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**Influence of relativistic effects on atomic
spectra**

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Title: Influence of relativistic effects on atomic spectra

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Abstract:

In this thesis we investigate solution of Dirac equation in spherically symmetric potential. The potential consist of Coulomb field of the nucleus and average potential of all other electrons in atom. We expand the solution of Dirac equation in finite Sturmian basis set. For this finite basis we introduce and investigate corresponding Foldy-Wouthuysen transformation. We apply the theory to the case of cesium atom. We find that non-relativistic energies are monotonically decreasing with increasing basis set. However, relativistic corrections cause oscillatory behaviour of energies present in fully relativistic case.

Keywords: quantum mechanics, relativity, atomic spectroscopy

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Introduction

The continuing advances in experimental atomic spectroscopy lead to ever increasing precision of position of atomic spectral lines. This opens up the possibility to test our fundamental theories of nature [1]. This demands high precision of atomic structure calculation. In particular the relativity has to be incorporated into the calculation from the very beginning. However it has been known, that the correct relativistic Hamiltonian describing electrons, particles with spin $1/2$, is not positive definite. This leads to the oscillatory behaviour of energies with increasing basis size. In this thesis we aim to investigate this phenomenon. We introduce the finite Foldy-Wouthyusen transformation (FWT) and investigate its properties.

The thesis is organized as follows in section 1.1 we summarize the basic features of the solution of Dirac Equation for particle moving in spherically symmetric potential. In section 2.1 we propose the finite FWT, give an illustrative example and describe general algorithm. In section 3 we discuss results obtained by this method in the case of cesium and hydrogen atom.

1. Solution of Dirac Equation in finite basis

1.1 Dirac Equation for particle moving in spherical symmetric potential

Within the framework of shell model the motion of electron in atom is described by Dirac equation [2]

$$\hat{H}_D \psi = E \psi, \quad (1.1)$$

where the Dirac Hamiltonian reads in natural units ($\hbar = c = 1$)

$$\hat{H}_D = \gamma_0 \vec{\gamma} \cdot \hat{\vec{P}} + \gamma_0 m_e - \frac{Z\alpha}{R} + V_{HF}(R). \quad (1.2)$$

Here γ 's denote Dirac matrices in Dirac representation

$$\gamma_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.3)$$

and

$$\vec{\gamma} = \begin{pmatrix} 0 & \vec{\sigma} \\ -\vec{\sigma} & 0 \end{pmatrix}, \quad (1.4)$$

where σ 's are well-known Pauli matrices and 1 stands for unit matrix dimension 2×2 . Further Z and $\alpha = 137.0359991^{-1}$ [3] denote atomic number and fine structure constant and m_e stands for electron mass. Furthermore V_{HF} stands for Hartree-Fock potential. This potential is averaged potential caused by all other electrons in atom.

Further, it is advantageous to make transformation to scaled atomic units [2]

$$\vec{R} = \frac{\vec{r}}{m_e Z \alpha}, \quad \hat{\vec{P}} = m_e Z \alpha \hat{\vec{p}}, \quad (1.5)$$

and subtract from Hamiltonian the constant corresponding to the electron rest mass m_e . Eqs. (1.1), (1.2), are transformed to equations

$$\hat{h}_D \psi = \varepsilon \psi, \quad \hat{h}_D = \frac{\hat{H}_D - m_e}{m_e (Z\alpha)^2}, \quad (1.6)$$

where

$$\hat{h}_D = \hat{z} + v_{HF}, \quad \hat{z} = \frac{1}{Z\alpha} \gamma_0 \vec{\gamma} \cdot \hat{\vec{p}} + \frac{\gamma_0 - 1}{(Z\alpha)^2} - \frac{1}{r} \quad (1.7)$$

and ε is electron energy in atomic units.

