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Algebraic calculation of atomic integrals

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In Prague on May 11, 2023   Vít Anderle

This thesis is dedicated to all who hunger for truth and knowledge.

Title: Algebraic calculation of atomic integrals

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Abstract: The objective of this thesis is the examination of a novel method for the calculation of spectra of helium-like ions. In the helium atom, the electron-electron interaction is difficult to account for as it often leads to numerical instabilities. A reformulation of this problem is proposed. A purely algebraic approach is then taken, yielding exact formulas for the atomic integrals. A numerically stable procedure is eventually employed, recovering back the physical Coulomb interaction.

Keywords: Quantum mechanics, Algebraic methods, Atomic physics

Název: Algebraický výpočet atomových integrálů

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Abstrakt: Cílem této práce je vyzkoušet novou metodu pro výpočet spekter heliu-podobných iontů. V atomu helia je obtížné započítat vliv elektron-elektronové interakce, protože často vede k numerických nestabilitám. Je předložena alternativní formulace tohoto problému. Poté je využit čistě algebraický přístup, s jehož pomocí jsou odvozeny přesné vzorce pro atomové integrály. Nakonec je použita numericky stabilní metoda pro získání fyzikální coulombické interakce.

Klíčová slova: Kvantová mechanika, algebraické metody, atomová fyzika

Contents

Introduction

Quantum mechanics has been considered a cornerstone of modern physics for almost a century, and as much as it is fundamental, it is not very user-friendly. It is a widely known fact that only a handful of problems can be solved analytically. One of the simplest systems that have to be calculated approximately are helium-like atoms, which are at the focal point of this thesis and which constitute the first non-trivial examination of the validity of quantum mechanics: *"As is well known, wave mechanics at once reproduced all correct results obtainable from Bohr's theory, and the use of its much more convenient perturbation theory added considerably more, however, not always in the strict numerical sense. Now, particularly by Max Born, it was argued that the simplest crucial test of the correctness of wave mechanics in general was to be found in its application to the helium atom—in particular to the ground state."* [1]

The field of atomic physics indeed was the backbone in the early development of quantum physics, and its essential role prevails to this day as well. Systems with a small number of particles, such as two body systems (H, He$^+$, μH, e^+e^-, μ^+e^-) or He-like ions represent a convenient way of testing the Standard Model. A major inconsistency between theoretical predictions and experimental results might be an indication of new physics or a hint that the values of fundamental constants are incorrect. In comparison with large particle collider experiments that require a lot of energy, empirical research in high-precision atomic physics offers an enormous reduction in financial costs. [2]

Some of the greatest achievements of atomic physics include the determination of the magnetic moment of the electron bound in the hydrogenlike carbon ion. The theoretical value calculated with methods of quantum electrodynamics is confirmed by experiment with a relative precision of 3×10^{-11}. Another important contribution is a problem called the proton radius puzzle. In a nutshell, the proton root-mean-square charge radius can be derived from what is called a Lamb shift. The discrepancy, however, lies in the fact that using this method, different values are obtained when measuring muonic μH and electronic H hydrogen, even though a single figure should be recovered. There is also the riddle of measuring the isotope shift between ^{3}He and ^{4}He where different experiments yield values of the nuclear charge radii difference with 4σ disagreement. [2] All of these results testify to the invaluableness of both theoretical as well as experimental atomic physics.

In this thesis, however, we will not try to resolve these contradictions, nor will we investigate the impact of some exotic effects. Rather, as mentioned above, the focus of our work will be the examination of a new method for the calculation of energies of helium-like atoms, where the only interaction we consider is the Coulomb interaction. In order to do that, the time-independent Schrödinger equation

$$\hat{\mathsf{H}} \ket{\Psi} = E \ket{\Psi} \tag{1}$$

needs to be solved. Not taking into account any relativistic or any other effects of secondary importance, the Hamiltonian provided by canonical quantization

postulate takes the form [1]

$$\hat{\mathsf{H}} = \frac{\hat{\mathsf{p}}_N^2}{2m_N} + \frac{\hat{\mathsf{p}}_{e1}^2}{2m_e} + \frac{\hat{\mathsf{p}}_{e2}^2}{2m_e} - \frac{Z\alpha}{\hat{\mathsf{r}}_{e1}} - \frac{Z\alpha}{\hat{\mathsf{r}}_{e2}} + \frac{\alpha}{\hat{\mathsf{r}}_{e12}}\,.$$

Using the approximation of infinite nuclear mass and by a transition to atomic units [2], the Hamiltonian can be rewritten as[3] [3]

$$\frac{\hat{\mathsf{H}}}{Z^2} = \hat{\mathsf{h}}_1 + \hat{\mathsf{h}}_2 + \frac{1}{Z\hat{\mathsf{r}}_{12}} = \frac{\hat{\mathsf{p}}_1^2}{2} - \frac{1}{\hat{\mathsf{r}}_1} + \frac{\hat{\mathsf{p}}_2^2}{2} - \frac{1}{\hat{\mathsf{r}}_2} + \frac{1}{Z\hat{\mathsf{r}}_{12}}\,, \tag{2}$$

where $\hat{\mathsf{r}}_{12}$ denotes the distance between electrons.

