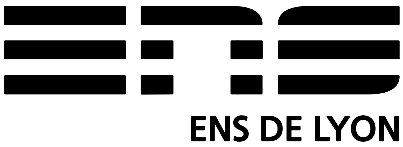

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One Dimensional Model for Relativistic Quantum Chemistry

Abstract: *In this article we provide a resolution of the relativistic Dirac equation in a one-dimensional model. In this model the Coulomb potential is replaced by a delta-interaction. We study three different systems: the free-particle system, the hydrogen-like system and the helium-like system. For the free and hydrogen-like systems we provide both an analytical solution and a basis set expansion to understand the relativistic effects that appear in these models. We also derive an analytical Hartree-Fock solution to the helium atom but the basis expansion is still to be made. We hope that this study will bring a better understanding of the relativistic effects and how to take them into account to develop sound relativistic electronic-structure computational methods.*

Keywords: *Relativistic quantum chemistry, One dimensional system, Delta interaction, Quantum electrodynamics, Dirac equation, Basis Set Expansion*

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Contents

I. INTRODUCTION

Relativity theory made a nice breakthrough in quantum chemistry calculations with its ability to explain some physical effects that were misunderstood. For instance, we present in our previous bibliographical report the importance of relativity in the color of gold and the explanation of the electromotive forces within lead-acid batteries. But some very recent articles have increased the importance of relativistic calculations. In 2017, Schwerdtfeger *et al.* have shown that by taking into accounts the relativistic effects into their calculations they managed to explain the liquid form of mercury at room temperature [1]. They also shown that by taking the Breit interaction and the QED effects into account it is possible to gain nearly two orders of magnitude for the convergence of the ionization potential and electronic affinity of gold [2].

Such studies demonstrate the importance of relativistic effects, especially in the case of systems which include heavy elements. If one wants to have accurate results and a precise physical description of such systems one could no longer neglect such effects. The difficulty of going into a relativistic framework is about the computational price that one has to give for his calculations. A lot of relativistic Hamiltonians have been developed, all more sophisticated than the previous one, some are including the Breit interaction, others the quantum electrodynamics (QED) effects but the four-component relativistic density functional theory (DFT) is mostly applied within the Kohn-Sham scheme with the no-pair approximation [3–5] and with non-relativistic exchange-correlation density functionals.

In this report we are using toy model to understand the properties of a no-photon QED Hamiltonian [6–10]. The ultimate goal would be to develop a relativistic DFT with sound density-functional approximations based on this no-photon QED Hamiltonian. We hope that the understanding of the one-dimensional delta-interaction model could help us in this goal.

In order to take most relativistic effects into account it is mandatory to look at the QED effects that come from the negative energy solutions of the Dirac equation. We must also take not only the Coulombic interaction (here delta-type interaction) but also the Breit term of the interaction.

This report is organized as follows. In Section II we establish the one-dimensional model and we find the analytical form of the free states in a one-dimensional space. In Section III we add to this one-dimensional system a delta-potential interaction with a nucleus to simulate the hydrogen atom. We solve this model and find the continuum states and the bound state of the hydrogen-like system. Then we recover the non-relativistic limits. In Section IV, we calculate analytically some QED effects such as the vacuum energy and the vacuum polarization density. Both effects arise because of the negative energy solutions of the Dirac equation. To verify these analytical results we expand, in Section V, the system into a basis set. And in the last Section VI we develop and solve the equivalent of the Dirac-Coulomb-Breit Hamiltonian for the helium atom. Then, we conclude the report and list further developments that still have to be done.

II. ONE-DIMENSIONAL MODEL

To simulate the full Dirac-Coulomb-Breit equation and the QED effects we use a one-dimensional system with delta type interactions [11, 12]. In the one-dimensional system one can consider particles of mass m as spinless.

Through this study we will work with the atomic units $\hbar = m = 1 = e^2/(4\pi\epsilon_0) = 1$ and will keep the velocity c as a parameter in order to be able to vary the strength of the relativistic effects. For clarity we will also keep the mass m in the equations.

For $c = 1$ a.u., we will have a system with high relativistic effects while for $c = 137.036$ a.u., which corresponds to the physical value, we will have a more realistic system on which the relativistic effects will be very small. Indeed, relativistic corrections start at second order in $Z/(2c)$ and account for less than 1% to the total energy for hydrogen [11]. Finally one can choose, for instance, $c = 500$ in order to study the non-relativistic limit and compare the results with those obtained by Traore, Giner and Toulouse [13] on the non-relativistic one-dimensional hydrogen and helium with delta-potential interactions.

Starting from the expression of the energy of a classical relativistic particle with mass m and momentum p, one has

$$E = \sqrt{p^2c^2 + m^2c^4}. \tag{1}$$

Then one can use the classical to quantum correspondence principle to propose a quantum Hamiltonian as

$$\hat{\mathcal{H}} = \sqrt{\hat{p}^2c^2 + m^2c^4\hat{1}}. \tag{2}$$

where $\hat{p} = -\mathrm{i}c\mathrm{d}/\mathrm{d}x$. To get rid of the square root Dirac [14] proposed the idea of searching for constants $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ such that the argument of the square root is a perfect square. Thus, one needs to solve the equation

$$\hat{p}^2c^2 + m^2c^4\hat{1} = \left(c\boldsymbol{\alpha}\hat{p} + \boldsymbol{\beta}mc^2\right)^2. \tag{3}$$

In order to solve this equation one derives two conditions for those constants. First we have, $\boldsymbol{\alpha}^2 = 1$, $\boldsymbol{\beta}^2 = 1$ and secondly $\{\boldsymbol{\alpha}, \boldsymbol{\beta}\} = \boldsymbol{\alpha}\boldsymbol{\beta} + \boldsymbol{\beta}\boldsymbol{\alpha} = 0$. Because of the anti-commutation condition, the constants cannot be of dimension 1, *i.e.* numerical constants. The hermiticity and anti-commutation conditions impose to be in an even dimension. By looking at dimension 2, it can be shown that these conditions are satisfied if $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are Pauli matrices. We will see right after which Pauli matrices to take.

The use of the Pauli matrices implies to work on the Hilbert space $\mathcal{H} = L^2(\mathbb{R}, \mathbb{C}^2) \cong L^2(\mathbb{R}, \mathbb{C}) \otimes \mathbb{C}^2$. The one-dimensional (spinless) free Dirac equation is [11]

$$\left[-\mathrm{i}c\boldsymbol{\alpha}\frac{\mathrm{d}}{\mathrm{d}x} + \boldsymbol{\beta}mc^2\right]\psi(x) = \varepsilon\psi(x), \tag{4}$$

with ψ a wave function solution of the one-dimensional (1D) Dirac equation. Given the matricial form of the one-dimensional Dirac equation, the wave function will be a two component spinor. One can write

$$\psi(x) = \begin{pmatrix}\psi^L(x)\\ \psi^S(x)\end{pmatrix}, \tag{5}$$

with ψ^L (resp. ψ^S) being the large (resp. small) component of the 2-spinor ψ.

A. Choice of the Pauli matrices

The 1D free Dirac equation, Eq. (4), has been derived from the squared form of the energy. But we still need to determine which Pauli matrices we have to use in order to describe the physics of the system. We have the Pauli matrices $\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y$ and $\boldsymbol{\sigma}_z$ as

$$\boldsymbol{\sigma}_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\ ;\ \boldsymbol{\sigma}_y = \begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}\ ;\ \boldsymbol{\sigma}_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \tag{6}$$

Several choices have been made for the matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. One choice can be $\boldsymbol{\alpha} = \boldsymbol{\sigma}_x$ and $\boldsymbol{\beta} = \boldsymbol{\sigma}_z$, which is the case in most articles [11, 12] which deal with the relativistic one-dimensional hydrogen.

However, one can look at another choice for the matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. In their article, Coutinho and Nogami [15] are using $\boldsymbol{\alpha} = \boldsymbol{\sigma}_y$ and $\boldsymbol{\beta} = \boldsymbol{\sigma}_z$ for the one-dimensional Dirac equation. Then it is legitimate to wonder which choice

is relevant and if both choices are equivalent what the main differences between these two choices are, which have to describe the same physics.

The choice of Coutinho and Nogami is interesting because choosing a pure imaginary matrix for $\boldsymbol{\alpha}$ leads to a real Dirac equation. And this has important consequences. Indeed having a real differential equation implies that the eigenfunctions of the system will be real. A quick proof is given by the fact that the Dirac equation, because it is real, commutes with the complex conjugate operator. Then one can expect the solution to have the form,

$$\boldsymbol{\psi}(x) = \begin{pmatrix} a(x) \\ b(x) \end{pmatrix}, \tag{7}$$

with a and b being two real functions of x.

In order to look if both choices of the Pauli matrices are equivalent one must be able to transform one choice into the other thanks to a unitary transformation. One can write the Dirac equation using the choice of Coutinho and Nogami, we will write this Dirac operator as $\hat{\mathcal{D}}_y$,

$$\hat{\mathcal{D}}_y \boldsymbol{\psi}(x) = \left[-\mathrm{i}c \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 \right] \begin{pmatrix} a(x) \\ b(x) \end{pmatrix} = \varepsilon \begin{pmatrix} a(x) \\ b(x) \end{pmatrix}. \tag{8}$$

If one applies the unitary operator U such that,

$$U = \begin{pmatrix} 1 & 0 \\ 0 & -\mathrm{i} \end{pmatrix} = \left(\frac{1}{2} + \frac{\mathrm{i}}{2}\right)\boldsymbol{\sigma}_z + \left(\frac{1}{2} - \frac{\mathrm{i}}{2}\right)\mathbb{I}_2, \tag{9}$$

to the previous eigensystem,

$$\begin{aligned} U\hat{\mathcal{D}}_y \boldsymbol{\psi}(x) &= U\hat{\mathcal{D}}_y U^\dagger \left[U\boldsymbol{\psi}(x)\right] \\ &= \varepsilon U \boldsymbol{\psi}(x) \end{aligned} \tag{10}$$

we obtain the new operator $U\hat{\mathcal{D}}_y U^\dagger$ which has the same eigenvalues as $\hat{\mathcal{D}}_y$ but with the eigenfunctions $U\boldsymbol{\psi}(x)$. Let us derive the form of this new operator,

$$\begin{aligned} U\hat{\mathcal{D}}_y U^\dagger &= U\left[-\mathrm{i}c \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 \right] U^\dagger \\ &= \left[-\mathrm{i}c \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 \right] \\ &= \hat{\mathcal{D}}_x, \end{aligned} \tag{11}$$

with $\hat{\mathcal{D}}_x$ the Dirac Hamiltonian corresponding to the choice of matrices $\boldsymbol{\alpha} = \boldsymbol{\sigma}_x$ and $\boldsymbol{\beta} = \boldsymbol{\sigma}_z$.

In the same way the eigenfunctions will be transformed and the 2-spinors will now be,

$$U\boldsymbol{\psi}(x) = \begin{pmatrix} a(x) \\ -\mathrm{i}b(x) \end{pmatrix}, \tag{12}$$

with a and b the same two reals functions as in Eq. (7).

One can remark that both choices of matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ to define the one-dimensional Dirac equation are identical up to a unitary transformation. But we already know that such transformation leave the system unchanged and does not have any influence over the physics of the system. The only difference is that the final eigenfunctions will be in one case real, and in the other case will have one component real and the other one purely imaginary.

In this work we mainly used the $\hat{\mathcal{D}}_x = \hat{\mathcal{D}}$ operator, which will lead to solution with the same form as in Eq. (12).

B. Solution of the free-particle Dirac equation

Determination of the eigenfunctions

In the free-particle case one must solve the equation,

$$\hat{\mathcal{D}}\boldsymbol{\psi}(x) = \left[-\mathrm{i}c\boldsymbol{\sigma}_x \frac{\mathrm{d}}{\mathrm{d}x} + \boldsymbol{\sigma}_z mc^2 \right] \boldsymbol{\psi}(x) = \varepsilon \boldsymbol{\psi}(x). \tag{13}$$

One can develop this equation over the 2-component spinor as,

$$\begin{cases} mc^2\psi^{\mathrm{L}}(x) - \mathrm{i}c\frac{\mathrm{d}\psi^{\mathrm{S}}(x)}{\mathrm{d}x} = \varepsilon\psi^{\mathrm{L}}(x) \\ -\mathrm{i}c\frac{\mathrm{d}\psi^{\mathrm{L}}(x)}{\mathrm{d}x} - mc^2\psi^{\mathrm{S}}(x) = \varepsilon\psi^{\mathrm{S}}(x) \end{cases}. \tag{14}$$

Using the second equation one can derive a link between the large and small components,

$$\psi^{\mathrm{S}}(x) \;=\; \frac{-\mathrm{i}c}{\varepsilon + mc^2}\frac{\mathrm{d}}{\mathrm{d}x}\psi^{\mathrm{L}}(x). \tag{15}$$

We can see that the small component must be proportional to the derivative of the large component. Moreover, by choosing the large component as a real function, one can see that the spinor will indeed have the form given by Eq. (12).

Without any potential, the spatial part of the eigenfunctions should be plane waves, we then expect a eigenfunction to have the form, $\psi_k(x) = A_k\begin{pmatrix} u_k \\ v_k \end{pmatrix}e^{\mathrm{i}kx}$ where $k \in \mathbb{R}$ and with energies ε_k. We then have the equations

$$\begin{cases} mc^2u_k + kcv_k = \varepsilon_k u_k \\ cku_k - mc^2v_k = \varepsilon_k v_k \end{cases}, \tag{16}$$

leading to

$$v_k = \frac{kc}{\varepsilon_k + mc^2}u_k \quad \text{or} \quad u_k = \frac{kc}{\varepsilon_k - mc^2}v_k, \tag{17}$$

and

$$\varepsilon_k^2 = k^2c^2 + m^2c^4. \tag{18}$$

Because of the squared form of the energies we then have two different cases: either the energy is negative or positive. Moreover, the energy depends on k^2, which means that the eigenfunctions for k and $-k$ are degenerate. We will then use the notation $\psi_{\pm,k}(x)$ in order to refer to the two different possibilities according to the sign of the energy of the eigenstates. With $k \in \mathbb{R}$ one remarks that the range of energies is $(-\infty, -mc^2] \cup [mc^2, +\infty)$. The continuum states of positive energies ε_k are

$$\psi_{+,k}(x) = A_k\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k+mc^2} \end{pmatrix}e^{\mathrm{i}kx} = A_k\begin{pmatrix} 1 \\ \frac{\varepsilon_k-mc^2}{kc} \end{pmatrix}e^{\mathrm{i}kx}, \tag{19}$$

and the continuum states of negative energies $-\varepsilon_k$ are

$$\psi_{-,k}(x) = A_k\begin{pmatrix} \frac{kc}{-\varepsilon_k-mc^2} \\ 1 \end{pmatrix}e^{\mathrm{i}kx} = A_k\begin{pmatrix} \frac{-\varepsilon_k+mc^2}{kc} \\ 1 \end{pmatrix}e^{\mathrm{i}kx}. \tag{20}$$

with $\varepsilon_k = \sqrt{k^2c^2 + m^2c^4}$ and A_k the normalization constant.

Determination of the normalization constant

In fact, these continuum states, Eqs. (19)-(20) are not normalizable, *i.e.* they do not belong to the Hilbert space $\hbar$. The consequence is that the eigenfunctions of the continuum are "generalized eigenfunctions". But for simplicity we will keep calling them eigenfunctions (or orbitals). In order to normalize these eigenfunctions one can use the generalized orthogonality relation,

$$\int_{-\infty}^{+\infty}\psi_{k_1}^{\dagger}(x)\psi_{k_2}(x)\mathrm{d}x = \delta(k_1 - k_2), \tag{21}$$

with δ the Dirac distribution. Using this relation over the positive energy states (which will be referred to as "electronic states") and the negative energy states ("positronic states"), we can obtain the normalization constant as

$$A_k = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{\varepsilon_k + mc^2}{2\varepsilon_k}}. \tag{22}$$

Here the k values belong to $\mathbb{R}$. Indeed we have a continuum of positive and negative energy states. But for simplicity we will keep discrete sum notations for all the quantities that depend on the continuum. For actual calculations, integrals will be used and we will make the transformation from discrete to continuum.