1.2 Integrals of motion

It is known, see e.g. [4], that there are three operators commuting with Dirac Hamiltonian for a particle described by Eq.(1.1): the square, \hat{J}^2 , and the third component, \hat{J}_z , of the total angular momentum given by the sum of orbital and spin angular momentum [2],

$$\hat{J} = \hat{L} + \frac{1}{2}\vec{\Sigma}, \quad \vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}$$

and the relativistic parity operator \hat{K} ,

$$\hat{K} = \gamma_0 \left(\vec{\Sigma} \cdot \hat{L} + 1 \right). \quad (1.8)$$

As done in [5], while dealing with purely Coulomb field, where $V_{HF} = 0$ in Eq. (1.2), one obtains another integral of motion for the Dirac Hamiltonian. After that can every single solution of Eq. (1.1) be rewritten as [2]

$$\psi = [\gamma_0(E - \hat{H}_D) + 2m_e]\phi,$$

Multiplying Eq. (1.1) by γ_0 from the left, we obtain the second-order Dirac equation,

$$\hat{\mathcal{H}}\phi = 0, \quad \hat{\mathcal{H}} = \gamma_0(E - \hat{H}_D)[\gamma_0(E - \hat{H}_D) + 2m_e], \quad (1.9)$$

where in the case of pure Coulomb potential, the second-order Dirac Hamiltonian $\hat{\mathcal{H}}$ is given by

$$\hat{\mathcal{H}} = E^2 - m_e^2 - 2(m_e Z\alpha)^2 \left[\frac{\hat{p}_r^2}{2} - \frac{\hat{G}(\hat{G} - 1)}{2r^2} - \frac{E/m_e}{r} \right], \quad (1.10)$$

where \hat{p}_r is radial momentum in coordinate representation $\hat{p}_r = -i \left(\frac{d}{dr} + \frac{1}{r} \right)$. The operator \hat{G} is the additional integral of motion.

$$\hat{G} = \gamma_0 \left(\hat{K} + i(Z\alpha)\vec{\gamma} \cdot \vec{n} \right), \quad (1.11)$$

where $\vec{n} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$ is the unit vector pointing in an arbitrary direction. The form (1.10) is almost the same as the non-relativistic Hamiltonian where $\hat{G}(\hat{G} - 1)$ is substituting the part of \hat{L}^2 .

Further calculation can show that [2]

$$\hat{K}^2 = \hat{J}^2 + \frac{1}{4}, \quad \hat{G}^2 = \hat{K}^2 - (Z\alpha)^2.$$

Where we obtain eigenvalues for \hat{K} and \hat{G} as follows

$$K = \kappa|K|, \quad \kappa = \pm 1, \quad |K| = j + 1/2 \quad (1.12)$$

and

$$G = g\kappa|G|, \quad g = \pm 1, \quad |G| = \sqrt{K^2 - (Z\alpha)^2}, \quad (1.13)$$

respectively. Special note of importance shall be given to the signs of G and K being relative to each other, this will simplify the following calculations even further, especially while dealing with the case of relativistic parity being static.

Since all the following operators commute with each other $\hat{G}, \hat{K}, \hat{J}^2$ and \hat{J}_z one can than see that they involve common eigenfunctions [2]

$$\hat{G}|g, \kappa, j, m\rangle = g\kappa|G||g, \kappa, j, m\rangle, \quad \hat{K}|g, \kappa, j, m\rangle = \kappa|K||g, \kappa, j, m\rangle \quad (1.14)$$

and

$$\hat{J}^2|g, \kappa, j, m\rangle = j(j+1)|g, \kappa, j, m\rangle, \quad \hat{J}_z|g, \kappa, j, m\rangle = m|g, \kappa, j, m\rangle.$$

Which can be rewritten in more explicit form

$$\langle \vec{n}|g, \kappa, j, m\rangle = \begin{pmatrix} c_1^g \langle \vec{n}|j, m\rangle^\kappa \\ c_2^g \langle \vec{n}|j, m\rangle^{-\kappa} \end{pmatrix}, \quad (1.15)$$

where the symbol $\langle \vec{n}|j, m\rangle^\kappa$ denotes the spherical spinors

$$\langle \vec{n}|j, m\rangle^\kappa = \sum_{S_z = -\frac{1}{2}}^{\frac{1}{2}} \left(j - \frac{\kappa}{2}, m - S_z, \frac{1}{2}, S_z |j, m\rangle \right) Y_{j-\frac{\kappa}{2}, m-S_z}(\vec{n}) \Big|_{\frac{1}{2}, S_z}. \quad (1.16)$$