When computing the energies of helium-like atoms, major difficulty arises with the calculation of matrix elements of the electron-electron Coulomb interaction $\langle k|\hat{\mathsf{r}}_{12}^{-1}|j\rangle$. As a consequence, no analytical solution can be found. Instead, variational method is exploited. Since the basis vectors can be expressed as products of a radial and an angular part, the computation can be split in this manner as well. This will be discussed in more detail in the first chapter. Now, the integration of the angular terms is basically trivial because the spherical functions are derived from commutation relations transforming the integral into an exact algebraic expression. In contrast, the radial functions are found as solutions of differential equation [4]. If we were to evaluate the radial integrals using methods of numerical integration, we would encounter serious numerical instabilities on account of radial functions having a large number of nodes.[4] In finite precision arithmetic, this corresponds to the subtraction of two infinities. If we used a nonorthogonal basis, we would just postpone the problem with instabilities to the diagonalization of Hamiltonian [4]. This issue might be addressed with the derivation of algebraic formulas for radial integrals obtained from commutation relations similar to the approach with which the angular terms are handled. For one such procedure, see [4]. We will employ this strategy as well. Unlike the article mentioned above with its rather intricate derivation of formulas, in this thesis, we will recover the $1/\hat{\mathsf{r}}_{12}$ operator in a purely algebraic manner using one simple trick.

As was suggested at the very end of [4], the Coulomb interaction matrix elements $\langle k|\hat{\mathsf{r}}_{12}^{-1}|j\rangle$ will not be calculated directly. Instead, we will determine the matrix elements of the operator $\hat{\mathsf{r}}_{12}^2$ first, as simple and exact formulas for their integrals can be derived. Subsequently, we will shift our focus to numerical methods that will enable us to compute the square root of $\hat{\mathsf{r}}_{12}^2$, which, after inversion, will yield our desired $1/\hat{\mathsf{r}}_{12}$ operator. This process will be the concern of the second chapter. In the third chapter, the matrix elements of the one-electron Hamiltonian will be calculated, and by solving the Schrödinger equation, the energy of the ground state will finally be acquired.

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[1]Subscript e at the given operator is used to distinguish the operators with the corresponding dimension and dimensionless operators in all following expressions.
Z is the proton number, α is the fine structure constant.

[2]Atomic units will be used in this entire thesis. In this system, the values of some key constants are set to one $e = \hbar = m_e = 1$.

[3]Throughout this thesis, if not specified otherwise, subscripts 1 or 2 at an operator imply that the operator applies to the electron 1 resp. 2, ie. $\hat{\mathsf{o}}_1 = \hat{\mathsf{o}} \otimes \hat{\mathsf{1}}$ and $\hat{\mathsf{o}}_2 = \hat{\mathsf{1}} \otimes \hat{\mathsf{o}}$.

[4]Especially for a large basis that is needed for convergence of the solution of Eq. (1).

1. Configuration interaction and Sturmian basis

Before we start with our own calculations, let us discuss some core ideas our work is based upon.

In this thesis, the method of configuration interaction (CI) is utilized. It is the most accurate method for the calculation of the Schrödinger equation of many-electron atoms [4]. In CI, the basis consists of antisymmetrized products of one-electron spin orbitals. When we increase the basis (i.e., when we make use of more basis states), the results converge to the accurate values.

As noted above, the basis states of the two electrons are antisymmetric. However, since the objective of this thesis is to calculate the energies of the first ^1S states, the antisymmetrization is secured by the spin part of the basis vectors leaving the coordinate part symmetric. Thus, the expression for the coordinate part of the basis functions $|j\rangle$ reads[1] [3]

$$|j\rangle = \frac{1}{\sqrt{2}} \bigg(|n_{1j}, n_{2j}, l_{1j} = l_j, l_{2j} = l_j, L_j = 0, M_j = 0\rangle +$$

$$+ |n_{2j}, n_{1j}, l_{2j} = l_j, l_{1j} = l_j, L_j = 0, M_j = 0\rangle \bigg) \tag{1.1}$$

$$= \frac{1}{\sqrt{2}} \bigg(|n_{1j}, l_j\rangle |n_{2j}, l_j\rangle \sum_{i=-l_j}^{l_j} (l_j, i, l_j, -i|0, 0) |l_j, i\rangle |l_j, -i\rangle +$$

$$+ |n_{2j}, l_j\rangle |n_{1j}, l_j\rangle \sum_{i=-l_j}^{l_j} (l_j, -i, l_j, i|0, 0) |l_j, -i\rangle |l_j, i\rangle \bigg) \tag{1.2}$$

where

$$(l_j, i, l_j, -i|0, 0) = \frac{(-1)^{l_j+i}}{\sqrt{2l_j + 1}}$$

are the Clebsch-Gordan coefficients, $|l_j, i\rangle$ are the spherical harmonics

$$Y_{lm}(\mathbf{n}) = \langle \mathbf{n}|l, m\rangle ,$$

and $|n_{1j}, l_j\rangle$, $|n_{2j}, l_j\rangle$ represent the radial part of the one-electron function. However, these functions are not the hydrogenic radial functions, as one might assume, since the system of eigenstates of hydrogen Hamiltonian is split into a discrete and a continuous part. Therefore, the discrete radial functions do not form a complete basis.

Instead, the so-called Sturmian functions will be used. These functions can be obtained from the hydrogenic functions via energy-dependent scaling $r \to rn$ [4] and are the eigenstates of the operator $\hat{\mathsf{T}}_3$, which is defined as [3]

$$\hat{\mathsf{T}}_3 \equiv \frac{\hat{\mathsf{r}}}{2}(\hat{\mathsf{p}}^2 + 1) .$$

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[1]If symmetrization is needed, i.e., if $n_1 \neq n_2$.

