{4!}\frac{1}{r^4} - \frac{\beta^6}{6!}\frac{1}{r^6} + \dots\right) + \frac{\alpha^2}{4}\frac{B}{\beta r}\left(\frac{\beta}{r} - \frac{\beta^3}{3!}\frac{1}{r^3} + \frac{\beta^5}{5!}\frac{1}{r^5} - \dots\right) - \frac{4!\cdot\frac{\alpha^2\beta^2}{4}}{6!}\frac{\alpha}{2}\frac{A}{r^7}\cdots \\
&= \frac{\alpha}{2}\left[\frac{A}{r}\cos\left(\frac{\beta}{r}\right) + \frac{\alpha\beta D}{2r}\sin\left(\frac{\beta}{r}\right) + O\left(\frac{1}{r^7}\right)\right] \\
&= \frac{\alpha}{2}A\left[\frac{1}{r}\cos\left(\frac{\beta}{r}\right) + \frac{\beta}{ar}\sin\left(\frac{\beta}{r}\right) + O\left(\frac{1}{r^7}\right)\right].
\end{aligned} \tag{4.3.62}$$

The appearance of the constant $\frac{\alpha}{2}$ is a sign of kinetic balance between the large and small components that could be predicted. The relativistic change to the calculations is minimal: it appears at the r^{-4} coefficient in the large component and in the r^{-7} of the small component, but in the advent of advanced calculations, the theory must be prepared to the highest precision.

Chapter 5

Results

In this part, I present the results that I obtained during my research. I calculated the electron-atom scattering lengths of argon, krypton, xenon, radon and oganesson with and without polarisation potential. I used two methods to do that: use the definition of scattering length (4.2.35) and by analysing the behaviour of the radial wavefunction away from the potentials and close to the polarisation potential. A part of those results was presented in the article [13], which I co-authored.

5.1 Preliminary

5.1.1 Review of the literature and used parameters

The polarisation potential is determined by two parameters: the dipole polarisability and the cut-off parameter. The dipole polarisabilities were taken from [36]. It is worth mentioning that the values for radon and oganesson were theoretically obtained. The cut-off parameter was determined by calculating the structure of the target atom. I utilised the computational package called GRASP2018 [37], using the MCDHF method. At first, by using the Dirac-Hartree-Fock method I calculated the standard orbitals of an atom. Then by adding extra configurational state functions (CSFs) with higher principal quantum numbers, I have taken into account the valence-valence excitations. As a result, the cutoff parameter $\langle r_0^3 \rangle$ is obtained from the topmost layer (L3) of the ground state. The method of construction of the active space layer using a layer-by-layer approach is presented in 5.3.3.

Previously I presented the definition of characteristic quantum length with the symbol β which correlates with the strength of the potential and has a unit of length. It could be interpreted as the radius of the area where the polarisation potential is the strongest. The area of influence of the Coulomb interaction is correlated with the size of an atom. In Table 5.1 I summarised the values of scattering lengths obtained by various groups through the years. There were no works on a calculation of the scattering length of radon and oganesson before the work [13], which I co-authored. My results are presented in part 5.3.1. Together for values of other groups I present in this table the values of α_d from [36], values of $\langle r_0^3 \rangle$ and $\langle r_0 \rangle$ calculated by GRASP2018 and the value of characteristic quantum length β as a reference to further discussions. There is a limited amount of articles calculating the scattering lengths of those atoms without polarisation, as these results are not possible to test in experiments and ignore the important effects that happen in atoms and are not taken into account by methods using frozen core approximation. However, they show how the character of interaction is drastically changed

by adding the polarisation potential. The theoretical results presented in this table were obtained by various methods with different degrees of sophistication. Therefore, the accuracy of the results differs. The methods vary from simple, such as approximating with the combination of the hard-sphere and the long-range polarisation potential (rigid sphere approach, [38]) to more advanced models, such as those based on the R-matrix method [39].

Table 5.1: Theoretical and experimental electron scattering lengths from atoms found in the literature. The parameters for the polarisation potential include the dipole polarizability α_d, as reported in the article by Schwerdtfeger [36], and a cutoff value of $\langle r_0^3 \rangle$ from the GRASP2018. To compare the size of the electron interaction and polarisation potential, the mean radius value of the largest orbital taken from GRASP2018 and characteristic polarisation length taken as $\beta = \sqrt{\alpha_d}$ are shown. All data are given in atomic units. Adapted from [13]

Atom	Experimental	Other theoretical	α_d	$\langle r_0^3 \rangle$	$\langle r \rangle$	β
Ar	-1.365^a, -1.488^b, -1.449^c	-1.39^i, -1.486^j, -1.441^k	11.083	7.651	1.6627	3.329
	-1.593^d, -1.442^e, -1.459^f	-1.386^l, -1.68^m, -1.4^n				
	-1.492^g, -1.5^h	1.48^{g*}				
Kr	-3.06^a, -3.19^o, -3.279^e	-3.10^s, -3.72^t, -3.23^u	16.78	11.803	1.9547	4.096
	-3.36^p, -3.43^q, -3.3528^r	-3.28^n, 1.5^{u*}				
Xe	-5.13^a, -6.09^p	-4.953^w, -6.21^n	27.32	19.302	2.3393	5.227
Rn			35.0	25.132	2.5462	5.916
Og			58.0	38.898	2.9529	7.616

* no polarisation,

^{a}Kurokawa *et al.* [40], ^{b}Haddad and O'Malley [41], ^{c}Ferch and Raith [42],

^{d}Weyhreter *et al.* [43], ^{e}Buckman and Mitroy [44], ^{f}Petrovic *et al.* [45],

^{g}Buckman and Lohmann [46], ^{h}Milloy *et al.* [47], ^{i}Cheng *et al.* [48], ^{j}Saha [49],

^{k}McEachran and Stauffer [50], ^{l}Mimnagh *et al.* [51], ^{m}Bell *et al.* [52],

^{n}Fedus [38], ^{o}Buckman and Lohmann [53], ^{p}Hunter *et al.* [54],

^{q}England and Elford [55], ^{r}Brennan and Ness [56], ^{s}McEachran and Stauffer [57],

^{t}Zatsarinny *et al.* [39], ^{u}Cheng *et al.* [58], ^{w}Meshkov *et al.* [59]

5.1.2 Continuum states

To calculate the continuum orbitals I used a modified version of the COWF [60] code. Originally, it was created as an additional part of the RATIP [61] package. The newest version is adapted to the latest version of the GRASP2018 [37] package. I focused on calculating only the s-wave ($\kappa = -1$) since it is the one used in calculations of scattering lengths.

The radial wavefunctions are obtained from solving the equations (4.1.1, 4.1.2) by outward integration, subject to the boundary condition $P(0) = Q(0) = 0$.

To study the behaviour of scattering length in the ultra-low energy range, continuum orbitals were

generated for ten electron energies from 0.0001 to 0.001 eV (0.0000036–0.000036 Hartree). For each energy, the phase shift is determined by comparing its asymptotic behaviour at large r with an undistorted wave, calculated by solving the same set of equations (4.1.1, 4.1.2) at zero potentials, which happened to be Bessel spherical functions. The phase shift is obtained by matching the corresponding maxima of both wave functions and evaluated as

$$\delta = k(x_m^0 - x_m^s), \tag{5.1.1}$$

where x_m^0 is the location of m-th extreme point of a free energy wave function, and x_m^s is the location of the corresponding extreme value of the scattered wave function. In my case, typically, the value of m was 25. [13] A more detailed description of continuum state generation and phase shift determination can be found in [62] and [63].