Symmetry adapted eigenfunctions

Because orbitals for k and $-k$ are degenerate the most general form of the eigenfunctions of energy ε_k is given by a linear combination of $\psi_k(x)$ and $\psi_{-k}(x)$. To find the proper linear combination, we will use the symmetries of the system. The parity operator for two-component spinors is

$$\hat{\mathcal{P}} = \boldsymbol{\sigma}_z \mathrm{P}(x \to -x), \tag{23}$$

with $\mathrm{P}(x \to -x)$ the spatial parity operator that flips the coordinate sign $x \to -x$. Because this operator $\hat{\mathcal{P}}$ commutes with the Hamiltonian, the orbitals are eigenfunctions of this operator. These eigenfunctions can have two different symmetry labels. We will labeled *gerade* the wave functions that are eigenfunctions of the parity operator with eigenvalue of +1 and *ungerade* those with eigenvalue of -1. We will use the superscript g and u to differentiate those two symmetry adapted eigenfunctions, such as

$$\hat{\mathcal{P}}\psi^g_{+,k}(x) = \psi^g_{+,k}(x) \quad \text{and} \quad \hat{\mathcal{P}}\psi^u_{+,k}(x) = -\psi^u_{+,k}(x) \tag{24}$$

$$\hat{\mathcal{P}}\psi^g_{-,k}(x) = \psi^g_{-,k}(x) \quad \text{and} \quad \hat{\mathcal{P}}\psi^u_{-,k}(x) = -\psi^u_{-,k}(x). \tag{25}$$

The four symmetry adapted eigenfunctions can be derived as linear combinations of the orbitals

$$\psi^g_{+,k}(x) = A_k \left[\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} 1 \\ \frac{-kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{-\mathrm{i}kx} \right] \quad \text{and} \quad \psi^u_{+,k}(x) = B_k \left[\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{\mathrm{i}kx} - \begin{pmatrix} 1 \\ \frac{-kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{-\mathrm{i}kx} \right], \tag{26}$$

$$\psi^g_{-,k}(x) = C_k \left[\begin{pmatrix} \frac{kc}{-\varepsilon_k - mc^2} \\ 1 \end{pmatrix} e^{\mathrm{i}kx} - \begin{pmatrix} \frac{-kc}{-\varepsilon_k - mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx} \right] \quad \text{and} \quad \psi^u_{-,k}(x) = D_k \left[\begin{pmatrix} \frac{kc}{-\varepsilon_k - mc^2} \\ 1 \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} \frac{-kc}{-\varepsilon_k - mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx} \right], \tag{27}$$

with

$$\begin{aligned} k &\in [0, \infty) \quad \text{for } \psi^g_{+,k} \text{ and } \psi^u_{-,k} \\ k &\in (0, \infty) \quad \text{for } \psi^u_{+,k} \text{ and } \psi^g_{-,k}. \end{aligned}$$

The normalization constants A_k, B_k, C_k, D_k can be derived using the relation, Eq. (21), to obtain

$$A_k = B_k = C_k = D_k = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{\varepsilon_k + mc^2}{2\varepsilon_k}}. \tag{28}$$

And using the expansion of the complex exponential into trigonometric functions it is possible to rewrite the eigenfunctions as,

$$\psi^g_{+,k}(x) = E_k \begin{pmatrix} \cos(k|x|) \\ \frac{\mathrm{i}kc}{\varepsilon_k + mc^2} \frac{x}{|x|} \sin(k|x|) \end{pmatrix} \qquad \psi^u_{+,k}(x) = F_k \begin{pmatrix} \frac{\mathrm{i}kc}{\varepsilon_k - mc^2} \frac{x}{|x|} \sin(k|x|) \\ \cos(k|x|) \end{pmatrix} \tag{29}$$

$$\psi^g_{-,k}(x) = F_k \begin{pmatrix} \cos(k|x|) \\ \frac{\mathrm{i}kc}{-\varepsilon_k + mc^2} \frac{x}{|x|} \sin(k|x|) \end{pmatrix} \qquad \psi^u_{-,k}(x) = E_k \begin{pmatrix} \frac{\mathrm{i}kc}{-\varepsilon_k - mc^2} \frac{x}{|x|} \sin(k|x|) \\ \cos(k|x|) \end{pmatrix}, \tag{30}$$

with E_k and F_k as

$$E_k = \sqrt{\frac{\varepsilon_k + mc^2}{2\pi\varepsilon_k}} \quad \text{and} \quad F_k = \sqrt{\frac{\varepsilon_k - mc^2}{2\pi\varepsilon_k}}, \tag{31}$$

with the relation

$$\frac{kc}{\varepsilon_k + mc^2} = \frac{\varepsilon_k - mc^2}{kc}. \tag{32}$$

One can remark that in Eqs. (29)-(30) the large component has always the same symmetry as the state, while the small component has always the symmetry opposite to as the symmetry of the state. This can be explained

when one looks at the parity operator for such spinors, Eq. (23), the use of the Pauli matrix $\boldsymbol{\sigma}_z$ forces the small component to have a symmetry which is opposite to the one of the state.

Non-relativistic limit

In the non-relativistic limit, $c \to \infty$, we have $\varepsilon_k \underset{c\to\infty}{\sim} mc^2$, and $\psi_{+,k}(x) = \begin{pmatrix}0\\1\end{pmatrix} e^{\mathrm{i}kx}/\sqrt{2\pi}$ and $\psi_{-,k}(x) = \begin{pmatrix}0\\1\end{pmatrix} e^{\mathrm{i}kx}/\sqrt{2\pi}$. One recovers plane waves, *i.e.* the non-relativistic continuum states.

III. ONE-DIMENSIONAL HYDROGEN-LIKE ATOM

Now that we have solved the free Dirac equation and found the generalized eigenfunctions of the system, we will interest ourself in solving the hydrogen-like Dirac equation on which we add the potential of the hydrogen nucleus. We will use a model with delta-potential interactions [11]. Indeed, this type of interaction can be considered as a good model for 3D equivalent systems with the Coulomb potential [16].

The Hamiltonian composed with the Dirac free operator and a delta-potential interaction term is written as

$$\hat{h} = -\mathrm{i}c\boldsymbol{\sigma}_x \frac{\mathrm{d}}{\mathrm{d}x} + \boldsymbol{\sigma}_z mc^2 - Z\delta(x). \tag{33}$$

where Z is the charge of the nuclei. However, because of the delta potential, the eigenfunctions will have a discontinuity at $x = 0$. But the action of a delta distribution over a discontinuous function presents an ambiguity. We will try to solve this ambiguity before going any further.

A. Definition of the delta-potential

We will focus on two different ways to deal with this ambiguity. Those two different ways will lead to two different matching conditions for ψ at $x = 0$. The first possible matching condition at $x = 0$ is [11, 17–19]

$$\begin{aligned}\begin{pmatrix}\psi^{\mathrm{L}}(0^+)\\ \psi^{\mathrm{S}}(0^+)\end{pmatrix} &= \frac{1}{1+\lambda^2}\begin{pmatrix}1-\lambda^2 & 2\mathrm{i}\lambda\\ 2\mathrm{i}\lambda & 1-\lambda^2\end{pmatrix}\begin{pmatrix}\psi^{\mathrm{L}}(0^-)\\ \psi^{\mathrm{S}}(0^-)\end{pmatrix}\\ &= \begin{pmatrix}\cos\theta & \mathrm{i}\sin\theta\\ \mathrm{i}\sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}\psi^{\mathrm{L}}(0^-)\\ \psi^{\mathrm{S}}(0^-)\end{pmatrix},\end{aligned} \tag{34}$$

where $\lambda = Z/(2c)$ and $\tan(\theta/2) = \lambda$. This matching condition can be obtained by different methods: (1) integrating the equation

$$\hat{h}\psi(x) = \varepsilon\psi(x) \tag{35}$$

around $x = 0$ and formally defining $\int_{0^-}^{0^+} \delta(x)\psi(x)\mathrm{d}x = (1/2)\left[\psi(0^+) + \psi(0^-)\right]$ [11, 17]; (2) using Colombeau's generalized theory of distributions allowing one to give a meaning to the product $\delta(x)\psi(x)$ [19]. The second possible matching condition at $x = 0$ is

$$\begin{pmatrix}\psi^{\mathrm{L}}(0^+)\\ \psi^{\mathrm{S}}(0^+)\end{pmatrix} = \begin{pmatrix}\cos\theta' & \mathrm{i}\sin\theta'\\ \mathrm{i}\sin\theta' & \cos\theta'\end{pmatrix}\begin{pmatrix}\psi^{\mathrm{L}}(0^-)\\ \psi^{\mathrm{S}}(0^-)\end{pmatrix}, \tag{36}$$

where $\theta'/2 = \lambda$. This matching condition can be obtained by considering the zero-width limit of a square-well potential [12, 20, 21]. Both matching conditions are consistent with self-adjointness and charge-conjugation symmetry [19].

In this paper we will refer to these two matching conditions as the first matching condition for Eq. (34) and the second matching condition for Eq. (36). We will mainly focus on the first matching condition but all the calculations have been made for both cases. Most of the time the results for the second matching condition will be given in Appendix A.

Now that the system is defined without any ambiguities we will focus on the derivation of the two-component eigenfunctions. First, we will focus on the bound state of the system, then we will look after the generalized eigenfunctions for both positive and negative energy states of the continuum.

B. Bound state

We consider the matching condition in Eq. (34). The case of the second matching condition is treated in Appendix A. We want to determine electron bound states with energies $0 \leq \varepsilon \leq mc^2$. For $x \neq 0$, we have the free Dirac equation,

$$\left[-\mathrm{i}c\boldsymbol{\sigma}_x \frac{\mathrm{d}}{\mathrm{d}x} + \boldsymbol{\sigma}_z mc^2\right] \tilde{\psi}(x) = \tilde{\varepsilon}\tilde{\psi}(x), \tag{37}$$

where $\tilde{\psi}$ is the wave function solution of the hydrogen-like Dirac equation. We will use the notation $\tilde{}$ for the eigenfunctions of the hydrogen-like Dirac equation.

To obtain the bound state, the equation

$$\hat{h}\tilde{\psi}(x) = \tilde{\varepsilon}\tilde{\psi}(x), \tag{38}$$

must be solved in $(-\infty, 0)$ and $(0, \infty)$ then the matching condition will give the actual form of the eigenfunctions. On the positive real half-line (and also the negative real half-line) the solution is an eigenfunction of the free Dirac equation (37). But because the bound state is "bound", it must goes to zero when $x \to \pm\infty$. Then a real κ exists such that $k = \mathrm{i}\kappa$, with $\kappa > 0$. Then the energy of such state is

$$\tilde{\varepsilon}_0 = \sqrt{k^2c^2 + m^2c^4} = \sqrt{-\kappa^2c^2 + m^2c^4} < mc^2. \tag{39}$$

The eigenfunctions in $(-\infty, 0)$ and $(0, \infty)$ are,

$$\tilde{\psi}(x) = A\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{\mathrm{i}kx} = A\begin{pmatrix} 1 \\ \frac{\mathrm{i}\kappa c}{\varepsilon_k + mc^2} \end{pmatrix} e^{-\kappa x} \quad \text{for } x > 0 \tag{40}$$

$$\tilde{\psi}(x) = B\begin{pmatrix} 1 \\ \frac{-kc}{\varepsilon_k + mc^2} \end{pmatrix} e^{-\mathrm{i}kx} = B\begin{pmatrix} 1 \\ \frac{-\mathrm{i}\kappa c}{\varepsilon_k + mc^2} \end{pmatrix} e^{\kappa x} \quad \text{for } x < 0. \tag{41}$$

Then, thanks to the matching condition we have at $x = 0$

$$A\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k + mc^2} \end{pmatrix} = \frac{1}{1+\lambda^2}\begin{pmatrix} 1-\lambda^2 & 2\mathrm{i}\lambda \\ 2\mathrm{i}\lambda & 1-\lambda^2 \end{pmatrix} B\begin{pmatrix} 1 \\ \frac{-kc}{\varepsilon_k + mc^2} \end{pmatrix}, \tag{42}$$

where we recall that $\lambda = Z/2c$, leading to $A = B$ and $\kappa = 2mc\lambda/(1+\lambda^2)$. We will assume $\lambda < 1$, then there is a single electron bound state with energy [11, 15, 22]

$$\tilde{\varepsilon}_0 = mc^2 \frac{1-\lambda^2}{1+\lambda^2}, \tag{43}$$

and wave function

$$\tilde{\psi}_0(x) = A\begin{pmatrix} 1 \\ \mathrm{i}\lambda\frac{x}{|x|} \end{pmatrix} e^{-\kappa|x|}. \tag{44}$$

The constant A is found from the normalization condition such that $A = \sqrt{\kappa/(1+\lambda^2)} = \sqrt{mZ}/(1+\lambda^2)$.

In the non-relativistic limit, $c \to \infty$, we recover the non-relativistic bound state wave function of the one dimensional hydrogen atom [13],

$$\lim_{c\to\infty} \tilde{\psi}_0(x) = \sqrt{mZ}\begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-mZ|x|}, \tag{45}$$

and the energy has the expansion

$$\tilde{\varepsilon}_0 = mc^2 - \frac{mZ^2}{2} + \frac{mZ^4}{8c^2} + O\left(\frac{1}{c^4}\right), \tag{46}$$

where we recognize the rest-mass energy, the non-relativistic energy, and the first relativistic correction. We recall that, for the 3D Dirac hydrogen-like atom, the ground-state energy is $\varepsilon_0 = mc^2\sqrt{1 - Z^2/c^2} = mc^2 - mZ^2/2 - mZ^4/(8c^2) + O(1/c^4)$. The sign of the relativistic correction is opposite!

C. Continuum positive states

Using the degeneracy in k and the first matching condition, one is able to derive the eigenfunctions for the electronic *gerade* state

$$\begin{aligned}\tilde{\psi}^{g}_{+,k}(x) = \; & A\left[\begin{pmatrix}1\\ \frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{\mathrm{i}kx} + \frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix}1\\ -\frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix}1\\ \frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{\mathrm{i}kx} + \begin{pmatrix}1\\ -\frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{-\mathrm{i}kx}\right]\theta(-x),\end{aligned} \tag{47}$$

for $k \in [0, \infty)$, and the *ungerade* state

$$\begin{aligned}\tilde{\psi}^{u}_{+,k}(x) = \; & B\left[\begin{pmatrix}-1\\ \frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{\mathrm{i}kx} + \frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix}1\\ -\frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix}-1\\ \frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{\mathrm{i}kx} + \begin{pmatrix}1\\ -\frac{kc}{\varepsilon_k+mc^2}\end{pmatrix}e^{-\mathrm{i}kx}\right]\theta(-x)\end{aligned} \tag{48}$$

for $k \in (0, \infty)$, and A, B are normalization constants that we need to determine.

We will use the notation

$$\zeta^{g}_{+,k} = \frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda} \tag{49}$$

$$\zeta^{u}_{+,k} = \frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}. \tag{50}$$

One can see that both complex numbers $\zeta^{g}_{+,k}$ and $\zeta^{u}_{+,k}$ have the same norm, $|\zeta^{g}_{+,k}|^2 = |\zeta^{u}_{+,k}|^2 = 1$. Then, we can write them using phase factors $\delta^{(1)}_k$ and $\delta^{(2)}_k$ such that

$$\begin{cases} e^{-2\mathrm{i}\delta^{(1)}_k} = \zeta^{g}_{+,k} & \Rightarrow \quad \tan\left(\delta^{(1)}_k\right) = \frac{\lambda(\varepsilon_k+mc^2)}{kc}, \\ e^{-2\mathrm{i}\delta^{(2)}_k} = \zeta^{u}_{+,k} & \Rightarrow \quad \tan\left(\delta^{(2)}_k\right) = \frac{\lambda(\varepsilon_k-mc^2)}{kc} \end{cases}. \tag{51}$$

In the same way we can derive the new expressions for the positronic wave functions. We then obtain the electronic eigenfunctions as [22]

$$\tilde{\psi}^{g}_{+,k}(x) = E_k\begin{pmatrix}\cos\left(k|x| + \delta^{(1)}_k\right)\\ \frac{\mathrm{i}kc}{\varepsilon_k+mc^2}\frac{x}{|x|}\sin\left(k|x| + \delta^{(1)}_k\right)\end{pmatrix} \qquad \tilde{\psi}^{u}_{+,k}(x) = F_k\begin{pmatrix}\frac{\mathrm{i}kc}{\varepsilon_k-mc^2}\frac{x}{|x|}\sin\left(k|x| + \delta^{(2)}_k\right)\\ \cos\left(k|x| + \delta^{(2)}_k\right),\end{pmatrix} \tag{52}$$

with the normalization constants E_k and F_k as

$$E_k = \sqrt{\frac{\varepsilon_k + mc^2}{2\pi\varepsilon_k}} \qquad \text{and} \qquad F_k = \sqrt{\frac{\varepsilon_k - mc^2}{2\pi\varepsilon_k}}. \tag{53}$$

One can remark the symmetry between the gerade and ungerade orbitals such that,

$$\tilde{\psi}^{u}_{+,k}(x) = \mathrm{P}(m \to -m)\boldsymbol{\sigma}_x\tilde{\psi}^{g}_{+,k}(x), \tag{54}$$

with $\boldsymbol{\sigma}_x$ the Pauli matrix and $\mathrm{P}(m \to -m)$ the operator that flips the sign of the mass $m \to -m$.