These functions satisfy

$$\hat{\mathsf{T}}_3 \, |n, l\rangle = n \, |n, l\rangle \tag{1.3}$$

and are denoted as

$$R_{n,l}^M(r) = \langle r|n, l\rangle \ .$$

The reason why we use the Sturmian basis is that the eigenstates of $\hat{\mathsf{T}}_3$ form a complete discrete basis, which is a crucial property when utilizing the CI method.

Unlike hydrogen eigenfunctions, Sturmian functions are orthonormal with respect to the inner product with the weight function r [3],

$$\langle n', l|n, l\rangle = \int_0^\infty \mathrm{d}r \, r R_{n',l}^M(r) R_{n,l}^M(r) = \delta_{n',n} \ . \tag{1.4}$$

Substituting the operator $\hat{\mathsf{T}}_3$ in Eq. (2), the equation Eq. (1) takes the form

$$\left(\frac{1}{\hat{\mathsf{r}}_1}(\hat{\mathsf{T}}_3 - \hat{\mathbb{1}})_1 + \frac{1}{\hat{\mathsf{r}}_2}(\hat{\mathsf{T}}_3 - \hat{\mathbb{1}})_2 + \frac{1}{Z\hat{\mathsf{r}}_{12}} \right) |\Psi\rangle = \Delta E \, |\Psi\rangle \ , \tag{1.5}$$

where ΔE satisfies

$$E = Z^2(\Delta E - 1) \ . \tag{1.6}$$

At this point, a variational parameter is often introduced [3]. We will not do so, however, as it would be of no benefit. The explanation will become apparent at the very end of this thesis.

The solution of Eq. (1.5) is the ultimate objective of our efforts.

2. Computation of the electron-electron interaction

In this chapter, the reader will find the evaluation of the operator $1/\hat{r}_{12}$ using a novel method making this chapter the essence of this entire thesis. As was mentioned in the introduction, at the core of this thesis lies the computation of the operator $\hat{r}_{12}^2$ from which the elements of the $1/\hat{r}_{12}$ operator are then determined.

The elegance of this approach and the reason why we chose it boils down to the fact that firstly, $\hat{r}_{12}^2$ takes a simple form

$$
\begin{aligned}
\hat{r}_{12}^2 &= (\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2) \cdot (\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2) \\
&= \hat{r}_1^2 - 2\,\hat{r}_1\hat{r}_2\,\hat{\mathbf{n}}_1 \cdot \hat{\mathbf{n}}_2 + \hat{r}_2^2 \\
&= \hat{r}_1^2 - 2\,\hat{r}_1\hat{r}_2\left(\frac{1}{2}(\hat{n}_1^+\hat{n}_2^- + \hat{n}_1^-\hat{n}_2^+) + \hat{n}_1^3\hat{n}_2^3\right) + \hat{r}_2^2\,,
\end{aligned}
$$

where all the operators are well-defined and act on the basis states Eq. (1.2) in a straightforward manner making their matrix elements easy to derive. Secondly, the Schur method offers a fast and numerically stable procedure to reconstruct $1/\hat{r}_{12}$ from the operator $\hat{r}_{12}^2$. Thus, we will obtain $1/\hat{r}_{12}$ without the need to evaluate a single integral.

Considering the symmetry of the ^1S states, the matrix elements of $\hat{r}_{12}^2$ require even fewer calculations as the following equalities hold,

$$
\hat{r}_1^2 = \hat{r}_2^2\,, \tag{2.1}
$$

$$
\hat{n}_1^+\hat{n}_2^- = \hat{n}_1^-\hat{n}_2^+\,. \tag{2.2}
$$

Furthermore, taking into account that $\hat{r}_{12}^2$ is hermitian with respect to the scalar product Eq. (1.4), the number of computations necessary drops to one third.

The non-hermitian operators $\hat{n}^+$ and $\hat{n}^-$ are defined as usual,

$$
\hat{n}^+ \equiv \hat{n}_x + i\hat{n}_y\,,
$$

$$
\hat{n}^- \equiv \hat{n}_x - i\hat{n}_y\,.
$$

It also holds that

$$
\hat{n}^3 \equiv \hat{n}_z\,,
$$

$$
\hat{\mathbf{n}} \equiv \frac{\hat{\mathbf{r}}}{\hat{r}}\,.
$$

With everything clarified, we can now proceed to the actual calculations. In the first subchapter, we will derive the form of $\hat{r}_1^2$. Subsequently, the elements of $\hat{r}_1\hat{r}_2\hat{n}_1^+\hat{n}_2^-$ and $\hat{r}_1\hat{r}_2\hat{n}_1^3\hat{n}_2^3$ will be calculated. Finally, at the end of this chapter, we will discuss the computation of the square root inverse of the $\hat{r}_{12}^2$ matrix.

2.1 Calculation of one-electron radial operator

In this subsection, the matrix elements $\langle k|\hat{r}_1^2|j\rangle$ are derived.

Taking into consideration that $\hat{r}_1^2$ acts only on the radial part of states, the concise form of the basis vectors Eq. (1.1) with factorized one-electron radial terms

$$|j\rangle = \frac{1}{\sqrt{2}} \bigg(|n_{1j}, l_j\rangle |n_{2j}, l_j\rangle + |n_{2j}, l_j\rangle |n_{1j}, l_j\rangle \bigg) |l_j, l_j, 0, 0\rangle \qquad (2.3)$$

will suffice and will, in fact, significantly reduce the number of computations.