5.2 Graphs

As presented in figures 5.1 and 5.2, we see the linear correlation between the phaseshifts and wavenumber which comes from the equation

$$\delta \sim -ak \tag{5.2.1}$$

obtained from the small angle approximation of the tangent function used in equation (4.2.35). The values of scattering length obtained by this method are presented later in Tables 5.2 and 5.3. It is visible that the oganesson behaves differently from other elements and its value of the scattering length has an opposite sign to other values. Without polarisation potential, noble gases lighter than oganesson behave similarly to each other and the values of their scattering length are alike. On the other hand, while using the polarisation potential, the values start to differ. Due to the fact that the scattering length is correlated to the slope of these lines, a conclusion can be made that if the noble gas is heavier, its scattering length is bigger in absolute values, which is understandable as it is correlated with the cross sections of the atoms which should be bigger for heavier atoms.

In Figures 5.3 – 5.12, the radial wavefunctions of the large component are calculated, excluding and including the polarisation potential. On Figures 5.3 and 5.4 are the results for argon, 5.5 and 5.6 for krypton, 5.7 and 5.8 for xenon, 5.9 and 5.10 for radon and finally on 5.11 and 5.12 for oganesson. In each figure, a close-up of the wavefunction is presented in the region near the origin. All the graphs behave similarly to the straight line which corresponds to the solution without the potientals presented in (4.2.18). This relation is used to calculate the scattering lengths presented in Table 5.2 and 5.3. It is visible that wavefunctions calculated using polarisation potential behave drastically differently around the point defined by the characteristic quantum length. This is manifested by an additional hump or recess in the aforementioned region. Here, the simple approximation by straight is not sufficient and higher-order approximation must be needed. In the equations (4.3.60) I presented how to obtain the additional coefficients. The biggest difference in behaviour is observed in oganesson. An additional fluctuation can be observed between the case of no-polarisation potential and polarisation potential. This could be explained by a possible bound state in oganesson induced by the polarisation of atom. This will also influence the value of the scattering length for oganesson. Comparing all of the graphs, it can be seen that the influence of polarisation potential is bigger for bigger atoms. When the atom is larger and the electrons in atoms are more dispersed, the atom is easier polarisable which has an effect on the value of dipole polarisation.

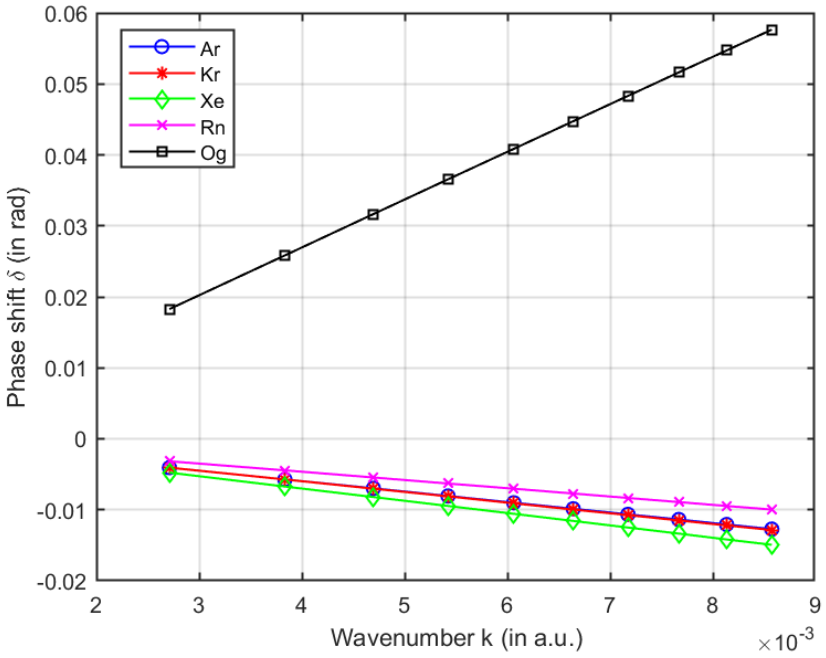

Figure 5.1: A graph presenting the correlation between the phase shift and the wavenumber for various atoms without the polarisation potential. Blue line with circles – argon, red line with stars – krypton, green line with diamonds – xenon, magenta line with crosses – radon and black line with squares – oganesson. Lines of argon and krypton lie close to each other.

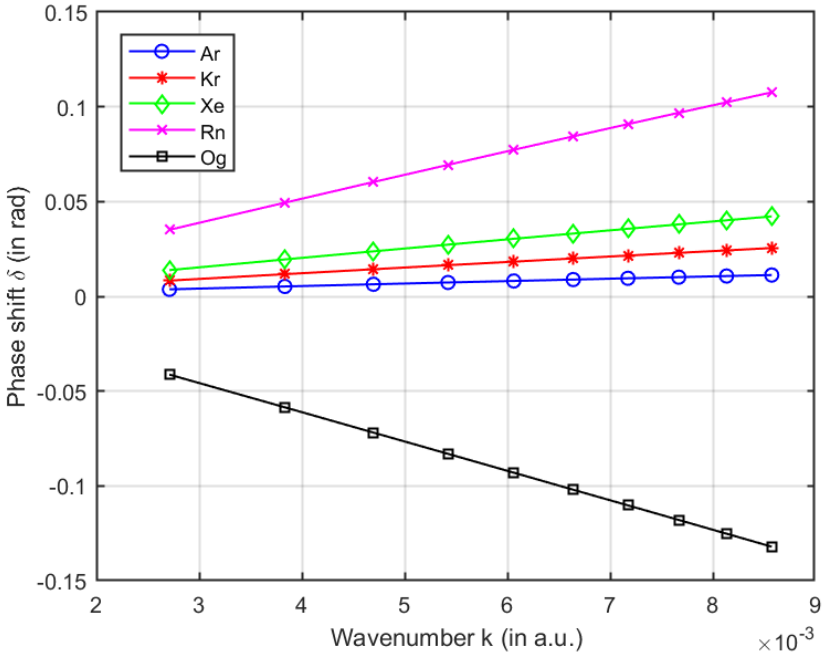

Figure 5.2: A graph presenting the correlation between the phase shift and the wavenumber for the same atoms as previously but including the polarisation potential. Symbols are the same as on the previous graph.