Here $Y_{l,m}(\vec{n})$, S_z and $|j, m\rangle$ are spherical harmonics, spin functions and Clebsch-Gordan coefficients, respectively, see any textbook on quantum mechanics, e.g. [6]. From Eqs. (1.8), (1.11) and (1.14) than follows, that the Clebsch-Gordan coefficients c in the expansion (1.15) satisfy

$$c_2^g = -\frac{i}{Z\alpha}(K - G)c_1^g. \quad (1.17)$$

Requiring normalization than yields

$$\langle g, \kappa, j, m | g, \kappa, j, m \rangle = |c_1^g|^2 + |c_2^g|^2 = 1, \quad (1.18)$$

the coefficients c can be determined with exception of the overall complex phase. They can be easily rewritten with introduction of the angle θ as given by the following relations

$$Z\alpha = |K|\sin\theta; \quad (1.19)$$

then, cf. Eq. (1.13),

$$|G| = |K|\cos\theta, \quad (1.20)$$

and, cf. Eqs. (1.15) and (1.17),

$$\langle \vec{n}|+, \kappa, j, m\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \langle \vec{n}|j, m\rangle^\kappa \\ -i\kappa \sin\frac{\theta}{2} \langle \vec{n}|j, m\rangle^{-\kappa} \end{pmatrix} \quad (1.21)$$

and

$$\langle \vec{n}|-, \kappa, j, m\rangle = \begin{pmatrix} \sin\frac{\theta}{2} \langle \vec{n}|j, m\rangle^\kappa \\ -i\kappa \cos\frac{\theta}{2} \langle \vec{n}|j, m\rangle^{-\kappa} \end{pmatrix}. \quad (1.22)$$

1.3 Expansion in Sturmian Basis

Next, we introduce the effective angular quantum number l_g [2]

$$l_g(l_g + 1) = G(G - 1). \quad (1.23)$$

We require $l_g > -1$ in order for the radial functions to stay normalized, we obtain $l_g = |G| - 1$ for $G > 0$ and $l_g = |G|$ for $G < 0$, that is

$$l_g = |G| - \delta_{g,\kappa}. \quad (1.24)$$

Next we look for solution of Eq. (1.10), in the form

$$\phi(\vec{r}) = R_{n,l_g}(\xi, r) \langle \vec{n} | g, \kappa, j, m \rangle \quad (1.25)$$

and setting

$$\xi = \frac{E}{m_e n}, \quad (1.26)$$

Eq. (1.10) is then transformed into equation suitable for Sturmian functions (see e.g. [6, 7, 8])

$$\frac{1}{2} \left[r \hat{p}_r^2 + \frac{l_g(l_g + 1)}{r} + r \right] R_{n,l_g}(r) = n R_{n,l_g}(r), \quad n = k + l_g + 1, \quad k = 0, 1, 2, \dots, \quad (1.27)$$

where

$$E = \frac{m_e}{\sqrt{1 + \left(\frac{Z\alpha}{n}\right)^2}} \quad (1.28)$$

and

$$R_{n,l}(\xi, r) = \xi R_{n,l}(\xi r). \quad (1.29)$$

The first order Dirac operator (1.7) combines states (1.25) with different signs of g and different quantum number n . Therefore we can look for a general eigenstate for the Dirac operator (1.7) in form of [2]

$$\langle \vec{r} | \psi \rangle = \langle \vec{r} | n, \kappa, j, m \rangle = \quad (1.30)$$

$$= \langle r | n, |G| - \delta_{\kappa,+} \rangle \langle \vec{n} | +, \kappa, j, m \rangle + \langle r | n, |G| - \delta_{\kappa,-} \rangle \langle \vec{n} | -, \kappa, j, m \rangle,$$

where, $|G| = \sqrt{(j + 1/2)^2 - (Z\alpha)^2}$, cf. Eqs. (1.12) and (1.13). Furthermore, the bispinors $\langle \vec{n} | g, \kappa, j, m \rangle$ are given by Eqs. (1.21), (1.22) and the radial parts can be expanded into Sturmian functions ((1.27), (1.29)) as well

$$\langle r | n, |G| - 1 \rangle = \sum_{k=0}^N c_k^+ R_{k,|G|-1}(\xi, r), \quad \langle r | n, |G| \rangle = \sum_{k=0}^{N-1} c_k^- R_{k,|G|}(\xi, r). \quad (1.31)$$

In terms of notation in Eq. (1.30) this can be written concisely as

$$\langle r | n, |G| - \delta_{\kappa,g} \rangle = \sum_{k=0}^{N - \delta_{\kappa,-g}} c_k^{\delta_{\kappa,g} - \delta_{\kappa,-g}} R_{k,|G| - \delta_{\kappa,g}}. \quad (1.32)$$