To evaluate $\langle k|\hat{r}_1^2|j\rangle$, three integrals need to be determined: the radial orthonormal relation Eq. (1.4), the angular orthonormal relation

$$\langle l', l', 0, 0|l, l, 0, 0\rangle = \delta_{l',l}, \qquad (2.4)$$

and above all

$$\langle n', l|\hat{r}^2|n, l\rangle = \int_0^\infty \mathrm{d}r r R_{n',l}^M(r) r^2 R_{n,l}^M(r). \qquad (2.5)$$

To calculate this integral the action of $\hat{r}$ on Sturmian functions [4]

$$r R_{n,l}^M(r) = n R_{n,l}^M(r) - \frac{1}{2}\sqrt{(n+l+1)(n-l)} R_{n+1,l}^M(r)$$
$$- \frac{1}{2}\sqrt{(n-l-1)(n+l)} R_{n-1,l}^M(r) \qquad (2.6)$$

is utilized. This recurrence relation, which we will apply only as a simple formula for now, is derived from the commutations of the radial so(2,1) algebra. For more details, see [4]. Substituting twice Eq. (2.6) and exploiting Eq. (1.4), the integral Eq. (2.5) yields

$$\langle n', l|\hat{r}^2|n, l\rangle = \int_0^\infty \mathrm{d}r r R_{n',l}^M(r) r^2 R_{n,l}^M(r)$$
$$= \left(\frac{3}{2}n^2 - \frac{1}{2}l(l+1)\right)\delta_{n',n}$$
$$- \frac{1}{2}\sqrt{(n+l+1)(n-l)}(2n+1)\delta_{n',n+1}$$
$$- \frac{1}{2}\sqrt{(n-l-1)(n+l)}(2n-1)\delta_{n',n-1}$$
$$+ \frac{1}{4}\sqrt{(n+l+1)(n-l)(n+l+2)(n-l+1)}\delta_{n',n+2}$$
$$+ \frac{1}{4}\sqrt{(n-l-1)(n+l)(n-l-2)(n+l-1)}\delta_{n',n-2}. \qquad (2.7)$$

Thus, with use of Eqs. (1.4), (2.4) and (2.7), an exact algebraic formula for matrix elements $\langle k|\hat{r}_1^2|j\rangle$ is derived. Keeping in mind Eq. (2.1), the elements $\langle k|\hat{r}_2^2|j\rangle$ are identical.

2.2 Calculation of the cross term

Having just acquired the expression for the one-electron part of the operator $\hat{r}_{12}^2$, we can continue by examining the $\langle k|\hat{r}_1\hat{r}_2\hat{n}_1^+\hat{n}_2^-|j\rangle$ and $\langle k|\hat{r}_1\hat{r}_2\hat{n}_1^3\hat{n}_2^3|j\rangle$ matrix elements.

To calculate these elements, the expanded form of the basis states Eq. (1.2) has to be used since the operators act on the radial as well as the angular part of the wave function. In the case of the cross term, four integrals need to be evaluated:

$$\langle n', l' | \hat{r} | n, l \rangle = \int_0^\infty \mathrm{d}r \, r R_{n',l'}^M(r) r R_{n,l}^M(r) \,, \tag{2.8}$$

$$\langle l', m' | \hat{n}^+ | l, m \rangle = \int_{S_2} \mathrm{d}\mathbf{n} Y_{l',m'}(\mathbf{n}) n^+ Y_{l,m}(\mathbf{n}) \,, \tag{2.9}$$

$$\langle l', m' | \hat{n}^- | l, m \rangle = \int_{S_2} \mathrm{d}\mathbf{n} Y_{l',m'}(\mathbf{n}) n^- Y_{l,m}(\mathbf{n}) \,. \tag{2.10}$$

$$\langle l', m' | \hat{n}^3 | l, m \rangle = \int_{S_2} \mathrm{d}\mathbf{n} Y_{l',m'}(\mathbf{n}) n^3 Y_{l,m}(\mathbf{n}) \,. \tag{2.11}$$

Let us begin with the computation of the angular terms first.

For their integration, we will make use of formulas [3]

$$n^+ Y_{l,m}(\mathbf{n}) = \sqrt{\frac{(l-m-1)(l-m)}{(2l-1)(2l+1)}} Y_{l-1,m+1}(\mathbf{n})$$
$$- \sqrt{\frac{(l+m+2)(l+m+1)}{(2l+1)(2l+3)}} Y_{l+1,m+1}(\mathbf{n}) \,,$$

$$n^- Y_{l,m}(\mathbf{n}) = -\sqrt{\frac{(l+m-1)(l+m)}{(2l-1)(2l+1)}} Y_{l-1,m-1}(\mathbf{n})$$
$$+ \sqrt{\frac{(l-m+2)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1,m-1}(\mathbf{n}) \,.$$

$$n^3 Y_{l,m}(\mathbf{n}) = \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}} Y_{l-1,m}(\mathbf{n})$$
$$+ \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1,m}(\mathbf{n})$$