In the non-relativistic limit ($c \to \infty$), one recovers the even and odd eigenfunctions of the non-relativistic one-dimensional hydrogen atom

$$\begin{cases} \tilde{\psi}^{g,NR}_{+,k}(x) = \frac{2k}{k+\mathrm{i}mZ}\begin{pmatrix}1\\0\end{pmatrix}\left[\cos(kx) - \frac{mZ}{k}\sin(k|x|)\right] \\ \tilde{\psi}^{u,NR}_{+,k}(x) = -2\mathrm{i}\begin{pmatrix}1\\0\end{pmatrix}\sin(kx) \end{cases}. \tag{55}$$

TABLE I: Different symmetries between the continuum eigenfunctions of the one-dimension hydrogen-like Dirac operator.

$$\begin{array}{ccc} \tilde{\psi}^{g}_{+,k}(x) & \xleftrightarrow{\mathrm{P}(m\to -m)\boldsymbol{\sigma}_x} & \tilde{\psi}^{u}_{+,k}(x) \\ \updownarrow \mathrm{P}(\varepsilon_k \to -\varepsilon_k) & & \mathrm{P}(\varepsilon_k \to -\varepsilon_k) \updownarrow \\ \tilde{\psi}^{g}_{-,k}(x) & \xleftrightarrow{\mathrm{P}(m\to -m)\boldsymbol{\sigma}_x} & \tilde{\psi}^{u}_{-,k}(x) \end{array}$$

D. Continuum negative states

As for the electronic states one can derive for the positronic states the eigenfunctions

$$\begin{aligned} \tilde{\psi}^{g}_{-,k}(x) = \; & C\left[\begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ -1 \end{pmatrix} e^{\mathrm{i}kx} + \frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ -1 \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(-x) \end{aligned} \tag{56}$$

for the *gerade* one, for $k \in (0, \infty)$, and for the *ungerade* state

$$\begin{aligned} \tilde{\psi}^{u}_{-,k}(x) = \; & D\left[\begin{pmatrix} -\frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{\mathrm{i}kx} + \frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda}\begin{pmatrix} -\frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} \frac{kc}{\varepsilon_k+mc^2} \\ 1 \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(-x) \end{aligned} \tag{57}$$

for $k \in [0, \infty)$, and C, D are normalization constants that we need to determine.

We will use the same notation as Eq. (50),

$$\zeta^{g}_{-,k} = \frac{kc(1+\lambda^2)-2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda} \tag{58}$$

$$\zeta^{u}_{-,k} = \frac{kc(1+\lambda^2)+2\mathrm{i}mc^2\lambda}{kc(1-\lambda^2)-2\mathrm{i}\varepsilon_k\lambda}. \tag{59}$$

As before, the complex numbers $\zeta^{g}_{-,k}$ and $\zeta^{u}_{-,k}$ are unitary. Then, we can write them using phase factors $\delta^{(1)}_k$ and $\delta^{(2)}_k$ such that

$$\begin{cases} e^{2\mathrm{i}\delta^{(1)}_k} = \zeta^{u}_{-,k} & \Rightarrow \quad \tan\left(\delta^{(1)}_k\right) = \frac{\lambda(\varepsilon_k+mc^2)}{kc}, \\ e^{2\mathrm{i}\delta^{(2)}_k} = \zeta^{g}_{-,k} & \Rightarrow \quad \tan\left(\delta^{(2)}_k\right) = \frac{\lambda(\varepsilon_k-mc^2)}{kc} \end{cases} . \tag{60}$$

One can now derive the positronic eigenfunctions as [22]

$$\tilde{\psi}^{g}_{-,k}(x) = F_k \begin{pmatrix} \cos\left(k|x| - \delta^{(2)}_k\right) \\ \frac{\mathrm{i}kc}{-\varepsilon_k+mc^2}\frac{x}{|x|}\sin\left(k|x| - \delta^{(2)}_k\right) \end{pmatrix} \qquad \tilde{\psi}^{u}_{-,k}(x) = E_k \begin{pmatrix} \frac{\mathrm{i}kc}{-\varepsilon_k-mc^2}\frac{x}{|x|}\sin\left(k|x| - \delta^{(1)}_k\right) \\ \cos\left(k|x| - \delta^{(1)}_k\right) \end{pmatrix}. \tag{61}$$

with the normalization constants E_k and F_k as

$$E_k = \sqrt{\frac{\varepsilon_k + mc^2}{2\pi\varepsilon_k}} \qquad \text{and} \qquad F_k = \sqrt{\frac{\varepsilon_k - mc^2}{2\pi\varepsilon_k}}. \tag{62}$$

We still have the same symmetry between the *gerade* and *ungerade* wave functions, and we have another symmetry between the positronic and electronic eigenfunction.

$$\tilde{\psi}^{g}_{-,k}(x) = \mathrm{P}(\varepsilon_k \to -\varepsilon_k)\tilde{\psi}^{g}_{+,k}(x), \tag{63}$$

with $\mathrm{P}(\varepsilon_k \to -\varepsilon_k)$ the operator that flips the sign of the energy $\varepsilon_k \to -\varepsilon_k$. We summarize the symmetries of the orbitals in Table I.

In the non-relativistic limit ($c \to \infty$), one recovers the even and odd eigenfunctions of the non-relativistic one-dimensional hydrogen atom,

$$\begin{cases} \tilde{\psi}^{g,NR}_{-,k}(x) = -2\mathrm{i}\begin{pmatrix}0\\1\end{pmatrix}\sin(kx) \\ \tilde{\psi}^{u,NR}_{-,k}(x) = \frac{2k}{k-\mathrm{i}mZ}\begin{pmatrix}0\\1\end{pmatrix}\Big[\cos(kx) + \frac{mZ}{k}\sin(k|x|)\Big] \end{cases} . \tag{64}$$

What we have done so far is summarized in Figure 1. We can see the difference between the free system (on the left) and the hydrogen-like system (on the right). We remark the creation of a bound state with energy, Eq. (43), lower than mc^2.

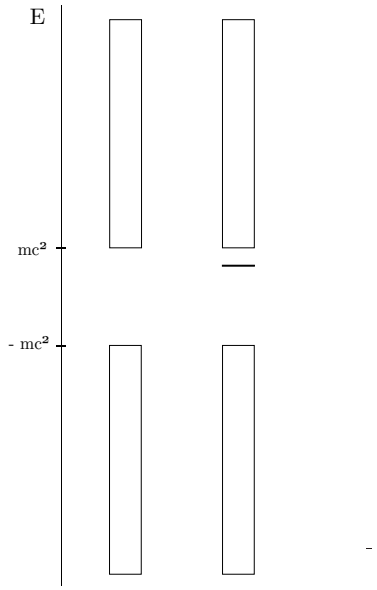


FIG. 1: Plot of the Dirac spectrum. On the left, the spectrum of the free system without any bound state, the only available states are in $(-\infty, -mc^2] \cup [mc^2, \infty)$. On the right the spectrum of the hydrogen-like system with the same range of energy and one bound state with energy $\varepsilon_0 \in (0, mc^2)$.

Then we will keep in mind the notation for the solutions of both systems

$$\begin{aligned} \hat{\mathcal{D}}\psi_p(x) &= \varepsilon_p\psi_p(x) \quad \text{for the free system} \\ \hat{h}\tilde{\psi}_p(x) &= \tilde{\varepsilon}_p\tilde{\psi}_p(x) \quad \text{for the hydrogen-like system.} \end{aligned}$$

IV. QUANTUM ELECTRODYNAMICS EFFECTS

A. Second quantization and vacuum definition

One can partition the states into two sets, one for the positive-energy states and the other for the negative-energy states. The set of positive-energy states will be written, PS, and the set of negative-energy states NS. We will now use the subscript indice p to refer to a state in PS $\cup$ NS.

In both cases, the Hilbert space can be decomposed as a direct sum of the positive-energy states and negative-energy states

$$\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_-, \tag{65}$$

where $\mathcal{H}_+ = \text{span}(\psi_p, p \in \text{PS})$ and $\mathcal{H}_- = \text{span}(\psi_p, p \in \text{NS})$.

1. Vacuum definition

In order to define an Hamiltonian in second quantization we need to define a vacuum reference state, $|\text{vac}\rangle$, on which one can define the creation and annihilation operators. Indeed, one has $\hat{a}_p$ and $\hat{a}_p^\dagger$ the annihilation and creation operators, with $p \in \text{PS} \cup \text{NS}$. One can define these operators thanks to their effects over the reference vacuum $|\text{vac}\rangle$

$$\hat{a}_p |\text{vac}\rangle = 0 \quad \text{and} \quad \hat{a}_p^\dagger |\text{vac}\rangle = \left|\psi_p\right\rangle. \tag{66}$$

The $|\text{vac}\rangle$ state is the one that is represented on the left of Fig. 2 where all the states are empty. These operators verify the relations

$$\{\hat{a}_p, \hat{a}_q^\dagger\} = \delta_{pq} \quad \text{and} \quad \{\hat{a}_p, \hat{a}_q\} = \{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = 0 \ \ \forall\ p, q \in \text{PS} \cup \text{NS}. \tag{67}$$

Now, one has a major issue. Indeed, by adding an electron to the $|\text{vac}\rangle$ it will go in the lower energy state, which means that it will fall in the infinite negative energy branch. This would imply that matter is not stable. In order to avoid such unphysical problem, another vacuum can be proposed. If the vacuum is a state where all the negative energy states are filled then, by adding an electron to this "filled vacuum", it will go in the lowest positive energy state. Then the unphysical problem is resolved. But taking this state as a reference, several problems may appear. First, if this state is "half-filled" with an infinite number of electrons then it has an energy that must be taken into account. Then, if there is electrons in the negative energy branch they can be excited in the positive energy branch. We need to figure out how to take these problems into account in the description of a QED second quantized Hamiltonian.

The starting point to describe this new state, that will be called "free vacuum state", $|0\rangle$, is to fill the negative-energy states. For this it is possible to use the creation operator over the negative energy spectrum as

$$|0\rangle = \prod_{p \in \text{NS}} \hat{a}_p^\dagger |\text{vac}\rangle. \tag{68}$$

A representation of this free vacuum state is given Fig. 2.

With this new vacuum one can define the proper annihilation and creation operators that act on it. The operator will be defined as electron or positron operator depending on which set of states they are dealing with. First, if p is in PS one has the electron annihilation and creation operator such that $\hat{b}_p \equiv \hat{a}_p$ and $\hat{b}_p^\dagger \equiv \hat{a}_p^\dagger$. Then, if p is in NS one has the positron annihilation and creation operator as $\hat{d}_p \equiv \hat{a}_p^\dagger$ and $\hat{d}_p^\dagger \equiv \hat{a}_p$. The corresponding free vacuum state $|0\rangle$ is such that,

$$\hat{b}_p |0\rangle = 0 \quad \text{for} \ \ p \in \text{PS} \quad \text{and} \quad \hat{d}_p |0\rangle = 0 \quad \text{for} \ \ p \in \text{NS}. \tag{69}$$

As we said previously, this state being half-filled with an infinite number of electrons, it must have a non zero energy. But the energy being always given up to an additive constant it is always possible to substract it to the Hamiltonian. First, the second quantized Hamiltonian is written as

$$\hat{\text{H}} = \sum_{p,q \in \text{PS} \cup \text{NS}} h_{pq} \hat{a}_p^\dagger \hat{a}_q \tag{70}$$

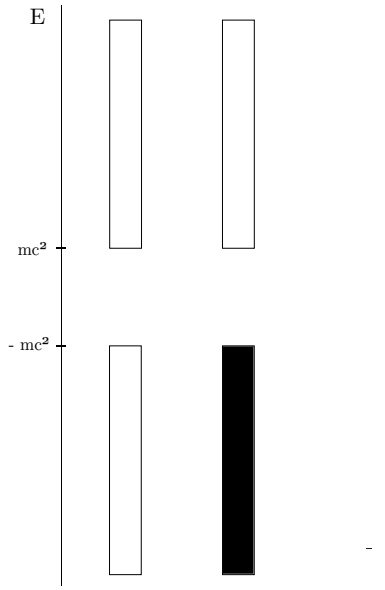


FIG. 2: Plot of the two vacuum states. On the left the reference empty vacuum state |vac⟩ and on the right the free vacuum state |0⟩.

with

$$\begin{aligned} h_{pq} &= \int_{-\infty}^{+\infty} \psi_p^\dagger(x)\hat{h}\psi_q(x)\mathrm{d}x \\ &= \int_{-\infty}^{+\infty} \psi_p^\dagger(x)\left[\hat{\mathcal{D}} - Z\delta(x)\right]\psi_q(x)\mathrm{d}x \\ &= \varepsilon_q\delta_{pq} - Z\psi_p^\dagger(0)\psi_q(0), \end{aligned} \tag{71}$$

where ψ_p the generalized eigenfunctions of the free Dirac equation and $\hat{h}$ the Hamiltonian defined in Eq. (33).