Substituting Eqs. (1.30) and (1.32) into the DHF equation (1.6) and projecting it onto mentioned basis vector yields so called Roothan form of (1.21) [2]

$$\begin{aligned} \sum_k \begin{pmatrix} (\hat{h}_D)_{ik}^{++} & (\hat{h}_D)_{ik}^{+-} \\ (\hat{h}_D)_{ik}^{-+} & (\hat{h}_D)_{ik}^{--} \end{pmatrix} \begin{pmatrix} C_k^{\delta_{\kappa,+} - \delta_{\kappa,-}} \\ C_k^{\delta_{\kappa,-} - \delta_{\kappa,+}} \end{pmatrix} &= \\ = \epsilon \sum_k \begin{pmatrix} S_{ik}^{++} & S_{ik}^{+-} \\ S_{ik}^{-+} & S_{ik}^{--} \end{pmatrix} \begin{pmatrix} C_k^{\delta_{\kappa,+} - \delta_{\kappa,-}} \\ C_k^{\delta_{\kappa,-} - \delta_{\kappa,+}} \end{pmatrix}, \end{aligned} \quad (1.33)$$

where

$$(\hat{h}_D)_{ik}^{g,\bar{g}} = z_{ik}^{g,\bar{g}} + (v_{HF})_{ik}^{g,\bar{g}}. \quad (1.34)$$

The operator \hat{z} is given by Eq. (1.7). The pertinent matrix elements are defined below in Eqs. (1.35) and (1.36). The matrix elements of Hartree-Fock potential are given in [2].

1.4 One-particle matrix elements

Further we are interested in matrix elements of operator \hat{z} [2]

$$z_{ik}^{g,\bar{g}} = \int_0^\infty dr r^2 R_{i,l_g}(\xi, r) \langle g, \kappa, j, m | \hat{z} | \bar{g}, \kappa, j, m \rangle R_{k,l_{\bar{g}}}(\xi, r), \quad (1.35)$$

and overlap matrix

$$S_{ik}^{g,\bar{g}} = \langle g, \kappa, j, m | \bar{g}, \kappa, j, m \rangle \int_0^\infty dr r^2 R_{i,l_g}(\xi, r) R_{k,l_{\bar{g}}}(\xi, r), \quad (1.36)$$

respectively. We recall $l_g = |G| - \delta_{g,\kappa}$, see Eq. (1.24).

We can than rewrite the spin-angular part of \hat{z} in terms of the operators \hat{G} , \hat{K} and γ_0 [2]

$$\hat{z} = -\frac{\hat{G} - \gamma_0 \hat{K}}{(Z\alpha)^2} \left(\frac{\partial}{\partial r} - \frac{\hat{G} - 1}{r} \right) + \frac{\gamma_0 - 1}{(Z\alpha)^2}. \quad (1.37)$$

Integrating spin-angular part in Eqs. (1.35) and (1.36) than reduces to

$$\langle g, \kappa, j, m | \gamma_0 | g, \kappa, j, m \rangle = g \cos \theta, \quad \langle -g, \kappa, j, m | \gamma_0 | g, \kappa, j, m \rangle = 0,$$

$$\langle g, \kappa, j, m | g, \kappa, j, m \rangle = 1, \quad \langle -g, \kappa, j, m | g, \kappa, j, m \rangle = \sin \theta$$

and

$$\langle g, \kappa, j, m | (\hat{G} - \gamma_0 \hat{K}) | g, \kappa, j, m \rangle = 0,$$

$$\langle -g, \kappa, j, m | (\hat{G} - \gamma_0 \hat{K}) | g, \kappa, j, m \rangle = G \sin \theta,$$

following from Eqs. (1.14)–(1.22). Substituting these results and Eq. (1.37) into Eq. (1.35) we get

$$\langle g, \kappa, j, m | \hat{z} | g, \kappa, j, m \rangle = \frac{g \cos \theta - 1}{(Z\alpha)^2} \quad (1.38)$$

and

$$\langle -g, \kappa, j, m | \hat{z} | g, \kappa, j, m \rangle = -\frac{\sin \theta}{(Z\alpha)^2} \left[1 + G \left(\frac{d}{dr} - \frac{G-1}{r} \right) \right]. \quad (1.39)$$