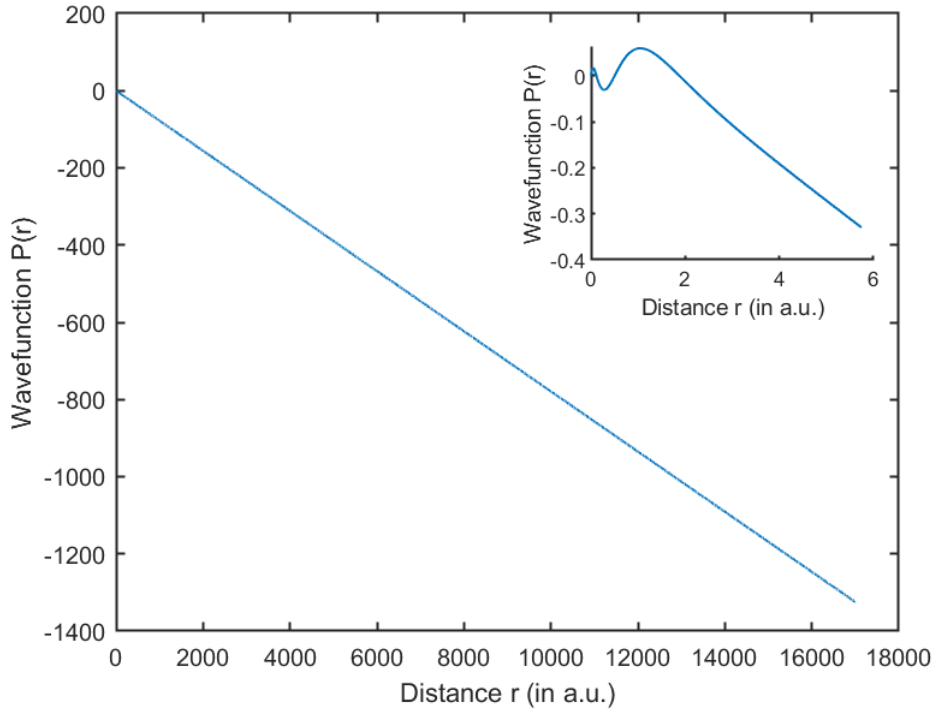

Figure 5.3: Large component of the radial wavefunction of argon without polarisation potential. The small graph is a close-up of the region near the origin.

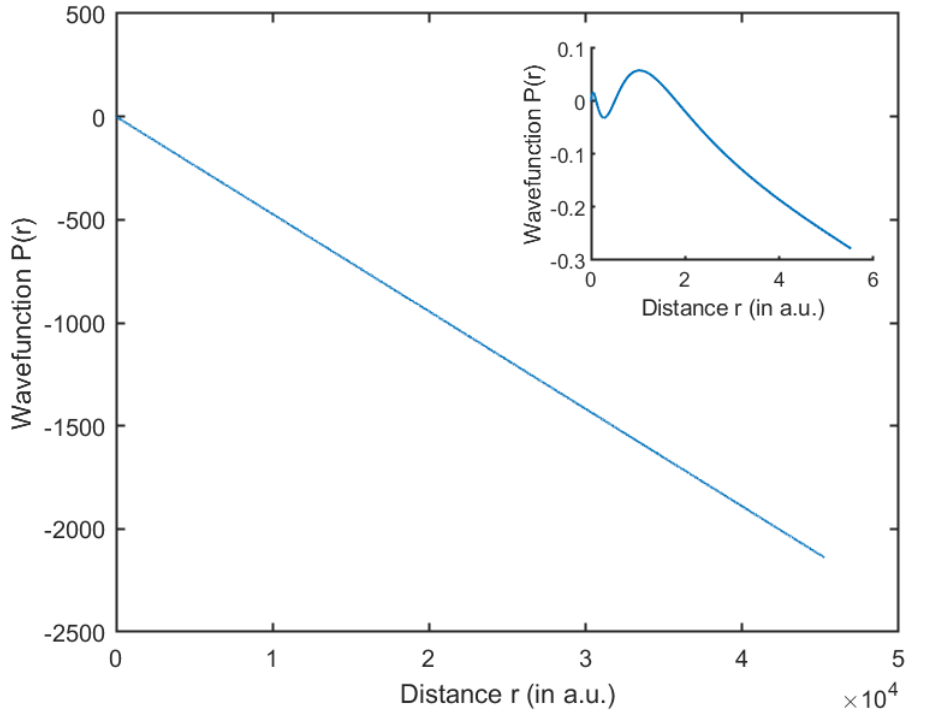

Figure 5.4: Similar as on the previous graph but including polarisation potential. A shallow recess could be seen at the distance of 3 a_0 due to the polarisation potential.

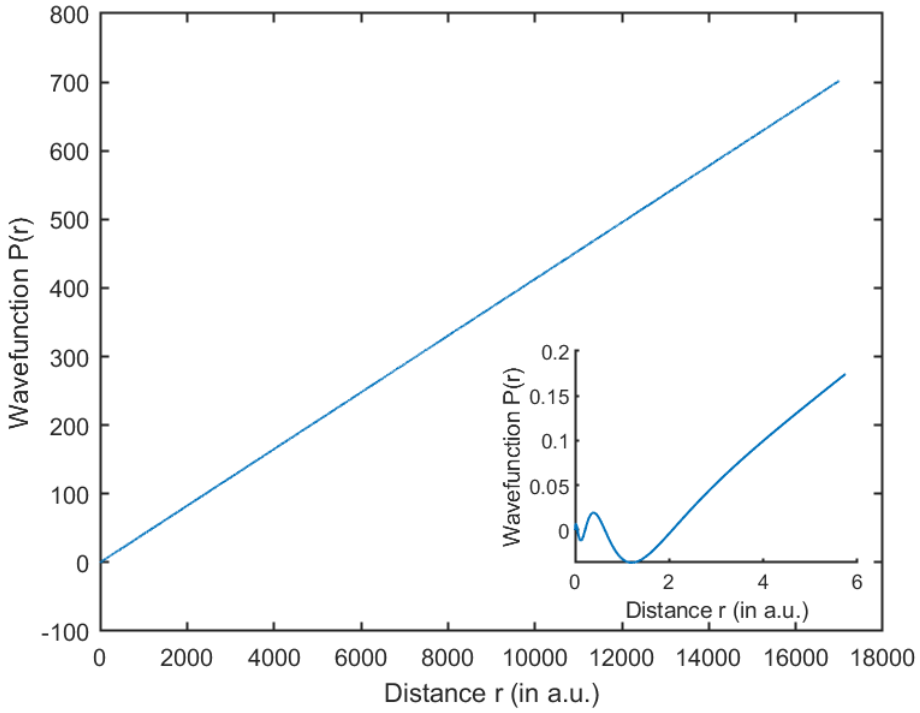

Figure 5.5: Large component of the radial wavefunction of krypton without polarisation potential.

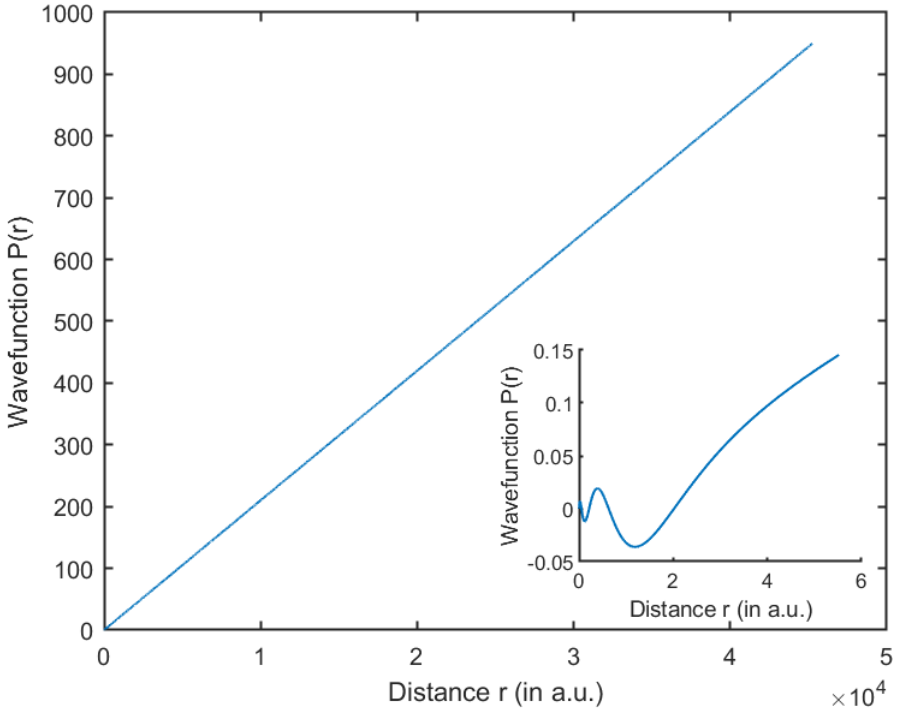

Figure 5.6: As on the previous graph, with polarisation. A small hump is visible around 4 a_0