The second quantized Hamiltonian, Eq. (70), can be developed as

$$\begin{aligned} \hat{\mathrm{H}} &= \sum_{p,q\in \mathrm{PS}\cup\mathrm{NS}} h_{pq}\hat{a}_p^\dagger\hat{a}_q \\ &= \sum_{p,q\in\mathrm{PS}} h_{pq}\hat{b}_p^\dagger\hat{b}_q + \sum_{p\in\mathrm{PS},q\in\mathrm{NS}} h_{pq}\hat{b}_p^\dagger\hat{d}_q^\dagger + \sum_{p\in\mathrm{NS},q\in\mathrm{PS}} h_{pq}\hat{d}_p\hat{b}_q + \sum_{p,q\in\mathrm{NS}} h_{pq}\hat{d}_p\hat{d}_q^\dagger. \end{aligned} \tag{72}$$

Then, when one looks for the expectation value of the energy of the vacuum, one needs to compute

$$\begin{aligned} E_0 = \langle 0|\hat{\mathrm{H}}|0\rangle &= \sum_{p,q\in\mathrm{NS}} h_{pq}\langle 0|\hat{d}_p\hat{d}_q^\dagger|0\rangle \\ &= \sum_{p,q\in\mathrm{NS}} \left[\varepsilon_q - Z\psi_p^\dagger(0)\psi_q(0)\right]\delta_{pq} \\ &= \sum_{p\in\mathrm{NS}} \varepsilon_p - Z\sum_{p\in\mathrm{NS}} \psi_p^\dagger(0)\psi_p(0) < 0, \end{aligned} \tag{73}$$

the sum being over the negative energy states one has $\varepsilon_p = -\varepsilon_k < 0$ for $p \in$ NS, then this energy is negative. And with the some being over the infinite number of negative energy states the free vacuum energy goes to $-\infty$. But this is not a problem, the energy being defined up to an additive constant, one can instead look at the operator $\hat{\mathcal{H}}$, written as

$$\hat{\mathcal{H}} = \hat{\mathrm{H}} - \langle 0|\hat{\mathrm{H}}|0\rangle \tag{74}$$

this operator is called the normal-ordered Hamiltonian with respect to the free vacuum state. This Hamiltonian can

be denoted as $\mathcal{N}[\hat{\mathrm{H}}]$. In second quantization it has the expression

$$\begin{aligned}\hat{\mathcal{H}} = \mathcal{N}[\hat{\mathrm{H}}] &= \hat{\mathrm{H}} - \langle 0|\hat{\mathrm{H}}|0\rangle \\ &= \sum_{p,q\in \mathrm{PS}} h_{pq}\hat{b}_p^\dagger \hat{b}_q + \sum_{p\in \mathrm{PS},q\in \mathrm{NS}} h_{pq}\hat{b}_p^\dagger \hat{d}_q^\dagger + \sum_{p\in \mathrm{NS},q\in \mathrm{PS}} h_{pq}\hat{d}_p \hat{b}_q + \sum_{p,q\in \mathrm{NS}} h_{pq}\hat{d}_p \hat{d}_q^\dagger - \sum_{p,q\in \mathrm{NS}} h_{pq}\delta_{pq} \\ &= \sum_{p,q\in \mathrm{PS}} h_{pq}\hat{b}_p^\dagger \hat{b}_q + \sum_{p\in \mathrm{PS},q\in \mathrm{NS}} h_{pq}\hat{b}_p^\dagger \hat{d}_q^\dagger + \sum_{p\in \mathrm{NS},q\in \mathrm{PS}} h_{pq}\hat{d}_p \hat{b}_q - \sum_{p,q\in \mathrm{NS}} h_{pq}\hat{d}_q^\dagger \hat{d}_p, \end{aligned} \tag{75}$$

then, by construction this Hamiltonian has a zero energy over the free vacuum as

$$\langle 0|\hat{\mathcal{H}}|0\rangle = \langle 0|\hat{\mathrm{H}} - \langle 0|\hat{\mathrm{H}}|0\rangle|0\rangle = \langle 0|\hat{\mathrm{H}}|0\rangle - \langle 0|\hat{\mathrm{H}}|0\rangle = 0. \tag{76}$$

But, one may wonder if this free vacuum state is the lowest energy state possible. The free vacuum is based on the free orbitals ψ_p, there might be others orbitals, generated by a rotation of the previous free orbitals that solve

$$\tilde{E}_0 = \min_{\{\tilde{\psi}_p\}} \left\langle \tilde{0}\middle|\hat{\mathcal{H}}\middle|\tilde{0}\right\rangle \tag{77}$$

with the orthonormalization condition $\left\langle \tilde{\psi}_p\middle|\tilde{\psi}_q\right\rangle = \delta_{pq}$. The state $\left|\tilde{0}\right\rangle$ being the state filled with the negative energy orbitals $\tilde{\psi}_p$ associated with the creation and annihilation operators $\hat{\tilde{a}}_p^\dagger$ as

$$\left|\tilde{0}\right\rangle = \prod_{p\in \mathrm{NS}} \hat{\tilde{a}}_p^\dagger \left|\mathrm{vac}\right\rangle. \tag{78}$$

2. *Dressed vacuum state*

To solve the minimization equation, Eq. (77), we are looking for the set of vectors $\tilde{\psi}_p$ such that they solve the Lagrange multiplier problem

$$\begin{aligned}\mathcal{L}\left[\{\tilde{\psi}_p\}\right] &= \left\langle \tilde{0}\middle|\hat{\mathcal{H}}\middle|\tilde{0}\right\rangle - \sum_{p\in \mathrm{NS}} \lambda_p\Big(\left\langle \tilde{\psi}_p\middle|\tilde{\psi}_p\right\rangle - 1\Big) \\ &= \sum_{p\in \mathrm{NS}} \left\langle \tilde{\psi}_p\middle|\hat{h}\middle|\tilde{\psi}_p\right\rangle - E_0 - \sum_{p\in \mathrm{NS}} \lambda_p\Big(\left\langle \tilde{\psi}_p\middle|\tilde{\psi}_p\right\rangle - 1\Big), \end{aligned} \tag{79}$$

with $\{\lambda_p\}$ the set of Lagrange multipliers. The wave functions that minimizes the energy must be such that,

$$\frac{\delta\mathcal{L}\left[\{\tilde{\psi}_p\}\right]}{\delta\left\langle \tilde{\psi}_p\right|} = 0 \Longrightarrow \hat{h}\left|\tilde{\psi}_p\right\rangle = \lambda_p\left|\tilde{\psi}_p\right\rangle. \tag{80}$$

Then, the set of vectors that are solutions of the problem are eigenfunctions of the operator $\hat{h}$, which means that they are the hydrogen-like eigenfunctions previously derived in Part III. The Lagrange multiplier λ_p then becomes the eigenvalue $\tilde{\varepsilon}_p$. We just found that a lower ground state is the state defined Eq. (78). This ground state will be called "dressed vacuum state" [6, 10] and corresponds to the state where all the negative energy hydrogen-like orbitals are filled. A proper representation of the difference between the free vacuum state and the dressed one is given Fig. 3.

The operators $\hat{\tilde{a}}_p^\dagger$ and $\hat{\tilde{a}}_p$ are the creation and annihilation operators associated with the hydrogen-like orbitals. As for the free vacuum, one can define the operators $\hat{\tilde{b}}_p$ and $\hat{\tilde{d}}_p$ such that,

$$\hat{\tilde{b}}_p\left|\tilde{0}\right\rangle = 0 \quad \text{for } p\in \mathrm{PS} \quad \text{and} \quad \hat{\tilde{d}}_p\left|\tilde{0}\right\rangle = 0 \quad \text{for } p\in \mathrm{NS}. \tag{81}$$

Because this dressed state is solution of the minimization of the energy $\tilde{E}_0$ it is necessary to derive the new form of the ground state energy, the dressed vacuum energy, with reference the free vacuum state

$$\tilde{E}_0 = \left\langle \tilde{0}\middle|\hat{\mathcal{H}}\middle|\tilde{0}\right\rangle, \tag{82}$$

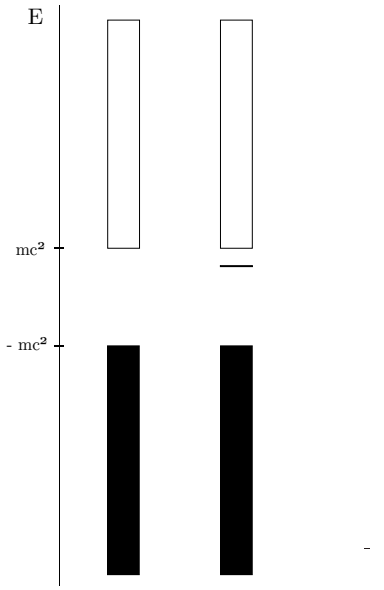


FIG. 3: On the left, the vacuum state $|0\rangle$ where all the negative energies states filled for the free system. On the right, the dressed vacuum state $\left|\tilde{0}\right\rangle$ where all the negative energies states filled for the hydrogen-like system.

then, using the definition of the normal-ordered Hamiltonian, Eq. (74)

$$\begin{aligned}\tilde{E}_0 &= \left\langle\tilde{0}\middle|\hat{\mathrm{H}}\middle|\tilde{0}\right\rangle - \langle 0|\hat{\mathrm{H}}|0\rangle \\ &= \sum_{p\in\mathrm{NS}} \tilde{\varepsilon}_p - \sum_{p\in\mathrm{NS}} \varepsilon_p + Z \sum_{p\in\mathrm{NS}} \psi_p^\dagger(0)\psi_p(0),\end{aligned} \tag{83}$$

which is supposedly negative.

3. *Vacuum Polarization*

With the state being half filled with an infinite number of electrons, it is possible for an electron to be excited from the negative energy branch to the positive one. Such excitation would create a positron, *i.e.* a hole in the negative energy branch, associated with a positive charge, and an electron in the positive energy branch, associated with a negative charge. This electron-positron pair can be spontaneously created due to an external potential field, here the nuclei. Such pair will polarize the vacuum and, if the interparticle interaction where to be taken into account this polarization would interact with the electrons (in the positive energy branch) of the system. Because this polarization is due to the external potential, it must verified to be zero when the external potential is switched off (when $Z = 0$).

To measure this vacuum polarization we can look at the density operator

$$\hat{n}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x). \tag{84}$$

As previously, it is important to look at such quantities with a reference state. We can define a normal-ordered density operator with respect to the free vacuum as

$$\mathcal{N}\left[\hat{n}(x)\right] = \hat{n}(x) - \langle 0|\hat{n}(x)|0\rangle\,. \tag{85}$$

Through this definition of the normal-ordered density operator, it is possible to define the vacuum polarization density operator as the average normal-ordered density over the dressed vacuum state

$$\begin{aligned}\tilde{n}^{vp}(x) &= \left\langle\tilde{0}\middle|\mathcal{N}\left[\hat{n}(x)\right]\middle|\tilde{0}\right\rangle \\ &= \left\langle\tilde{0}\middle|\hat{n}(x)\middle|\tilde{0}\right\rangle - \langle 0|\hat{n}(x)|0\rangle \\ &= \sum_{p\in\mathrm{NS}} \tilde{\psi}_p^\dagger(x)\tilde{\psi}_p(x) - \sum_{p\in\mathrm{NS}} \psi_p^\dagger(x)\psi_p(x).\end{aligned} \tag{86}$$

We remark that if $Z = 0$ then, $\tilde{\psi}_p = \psi_p$ because both orbitals are eigenfunctions of the same operator and the vacuum polarization density goes to zero.

Moreover, this expression reminds us of the expression of the vacuum energy Eq. (83). They are the two main QED effects that we will be interested in.

4. Alternative definition of the Hamiltonian

There is another equivalent definition of the Hamiltonian normal-ordered with respect to the free vacuum state, which is an electron-positron Hamiltonian defined with commutators [8]. We will note the Hamiltonian and all the properties linked with this definition with superscript c. The second quantized Hamiltonian is now defined as

$$\hat{\mathcal{H}}^c = \frac{1}{2} \sum_{p,q \in \mathrm{PS} \cup \mathrm{NS}} h_{pq} \left[\hat{\hat{a}}_p^\dagger, \hat{\hat{a}}_p \right], \tag{87}$$

with $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$ the commutator between the operators $\hat{A}$ and $\hat{B}$. The vacuum energy can also be derived as

$$\begin{aligned} \tilde{E}_0^c &= \left\langle \tilde{0} \middle| \hat{\mathcal{H}}^c \middle| \tilde{0} \right\rangle \\ &= \frac{1}{2} \Bigg[\sum_{p \in \mathrm{NS}} \tilde{\varepsilon}_p - \sum_{p \in \mathrm{PS}} \tilde{\varepsilon}_p \Bigg]. \end{aligned} \tag{88}$$

The two definition for the Hamiltonians are a bit different but must have the same physics. The vacuum energy being a physical quantity it must have the same definition in both formalisms. Because the energy is defined from a reference, up to an additive constant, it can be shown that we have the relation between both vacuum energies [8]

$$\begin{aligned} \tilde{E}_0 &= \left\langle \tilde{0} \middle| \hat{\mathcal{H}}^c \middle| \tilde{0} \right\rangle - \langle 0 | \hat{\mathcal{H}}^c_{(Z=0)} | 0 \rangle \\ &= \frac{1}{2} \Bigg[\sum_{p \in \mathrm{NS}} \tilde{\varepsilon}_p - \sum_{p \in \mathrm{PS}} \tilde{\varepsilon}_p \Bigg] - \frac{1}{2} \Bigg[\sum_{p \in \mathrm{NS}} \varepsilon_p - \sum_{p \in \mathrm{PS}} \varepsilon_p \Bigg]. \end{aligned} \tag{89}$$

We also introduce a new density operator as

$$\hat{n}^c(x) = \frac{1}{2} \left[\hat{\psi}^\dagger(x), \hat{\psi}(x) \right], \tag{90}$$

which leads to the expression of the vacuum polarization density as [9, 10]

$$\begin{aligned} \tilde{n}^{c,vp}(x) &= \left\langle \tilde{0} \middle| \hat{n}^c(x) - \langle 0 | \hat{n}^c(x) | 0 \rangle \middle| \tilde{0} \right\rangle \\ &= \frac{1}{2} \Bigg(\left\langle \tilde{0} \right| \left[\hat{\psi}^\dagger(x), \hat{\psi}(x) \right] \left| \tilde{0} \right\rangle - \langle 0 | \left[\hat{\psi}^\dagger(x), \hat{\psi}(x) \right] | 0 \rangle \Bigg) \\ &= \frac{1}{2} \Bigg(\sum_{p \in \mathrm{NS}} \tilde{\psi}_p^\dagger(x) \tilde{\psi}_p(x) - \sum_{p \in \mathrm{PS}} \tilde{\psi}_p^\dagger(x) \tilde{\psi}_p(x) \Bigg) \end{aligned} \tag{91}$$

Most of the derivations will be done using both definitions of the Hamiltonian. The commutator expressions and derivations will mostly be given in the Appendix but the main results will be presented and compared throughout this report. We will also demonstrate the equality between both definitions of the vacuum polarization density

$$\tilde{n}^{c,vp}(x) = \tilde{n}^{vp}(x) \tag{92}$$

B. Analytical calculation of the vacuum polarization density

In order to derive the vacuum polarization density defined in Eq. (86) one will need the analytical formulas for the ψ_p and $\tilde{\psi}_p$ for $p \in \mathrm{NS}$. This means that for the vacuum polarization density in the normal ordered definition we will only look at the *gerade* and *ungerade* positronic wave functions. We have those formulas, Eq. (27), for the free wave functions and, Eqs. (56)-(57), for the hydrogen-like positronic wave functions. In most calculations, because the wave functions belong to the continuum we will work with integrals. Furthermore, because we already

took into account the degeneracy in k we can integrate only over the domain $k \in \mathbb{R}^+$. One can develop the free part of the vacuum polarization density,

$$\begin{aligned}\sum_{p\in \mathrm{NS}} \psi_p^\dagger(x)\psi_p(x) &= \int_{\mathbb{R}^+} \Big(\psi_{-,k}^{g,\dagger}(x)\psi_{-,k}^{g}(x) + \psi_{-,k}^{u,\dagger}(x)\psi_{-,k}^{u}(x)\Big)\mathrm{d}k \\ &= \int_0^{+\infty} \frac{\mathrm{d}k}{\pi}, \end{aligned} \tag{93}$$

and the hydrogen-like part

$$\begin{aligned}\sum_{p\in \mathrm{NS}} \tilde{\psi}_p^\dagger(x)\tilde{\psi}_p(x) &= \int_{\mathbb{R}^+} \Big(\tilde{\psi}_{-,k}^{g,\dagger}(x)\tilde{\psi}_{-,k}^{g}(x) + \tilde{\psi}_{-,k}^{u,\dagger}(x)\tilde{\psi}_{-,k}^{u}(x)\Big)\mathrm{d}k \\ &= \int_0^{+\infty} \mathrm{d}k \frac{1}{\pi}\Big(1 + \mathrm{i}\frac{mc^2}{2\tilde{\varepsilon}_k} 2mc^2\lambda\Big[\frac{e^{-2\mathrm{i}kx}}{kc(1-\lambda^2) - 2\mathrm{i}\tilde{\varepsilon}_k\lambda} - \frac{e^{2\mathrm{i}kx}}{kc(1-\lambda^2) + 2\mathrm{i}\tilde{\varepsilon}_k\lambda}\Big]\Big). \end{aligned} \tag{94}$$

Having the two terms of the vacuum polarization density, by substracting them it give the analytical form of this quantity as

$$\tilde{n}^{vp}(x) = \int_0^{+\infty} \mathrm{d}k \frac{\mathrm{i}}{\pi} \frac{mc^2}{2\tilde{\varepsilon}_k} 2mc^2\lambda \left[\frac{e^{-2\mathrm{i}kx}}{kc(1-\lambda^2) - 2\mathrm{i}\tilde{\varepsilon}_k\lambda} - \frac{e^{2\mathrm{i}kx}}{kc(1-\lambda^2) + 2\mathrm{i}\tilde{\varepsilon}_k\lambda}\right]. \tag{95}$$

Then thanks to the relations that we previously defined for the bound state in the first matching condition, Eq. (43)

$$\tilde{\varepsilon}_0 = mc^2 \frac{1-\lambda^2}{1+\lambda^2} \tag{96}$$

$$\kappa = \frac{2mc\lambda}{1+\lambda^2}, \tag{97}$$

one can derive a much simpler formula for the vacuum polarization density as

$$\tilde{n}^{vp}(x) = \int_0^{+\infty} \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2}\Big[\frac{\tilde{\varepsilon}_0}{\tilde{\varepsilon}_k} k\sin(2k|x|) - \kappa\cos(2k|x|)\Big]. \tag{98}$$

We can make some remarks about this expression. First, one can see that this function is even in x. Indeed this is unsurprising because the system is symmetric with respect to $x = 0$. It seems logical that the vacuum polarization density is symmetric. Secondly, one can derive the exact same formula for the vacuum polarization density from the second matching condition with the positronic wave functions derived in Appendix A. The only difference between the first and the second matching condition is in the choice of λ. Indeed in the first matching condition one has to choose $\lambda = Z/(2c)$ while in the second matching condition one has to choose $\lambda = \arctan(Z/2c)$.