With the help of these relations as well as by utilizing the angular orthonormality relation [3]

$$\langle l', m' | l, m \rangle = \delta_{l',l} \delta_{m',m} \,,$$

the integrals Eqs. (2.9), (2.10) and (2.11) take the form

$$\langle l', m' | \hat{n}^+ | l, m \rangle = \left(\sqrt{\frac{(l-m-1)(l-m)}{(2l-1)(2l+1)}} \delta_{l',l-1} \right.$$
$$\left. - \sqrt{\frac{(l+m+2)(l+m+1)}{(2l+1)(2l+3)}} \delta_{l',l+1} \right) \delta_{m',m+1} \tag{2.12}$$

$$\langle l', m' | \hat{n}^- | l, m \rangle = \left(-\sqrt{\frac{(l+m-1)(l+m)}{(2l-1)(2l+1)}} \delta_{l',l-1} \right.$$
$$\left. + \sqrt{\frac{(l+m+2)(l+m+1)}{(2l+1)(2l+3)}} \delta_{l',l+1} \right) \delta_{m',m-1} \tag{2.13}$$

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$$\langle l', m'|\hat{\mathsf{n}}^3|l, m\rangle = \left(\sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}\delta_{l',l-1} \right.$$

$$\left. + \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}\delta_{l',l+1} \right)\delta_{m',m} \tag{2.14}$$

Now, let us shift our focus to the radial part.

Thanks to the Kronecker deltas in the expressions above, the equality $|l' - l| = 1$ is ensured. As a consequence, Eq. (2.6) cannot be applied since the orthonormality Eq. (1.4) holds only for $l' = l$. Instead, another set of relations

$$rR_{n,l}^M(r) = \frac{1}{2}\sqrt{(n+l+1)(n+l+2)}R_{n+1,l+1}^M(r)$$
$$+ \frac{1}{2}\sqrt{(n-l-1)(n-l-2)}R_{n-1,l+1}^M(r)$$
$$- \sqrt{n^2-(l+1)^2}R_{n,l+1}^M(r)$$

$$rR_{n,l}^M(r) = \frac{1}{2}\sqrt{(n-l)(n-l+1)}R_{n+1,l-1}^M(r)$$
$$+ \frac{1}{2}\sqrt{(n+l)(n+l-1)}R_{n-1,l-1}^M(r)$$
$$- \sqrt{n^2-l^2}R_{n,l-1}^M(r)$$

will be used to raise or lower l so that the application of Eq. (1.4) is justified. The algebraic expression for the integral Eq. (2.8) then reads

$$\langle n', l+1|\hat{\mathsf{r}}|n, l\rangle = \int_0^\infty \mathrm{d}r r R_{n',l+1}^M(r) r R_{n,l}^M(r)$$
$$= \frac{1}{2}\sqrt{(n+l+1)(n+l+2)}\delta_{n',n+1}$$
$$+ \frac{1}{2}\sqrt{(n-l-1)(n-l-2)}\delta_{n',n-1}$$
$$- \sqrt{n^2-(l+1)^2}\delta_{n',n} \tag{2.15}$$

$$\langle n', l-1|\hat{\mathsf{r}}|n, l\rangle = \int_0^\infty \mathrm{d}r r R_{n',l-1}^M(r) r R_{n,l}^M(r)$$
$$= \frac{1}{2}\sqrt{(n-l)(n-l+1)}\delta_{n',n+1}$$
$$+ \frac{1}{2}\sqrt{(n+l)(n+l-1)}\delta_{n',n-1}$$
$$- \sqrt{n^2-l^2}\delta_{n',n}.$$

Since Eq. (2.8) is symmetric and since we could always make the substitution $l - 1 \to l$, a single formula would suffice. Nevertheless, both expressions are included for the sake of completeness.

With integrals Eqs. (2.12), (2.13), (2.14) and (2.15), the matrix elements $\langle k|\hat{\mathsf{r}}_1\hat{\mathsf{r}}_2\hat{\mathsf{n}}_1^+\hat{\mathsf{n}}_2^-|j\rangle$ and $\langle k|\hat{\mathsf{r}}_1\hat{\mathsf{r}}_2\hat{\mathsf{n}}_1^3\hat{\mathsf{n}}_2^3|j\rangle$ can be evaluated. And because of the equality Eq. (2.2), we will kill two birds with one stone by obtaining the elements $\langle k|\hat{\mathsf{r}}_1\hat{\mathsf{r}}_2\hat{\mathsf{n}}_1^-\hat{\mathsf{n}}_2^+|j\rangle$ as well. Thus, a formula for the whole cross term was recovered.

2.3 The Schur method for the square root of a matrix

With formulas derived in the previous two sections, we acquired exact algebraic expressions for the calculation of the matrix elements of the $\hat{r}_{12}^2$ operator. The interaction potential between two electrons in a Helium atom is however not proportional to the square of their distance. Instead, it is proportional to the inverse of their distance. Thus, if we recovered the matrix of the operator $1/\hat{r}_{12}$ from the matrix $\hat{r}_{12}^2$, we would obtain an operator that corresponds to the physical Coloumb interaction.

Luckily for us, thorough research regarding the matrix square roots has been conducted, allowing us to reap the benefits and apply the algorithm that suits our needs the best.

The problem we want to solve is to find a matrix X for a given matrix A such that $A = X^2$. A solution exists for any nonsingular $A \in \mathbb{C}^{n \times n}$. Moreover, a sufficient condition for X to be real is if A is real and has a real non-negative spectrum. [5] In view of the fact that $\hat{r}_{12}^2$ satisfies this condition, it is ensured that we will not burden the computer with the use of complex numbers. This implies another reduction in the number of operations. Furthermore, because $\hat{r}_{12}^2$ is a symmetric positive definite matrix, it has a unique symmetric positive definite square root [5].