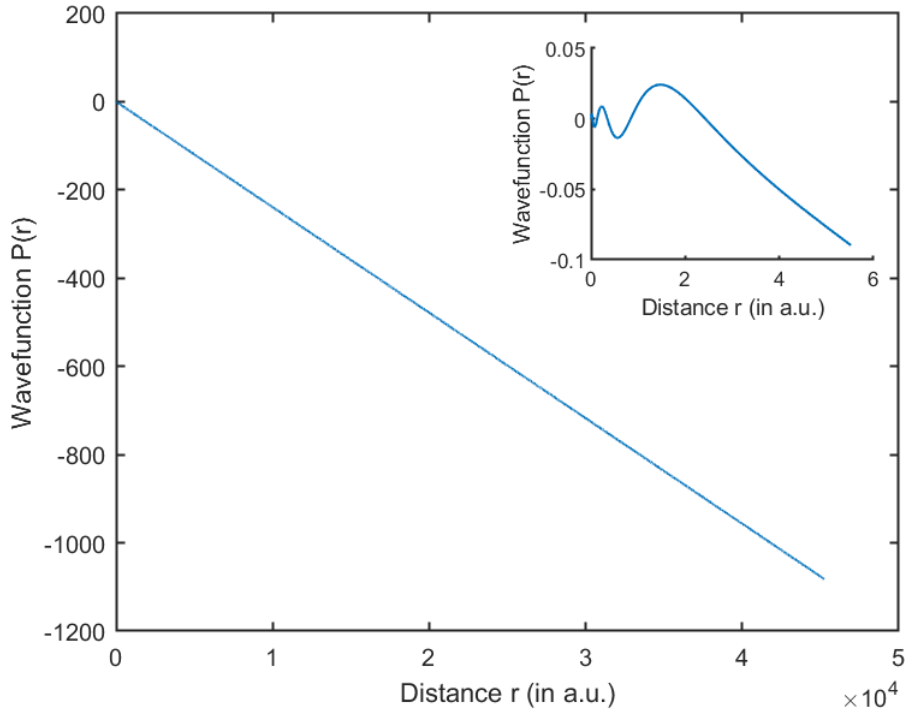

Figure 5.7: Large component of the radial wavefunction of xenon without polarisation potential.

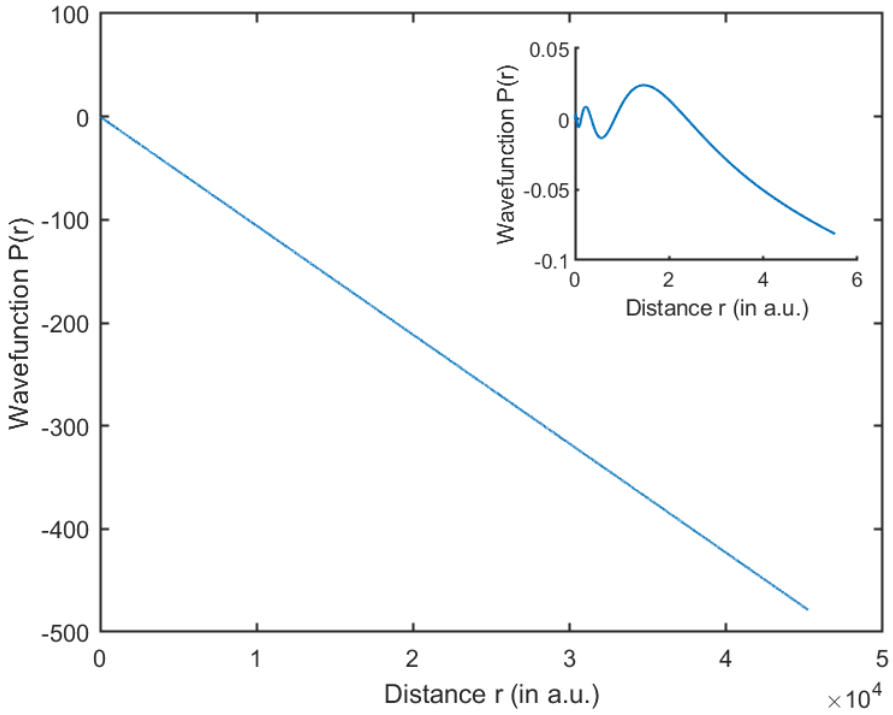

Figure 5.8: Large component of radial wavefunction calculated with polarisation potential for xenon. There is a slight but visible difference between these two graphs in the range of 2 and 6 a_0

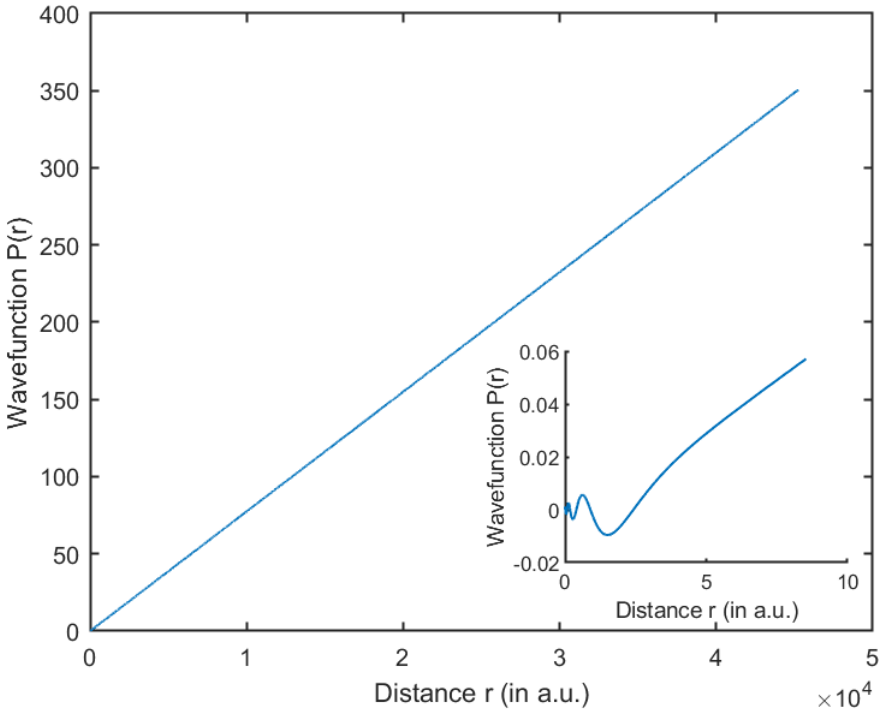

Figure 5.9: Large component of the radial wavefunction of radon without polarisation potential.