1.5 Analysis of the matrix elements in orders of $Z\alpha$

Henceforth we restrict our attention to the case of positive parity $\kappa = 1$. Eq. (1.33) can be schematically written as

$$\begin{pmatrix} D_+ + V_+ & B + (Z\alpha)W \\ B^T + (Z\alpha)W^T & D_- + V_- \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \varepsilon \begin{pmatrix} A_+ & C \\ C^T & A_- \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix}, \quad (1.40)$$

where the expansion of matrices in powers of $Z\alpha$ reads, cf Eqs. (1.19), (1.20), (1.38)

$$D_g = \frac{g\sqrt{1 - \frac{(Z\alpha)^2}{|K|}} - 1}{(Z\alpha)^2} A_g, \quad g = \pm 1, \quad (1.41)$$

as A_g is denoted further in Eq. (1.45). We expand this expression into the series in power of $Z\alpha$

$$D_{\pm} = \frac{\pm \sum_{n=0}^{\infty} \frac{(Z\alpha)^{2n} (-1/2)_n}{n!} - 1}{(Z\alpha)^2} A_{\pm}. \quad (1.42)$$

Here the symbol $(-1/2)_n$ is denoting the Pochhammer symbol [9]

$$(-1/2)_n = \frac{\Gamma(-1/2 + n)}{\Gamma(-1/2)} = (-1/2)(-1/2 + 1) \dots (-1/2 + n). \quad (1.43)$$

Further expansion on other terms leads to

$$B_{ik} = -\frac{1}{Z\alpha} \int_0^{\infty} dr r^2 R_{i,l_g}(\xi, r) \left[1 + G \left(\frac{d}{dr} - \frac{G-1}{r} \right) \right] R_{k,l_{-g}}(\xi, r) \quad (1.44)$$

,

$$(A_g)_{ik} = \int_0^{\infty} dr r^2 R_{i,l_g}(\xi, r) R_{k,l_g}(\xi, r), \quad (1.45)$$

and finally

$$C_{ik} = \frac{Z\alpha}{|K|} \int_0^{\infty} dr r^2 R_{i,l_g}(\xi, r) R_{k,l_{\bar{g}}}(\xi, r). \quad (1.46)$$

The dependence of matrix elements of Hartree-Fock potential on $Z\alpha$ is supposed to be as indicated in Eq. (1.40), but more detailed analysis is needed. This will be done in future investigation.

2. Foldy-Wouthuysen Transformation

2.1 The method

Foldy-Wouthuysen transformation, or FWT, was introduced in 1949 by Leslie Lawrance Foldy and Siegfried Adolf Wouthuysen. Its standard formulation can be found in many places, see e.g. [10]. Here we introduce its finite form. First we rewrite Eq. (1.40) into the form

$$\Omega \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = 0, \quad (2.1)$$

where

$$\Omega = \begin{pmatrix} D_+ + V_+ & B + (Z\alpha)W \\ B^T + (Z\alpha)W^T & D_- + V_- \end{pmatrix} - \varepsilon \begin{pmatrix} A_+ & C \\ C^T & A_- \end{pmatrix}. \quad (2.2)$$

We search for solution in the form

$$\begin{pmatrix} c_+ \\ c_- \end{pmatrix} = e^{(-iT)} \begin{pmatrix} c_{FW} \\ 0 \end{pmatrix}, \quad T = \begin{pmatrix} 0 & U \\ U^T & 0 \end{pmatrix}. \quad (2.3)$$

We multiply the last equation by e^{iT} from the left and obtain

$$\Omega_{FW} \begin{pmatrix} c_{FW} \\ 0 \end{pmatrix} = 0, \quad \Omega_{FW} = e^{iT} \Omega e^{-iT}. \quad (2.4)$$