From the vacuum polarization defined using the commutators, in Appendix B, the same formula is also derived for the vacuum polarization density

$$\tilde{n}^{c,vp}(x) = -\frac{\kappa}{2}e^{-2\kappa|x|} + \int_0^{+\infty} \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2} \frac{\tilde{\varepsilon}_0}{\tilde{\varepsilon}_k} k\sin(2k|x|). \tag{99}$$

But, because we have

$$\int_0^{+\infty} \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2} \kappa\cos(2k|x|) = -\frac{\kappa}{2}e^{-2\kappa|x|}, \tag{100}$$

then

$$\tilde{n}^{vp}(x) = \tilde{n}^{c,vp}(x). \tag{101}$$

Before looking at the shape of the vacuum polarization density it is interesting to see what is the non-relativistic limit. Using the non-relativistic limit ($c \to \infty$)

$$\tilde{\varepsilon}_0 = mc^2 \frac{1-\lambda^2}{1+\lambda^2} \to mc^2 \tag{102}$$

$$\tilde{\varepsilon}_k = \sqrt{m^2c^4 + k^2c^2} \to mc^2, \tag{103}$$

it is possible to derive the non-relativistic vacuum polarization density as

$$\begin{aligned}\lim_{c\to\infty}\tilde{n}^{vp}(x) &= -\frac{\kappa}{2}e^{-2\kappa|x|}+\int_0^{+\infty}\frac{\mathrm{d}k}{\pi}\frac{\kappa k}{k^2+\kappa^2}\sin(2k|x|)\\ &= \begin{cases}-\frac{\kappa}{2}e^{-2\kappa|x|}+\frac{\kappa}{2}e^{-2\kappa|x|} & \text{if } x\neq 0\\ -\frac{\kappa}{2}e^{-2\kappa|x|}+0 & \text{if } x=0\end{cases}\\ &= \begin{cases}0 & \text{if } x\neq 0\\ -\frac{\kappa}{2} & \text{if } x=0\end{cases}.\end{aligned} \tag{104}$$

Indeed, the system being not relativistic anymore, the negative energy solutions do not exist, then the vacuum polarization density does not have any physical meaning anymore, and it is zero, except for the irrelevant value at $x = 0$.

C. Plots of the vacuum polarization density

High relativistic regime

We will call the "high relativistic regime" when the speed of light is taken as $c = 1$ a.u.. In this case the speed of the electron will be very close to the speed of light and the relativistic effects will be very strong. Using this value for the speed of light we have the plotting parameters $m = 1$ and $\lambda = 0.5$. We plotted both commutator and normal-ordered vacuum polarization density in Fig. 4). It can be seen that as we show previously both plots are exactly the same and both expressions of the vacuum polarization density are the same.

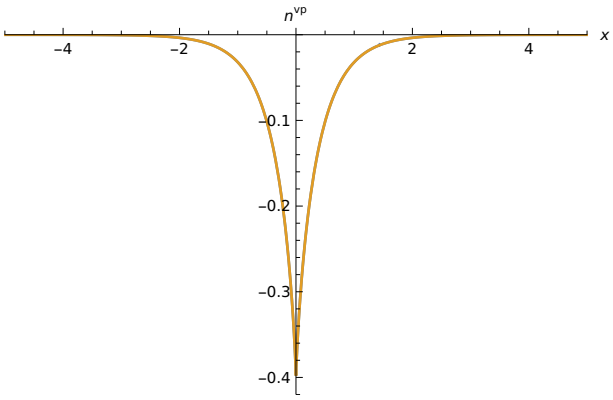


FIG. 4: Plot of the vacuum polarization density calculated either by Eq. (86) or by Eq. (91) for $Z = 1$ and $c = 1$ a.u.. We remark that both plots are equal for all x.

But, we can plot the commutator expression of the vacuum polarization density, Fig. 5, for larger x values and it seems that there is some numerical instabilities for $|x| > 6$. When, looking at both expressions for the vacuum polarization density, we can remark that for the normal-ordered one the integral involves a difference between trigonometric functions. Maybe this helps to cancel some numerical instabilities during the integration over k.

But both expressions being the same, we will always use the normal-ordered expression of the vacuum polarization density for future plots.

Low relativistic regime

As opposed to the previous high relativistic regime, the "low relativistic regime" is the regime where the velocity of light has its physical value $c = 137.036$ a.u. In this regime the speed of the electron is (for the hydrogen) less than 1% of the light velocity. Then the relativistic effects are much smaller. Here we have $Z = 1$. We plotted the effect of the increasing value of c for the vacuum polarization density in Fig. 6.

The effect of increasing the light velocity seems to contract the vacuum polarization density around the nucleus.

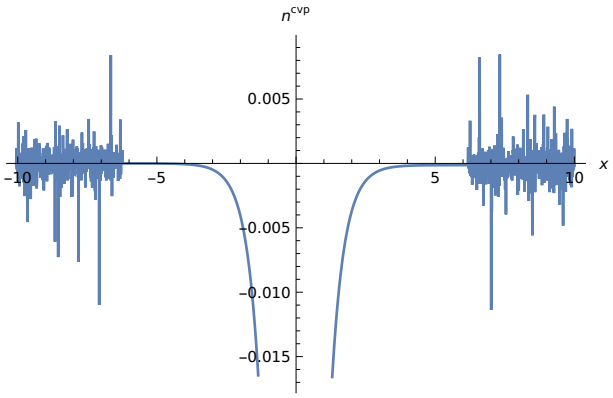


FIG. 5: Convergence problems for the commutator definition of the vacuum polarization density.

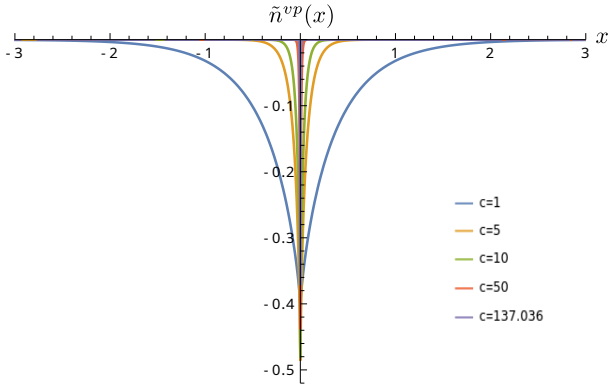
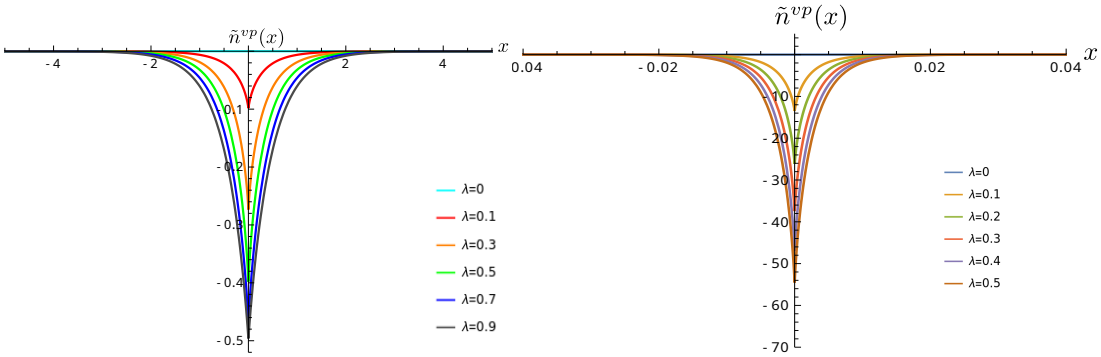


FIG. 6: Vacuum polarization density for different values of the parameter c.

Dependence over λ

Here it is interesting to plot the evolution of the density over all space depending on the values of λ, see Fig. 7. In order to see the effect of λ we plotted the vacuum polarization density for different λ for two different values of c.



(a) Variation of λ at $c = 1$

(b) Variation of λ at $c = 137.036$

FIG. 7: Variations of the vacuum polarization density as a function of x for different λ for two different values of c. Scales are different!

We can remark that the variations of λ seems to make the vacuum polarization wider at c fixed, and for two different values of c the vacuum polarization seems to be much more contracted around $x = 0$ and to have a deeper value at $x = 0$. Indeed with Eq. (104) the value of the vacuum polarization density at $x = 0$ is given by $\tilde{n}^{vp}(0) = -\kappa/2 = -mZ/(2(1 + \lambda^2))$, which is proportional to Z.

V. BASIS SET EXPANSION

So far, we have developed the one-dimensional relativistic Dirac equation in the free and the hydrogen-like system. In order to verify the analytical results, an expansion over a basis set will be used. We are looking for solutions of the one-dimensional Dirac Hamiltonian with delta-interaction as [11]

$$\left[-\mathrm{i}c\boldsymbol{\sigma}_x\frac{\mathrm{d}}{\mathrm{d}x}+\boldsymbol{\sigma}_z mc^2-Z\delta(x)\right]\tilde{\psi}(x)=\tilde{\varepsilon}\tilde{\psi}(x), \tag{105}$$

with the eigenfunction being a two-spinor

$$\tilde{\psi}(x)=\begin{pmatrix}\tilde{\psi}^L(x)\\ \tilde{\psi}^S(x)\end{pmatrix}. \tag{106}$$

As a useful reminder we will recall the relation between the large and small component of the two spinor solution of the free Dirac equation (which is true even for the hydrogen-like system at $x \neq 0$)

$$\tilde{\psi}^S(x) \;=\; \frac{-\mathrm{i}c}{\tilde{\varepsilon}+mc^2}\frac{\mathrm{d}}{\mathrm{d}x}\tilde{\psi}^L(x). \tag{107}$$

In order to expand the solution of Eq. (105) over a basis set, the first step is to choose a basis set. For this, we will use a very convenient basis set, the Hermite-Gaussian basis set.

A. Hermite functions

The Hermite-Gaussian basis functions is a useful basis set defined as

$$\forall x\in\mathbb{R},\; f_n^\alpha(x)=N_n^\alpha H_n(\sqrt{2\alpha}x)e^{-\alpha x^2}, \tag{108}$$

where n is a natural number, H_n the Hermite polynomials, $N_n^\alpha=(2^n n!)^{-1/2}(2\alpha/\pi)^{1/4}$ a normalization factor and α a real positive constant. This basis set is very convenient because of its orthonormality and the fact that in the limit where we take all integers n it becomes a complete orthonormal basis of $L^2(\mathbb{R},\mathbb{C})$ for all values of α.

This kind of basis set has already been used by Traore, Giner and Toulouse [13] in their work on the non-relativistic one-dimensional delta-interaction helium and hydrogen atoms. We will use their work as a reference for the non-relativistic limit of the results that will be obtained in this report.

The eigenfunctions being a two-spinor, both components will be expanded over the basis set independently as

$$\begin{pmatrix}\tilde{\psi}^L(x)\\ \tilde{\psi}^S(x)\end{pmatrix}=\begin{pmatrix}\sum_\mu \tilde{c}_\mu^L\chi_\mu^L(x)\\ \sum_\mu \tilde{c}_\mu^S\chi_\mu^S(x)\end{pmatrix}, \tag{109}$$

with, $\chi_\mu^{L/S}$ a basis function from the Hermite-Gaussian basis set.

In the previous analytical part the eigenfunctions of the system have been derived as eigenfunctions of the parity operator. Hence, the basis set will be chosen such that this parity is still verified. Another convenient aspect of this basis set is that the even Hermite functions $f_{2n}^\alpha(x)$ are even function for the spatial transformation $x\to -x$ and the odd Hermite functions $f_{2n+1}^\alpha(x)$ are odd for such transformation. We will see right after how to choose the even and odd basis set functions to describe the *gerade* and *ungerade* eigenfunctions.

The parity of the Hermite-Gaussian basis functions is going to be used because the eigenfunctions that we derived are eigenfunctions of the parity operator, Eq. (23). Indeed, a *gerade* eigenfunction will have its large component expanded over the even basis functions while its small component will be expanded over the odd basis functions. The opposite happens for the *ungerade* states whose large component will be expanded over the odd basis functions and the small component over the even. This parity relation between the large and small component is enhanced with the kinetic balance condition.

Kinetic balance

Furthermore, another useful aspect of this basis set is to calculate derivatives. It can be shown that

$$\frac{\mathrm{d}}{\mathrm{d}x}f_n^\alpha(x)=\sqrt{2\alpha}\left[\sqrt{\frac{n}{2}}f_{n-1}^\alpha(x)-\sqrt{\frac{n+1}{2}}f_{n+1}^\alpha(x)\right]. \tag{110}$$

Then, with the relation between both large and small component, Eq. (107), the small component must be expanded as the derivative of the large component. Hence, if the large component is developed over even Hermite functions (for a *gerade* eigenfunction) then the small component must be expanded over odd Hermite functions.

Here, there are two possibilities to expand the eigenfunctions. First, the *restricted kinetic balance* where the small component is forced to have the exact coefficients that verify the relation Eq. (107). Then, the *unrestricted kinetic balance* where the small component must be expanded over functions that are derivatives of the large component ones but the coefficients in front of each function are kept free and must be found exactly in the same way as the other coefficients.

Through this report, for the *gerade* wave functions the large component will be expanded over the even Hermite functions and the small component over the odd ones but we will use the unrestricted kinetic balance.

The kinetic balance is a very important condition in order to recover the non-relativistic limit within the basis set [23].

Calculation of the matrix elements

By using the decomposition given in Eq. (109) and injecting these expressions in the eigenvalue equation, Eq. (105) the following system of equations is obtained

$$\begin{cases} \sum_\mu \Big[mc^2 - Z\delta(x)\Big]\tilde{c}^L_\mu \chi^L_\mu(x) - \mathrm{i}c \sum_\mu \tilde{c}^S_\mu \frac{\mathrm{d}\chi^S_\mu(x)}{\mathrm{d}x} = \tilde{\varepsilon} \sum_\mu \tilde{c}^L_\mu \chi^L_\mu(x) \\ -\mathrm{i}c \sum_\mu \tilde{c}^L_\mu \frac{\mathrm{d}\chi^L_\mu(x)}{\mathrm{d}x} + \sum_\mu \Big[- mc^2 - Z\delta(x)\Big]\tilde{c}^S_\mu \chi^S_\mu(x) = \tilde{\varepsilon} \sum_\mu \tilde{c}^S_\mu \chi^S_\mu(x) \end{cases}. \tag{111}$$

By multiplying the first (resp. second) equation by the left by χ^L_ν (χ^S_ν) and by integrating over the whole space we obtain,

$$\begin{cases} \sum_\mu \Big[mc^2 S^{LL}_{\mu\nu} + V^{LL}_{\mu\nu}\Big]\tilde{c}^L_\mu + c \sum_\mu \tilde{c}^S_\mu P^{LS}_{\mu\nu} = \tilde{\varepsilon} \sum_\mu \tilde{c}^L_\mu S^{LL}_{\mu\nu} \\ c \sum_\mu \tilde{c}^L_\mu P^{SL}_{\mu\nu} + \sum_\mu \Big[- mc^2 S^{SS}_{\mu\nu} + V^{SS}_{\mu\nu}\Big]\tilde{c}^S_\mu = \tilde{\varepsilon} \sum_\mu \tilde{c}^S_\mu S^{SS}_{\mu\nu} \end{cases}, \tag{112}$$

or

$$\begin{pmatrix} mc^2 S^{LL} + V^{LL} & cP^{LS} \\ cP^{SL} & -mc^2 S^{SS} + V^{SS} \end{pmatrix} \begin{pmatrix} \tilde{c}^L \\ \tilde{c}^S \end{pmatrix} = \tilde{\varepsilon} \begin{pmatrix} S^{LL} & 0 \\ 0 & S^{SS} \end{pmatrix} \begin{pmatrix} \tilde{c}^L \\ \tilde{c}^S \end{pmatrix}, \tag{113}$$

with the following matrices elements

$$S^{XX}_{\mu\nu} = \int_{-\infty}^{\infty} \mathrm{d}x\ \chi^X_\mu(x)\chi^X_\nu(x) \tag{114}$$

$$V^{XX}_{\mu\nu} = \int_{-\infty}^{\infty} \mathrm{d}x\ \chi^X_\mu(x)\Big[- Z\delta(x)\Big]\chi^X_\nu(x) = -Z\chi^X_\mu(0)\chi^X_\nu(0) \tag{115}$$

$$P^{XY}_{\mu\nu} = \int_{-\infty}^{\infty} \mathrm{d}x\ \chi^X_\mu(x)\Big[- \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}x}\Big]\chi^Y_\nu(x) \tag{116}$$

with $X, Y \in \{L, S\}$. We can now use the properties of the Hermite-Gaussian basis set that we underlined before to obtain analytical terms for those integrals. Using these relations we can choose for the *gerade* (resp. *ungerade*) case to expand the large component over the f^α_{2n} (resp. f^α_{2n+1}) and the small one over the f^α_{2n+1} (resp. f^α_{2n}).