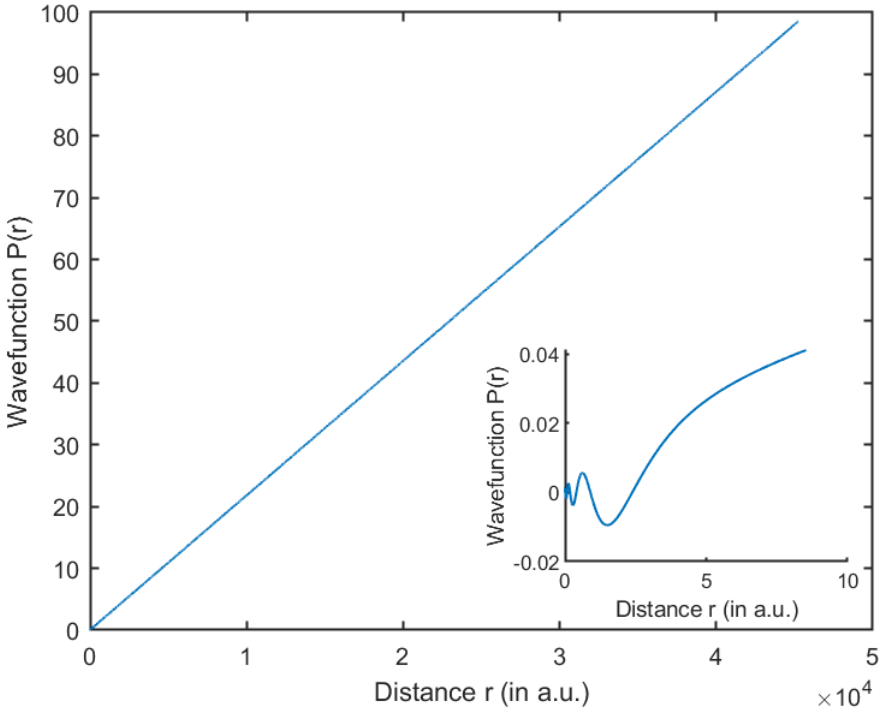

Figure 5.10: As previously but with polarisation potential. There exists a large hump in the wavefunction

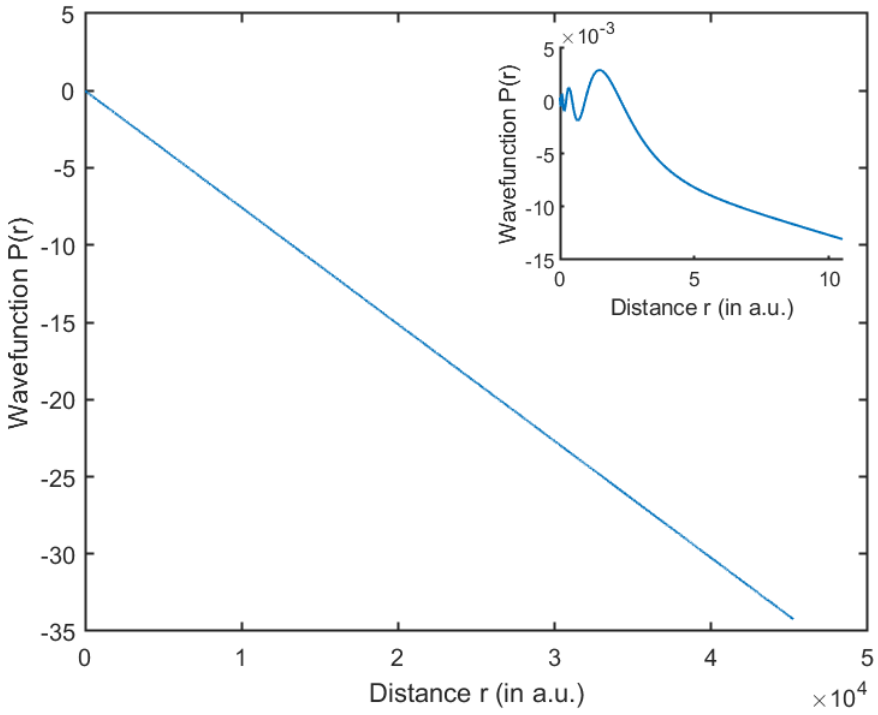

Figure 5.11: Large component of the radial wavefunction of oganesson without polarisation potential.

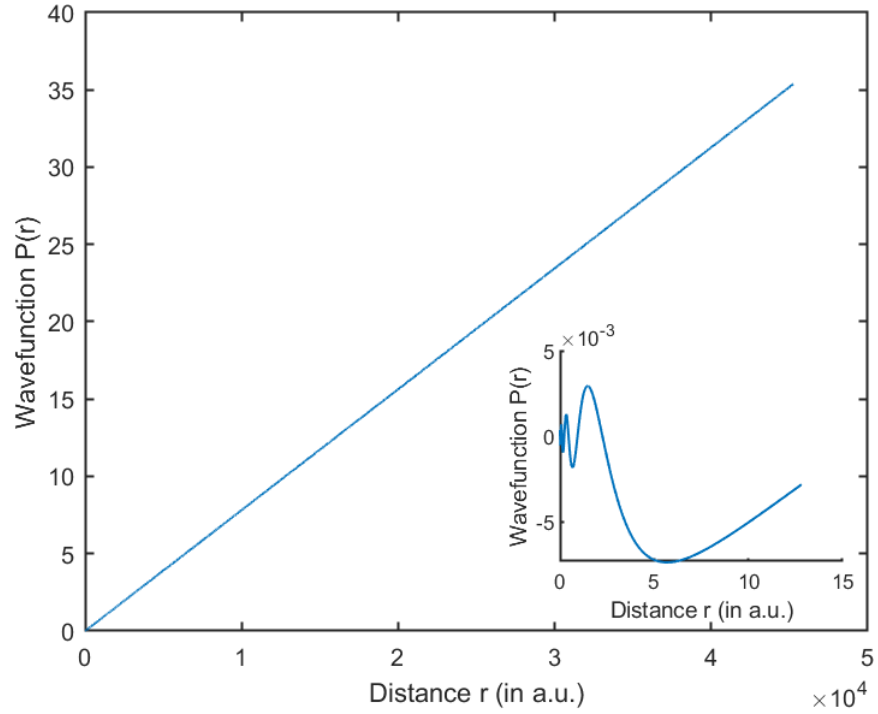

Figure 5.12: Similar to the previous graph but including polarisation potential. There exists an additional bend of the radial wavefunction, which could be connected to an additional bound state.