The matrix U is determined from the requirement, that up to the given order of $Z\alpha$ the matrix Ω_{FW} has the form

$$\Omega_{FW} = \begin{pmatrix} X & 0 \\ 0^T & Y \end{pmatrix}. \quad (2.5)$$

For illustrative purposes we provide calculation at the leading order of $Z\alpha$. The expansion of the matrix Ω in power of $Z\alpha$ reads, see Section 1.5

$$\begin{aligned} \Omega = & \frac{1}{(Z\alpha)^2} \begin{pmatrix} 0 & 0 \\ 0^T & D_-^{(-2)} \end{pmatrix} + \frac{1}{(Z\alpha)} \begin{pmatrix} 0 & B^{(-1)} \\ B^{T(-1)} & 0 \end{pmatrix} \\ & + \begin{pmatrix} D_+^{(0)} + V_+^{(0)} & 0 \\ 0 & D_-^{(0)} + V_-^{(0)} \end{pmatrix} - \varepsilon \begin{pmatrix} A_+^{(0)} & 0 \\ 0 & A_-^{(0)} \end{pmatrix} + O(Z\alpha). \end{aligned} \quad (2.6)$$

Now expanding the expression

$$e^{iT} \Omega e^{-iT} \simeq \Omega + i[T, \Omega] - \frac{1}{2}[T, [T, \Omega]] + \dots \quad (2.7)$$

and assuming T has the form

$$T = (Z\alpha) \begin{pmatrix} 0 & U^{(1)} \\ U^{T(1)} & 0 \end{pmatrix} + \dots, \quad (2.8)$$

one obtains from requirement of vanishing terms of the order $(Z\alpha)^{(-1)}$

$$0 = \frac{1}{(Z\alpha)} \begin{pmatrix} 0 & B^{(-1)} \\ B^{T(-1)} & 0 \end{pmatrix} + \imath \left[\begin{pmatrix} 0 & U^{(1)} \\ U^{T(1)} & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 \\ 0^T & D_-^{(-2)} \end{pmatrix} \right], \quad (2.9)$$

written in reduced form

$$0 = \frac{1}{Z\alpha} B^{(-1)} + \frac{\imath}{Z\alpha} U^{(1)} D_-^{(-2)}. \quad (2.10)$$

At the order $(Z\alpha)^{(0)}$ one gets the diagonal Hamiltonian

$$\begin{aligned} \Omega^{(0)} = & (Z\alpha)^{-2} \begin{pmatrix} 0 & 0 \\ 0^T & D_-^{(-2)} \end{pmatrix} + \begin{pmatrix} D_+^{(0)} + V_+^{(0)} & 0 \\ 0^T & D_-^{(0)+V_-^{(0)}} \end{pmatrix} \\ & + \imath \left[\begin{pmatrix} 0 & U^{(1)} \\ U^{T(1)} & 0 \end{pmatrix}, \begin{pmatrix} 0 & B^{(-1)} \\ B^{T(-1)} & 0 \end{pmatrix} \right] \\ & - \frac{1}{2!} \left[\begin{pmatrix} 0 & U^{(1)} \\ U^{T(1)} & 0 \end{pmatrix}, \left[\begin{pmatrix} 0 & U^{(1)} \\ U^{T(1)} & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 \\ 0^T & D_-^{(-2)} \end{pmatrix} \right] \right] - \varepsilon \begin{pmatrix} A_+^{(0)} & 0 \\ 0 & A_-^{(0)} \end{pmatrix}. \end{aligned} \quad (2.11)$$

Now we can recall that all matrix equations of the form of Eq. (2.9):

$$AX + XB = C, \quad (2.12)$$

are called Sylvester equations, and their solutions have been known for more than a century [11]. This equation follows every calculation of transformation matrix and its uses are discussed further.

2.2 Practical implementation

Since computer-based calculations are almost the only feasible approach for solving this problem, let us formulate an iterative scheme that was used for the calculation. This algorithm will also serve as a guide for the reader to understand how the problem was computed.

1. Expand the matrix Ω in powers of $(Z\alpha)$ up to the terms of the order $(Z\alpha)^{2n}$.
2. Perform the expansion of Eq. (2.7) up to the order $(2 + 2n)$.
3. Set the resulting equation for the off-diagonal terms equal to zero and solve for $U^{(2n+1)}$.
4. Use the newly found matrix $T^{(2n+1)}$ to calculate the transformed, perturbed Hamiltonian by considering all possible combinations that contribute to the $2n$ th order.
5. Solve the generalized eigenvalue problem to obtain the energy up to the $2n$ th order.
6. Repeat the entire process, increment the orders of all terms by one in n .