Since we now know what properties our A and X have, let us examine some specific algorithms for finding the solution of $A = X^2$. In the field of numerical linear algebra, several methods for the computation of the square root of a matrix have been developed. We will take a look at some of them and select the one that fits our purposes the best. All of the following methods are in extensive detail analyzed in [5].

The first method is the well-known Newton algorithm given by the iteration relation

$$X_{k+1} = \frac{1}{2}(X_k + X_k^{-1} A) , \qquad\qquad X_0 = A .$$

Although it has good theoretical properties, especially for symmetric positive definite matrices, it suffers from such poor numerical instabilities that it is useless for practical application.

Another iterative algorithm derived by Denman and Beavers [1]

$$Y_{k+1} = \frac{1}{2}(Y_k + Z_k^{-1}) , \qquad Y_0 = A , \qquad Y_k \to A^{1/2} ,$$

$$Z_{k+1} = \frac{1}{2}(Z_k + Y_k^{-1}) , \qquad Z_0 = I , \qquad Z_k \to A^{-1/2}$$

is recommended in general as it is numerically stable and converges quadratically. For our purposes, it would offer the added benefit that it calculates the inverse of the matrix square root right away, saving us the need for the inversion. Nevertheless, let us examine some other algorithms.

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[1]The convergence holds for A positive definite.

Especially for a symmetric positive definite $A \in \mathbb{R}^{n \times n}$, the algorithm

1. $A = R^T R$ (Cholesky factorization)

2. $Y_{k+1} = \dfrac{1}{2}(Y_k + Y_k^{-1})$, $Y_0 = R$

3. $X = Y_\infty^T R$

is a very good alternative.

The ideal choice, however, is the Schur method [5]. It is actually not a single method. Rather, it is a family of algorithms for the matrix roots. Some of them are described in great detail in [6] or [7]. All of the algorithms have in common that the first step is the calculation of the Schur decomposition $A = Q^* R Q$. Then, the square root of the upper triangular matrix R is determined, often with the use of procedures based on the algorithms discussed above. After that, the square root of A is given by $A^{1/2} = Q^* R^{1/2} Q$.

The main point of the Schur method is that it is much easier to compute the root of an upper triangular matrix than that of a general square matrix. For us, it is, in fact, trivial. Considering that $\hat{r}_{12}^2$ is symmetric, R has to be a diagonal matrix allowing us to compute $R^{-1/2}$ right away with $(R^{-1/2})_{ii} = 1/\sqrt{R_{ii}}$. The Coloumb potential between electrons is then given by $1/\hat{r}_{12} = Q^* R^{-1/2} Q$.

Thus, we have achieved the goal of this chapter as we calculated $1/\hat{r}_{12}$ in a numerically stable way.

3. Computation of the ground-state energy

In the previous chapter, the primary object of our enterprise was achieved when the matrix form of the $1/\hat{r}_{12}$ operator was recovered. A significant portion of our endeavor still lies ahead, however, as our final goal is the computation of the energies of the first singlet S states.

For that, the solution to the eigenvalue problem Eq. (1.5) needs to be found. The evaluation of the most problematic part of the Hamiltonian, the $1/\hat{r}_{12}$ operator, was already discussed in the previous chapter. Nonetheless, the form of the one-electron Hamiltonian $\frac{1}{\hat{r}}(\hat{T}_3 - \hat{1})$ is still to be determined. Thanks to the symmetry of singlet states, the equality of operators

$$\frac{1}{\hat{r}_1}(\hat{T}_3 - \hat{1})_1 = \frac{1}{\hat{r}_2}(\hat{T}_3 - \hat{1})_2$$

allows us to cut the number of operations by one half. The calculation of the one-electron Hamiltonian will be the concern of the first subsection.

In the second subsection, we will exploit all derived formulas for the Hamiltonian, and by solving the time-independent Schrödinger equation, we will obtain the sought-after energy spectrum.

3.1 Calculation of one-electron Hamiltonian

Let us calculate the matrix elements $\langle k|\frac{1}{\hat{r}}(\hat{T}_3 - \hat{1})|j\rangle$. Taking into consideration that all the operators of the one-electron Hamiltonian act only on the radial part of the wave function, the compact form of the basis vectors Eq. (2.3) will be used. To determine $\langle k|\frac{1}{\hat{r}}(\hat{T}_3 - \hat{1})|j\rangle$, a single remaining integral

$$\langle n', l'|\frac{1}{\hat{r}}(\hat{T}_3 - \hat{1})|n, l\rangle = \int_0^\infty \mathrm{d}r\, r R_{n',l'}^M(r)\frac{1}{r}(T_3 - 1)R_{n,l}^M(r)$$

$$= (n-1)\int_0^\infty \mathrm{d}r\, R_{n',l'}^M(r)R_{n,l}^M(r)$$

needs to be evaluated. In the second equality, Eq. (1.3) is utilized.

In contrast to our approach in the previous chapter, where closed formulas for the atomic integrals were found, only a recurrence relation for the radial integral

$$\langle n', l'|\frac{1}{\hat{r}}|n, l\rangle = \int_0^\infty \mathrm{d}r\, R_{n',l'}^M(r)R_{n,l}^M(r) \tag{3.1}$$

will be derived. Since the one-electron Hamiltonian contains no angular operators, the orthonormality relation Eq. (2.4) ensures the equality $l' = l$.