5.3 Tables

5.3.1 Scattering lengths

In the Tables 5.2 and 5.3 I present the values of scattering lengths without and with polarisation elements for noble gases obtained from my calculations. I used two methods: by using the phase shifts and by approximation of the zero-energy wavefunction. For both cases, the linear approximation was used away from the centre and close to the atom. The distance away from the atom revolves around 30000 a_0. The distance close to the atom was chosen to be 5β due to the approximation used in the case, including polarisation potential. Results for the case without polarisation potential do not differ whether they were taken far away or close at the distance of 5β. In the case with polarisation potential, three orders of approximation were used. As I presented in (4.3.61), the radial wavefunction should behave as

$$P(r) \sim \frac{r}{a}\cos\left(\frac{\beta}{r}\right) - \frac{r}{\beta}\sin\left(\frac{\beta}{r}\right) + \alpha^2 O\left(\frac{1}{r^4}\right). \tag{5.3.1}$$

In the first order of approximation, I used only the terms whose index is non-negative i.e. p_1 and p_0, which is a linear approximation

$$P^{(1)}(r) \approx p_1 r + p_0 \tag{5.3.2}$$

. In the second order, I also used the term with the index -1 which creates a combination of the straight line with hiperbola

$$P^{(2)}(r) \approx p_1 r + p_0 + \frac{p_{-1}}{r}. \tag{5.3.3}$$

In the third order of approximation, I added an additional term behaving as r^{-2}

$$P^{(3)}(r) \approx p_1 r + p_0 + \frac{p_{-1}}{r} + \frac{p_{-2}}{r^2}. \tag{5.3.4}$$

They come from the small angle approximation of sine and cosine

$$\sin x \approx x \qquad \sin x \approx x - \frac{x^3}{3!} \tag{5.3.5}$$

$$\cos x \approx 1 \qquad \cos x = 1 - \frac{x^2}{2!} \tag{5.3.6}$$

In my case, $x = \beta/r$. This approximation has respective errors of 0.6%, 0.001%, 2% and 0.006% for value $x = 0.2$ and this is the reason I used the distance of $r = 5\beta$ to perform my calculations. By using the symbols used in (4.3.59), those approximations could be written as

$$P^{(1)}(r) \approx \frac{\alpha}{2} D r - A \tag{5.3.7}$$

$$P^{(2)}(r) \approx \frac{\alpha}{2} D r - A - \frac{\beta^2}{2}\frac{\alpha}{2}\frac{D}{r} \tag{5.3.8}$$

$$P^{(3)}(r) \approx \frac{\alpha}{2} D r - A - \frac{\beta^2}{2}\frac{\alpha}{2}\frac{D}{r} + \frac{\beta^2}{3!}\frac{A}{r^2} \tag{5.3.9}$$

As we can see in Table 5.2, the values of the phase scattering length using both methods for the case without polarisation potential are in great accordance with each other and match the values presented in Table 5.1. The most important case is presented in Table 5.3. The values of scattering lengths using phase shifts, linear approximation at large distances and the higher than linear approximation close to the origin give matching results. Significantly, ordinary linear approximation close to the origin presents

results that cannot be compared to their values. Basic linear approximation does not take into account polarisation and at the distance of 5β, the polarisation potential is still significant. It is also noticeable that with the higher order of approximation, the values of scattering length close to the origin are getting closer to the values obtained far away from the atom. This shows that the approximations presented in (5.3.8) and (5.3.9) can be relatively successfully used to evaluate the value of scattering length without the need to calculate the wavefunction further from the atom, where the possibility of accumulation of numerical error is higher.

From Table 5.3, we can notice that the absolute value of scattering length is bigger for heavier atoms, which coincides with the relation between the scattering length and the total cross-section of a target atom. The results for radon follow the trend for lighter noble gases, where the scattering length has a negative sign, which means that radon polarisation potential creates the additional attractive force without creating the bound state. As the negative value of scattering length is a suggestion of the existence of the Ramsauer-Towsend effect [3], I suspect that radon may be observed in the Ramsauer minimum in the total cross-section. It was also suggested in [64] by working in higher energy regimes than my work. Surprisingly, this is not the case for the oganesson. The large absolute value of the scattering length, combined with its sign, suggests that there exists a low-lying bound state. Another clue supporting this suggestion is the behaviour of the radial wavefunction, which was presented in Figure 5.12. The investigation of phase shits in higher regimes than presented in this work is needed to further support this thesis.

Table 5.2: Values of scattering length obtained from calculation without polarisation potential. Two methods were used – by using the formula (4.2.35) and by linear approximation of the radial wavefunction far away from the atom.

Atom	Using phase shifts (in a_0)	Using linear approximation (in a_0)
Ar	1.500	1.505
Kr	1.495	1.509
Xe	1.762	1.737
Rn	1.162	1.162
Og	-6.751	-6.761

Table 5.3: Values of scattering length obtained from calculation with polarisation potential. Two methods were used - using the formula (4.2.35) and by approximation of the radial wavefunction. First order of approximation is by using a straight line $p_1 r + p_0$, second order is by adding the term with the inverse of the distance $p_1 r + p_0 + p_{-1}/r$, third order is by adding the additional term with the inverse of distance squared $p_1 r + p_0 + p_{-1}/r + p_{-2}/r^2$. Calculations categorised as closed were calculated at the distance 5β, where β is a characteristic quantum length $\beta = \sqrt{\alpha_d}$.

		Far away	Close		
Atom	Using phase shifts (in a_0)	1st order (in a_0)	1st order (in a_0)	2nd order (in a_0)	3rd order (in a_0)
Ar	-1.394	-1.4171	-0.7858	-1.4327	-1.4222
Kr	-3.112	-3.1468	-2.2267	-3.1991	-3.1555
Xe	-5.199	-5.2095	-3.9247	-5.3101	-5.2225
Rn	-13.13	-13.3147	-11.635	-13.5847	-13.3295
Og	15.13	15.0978	16.1813	15.5203	15.0826

5.3.2 The internal coherence of the solutions

From the theory, we can approximate the behaviour of radial wavefunction for large and small components. From equations (4.3.60) and (4.3.62), the approximation is

$$P^{(3)}(r) \approx \frac{\alpha}{2} D r - A - \frac{\beta^2}{2}\frac{\alpha}{2}\frac{D}{r} + \frac{\beta^2}{3!}\frac{A}{r^2} = p_1 r + p_0 + \frac{p_{-1}}{r} + \frac{p_{-2}}{r^2} \tag{5.3.10}$$

$$Q^{(2)}(r) \approx \frac{\alpha}{2}\frac{A}{r} + \frac{\alpha^2\beta^2}{2}\frac{D}{r^2} - \frac{\alpha}{2}\frac{\beta^2}{2!}\frac{A}{r^3} = \frac{q_{-1}}{r} + \frac{q_{-2}}{r^2} + \frac{q_{-3}}{r^3} \tag{5.3.11}$$

From those approximations, it may be concluded that

$$-\frac{p_0}{2q_{-1}} = -\frac{-A}{2\frac{\alpha}{2}A} = \frac{1}{\alpha} \tag{5.3.12}$$

is a reciprocal of a fine-structure constant, which is well-known. In the Table 5.4) I present obtained values of α^{-1} from small and large components of radial wavefunctions calculated with and without polarisation potentials. The components were compared at the distance of 5β, as the small component falls rather quickly and investigation of the small component far away would be contaminated with numerical error. The values presented in the table are compared with the value of α^{-1} taken from CODATA2018 [65], where I present the difference in values as a percentage. In the case with polarisation potential, two types of approximations were tested. In the first one, labeled α_2^{-1}, large component was approximated up to p_{-1} and small component up to q_{-2}. In the second one, marked α_3^{-1}, approximation of large component ended at p_{-2} and of small component at q_{-3}. As it is presented in Table 5.4, the values of the fine structure constant are rather accurately obtained from this method, which proves an internal coherence between those two solutions. This is also a sign of kinetic balance being satisfied as the ratio between large and small components is $\frac{\alpha}{2}$. Using higher order approximation makes the difference slightly worse, which may be a result of over-fitting and the difficulty of calculating the coefficients of q_{-3} with high enough precision. On one hand, reaching the approximation further should improve the results, but on the other hand, the coefficients p_{-n} and q_{-n} for $n > 2$ get lower and lower, which are then harder to accurately estimate.