Further notes regarding this algorithm:

- Last term while, finding all combinations should always involve $D_{\pm}^{(-2)}$. Since it's the term with smallest order.
- In the first iteration, $-\varepsilon S$ is not included until the 5th step, as it belongs to the 0th order.
- When calculation of $\varepsilon^{(k)}$ is finished, one needs to add $\varepsilon^{(k)}S$ to certain order. This might create same orders for different $S^{(k)}$! Difference being in, if the diagonal or off-diagonal structure is used.
- When calculating the elements of the transformation matrix, it is important to consider the following:
 - When "cutting" the transformation matrix into a rectangular form, transpose every second element in commutators of even length.
 - Transpose every even U in commutators of odd length.
- Multi-commutators, such as those of length 4, follow the structure of Pascal's triangle. For example, when computing a commutator of length 4, the resulting terms follow the coefficients of the 5th row of Pascal's triangle. As an example:

$$[A, [A, [A, [A, B]]]] = A^4B - 4A^3BA + 6A^2BA^2 - 4ABA^3 + BA^4, \quad (2.13)$$

whole calculation of commutator than follows this structure:

$$\begin{array}{cccccc}
 & & & & & 1 \\
 & & & & & 1 & -1 \\
 & & & & 1 & -2 & 1 \\
 & & 1 & -3 & 3 & -1 \\
 1 & -4 & 6 & -4 & 1
 \end{array}$$

starting at the second row is every commutator of length 1, and so on. Length of the commutator also carries the information about which term of exponential has to be used.

- Solving Sylvester equation is especially helpful for the algorithmic rule. Since it does not require any extra matrix manipulation.

3. Results

In the last chapter, we formulated the core structure required for calculating energies in a perturbed manner, along with the calculation algorithm. However, it is important to note that the results obtained in Chapter 1 only apply to the s and p states of electrons in the valence orbital. Therefore, the final results will correspond to the energies of these states. Additionally, we present the results up to the 7th decimal place due to the sensitivity of the aforementioned calculations to the exact structure of the algorithm. The Python programming language was used for these calculations.

Let us first present the results for the s-state as obtained in [2]. Now, we

Table 3.1: Reference energies of Cs atom for s-state electrons, depended on size of the basis and main quantum number [2]

basis	1s	2s	3s	4s	5s	6s
10	-0.457772	-0.042769	-0.008609	-0.001699	-0.000287	-0.000009
20	-0.445741	-0.065640	-0.014494	-0.003037	-0.000480	-0.000042
30	-0.441569	-0.069959	-0.015179	-0.003144	-0.000492	-0.000042
40	-0.440233	-0.070267	-0.015199	-0.003145	-0.000493	-0.000042
50	-0.439866	-0.070275	-0.015198	-0.003145	-0.000493	-0.000042
60	-0.439776	-0.070275	-0.015198	-0.003145	-0.000493	-0.000042
70	-0.439755	-0.070274	-0.015198	-0.003145	-0.000493	-0.000042
80	-0.439751	-0.070274	-0.015198	-0.003145	-0.000493	-0.000042
90	-0.439750	-0.070274	-0.015198	-0.003145	-0.000493	-0.000042
100	-0.439750	-0.070274	-0.015198	-0.003145	-0.000493	-0.000042

will demonstrate the results for the 1s-state of the Cs atom obtained through the perturbation method discussed in Chapter 3.

Before moving on to higher energy states, let's discuss these results. Although

Table 3.2: Energies obtained via perturbation method 1s state. X-axis shows size of the basis, Y-axis shows order of perturbation.

	10	20	30	40	50
0	-0.436226	-0.424077	-0.419447	-0.417710	-0.417140
2	-0.456179	-0.444676	-0.441187	-0.440454	-0.440525
4	-0.456632	-0.446322	-0.443282	-0.443218	-0.446952
6	-0.457638	-0.445702	-0.441876	-0.450717	-1.403509
8	-0.457645	-0.445643	-0.441995	-	-

our main goal is to replicate these results for the 6s-state using HF interaction, the current results still provide relevant and accurate data. It is important to note that as we increase the basis size, the precision of the results improves. However, there are a few points to consider regarding the errors. There is a

Table 3.3: Energies obtained via perturbation method 1s state. X-axis shows size of the basis, Y-axis shows order of perturbation.