B. Results

1. Definition of n_{max}

The basis set, defined Eq. (108), depends on a constant α. In the complete basis set limit, it does not depend anymore on this constant but for a finite number of basis functions, it must be taken into account. We will use the notation $n_{\max}$ to refer to the highest principal quantum number of the basis functions used for the large component of the *gerade* eigenfunctions.

However this definition of $n_{\max}$ has a small subtility. This ambiguity is due to the kinetic balance condition. We will choose $n_{\max}$ as an even number, such that $n_{\max}/2 \in \mathbb{N}$. Then, the large component of a *gerade* eigenfunction will be expanded as

$$\tilde{\psi}^{L,g}(x) = \sum_{n=0}^{n_{\max}/2} \tilde{c}^L_n f^\alpha_{2n}(x). \tag{117}$$

Thus, this component is expanded over $n_{\max}/2+1$ even basis functions from f_0^α to $f_{n_{\max}}^\alpha$. Now because of the kinetic balance, if the expansion of the large component includes the Hermite function $f_{n_{\max}}^\alpha(x)$ then the expansion of the small component must include the Hermite function $f_{n_{\max}+1}^\alpha(x)$. The small component of a *gerade* eigenfunction must be expanded as

$$\tilde{\psi}^{S,g}(x) = \sum_{n=0}^{n_{\max}/2} \tilde{c}_n^S f_{2n+1}^\alpha(x). \tag{118}$$

This expansion is over $n_{\max}/2+1$ odd basis functions from f_1^α to $f_{n_{\max}+1}^\alpha$. The gerade eigenfunction being expanded over $n_{\max}+2$ basis functions, we have a total of $n_{\max}+2$ *gerade* eigenstates, with $n_{\max}+1$ ones of positive energy and $n_{\max}+1$ ones of negative energy. This is the first subtility, the number $n_{\max}$ corresponds to $n_{\max}+2$ eigenstates. This definition of $n_{\max}$ matches the definition of Traore, Giner and Toulouse [13] in the non-relativistic limit.

Then, there is a second subtility in the *ungerade* eigenfunctions. As the previous case of the *gerade* states, we keep the expansion of the large component over $n_{\max}/2+1$ odd basis functions from f_1^α to $f_{n_{\max}+1}^\alpha$ (indeed the *ungerade* large component is an odd function of x). But, again because of the kinetic balance, the expansion of the small component for this *ungerade* eigenfunction must include the even Hermite function $\chi_{n_{\max}+2}^\alpha$. We then have the expansion

$$\tilde{\psi}^{L,u}(x) = \sum_{k=0}^{n_{\max}/2} \tilde{c}_n^S f_{2n+1}^\alpha(x) \tag{119}$$

$$\tilde{\psi}^{S,u}(x) = \sum_{k=0}^{n_{\max}/2+1} \tilde{c}_n^S f_{2n}^\alpha(x). \tag{120}$$

The *ungerade* states are decomposed over $n_{\max}+3$ basis functions, which means that we have one more *ungerade* state compared to the *gerade* ones.

For example, for $n_{\max}=20$, we have 22 *gerade* states expanded over the basis functions f_0^α to f_{22}^α. And there are 23 *ungerade* states expanded over the basis functions f_0^α to f_{23}^α.

2. *Find the optimal value for α*

First, in order to find the best value for α it is necessary to define what is this value and how to find it. As an example a first system will be solved. Taking the parameters, $n_{\max}=50$, $c=1$, $Z=1$, $m=1$ and $\alpha=3.1$ (arbitrary value of α) it is possible to solve the Hamiltonian expanded over the basis, Eq. (113) in both the free and hydrogen-like system. We obtained the spectrum represented in Fig. 8.

The main difference between the free and the hydrogen-like system is the creation of a bound state with an energy $\tilde{\varepsilon}_0 = 0.614$ a.u. (lower than $mc^2=1$ a.u.). But because the number of basis functions is not infinite, the system depends on the value of α. Then, it is possible to use α as a parameter to find the lowest possible energy for this bound state. The optimal α, α_{opt}, is defined as

$$\alpha_{\text{opt}} = \underset{\alpha>0}{\text{argmin}}\ \tilde{\varepsilon}_0. \tag{121}$$

The optimal value of α for each value of $n_{\max}$ is obtained by plotting the energy as a function of α. We obtained the plots in Fig. 9 for three different values of $n_{\max}$. However, it can be remarked that when all curves are plotted together the larger $n_{\max}$ is, the less sensitive to α the energy is (see Fig. 10). Indeed, the more basis functions are used, the closer it gets to the complete basis limit and, in the limit $n_{max} \to \infty$ the energy does not depend on α anymore. We report in Table II the results in the high-relativistic regime and in Table III the results in the low-relativistic regime.

TABLE II: Values of α_{opt} for different values of $n_{\max}$, high-relativistic regime ($c=1$ a.u.).

$n_{\max}$	10	20	30	40	50	100	150	200	500	700	1000
α_{opt}	1.1	1.8	2.2	2.7	3.1	5.1	6.7	8.4	16.8	21.8	27.8

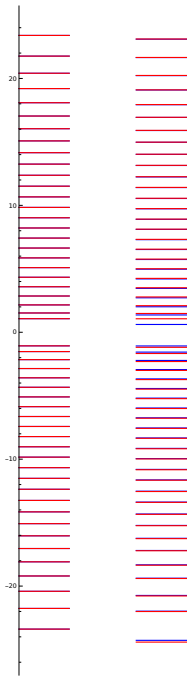
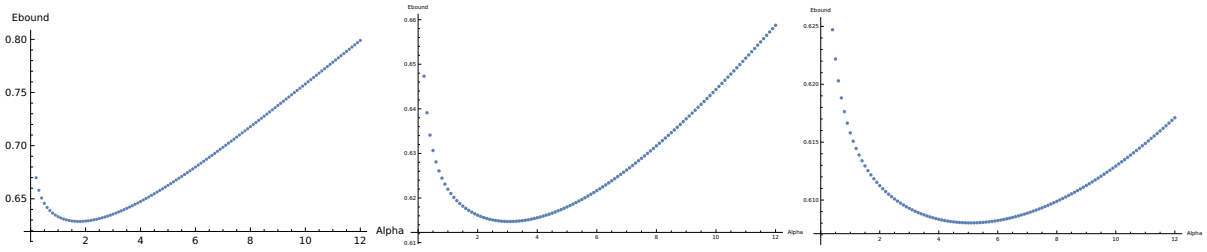


FIG. 8: Energetic diagram for the free system (on the left) and the hydrogen-like system (on the right). In blue, the *gerade* negative and positive solutions and in red the *ungerade* ones. Those energies have been calculated for $n_{max} = 50$, $c = 1$, $Z = 1$, $m = 1$ and $\alpha = 3.1$.



(a) $n_{\max} = 20$, $\alpha_{opt} = 1.8$ (b) $n_{\max} = 50$, $\alpha_{opt} = 3.1$ (c) $n_{\max} = 100$, $\alpha_{opt} = 5.1$

FIG. 9: Plots of minimization of the bound state energy as a function of α.

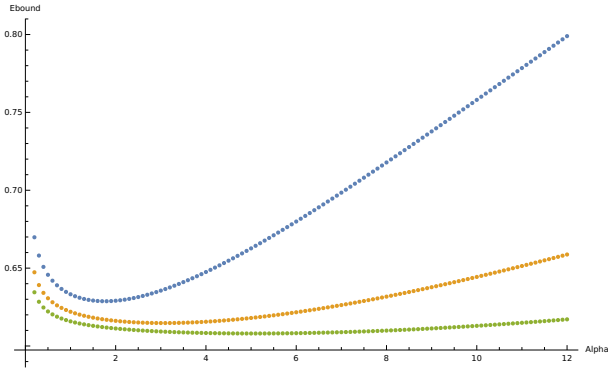


FIG. 10: Plots of the minimization of the bound state energy for $n_{max} = 20$ (in blue), $n_{max} = 50$ (in yellow) and $n_{max} = 100$ (in green).

TABLE III: Values of α_{opt} for different values of n_{max}, low-relativistic regime ($c = 137.036$ a.u.).

n_{max}	10	20	30	40	50	100	150	200	500	700	1000
α_{opt}	1.6	2.7	3.3	4.2	4.7	7.9	10.4	13.	26.1	33.9	44.8

3. *Convergence of the bound state energy as a function of n_{max}.*

Now that we have the minimum energy for the bound state for each values of n_{max} it is possible to look at the convergence of the bound state energy as a function of n_{max}. We will plot the bound state energy for both matching condition with parameters $c = 1$, $m = 1$, $Z = 1$. As a reminder for the first matching condition we have

$$\tilde{\varepsilon}_0 = mc^2 \frac{1-\lambda^2}{1+\lambda^2} = 0.6 \text{ a.u.}, \tag{122}$$

and for the second matching condition (SMC), Eq. (A2)

$$\tilde{\varepsilon}_0^{\text{SMC}} = mc^2 \cos(2\lambda) \approx 0.54 \text{ a.u.} \tag{123}$$

We will look at two different minimization processes. First, by choosing the optimal value of α for each n_{max} and then by keeping α fixed such as $\alpha_{\text{opt}}(n_{\text{max}} = 1000) = 27.8$. Both convergences are plotted in Fig. 11.

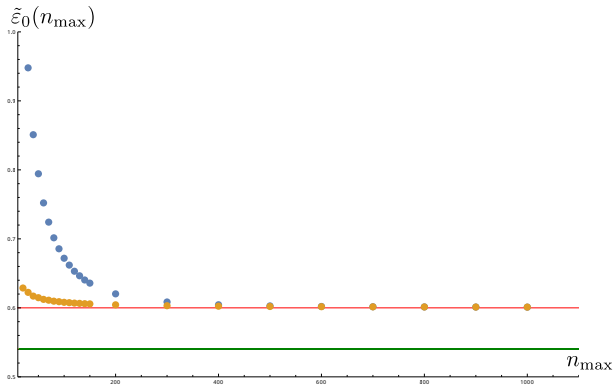


FIG. 11: Bound state energy as a function of n_{max}. The blue dots correspond to the plot when we kept the value of α as its maximal value ($\alpha = 27.8$). The orange dots correspond to the plot when we used the optimal values of α for every n_{max} (see Table II). Then the red line correspond to the energy of the bound state in the first matching condition, while the green line corresponds to the energy of the bound state in the second matching condition.

In orange we are optimizing the value of α at each point and we can see that we have a convergence which is much faster that the blue curve in which we kept α fixed. But by getting closer to the complete basis set limit we can see that for $n_{\text{max}} > 300$ the difference between the two approaches becomes very small.

Then we remark that both curves are converging to the bound state energy of the first matching condition. Then, for the next convergence studies we will keep the first matching condition as reference.

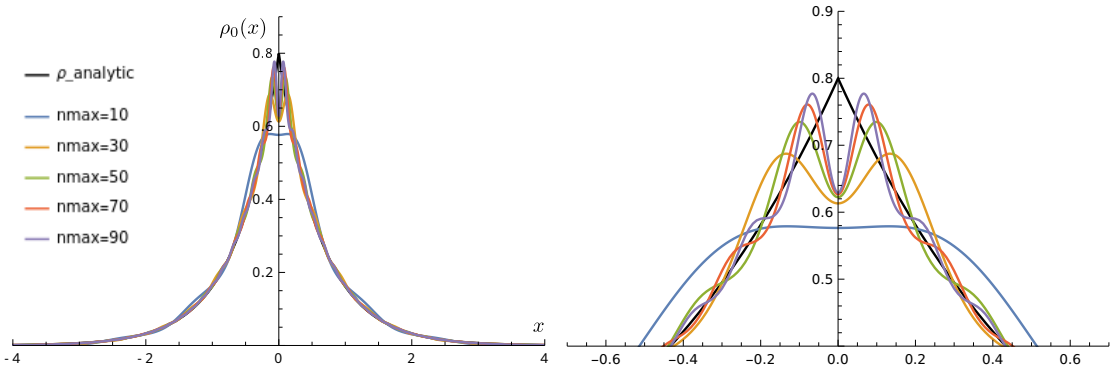
4. *Convergence of the bound state density as a function of n_{max}*

We have seen the basis set convergence of the bound state energy, we can now look at the basis set convergence of the bound state density. Using the analytical form of the bound state eigenfunction, Eq. (44), the analytical bound state density is derived as

$$\begin{aligned} \rho_0(x) &= |\tilde{\psi}_0(x)|^2 \\ &= \frac{\kappa}{1+\lambda^2} \begin{pmatrix} 1 & -\mathrm{i}\lambda\frac{x}{|x|} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ \mathrm{i}\lambda\frac{x}{|x|} \end{pmatrix} e^{-2\kappa|x|} \\ &= \kappa e^{-2\kappa|x|}. \end{aligned} \tag{124}$$

This density is derived for the first matching condition but we will keep to this condition as it gives the good ground state energy for the basis set.

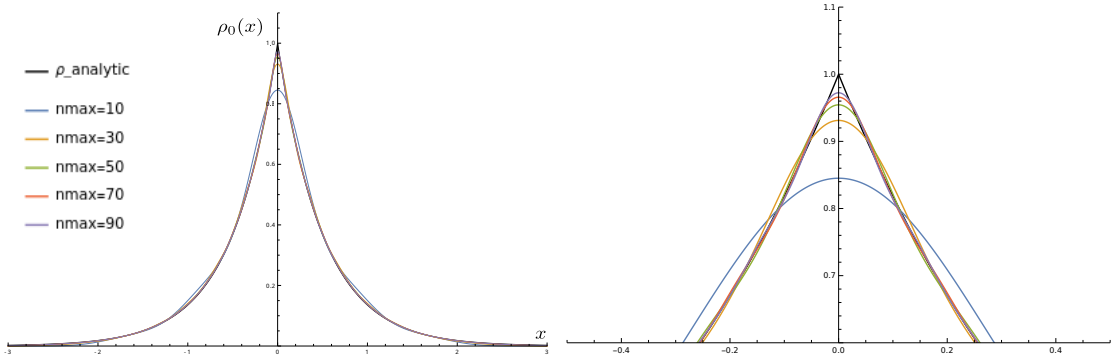
Then, it is possible to plot the analytical density and the density obtained in the basis set as a function of x for different values of $n_{\max}$. We will keep the optimal value of α obtained for each $n_{\max}$. The plots in Figs. 12 and 13, have been done for two values of the light velocity $c = 1$ a.u., in the high-relativistic limit and $c = 137.036$ a.u., in the low-relativistic limit.



(a) Bound state density as a function of x.

(b) Zoom of the bound state density around the origin.