Table 5.4: Values of the reciprocals of the fine structure constant obtained from the approximations of radial wavefunctions without and with polarisation. For the values without polarisation, the approximation was done far away from the atom, for the values with polarisation it was done at the distance of 5β using second and third order of approximation. The differences stated as percentages are between obtained values of $1/\alpha$ and $1/\alpha = 137.035999084$ taken from CODATA 2018 [65].

	Without polarisation		With polarisation			
Atom	α^{-1}	Diff. (%)	α_2^{-1}	Diff. (%)	α_3^{-1}	Diff. (%)
Ar	136.9367	0.072443	137.007	-0.0212	138.0219	0.7194
Kr	137.0656	-0.02157	137.0045	-0.023	138.8126	1.2964
Xe	137.0712	-0.02572	136.9839	-0.038	139.1876	1.5701
Rn	137.0472	-0.00816	137.0222	-0.0101	139.3235	1.6693
Og	137.0311	0.003588	136.9532	-0.0604	141.8008	3.4771

Another method of checking the accordance between the theory and computed results is estimating the value of dipole polarisability. From the equation (5.3.10), the relation between p_1 ad p_{-1} can be derived as

$$\frac{p_{-1}}{p_1} = \frac{\frac{\beta^2}{2}\frac{\alpha}{2}D}{\frac{\alpha}{2}D} = -\frac{\beta^2}{2}, \tag{5.3.13}$$

where β is the characteristic quantum length. From the direct comparison of the definition of polarisation potential presented in (3.1.41) and a model at (4.3.1), it can be shown that

$$-\frac{1}{2}\frac{\alpha_d r^2}{(r^3 + \langle r_0^3\rangle)^2} = -\frac{1}{2}\frac{\beta^2}{r^4}$$

$$\alpha_d = \frac{\beta^2}{\left(1 + \frac{\langle r_0^3\rangle}{r^3}\right)^2} \tag{5.3.14}$$

$$\alpha_d \approx \beta^2. \tag{5.3.15}$$

Which combined with the previous result, I get

$$-\frac{2p_{-1}}{p_1} \approx \alpha_d \tag{5.3.16}$$

The approximation gets better further from the centre, when the denominator is getting closer to 1. In Table 5.5 I present the values of α_d obtained from this method using the second and third-order approximation of the radial wavefunction at the distance of 5β from Table 5.1 compared with the theoretical values of α_d taken from [36]. Although the second-order approximation does not achieve a great agreement with theoretical results (it is clearly visible for heavier atoms), the third-order approximation, where the term p_{-1} is not the lowest coefficient obtained in approximation, yields higher quality results which differ not to so much from theory. This method can be used when the polarisation of the atom may be implemented in other ways, such as taking into account the orbitals of the negatively charged

atom with an additional electron. Then, by using the approximation, we may check the supposed value of dipole static polarisability of the atom, using the polarisation potential suggested in (3.1.41). There is also a difference between the simple potential stated in (4.3.1) and the more advanced potential suggested in (3.1.41), but at a sufficiently large distance, the denominator of (3.1.41) does not create a change which is significant enough. There is also a constant problem of establishing the area where the atomic potential is small enough to be omitted and the polarisation potential still has an influence. At large distances, both those interactions diminish and finding the coefficients of the higher inverse powers coefficients stand before the difficulties created by numerical errors.

Table 5.5: Comparison of values of dipole polarisabilities taken from [36] (marked as α_d^t) and the values obtained from 2nd and 3rd order of approximation (namely $\alpha_d^{(2)}$ and $\alpha_d^{(3)}$) at the distance of 5β. Differences between the values are presented as percentages.

Atom	α_d^t	$\alpha_d^{(2)}$	Diff (%)	$\alpha_d^{(3)}$	Diff (%)
Ar	11.083	11.7197	5.7651	11.3358	2.2809
Kr	16.78	18.9736	13.0727	17.2502	2.8019
Xe	27.32	32.3258	18.32	28.1662	3.0973
Rn	35	49.692	41.9972	36.0708	3.0593
Og	58	27.254	-53.0104	59.4192	2.4469

5.3.3 Uncertainty estimates

As with any calculation, those calculations have uncertainties. Various sources of uncertainty impact the end value differently. The first one, which causes the largest uncertainties, is related to the polarisation potential. The polarisation potential is described by two free parameters: dipole polarizability α_d and cutoff parameter $\langle r_0^3 \rangle$. The article by Schwedtfeger [36] provides the summary of current knowledge in the field of values of dipole polarisabilities of various atoms. Table 5.6 lists the uncertainties in the determination of α_d and their impact on the calculated scattering lengths, obtained by performing test calculations with extreme values of α_d measured by using the relationship between scattering length and phase shift. In my calculations, I disregarded the quadrupole term, presented in (3.1.42), as it is insignificant compared to the dipole term, mainly for its behaviour for larger distances, where it behaves as α_q'/r^6. Moreover, the value of quadrupole polarisability is significantly smaller than that of dipole polarisability. For instance, in the case of argon, its value is only 0.14 [66]. The values of dipole polarisabilities of radon and oganesson are only theoretically calculated and have the biggest uncertainty, which has the biggest impact on the value of scattering length.

The second cause of errors in the results is the uncertainty that arises during the calculation of atomic bound states. This uncertainty is a result of the finite expansion of the atomic state function, and the omission of certain components of the energy functional, such as the interaction of transverse photons (Breit), vacuum polarisation, and self-energy correction (QED).

Table 5.6: Uncertainties of α_d used in calculations, and related uncertainties of calculated scattering lengths.

		Uncertainty
Element	α_d [36]	Scattering length
Ar	0.06%	<0.0001%
Kr	0.12%	0.43%
Xe	0.73%	1.5%
Rn	5.72%	15%
Og	10.34%	15%

The layer-by-layer procedure was used to check and estimate the size of the contribution, which results from the limited, finite expansion of the ASF based on the CSF (3.1.13). This is done by systematically increasing the active space of CSF. The results for all elements are collected in Table 5.7, which shows that increasing the size of the active space reduces the relative change between the scattering lengths calculated in different layers. This is also the part which consumes the biggest computational power as the number of CSFs rapidly increases with each layer. The careful analysis shows that the values of the scattering length for the full, infinite active space should not differ from the result from the last calculated layer L3 by more than the difference between the results for L2 and L3, as the difference in obtained values is getting smaller. Moreover, those errors are relatively small and even using L1 yields sufficiently enough results. This is expected because noble gases have closed shells and for them, the most important configuration in the active space is their ground state. Surprisingly, those errors are smaller for heavier atoms due to the fuller CSF base, with the cost of longer calculations.

Additionally, to estimate the effect of the previously mentioned factors, the Breit interaction as a perturbation, along with other interactions, were used in the configuration-interaction procedure. I observed no significant change in the results for Ar, Kr and Xe. For Rn and Og, the change is less than 0.01% which, compared to uncertainties arising from polarisation potential, is practically insignificant.