Our starting point is the formula Eq. (2.6)

$$\hat{r}\,|n, l\rangle = n\,|n, l\rangle - \frac{1}{2}\sqrt{(n+l+1)(n-l)}\,|n+1, l\rangle$$

$$- \frac{1}{2}\sqrt{(n-l-1)(n+l)}\,|n-1, l\rangle.$$

When we apply $\langle n', l | \frac{1}{\hat{r}}$ from the left, it takes the form

$$\delta_{n',n} = n \langle n', l | \frac{1}{\hat{r}} | n, l \rangle - \frac{1}{2} \sqrt{(n+l+1)(n-l)} \langle n', l | \frac{1}{\hat{r}} | n+1, l \rangle$$
$$- \frac{1}{2} \sqrt{(n-l-1)(n+l)} \langle n', l | \frac{1}{\hat{r}} | n-1, l \rangle .$$

With the transformation $n \to n - 1$ and some algebraic manipulation

$$\langle n', l | \frac{1}{\hat{r}} | n, l \rangle = \left(-\frac{1}{2} \sqrt{(n-l-2)(n+l-1)} \langle n', l | \frac{1}{\hat{r}} | n-2, l \rangle - \right.$$
$$\left. - (n-1) \langle n', l | \frac{1}{\hat{r}} | n-1, l \rangle - \delta_{n',n-1} \right) \frac{2}{\sqrt{(n+l)(n-l-1)}} ,$$
$$(3.2)$$

we obtain the recurrence relation for the integral Eq. (3.1).

With the use of Mathematica software, formulas for the master integrals

$$\langle n, l | \frac{1}{\hat{r}} | n, l \rangle \quad = \int_0^\infty dr R_{n,l}^M(r) R_{n,l}^M(r) \quad = \frac{2}{2l+1} \tag{3.3}$$

$$\langle l+1, l | \frac{1}{\hat{r}} | l+2, l \rangle = \int_0^\infty dr R_{l+1,l}^M(r) R_{l+2,l}^M(r) = \frac{2}{2l+1} \sqrt{\frac{1}{2l+2}} \tag{3.4}$$

were found.

Utilizing Eqs. (3.2), (3.3), (3.4) as well as the symmetry of the integral Eq. (3.1), we are able to evaluate all the matrix elements $\langle k | \frac{1}{\hat{r}} (\hat{T}_3 - \hat{1}) | j \rangle$.

3.2 Numerical results

In the second chapter, together with the first section of this chapter, we examined the procedures employed to determine the values of the atomic integrals using only algebraic methods. Thus, having completed the derivation of the Hamiltonian matrix elements, we can finally advance to the solution of the Schrödinger equation Eq. (1.5).

There still remains one detail left to be clarified, though. In all the formulas above, the integrals depend on the quantum numbers n and l of a given state $|j\rangle$. The quantum numbers are yet to be assigned to the basis states, however, as there exists no canonical specification of their values. Let us resolve this ambiguity.

For the first 14 states denoted by j, numbers n_1, n_2, and l are displayed in table 3.1. Hopefully, the reader will recognize the pattern and will be able to extrapolate to more basis states if needed. This sequence was adopted from [3] and was chosen for more rapid convergence. We introduce a new number $n_{12} = n_1 + n_2$, according to which the states are ordered. With this approach, radial functions with higher values of n_2 are included from the beginning making the convergence of the energies faster.

Given that we have discussed everything needed, we can finally present the calculated energies of the Helium spectral lines. The energies were obtained as a solution to the eigenvalue problem Eq. (1.5) and with the use of Eq. (1.6).

The numerical results for the first two energy levels are displayed in table 3.2[1].

j	n_1	n_2	l	n_{12}
1	1	1	0	2
2	1	2	0	3
3	1	3	0	4
4	2	2	0	4
5	2	2	1	4
6	1	4	0	5
7	2	3	0	5
8	2	3	1	5
9	1	5	0	6
10	2	4	0	6
11	2	4	1	6
12	3	3	0	6
13	3	3	1	6
14	3	3	2	6

Table 3.1: Quantum numbers

n_{12}	N	$E(1\,^1S)$	$E(2\,^1S)$
2	1	-2.845 299	
3	2	-2.974 065	5.273 725
4	5	-2.984 372	-1.078 245
5	8	-2.957 090	-1.856 181
6	14	-2.951 889	-1.992 264
7	20	-2.943 705	-2.087 557
8	30	-2.938 345	-2.113 734
9	40	-2.934 122	-2.132 869
10	55	-2.930 806	-2.139 475
11	70	-2.928 126	-2.143 976
12	91	-2.925 917	-2.145 583
13	112	-2.924 068	-2.146 600
14	140	-2.922 497	-2.146 901
15	168	-2.921 147	-2.147 068
16	204	-2.919 975	-2.147 068
17	240	-2.918 948	-2.147 050
$\vdots$			
40	2870	-2.909 859	-2.146 420
∞	∞	-2.903 686	-2.145 971
Ref. [8]		-2.903 724	-2.145 974

Table 3.2: Energies of the first two states

The energies were calculated for the values of n_{12} in the range 2-40 and then were extrapolated to infinity. The number of all basis states taken into expansion of the reference state is denoted by N.