FIG. 12: For $c = 1$ a.u.. Bound state density as a function of x for differents $n_{\max}$. As the basis set is increased the bound state density tends to get closer to the analytical density but the cusp is far from being recovered.



(a) Bound state density as a function of x.

(b) Zoom of the bound state density around the origin.

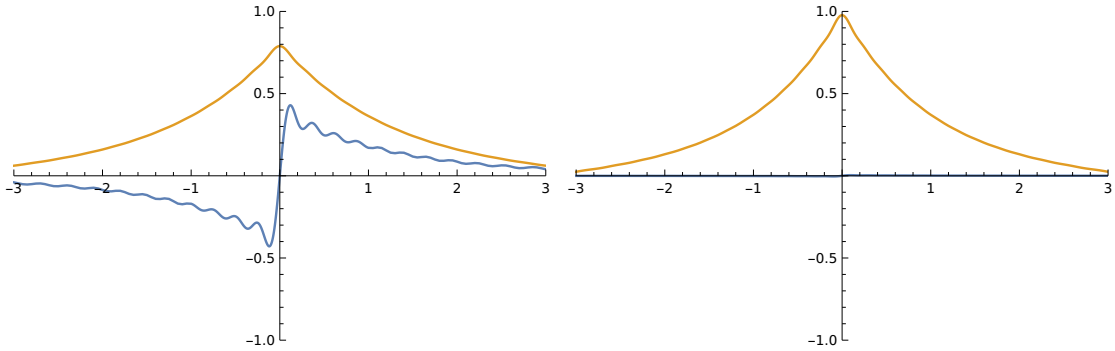
FIG. 13: For $c = 137.036$ a.u.. Bound state density as a function of x for differents $n_{\max}$. As the basis set is increased the bound state density tends to converge to the analytical density. The cusp at $x = 0$ is not recovered but it converges.

We can remark that in the high-relativistic limit the calculation has more trouble to obtain the cusp at $x = 0$. This can be understood because the relativistic effect are very important. In order to understand this effects it is possible to plot the large and small components of the bound state in both low and high-relativistic regimes, see Fig. 14.

The convergence problem of the cusp in the high-relativistic regime is due to the small component of the bound state eigenfunction. Indeed, the sign function in the small component makes it discontinuous at $x = 0$. But as shown in Fig. 14, the basis set is not able to represents a discontinuous function with the continuous Hermite-Gaussian functions. Then the small component, in the high-relativistic regime, is still continuous and in the vicinity of $x = 0$ the analytical small component is far away from the basis set expansion. By looking at the bound state density, the squared small component is included but its value at $x = 0$ is zero for the basis set expansion while it is not zero in the analytical form.

So far, we resolved the bound state of the hydrogen-like system and we saw that as a function of $n_{\max}$ the bound state energy and density are converging reasonably well in the low-relativistic regime but the high-relativistic regime can be improved. The use of a discontinuous basis function could help but in this case we would lost the orthogonalization of the basis. It will then complicate the resolution of the system.

After the bound state convergence study we can look at the convergence of the QED effects as the vacuum energy or the vacuum polarization density.



(a) High-relativistic regime.

(b) Low-relativistic regime.

FIG. 14: Plots of large and small components of the bound state wave function as a function of x for both relativistic regimes ($n_{\max} = 50$). In the high-relativistic regime the small component as a much bigger amplitude than in the low-relativistic regime.

5. *Convergence of the vacuum energy*

First the vacuum energy has already been derived, Eq. (83) for the normal ordered Hamiltonian and Eq. (89) for the Hamiltonian with the commutator. Once the basis set expansion has been done we obtained a discrete set of eigenstates with different energies, Fig. 8. It is then possible to use those eigenvalues ε_n and $\tilde{\varepsilon}_n$ to plot in Fig. 15 the evolution of the vacuum energy as a function of $n_{\max}$ for both expressions of the Hamiltonian.

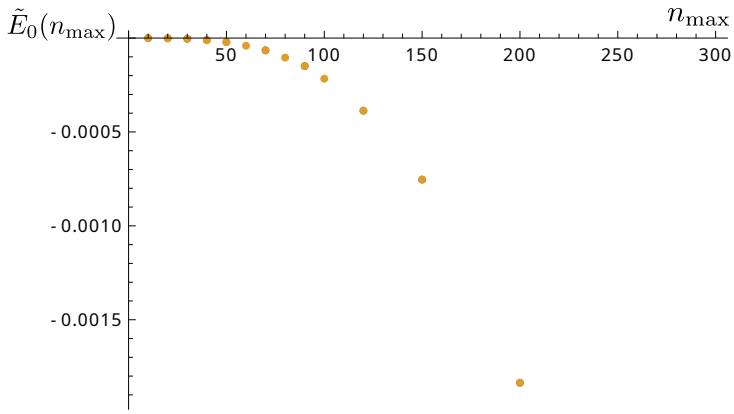


FIG. 15: Vacuum energy as a function of $n_{\max}$. The curve is decreasing as n_{max}^3.

The first remark that is done on this plot is that both expressions for the vacuum energy are exactly the same. This is what we expected for the alternative commutator definition when substracting the free vacuum energy with the commutator definition. Then, it seems that the vacuum energy goes to $-\infty$ when $n_{\max} \to \infty$. It is possible to conclude what we expected, the dressed vacuum state has a lower energy than the free vacuum state.

6. *Convergence to the vacuum polarization density*

As for the vacuum energy, having the eigenfunction of each eigenstate of the basis set expansion, it is possible to reproduce the analytical formulas we derived for the vacuum polarization density, for both the normal-ordered and commutator Hamiltonians. We derived the analytical expression as

$$\tilde{n}^{vp}(x) = \int_0^{+\infty} \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2} \Big[\frac{\tilde{\varepsilon}_0}{\tilde{\varepsilon}_k} k \sin(2k|x|) - \kappa \cos(2k|x|) \Big], \tag{125}$$

and we will use for the basis set expansion the formula given in Eq. (86). We obtain the plots given in Fig. 16 for the high-relativistic regime and in Fig. 17 in the low-relativistic regime.

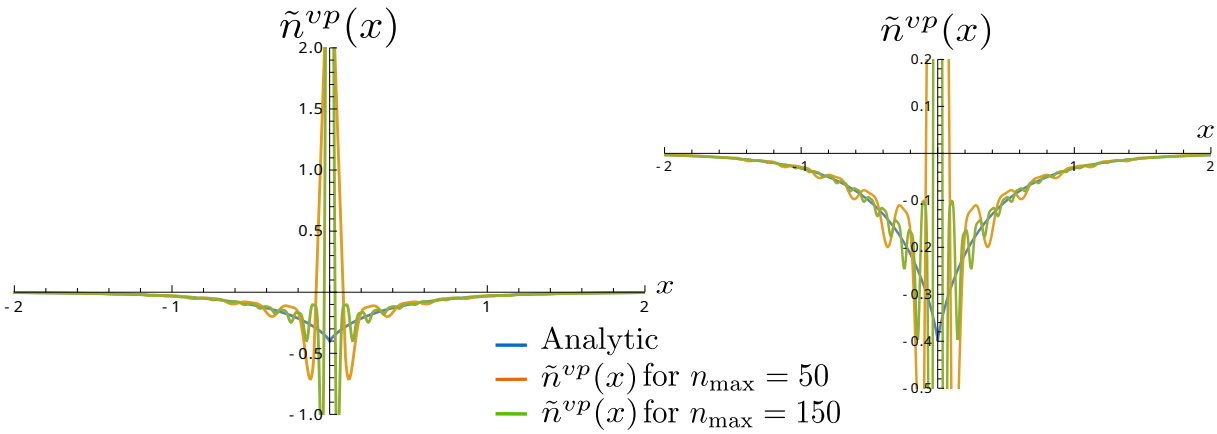


FIG. 16: Vacuum polarization density as a function of x for different values of $n_{\max}$ in the high-relativistic limit, $c = 1$ a.u.. The plot on the right is a zoom around the origin.

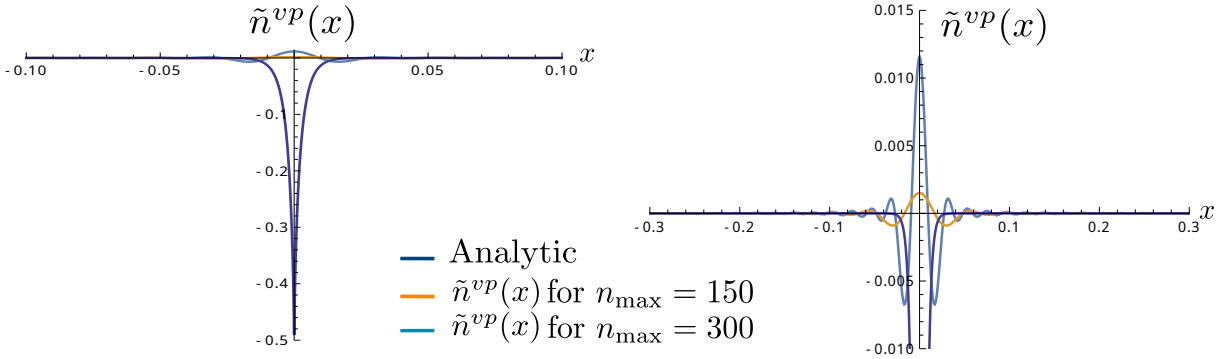


FIG. 17: Vacuum polarization density as a function of x for different values of $n_{\max}$ in the low-relativistic limit, $c = 137.036$ a.u.. The plot on the right is a zoom around the origin.

From those two plots is it possible to remark that the basis set expansion of the vacuum polarization density is recovering the analytical formula away from the origin. But the closer it gets to the origin the bigger the oscillations of the basis set expanded vacuum polarization density. In both regimes there is at $x = 0$ a positive value for the density, which is totally not expected in the analytical formula. This positive weight at $x = 0$ could be an artefact of the basis set expansion. Indeed, the eigenfunctions being in a finite number and all normalized, then the integration over the whole space should give a value close to zero.

VI. ONE-DIMENSIONAL HELIUM-LIKE ATOM

For the helium like atom one needs to consider the two-electron interaction. We have the equivalent of the relativistic Dirac-Coulomb-Breit (DCB) Hamiltonian for the one dimensional system

$$\hat{\mathcal{H}}^{DCB} = \sum_i \Big[c\hat{p}_i\boldsymbol{\alpha}_i + mc^2\boldsymbol{\beta}_i - Z\delta(x_i)\Big] + \Big[1 - \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2\Big]\delta(x_1 - x_2), \tag{126}$$

with $i = 1, 2$ refers to the two electrons of the system, and $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are 2×2 Pauli matrices. We remind that there are different possibilities for the $\boldsymbol{\alpha}$ matrix. Here, we will use the same choice of Pauli matrix as Coutinho and Nogami [15] and put $\boldsymbol{\alpha} = \boldsymbol{\sigma}_y$. The DCB Hamiltonian in Eq. (126) is then a real operator.

A. Hartree-Fock solution

If we are looking for the HF solution the wave function will have the following form

$$\Psi_{HF}(x_1, x_2) = \psi(x_1) \otimes \psi(x_2), \tag{127}$$

because we do not take the spin into account in our model the wave function does not have to be antisymmetric. Then a Hartree product of monoelectronic wave function is enough. We have the energy functional

$$E[\psi] = \langle\Psi_{HF}|\hat{\mathcal{H}}^{DCB}|\Psi_{HF}\rangle = 2\langle\psi|\hat{h}|\psi\rangle + \langle\psi\psi|\hat{W}|\psi\psi\rangle, \tag{128}$$

using the classical method of the Lagrange multiplier we have the Lagrange functional

$$L[\psi] = E[\psi] - \lambda\left(\langle\psi|\psi\rangle - 1\right) \tag{129}$$

where $\lambda \in \mathbb{R}$ is the Lagrange multiplier. We will look for a stationary point of $L[\psi]$. But, because L is symmetric we can look at a stationary point in $\psi^\dagger$

$$\begin{aligned}\frac{\delta L[\psi]}{\delta\psi^\dagger(x)} &= 0 = 2\Big[c\hat{p}\boldsymbol{\sigma}_y + mc^2\boldsymbol{\sigma}_z - Z\delta(x)\Big]\psi(x) + 2\Big[\psi^\dagger(x)\psi(x) - \Big(\psi^\dagger(x)\boldsymbol{\sigma}_y\psi(x)\Big)\boldsymbol{\sigma}_y\Big]\psi(x) - \lambda\psi(x) \\ &\Leftrightarrow \Big[c\hat{p}\boldsymbol{\sigma}_y + mc^2\boldsymbol{\sigma}_z - Z\delta(x)\Big]\psi(x) + \Big[\psi^\dagger(x)\psi(x) - \Big(\psi^\dagger(x)\boldsymbol{\sigma}_y\psi(x)\Big)\boldsymbol{\sigma}_y\Big]\psi(x) = \varepsilon\psi(x).\end{aligned} \tag{130}$$

With the choice of the Pauli matrix, each of the two-component solution must be real. We have then

$$\psi^\dagger(x)\boldsymbol{\sigma}_y\psi(x) = \mathrm{i}\psi^L(x)\psi^S(x) + (-\mathrm{i})\psi^S(x)\psi^L(x) = 0. \tag{131}$$

Then the Breit part of the interaction is zero and the only remaining two-electron interaction is the equivalent of the Coulombic term

$$\Big[cp\boldsymbol{\sigma}_y + mc^2\boldsymbol{\sigma}_z - Z\delta(x)\Big]\psi(x) + \Big[|\psi^L(x)|^2 + |\psi^S(x)|^2\Big]\psi(x) = \varepsilon\psi(x). \tag{132}$$

We obtain the two coupled equations for the large and small components as, for $x \neq 0$

$$\begin{pmatrix} mc^2 + |\psi^L(x)|^2 + |\psi^S(x)|^2 & -\mathrm{i}cp \\ \mathrm{i}cp & -mc^2 + |\psi^L(x)|^2 + |\psi^S(x)|^2 \end{pmatrix}\begin{pmatrix}\psi^L(x)\\ \psi^S(x)\end{pmatrix} = \varepsilon\begin{pmatrix}\psi^L(x)\\ \psi^S(x)\end{pmatrix}. \tag{133}$$

B. Bound state

We are looking for the bound state of the system [15], which is a *gerade* state. We can transform the large and small component as

$$\begin{pmatrix}\psi^L(x)\\ \psi^S(x)\end{pmatrix} = \eta(x)\begin{pmatrix}\cos\phi(x)\\ \sin\phi(x)\end{pmatrix}, \tag{134}$$

with η (resp. ϕ) is an even (resp. odd) function of x. Thanks to the relations obtained in Eq. (133) it is possible to derive the system of coupled equations as

$$c\frac{\mathrm{d}\phi}{\mathrm{d}x} = mc^2\cos(2\phi(x)) - \varepsilon - Z\delta(x) + \eta^2(x) \tag{135}$$
$$c\frac{\mathrm{d}\eta}{\mathrm{d}x} = mc^2\eta(x)\sin(2\phi(x)), \tag{136}$$

which gives the equation for the energy, for $x \neq 0$

$$\varepsilon - mc^2\cos(2\phi(x)) - \frac{1}{2}\eta^2(x) = 0, \qquad \forall x \in \mathbb{R}^*. \tag{137}$$

The bound state being bound, it must vanish far away from the nucleus, *i.e.* η must be localized $\eta(\pm\infty) = 0$. The energy ε being a constant it can be evaluated at any position. For x very far of the nuclei, $x \to \infty$ we have

$$\varepsilon = mc^2\cos[2\phi(\infty)]. \tag{138}$$

Then, using again Eq. (137) the following differential equation for ϕ can be derived by injecting the value of η, for $x \neq 0$

$$c\frac{\mathrm{d}\phi}{\mathrm{d}x} = -\varepsilon + mc^2\cos[2\phi], \tag{139}$$

which gives a solution for $\phi(x)$ as

$$\phi(x) = \arctan\Big[\sqrt{\beta}\ \coth(\kappa x')\Big], \tag{140}$$

with $\beta = (mc^2 - \varepsilon)/(mc^2 + \varepsilon)$, $\kappa = \sqrt{(mc^2)^2 - \varepsilon^2}/c$ and $x' = x + \mathrm{sgn}(x)x_0$ with x_0 an integration constant.