Another source of uncertainty comes from the procedure of calculating the phase shift. In the programme used, it is done by the comparison between the behaviour of the wave at a large distance, treated as an infinity, with that of an undisturbed wave. However, the expansion of the numerical grid to encapsulate in the calculations the appropriate distance from the origin will introduce some numerical errors. Careful control of the numerical integration is used to minimise the error. One of those control measurements is a comparison between calculated and theoretical wavelengths $\lambda = 2\pi/k$ far from the origin. Error due to calculating phase shift is estimated to be no more than 0.5%.

The last type of error, which is present in both cases, is the fit of the straight line in both cases. In the phaseshift method, the relation between the tangent of the phase shift (and for the small angles also for the phaseshifts alone) is linear and the scattering length is a value of the slope of this approximation taken with a negative sign. The calculation involves extrapolating scattering lengths calculated for electron energies that are close to zero but not exactly zero. In the wavefunction method, a linear approximation was used to calculate the slope and the intercept of the asymptote. The scattering length is an interception of this asymptote with the r-axis, which can be calculated as

$$a = -\frac{p_0}{p_1}, \tag{5.3.17}$$

where p_1 is the slope, and p_0 is the intercept. In all tested atoms, the fitting error was found to be approximately 0.3% in both cases.

Table 5.7: Changes in scattering lengths calculated from method A for different layers, used on the calculation of the bound states. Layers (L1, L2 and L3) are constructed by single and double excitations from the ground configuration into an increasing set of active orbitals. DF (Dirac-Fock) means no excitations. The last column displays the relative changes between the previous and current layers. Taken from [13]

Layer	Active orbitals	No. of CSFs	Scattering length	Relative change
Ar, ground configuration: $[\mathrm{Ne}]3s^2 3p^6$				
DF	–	1	−1.468	–
L1	$4s, 4p, 3d, 3f$	53	−1.426	2.96%
L2	L1 + $5s, 5p, 4d, 4f, 4g$	238	−1.404	1.58%
L3	L2 + $6s, 6p, 5d, 5f, 5g, 5h$	620	−1.394	0.72%
Kr, ground configuration: $[\mathrm{Ar}]3d^{10}4s^2 4p^6$				
DF	–	1	−2.947	–
L1	$5s, 5p, 4d, 4f, 4g$	306	−3.051	3.43%
L2	L1 + $6s, 6p, 5d, 5f, 5g, 5h$	1442	−3.101	1.61%
L3	L2 + $7s, 7p, 6d, 6f, 6g, 6h$	3782	−3.112	0.34%
Xe, ground configuration: $[\mathrm{Kr}]4d^{10}5s^2 5p^6$				
DF	–	1	−5.088	–
L1	$6s, 6p, 5d, 5f, 5g, 5h$	729	−5.182	1.80%
L2	L1 + $7s, 7p, 6d, 6f, 6g, 6h$	2592	−5.193	0.22%
L3	L2 + $8s, 8p, 7d, 7f, 7g, 7h$	5616	−5.199	0.11%
Rn, ground configuration: $[\mathrm{Xe}]4f^{14}5d^{10}6s^2 6p^6$				
DF	–	1	−12.7195	–
L1	$7s, 7p, 6d, 6f, 6g, 6h$	3312	−13.007	2.21%
L2	L1 + $8s, 8p, 7d, 7f, 7g, 7h$	9384	−13.108	0.77%
L3	L2 + $9s, 9p, 8d, 8f, 8g, 8h$	18554	−13.129	0.15%
Og, ground configuration: $[\mathrm{Rn}]5f^{14}6d^{10}7s^2 7p^6$				
DF	–	1	14.883	–
L1	$8s, 8p, 7d, 7f, 7g, 7h$	5439	15.100	1.44%
L2	L1 + $9s, 9p, 8d, 8f, 8g, 8h$	12733	15.117	0.12%
L3	L2 + $10s, 10p, 9d, 9f, 9g, 9h$	23125	15.126	0.05%

According to [16], all the above components are combined by taking the square root of the sum of squares. In Table 5.8 I present the results published in [13], together with the uncertainties.

Table 5.8: Theoretical values of scattering lengths from atoms presented in [13]. Results obtained with two different methods, along with the estimated uncertainties are presented. Star denotes the value of scattering length when there is no polarisation potential. All data are given in atomic units.

Atom	Phase shifts	Linear approx.	Uncertainty
Ar	−1.394	−1.417	0.92%
	1.483*	1.479*	
Kr	−3.112	−3.147	0.8%
	1.495*	1.499*	
Xe	−5.199	−5.209	1.61%
	1.755*	1.737*	
Rn	−13.129	−13.315	15.01%
	1.161*	1.162*	
Og	15.126	15.098	15.01%
	−6.747*	−6.761*	

Compared to values in Table 5.1, the values of scattering length for argon, krypton and xenon are in good agreement with the values obtained by different groups, both theoretically and experimentally. A novelty of those results is the value of the scattering length for radon and oganesson not previously seen in the literature. The existence of the Ramsauer-Towsend effect in radon was stipulated [64], which connects with the negative value of the scattering length for radon. The most surprising result is that of oganesson. Even without polarisation, oganesson should behave drastically differently than other noble gases. The physics and chemistry of oganesson are in their beginning stage as only a few atoms of this element were produced and experiments are arduous to conclude. Nevertheless, there is a possibility that the behaviour of ultra-massive atoms could be described by more complex theories and further studies are needed.

Chapter 6

Conclusions

Currently, the scattering theory could be described using three different types of theory: Schrödinger non-relativistic equation, Dirac relativistic equation and Quantum Electrodynamics developed by Feynmann, Schwinger and Tomanaga. When the relativistic effects are disregarded, mainly the Schrödinger theory is used. For better estimates and calculations, relativistic corrections are added to the Schrödinger equation. In highly relativistic cases, such as those observed in super-colliders, the QED is used with its Feynmann diagrams and Lippmann-Schwinger equation. This method is significantly harder to use in electron-atom collisions and thus is never used. A bridge between those two theories, which is the Dirac equation, is rarely used as a medium to obtain the results for semi-complex models such as atoms and molecules when it is only slightly harder than the classic non-relativistic case with relativistic addition. The aim of this dissertation, which was to present the theory of elastic scattering in the relativistic equation, is one of the steps to build the bridge. In this work, I presented how the effective range theory changes when the relativistic equations are applied and how the polarisation potential influences the solutions of zero-energy particles in the Dirac equation. The corrections are small. However, they give a better insight into the theory and connection between relativistic and non-relativistic regimes. Additionally, those equations were used to calculate the scattering length for argon, krypton, xenon, radon and oganesson. For the first three elements, this is mainly a proof of the method to use in calculations, but for the radon and oganesson, it is a source of new information about those atoms. The development of relativistic theory has additional benefits such as easier treatment of positron-atom scattering, which I plan to focus on in the feature. The main difference between the positron-atom and electron-atom scattering is the behaviour of polarisation potential which, as shown in this dissertation, has a great impact on the result. I also plan to use this method to calculate the scattering lengths for other elements. At first, I will focus on elements with closed subshell structures, like those in groups 2 and 12 (Sr, Hg, Zn, Cd, Mg, Ca, Ba, Ra), and later on other elements. The elements of the theory presented in this dissertation, such as the description of the atom and radial wavefunction of the scattered electron, will be later used to develop the theory of inelastic relativistic electron-atom scattering.

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