	60	70	80	90	100
0	-0.416973	-0.416928	-0.416916	-0.416913	-0.416913
2	-0.440732	-0.440909	-0.441040	-0.441135	-0.441206
4	-0.584427	-1.137043	-2.146258	-3.812341	-6.386750
6	-4.473480	-	-	-	-
8	-	-	-	-	-

noticeable jump between orders 0 and 2 in all energies, but this should not come as a surprise since both depend solely on the transformation matrices $T^{(1)}$ and $T^{(3)}$, where only the largest terms of other matrices and HF interaction play a significant role, making these two orders practically the same. Additionally, the HF interaction is well below the precision of this calculation, as can be observed in the case of the hydrogen atom.

Another mistake occurs towards the end of the calculation, where the allowed error is greater than $O(Z\alpha)^{(i)}$ as expected. This is accompanied by larger errors, particularly in basis 50 and larger. This divergence may be attributed to the use of single-float precision in macros during the Python calculation. As numerous matrix multiplications of small values (presumably transformation matrices) accumulate, the calculation diverges when multiplying higher numbers. This problem is primarily encountered while attempting to solve the Sylvester equation, as this macro only allows cfloat128. Additionally, another issue arises during the calculation as the matrices become gradually asymmetrical due to multiple operations. Although this problem is partially addressed by making them symmetrical towards the end, it becomes increasingly significant, particularly in higher orders of perturbation. Notably, calculating order 10 and further in basis 10 takes approximately hours, whereas calculating orders 6+ in basis 100 takes a similar amount of time. This correlation indicates a potential relationship between divergence in lower orders of higher bases and higher orders of lower bases. This serves as further evidence supporting the explanation for the observed errors.

Now we show the result for higher states, please take note that due to the discussion above the most accurate results (the ones showed) are around 2nd to 4th order. In the higher basis we can clearly see correspondence as expected. We

Table 3.4: Result for higher electron states of Cs atom - 2nd order of perturbation

s-states	10	20	40	60	100
2	-0.0749022	-0.0561407	-0.0603758	-0.0603858	-0.0603873
3	-0.0072651	-0.0128648	-0.0128648	-0.0128645	-0.0128648
4	-0.0014440	-0.0025748	-0.0026628	-0.0026627	-0.0026628
5	-0.0002481	-0.0004113	-0.0004212	-0.0004925	-0.0004212
6	-0.0000072	-0.0000346	-0.0000351	-0.0000351	-0.0000351

would also like to acknowledge reader that since the complexity of this algorithm

is enormous, 2-3 thousands of lines of code written all together. We used side program that was designed by hand to check the correctness of these calculations up to 4th order, depending on the case.

Now lastly for s-state there is hydrogen case. Referential value as in [2] is: -0.5000066566 . Obtained value in 2nd order of precision is: -0.5000066568 . This result is not proceeded to further perturbation, since the dependence on exact algorithm usually ensures that the error to this value lies in $10^{-9} - 10^{-10}$.

For p-states belong following referential results. And the results obtained by

Table 3.5: Referential values for p-states as in [2]

basis	2p	3p	4p	5p
10	-0.0358412	-0.0068364	-0.0011321	-0.0001388
30	-0.0614290	-0.0131427	-0.0024251	-0.0002970
50	-0.0620611	-0.0132128	-0.0024351	-0.0002980
100	-0.0620659	-0.0132133	-0.0024352	-0.0002980

perturbation with precision set to 2nd order.

Table 3.6: Results obtained by perturbation method

basis	2p	3p	4p	5p
10	-0.0317684	-0.0057263	-0.0007683	-0.0000591
30	-0.0551771	-0.0105962	-0.0016688	-0.0001433
50	-0.0555190	-0.0106100	-0.0016688	-0.0001432
100	-0.0555182	-0.0106100	-0.0016688	-0.0001432

Conclusion

In this thesis we introduced and investigated the finite FWT and applied it to the case of cesium and hydrogen atoms. The main motivation for doing this is to understand and possibly eliminate the oscillatory behaviour of energies with increasing basis size. We found that at the leading order of $Z\alpha$ the energies are monotonically decreasing. While in larger order of $Z\alpha$ not so much. This is highly dependent of the size of the basis as well as the error mentioned above. Possible room for improvement lies possibly in perturbing in slightly different manner as-well as processing the referential data in different manner through the algorithm, avoiding single-float precision.

Even though we investigated this for the case of hydrogen and cesium and only for p and s states, this method can be easily expanded to other alkali metal atoms as well as the rest of their spin-orbital states.

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