Having obtained the final results for energies we may keep the promise given to the reader in the first chapter and finally justify why we do not make use of any variational parameter. In the third column, we can see that the first energy level is lower than the accurate value and converges to it from the bottom up. Usually in the variational method the obtained energies lie above the ground state and by optimizing the variational parameter we obtain the lowest lying result. However, since in our case the results are converging from bellow it is unclear what the procedure of optimizing the parameter should lead to and thus we will not use it.

For the $2\,^1S$ state, the situation is not that simple. We can see that for $n_{12} \leq 12$, the energy is greater than the correct value and is slowly decreasing and continues to decrease until $n_{12} = 15$, where it reaches its minimum and then it begins to converge to the proper value from the bottom up, just like $1\,^1S$. However, if we take a closer look, this is the case for the ground state as well because, for $n_{12} = 2$, the energy is $E_2 \doteq -2.85 > -2.90 \doteq E_\infty$, and only after that the energy drops below E_∞ and starts rising to the right value.

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[1]The energies are in Hartrees. $1\,\mathrm{Ha} \doteq 27.211\,\mathrm{eV}$.

Thus, for the calculation of the first excited state, the use of a variational parameter would be a hindrance too.

For the $3\,^1S$ state, similar behavior is observed. In this case, the energy reaches its minimum for $n_{12} = 34$.

Let us now have a look at the precision our method offers in the problem of Helium-like ions. In comparison with the exact theoretical values [8], which are shown in the ultimate row of table 3.2, we can see that for $1\,^1S$, the relative precision is 1×10^{-5}. For the $2\,^1S$ state, we observe a finer performance with the relative precision 1×10^{-6}. For other states, the accuracy of the obtained values is not significant as the use of a larger basis is required.

To conclude, we have demonstrated that our method indeed produces results with considerable precision, although the evaluation is hindered by the impossibility of the optimization of the variational parameter.

Conclusion

The objective of this thesis was to utilize a novel method for the calculation of helium spectra. We explored the advantages as well as the disadvantages it has to offer. To summarize the results of our work, the major achievement was accomplished when the operator of the electron-electron interaction $1/\hat{r}_{12}$ was determined with the use of a unique method that had not been employed before.

This new method was the subject of the second chapter and consists of two steps. Firstly, we derived exact algebraic formulas for the atomic integrals of the operator $\hat{r}_{12}^2$: Eqs. (2.7), (2.12), (2.13), (2.14), (2.15). Then, we computed the inverse square root of $\hat{r}_{12}^2$ utilizing the Schur method. Thus, the operator $1/\hat{r}_{12}$ was recovered.

In the third chapter, the recurrence relation for the integrals of the one-electron Hamiltonian Eqs. (3.2), (3.3), (3.4) was derived. We then concluded with an analysis of the numerical results.

The primary benefit of the method presented in this thesis is the fact that all integrals are evaluated strictly algebraically without any potential for the emergence of numerical instabilities. The only numerical calculation is the Schur decomposition in the computation of the square root of $\hat{r}_{12}^2$. This mathematical operation is well understood and poses no threat to the final results since it is numerically stable and is, from the numerical point of view, analogous to the eigenvalue problem Eq. (1).

In comparison with another method that also utilizes a purely algebraic approach [4], our procedure offers the advantage that the expressions for the atomic integrals take a much simpler form. On the other hand, considering that in our method, the energy converges to the accurate value from below, it is not possible to optimize a variational parameter. This is a major drawback since, as a result, calculations with more basis states are needed. That further translates into manipulations with larger matrices, significantly increasing the number of operations. For comparison, in [4], with $N = 862$, the relative precision achieved is at the order of 10^{-5}. In our case, for $N = 910$, the relative precision is only at the order of 10^{-3}.

Although in this thesis, we examined only singlet S states, our method can be easily extended to other states as well. The use of this method for atoms with multiple electrons is theoretically possible, even though it is rather impractical because of the rapid growth of the Slater determinant. Instead, our method can be applied without difficulty when dealing with relativistic corrections.

Further research involving this inverse square root method thus seems promising. Considering the possibility that the problematic direction of the convergence might not be an inherent feature of this approach and would disappear in some cases, the variational parameter could then be optimized, allowing our method to reach its full potential.

Bibliography

[1] Egil A. Hylleraas. Reminiscences from early quantum mechanics of two-electron atoms. *Rev. Mod. Phys.*, 35:421–430, Jul 1963.

[2] Krzysztof Pachucki, Vojtěch Patkóš, and Vladimir A. Yerokhin. Testing fundamental interactions on the helium atom. *Phys. Rev. A*, 95:062510, Jun 2017.

[3] Jaroslav Zamastil. *Quantum mechanics and electrodynamics*. Springer, Cham, 2017.

[4] J. Zamastil, F. Vinette, and M. Šimánek. Calculation of atomic integrals using commutation relations. *Phys. Rev. A*, 75:022506, Feb 2007.

[5] Nicholas J. Higham. Stable iterations for the matrix square root. *Numerical Algorithms*, 15:227–242, Sep 1997.

[6] Åke Björck and Sven Hammarling. A schur method for the square root of a matrix. *Linear Algebra and its Applications*, 52/53:127–140, 1983.

[7] Chun-Hua Guo and Nicholas J. Higham. A schur–newton method for the matrix pth root and its inverse. *SIAM Journal on Matrix Analysis and Applications*, 28(3):788–804, 2006.

[8] D. T. Aznabayev, A. K. Bekbaev, I. S. Ishmukhamedov, and V. I. Korobov. Energy levels of a helium atom. *Physics of Particles and Nuclei Letters*, 12:689–694, Sep 2015.