Then using the first or second matching condition when integrating Eq. (135) around $x = 0$ it can be found that

$$\phi(0^+) = -\phi(0^-) = \lambda = \arctan\Big[\sqrt{\beta}\ \coth(\kappa x_0)\Big], \tag{141}$$

with $\lambda = \arctan(Z/2c)$ in the first matching condition and $\lambda = Z/(2c)$ in the second matching condition. We will keep the first matching condition for now.

Then, using the normalization of the bound state over space and the new relations that have just been derived previously it is possible to derive a simpler formula for the bound-state energy

$$\varepsilon = mc^2\cos\left(2\lambda - \frac{1}{2c}\right), \tag{142}$$

and by writing $\gamma = 2\lambda - 1/(2c)$ we have the formula for β and κ as

$$\beta = \tan^2[\gamma/2c] \tag{143}$$
$$\kappa = c\sin[\gamma/c]. \tag{144}$$

Non-relativistic limit

Now that we derived the total bound state wave function at the HF level for the relativistic one dimensional Helium, we can see if it represents the non-relativistic one. Using the work of Traore *et al.* [13] we have for the non-relativistic HF bound state wave function

$$\forall x \in \mathbb{R},\ \ \psi(x) = 2\gamma\sqrt{\zeta}\frac{e^{-\gamma|x|}}{1 - \zeta e^{-2\gamma|x|}}, \tag{145}$$

with $\gamma = Z - \frac{1}{2}$ and $\zeta = \frac{1}{4Z-1}$.

From the relativistic wave function we will derive how to obtain the non-relativistic one in the limit $c \to \infty$. When c goes to ∞ we have $\beta \to \frac{\gamma}{4c^2} \to 0$. Because $\phi(x) = \arctan\Big[\sqrt{\beta}\ \coth(\kappa x')\Big]$ we have $\phi(x) \to 0$ when $c \to \infty$.

The HF wave function is then reduced to

$$\Psi_{HF}^{NonRelat}(x) = \eta(x)\begin{pmatrix}1\\0\end{pmatrix}. \tag{146}$$

Now we have to calculate the non relativistic limit of the η function.

$$\begin{aligned}\eta^2(x) &= \frac{2(mc^2-\varepsilon)(mc^2+\varepsilon)}{mc^2}\frac{1}{\cosh(2\kappa x')-\cos(\gamma/c)}\\ \eta^2(x) &= 2mc^2\frac{(1-\cos(\gamma/c))(1+\cos(\gamma/c))}{\cosh(2\kappa x')-\cos(\gamma/c)},\end{aligned} \tag{147}$$

for $c \to \infty$ we have

$$1-\cos(\gamma/c) \;\to\; (\gamma/c)^2/2 \tag{148}$$

$$1+\cos(\gamma/c) \;\to\; 2, \tag{149}$$

then we have, for $m = 1$

$$\eta^2(x) = 4m\frac{\gamma^2/2}{\cosh(2\kappa x')-1} = (2\gamma)^2\frac{1}{e^{2\kappa x'}+e^{-2\kappa x'}-2}. \tag{150}$$

For $x > 0$ we have

$$\eta^2(x) = (2\gamma)^2\frac{e^{-2\kappa(x+x_0)}}{(1-e^{-2\kappa(x+x_0)})^2}, \tag{151}$$

and for $x < 0$

$$\eta^2(x) = (2\gamma)^2\frac{e^{2\kappa(x-x_0)}}{(1-e^{2\kappa(x-x_0)})^2}. \tag{152}$$

Using the phase factor

$$e^{-2\kappa x_0} = \frac{1}{4Z-1} = \zeta, \tag{153}$$

we find the non-relativistic squared form of the η function as

$$\eta^2(x) \;=\; (2\gamma)^2\frac{\zeta e^{-2\kappa|x|}}{(1-\zeta e^{-2\kappa|x|})^2}. \tag{154}$$

Using this non-relativistic form of the η function, one is able to take the square root of such function in order to obtain the analytical form of the non-relativistic Hartree-Fock eigenfunction for the helium bound state as

$$\Psi^{NR}_{HF}(x) \;=\; 2\gamma\sqrt{\zeta}\frac{e^{-\kappa|x|}}{1-\zeta e^{-2\kappa|x|}}. \tag{155}$$

We recover the non-relativistic Hartree-Fock bound-state wavefunction obtained by Traore, Giner and Toulouse, Eq. (145) as we expected. We now have to develop this expression in the basis-set of the Hermite-Gaussian functions as in the hydrogen-like case.

VII. CONCLUSION AND FURTHER DEVELOPMENTS

In this report we presented an analytical development of the Dirac equation over a one-dimensional toy model. We compared this analytical development with a basis set expansion for the free part and the hydrogen-like model and we have verified our analytical results. We have also shown that the first matching condition for defining the action of the delta potential is more interesting than the second one if one wants to compare the analytical results with numerical ones. We also managed to recover the non-relativistic limit even in the case of the one-dimensional model for the Helium atom. After developing the analytical solution of the Hartree-Fock bound state of the helium we still have to develop this model in a basis. Once the expansion will be made it will be possible to develop a full configuration interaction (FCI) code to converge to the one-dimensional bound-state energy of the helium. Then it will be interesting to see the influence of the negative energy states for this numerical result. After reaching a sufficient convergence for the bound-state energy it would be possible to try to develop a functional for DFT thanks to the FCI code and to see the convergence in the one-dimensional model of a fully relativistic energy functional.

[1] K. Steenbergen, E. Pahl and P. Schwerdtfeger, J. Phys. Chem. Lett. **8**, 1407 (2017).
[2] L. Pasteka, E. Eliav, A. Borschevsky, U. Kaldor, and P. Schwerdtfeger, Phys. Rev. Lett. **118**, 023002 (2017).
[3] A. F. B. H. M. E. Engel, S. Keller and R. M. Dreizler, Phys. Rev. A **52**, 2750 (1995).
[4] T. Yanai, H. Iikura, T. Nakajima, Y. Ischikawa and K. Hirao, J. Chem. Phys. **115**, 8267 (2001).
[5] T. Saue and T. Helgaker, J. Comput. Chem. **23**, 814 (2002).
[6] P. Chaix and D. Iracane, J. Phys. B **22**, 3791 (1989).
[7] T. Saue and L. Visscher, in *Theoretical Chemistry and Physics of Heavy and Superheavy Elements*, edited by S. Wilson and U. Kaldor (Kluwer, Dordrecht, 2003), pp. 211–267.
[8] C. Hainzl, M. Lewin, E. Séré and J. P. Solovej, Phys. Rev. A **76**, 052104 (2007).
[9] W. Liu and I. Lindgren, J. Chem. Phys. **139**, 014108 (2013).
[10] J. Toulouse, SciPost Chem. **1**, 2 (2021).
[11] I. R. Lapidus, Am. J. Phys. **51**, 1036 (1983).
[12] J. M. Guilarte, J. M. Munoz-Castaneda, I. Pirozhenko and L. Santamaria-Sanz, Frontiers in Physics **7** (2019).
[13] D. Traore, E. Giner and J. Toulouse, J. Chem. Phys. **156**, 044113 (2022).
[14] P. A. M. Dirac, Royal Society of London **117**, 610 (1928).
[15] F. A. B. Coutinho and Y. Nogami, Phys. Rev. A **36**, 1008 (1987).
[16] D. R. Herschbach, J. Chem. Phys. **84**, 838 (1986).
[17] R. Subramanian and K. V. Bhagwat, J. Phys. C **5**, 798 (1972).
[18] R. J. Hughes, Rep. Math. Phys. **39**, 425 (1997).
[19] F. Fillion-Gourdeau, E. Lorin and A. D. Bandrauk, J. Phys. A **45**, 215304 (2012).
[20] M. G. Calkin, D. Kiang and Y. Nogami, Am. J. Phys. **55**, 737 (1987).
[21] B. H. J. McKellar and G. J. Stephenson, Jr., Phys. Rev. C **35**, 2262 (1987).
[22] Y. Nogami and D. J. Beachey, Europhysics Letters **2**, 661 (1986).
[23] K. G. Dyall and K. Fægri, Jr., *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, 2007).

Appendix A: Second Matching Condition

In this part one will rederive all the equations obtained in the first matching condition part but using the second matching condition defined in Eq. (36). As previously we have $\lambda = Z/2c$ but now instead of λ, we will see that in the equations, λ will be replaced by $\tan(\lambda)$. Then the first matching condition can always be recovered by using the transformation $\lambda \to \arctan(\lambda)$ in the second matching condition results. Then, because $\lambda = Z/(2c)$ it has the same non-relativistic limit as $\arctan(\lambda)$, then no matter the matching condition, the non-relativistic limit is always the same.

1. Bound state

Starting from Eqs. (40) and (41), the second matching condition at $x = 0$ gives

$$A\begin{pmatrix} 1 \\ \frac{kc}{\varepsilon_k+mc^2} \end{pmatrix} = \begin{pmatrix} \cos(2\lambda) & \mathrm{i}\sin(2\lambda) \\ \mathrm{i}\sin(2\lambda) & \cos(2\lambda) \end{pmatrix} B\begin{pmatrix} 1 \\ \frac{-kc}{\varepsilon_k+mc^2} \end{pmatrix}, \tag{A1}$$

leading to $A = B$ and $\kappa = mc\sin(2\lambda)$, assuming that $\lambda < \pi/4$. There is a single electron bound state with energy [15]

$$\tilde{\varepsilon}_0 = mc^2\cos(2\lambda), \tag{A2}$$

and wave function

$$\tilde{\psi}_0(x) = A\begin{pmatrix} 1 \\ \mathrm{i}\tan(\lambda)\frac{x}{|x|} \end{pmatrix} e^{-\kappa|x|}, \tag{A3}$$

with $A = \sqrt{\kappa/(1+\tan(\lambda)^2)} = \sqrt{2mc\sin(\lambda)\cos(\lambda)^3}$.

In the non-relativistic limit, $c \to \infty$ or $\lambda \to 0$, the energy has the expansion

$$\tilde{\varepsilon}_0 = mc^2 - \frac{mZ^2}{2} + \frac{mZ^4}{24c^2} + O\left(\frac{1}{c^4}\right), \tag{A4}$$

where the first relativistic correction is three times smaller compared to Eq. (46). In the same limit, we correctly recover the non-relativistic ground-state wave function of the 1D hydrogen-like atom: $\psi_0(x) = \sqrt{mZ}\begin{pmatrix}1\\0\end{pmatrix}e^{-mZ|x|}$.

2. Continuum positive states

With the same method as in the first matching condition we obtain the electronic wave function of the continuum as

$$\begin{aligned}\tilde{\psi}^g_{+,k}(x) = \; & A_k\left[\begin{pmatrix} 1 \\ \frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{\mathrm{i}kx} + \frac{kc-\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)}\begin{pmatrix} 1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc-\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)}\begin{pmatrix} 1 \\ \frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} 1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(-x),\end{aligned} \tag{A5}$$

for the *gerade* one, and for the *ungerade*

$$\begin{aligned}\tilde{\psi}^u_{+,k}(x) = \; & B_k\left[\begin{pmatrix} -1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{\mathrm{i}kx} + \frac{kc+\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)}\begin{pmatrix} 1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(x) + \\ & \left[\frac{kc+\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)}\begin{pmatrix} -1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{\mathrm{i}kx} + \begin{pmatrix} 1 \\ -\frac{kc}{\tilde{\varepsilon}_k+mc^2} \end{pmatrix} e^{-\mathrm{i}kx}\right]\theta(-x).\end{aligned} \tag{A6}$$

We will use the notations

$$\xi^g_{+,k} = \frac{kc - \mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda) + \mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)} \tag{A7}$$

$$\xi^u_{+,k} = \frac{kc + \mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda) + \mathrm{i}\tilde{\varepsilon}_k\sin(2\lambda)}. \tag{A8}$$

One can see that both complex numbers $\xi^g_{+,k}$ and $\xi^u_{+,k}$ have the same norm, $|\xi^g_{+,k}|^2 = |\xi^u_{+,k}|^2 = 1$. Then, one can write them by using phase factors τ_1 and τ_2 such that,

$$\begin{cases} e^{-2i\tau_1} = \xi^g_{+,k} \\ e^{-2i\tau_2} = \xi^u_{+,k} \end{cases}. \tag{A9}$$

With these notations we obtain the two electronic wave-functions as

$$\tilde{\psi}^g_{+,k}(x) = E_k \begin{pmatrix} \cos(k|x| + \tau_1) \\ \frac{ikc}{\tilde{\varepsilon}_k + mc^2} \frac{x}{|x|} \sin(k|x| + \tau_1) \end{pmatrix} \qquad \tilde{\psi}^u_{+,k}(x) = F_k \begin{pmatrix} \frac{ikc}{\tilde{\varepsilon}_k - mc^2} \frac{x}{|x|} \sin(k|x| + \tau_2) \\ \cos(k|x| + \tau_2) \end{pmatrix}, \tag{A10}$$

with the normalization constants E_k and F_k as

$$E_k = \sqrt{\frac{\tilde{\varepsilon}_k + mc^2}{2\pi\tilde{\varepsilon}_k}} \qquad \text{and} \qquad F_k = \sqrt{\frac{\tilde{\varepsilon}_k - mc^2}{2\pi\tilde{\varepsilon}_k}}. \tag{A11}$$

And we obtain the same non-relativistic limit as in the first matching condition.

3. Continuum negative states

With the same method as in the first matching condition we obtain the positronic wave function of the continuum as

$$\begin{aligned} \tilde{\psi}^g_{-,k}(x) = \; & C_k \left[\begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ -1 \end{pmatrix} e^{ikx} + \frac{kc - imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)} \begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{-ikx} \right] \theta(x) + \\ & \left[\frac{kc - imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)} \begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ -1 \end{pmatrix} e^{ikx} + \begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{-ikx} \right] \theta(-x), \end{aligned} \tag{A12}$$

for the *gerade* one, and for the *ungerade*

$$\begin{aligned} \tilde{\psi}^u_{-,k}(x) = \; & D \left[\begin{pmatrix} -\frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{ikx} + \frac{kc + imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)} \begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{-ikx} \right] \theta(x) + \\ & \left[\frac{kc + imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)} \begin{pmatrix} -\frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{ikx} + \begin{pmatrix} \frac{kc}{\tilde{\varepsilon}_k + mc^2} \\ 1 \end{pmatrix} e^{-ikx} \right] \theta(-x). \end{aligned} \tag{A13}$$

We will use the notations

$$\xi^g_{-,k} = \frac{kc - imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)} \tag{A14}$$

$$\xi^u_{-,k} = \frac{kc + imc^2 \sin(2\lambda)}{kc\cos(2\lambda) - i\tilde{\varepsilon}_k \sin(2\lambda)}. \tag{A15}$$

One can see that both complex numbers $\xi^g_{-,k}$ and $\xi^u_{-,k}$ have the same norm, $|\xi^g_{-,k}|^2 = |\xi^u_{-,k}|^2 = 1$. Then, one can write them by using phase factors τ_1 and τ_2 such that,

$$\begin{cases} e^{2i\tau_1} = \xi^u_{-,k} \\ e^{2i\tau_2} = \xi^g_{-,k} \end{cases}. \tag{A16}$$

Thanks to these notation we obtain the two electronic wave-functions as

$$\tilde{\psi}^g_{-,k}(x) = F_k \begin{pmatrix} \cos(k|x| - \tau_2) \\ \frac{ikc}{-\tilde{\varepsilon}_k + mc^2} \frac{x}{|x|} \sin(k|x| - \tau_2) \end{pmatrix} \qquad \tilde{\psi}^u_{-,k}(x) = E_k \begin{pmatrix} \frac{ikc}{-\tilde{\varepsilon}_k - mc^2} \frac{x}{|x|} \sin(k|x| - \tau_1) \\ \cos(k|x| - \tau_1) \end{pmatrix}, \tag{A17}$$

with the normalization constants E_k and F_k as

$$E_k = \sqrt{\frac{\tilde{\varepsilon}_k + mc^2}{2\pi\tilde{\varepsilon}_k}} \qquad \text{and} \qquad F_k = \sqrt{\frac{\tilde{\varepsilon}_k - mc^2}{2\pi\tilde{\varepsilon}_k}}. \tag{A18}$$

And we obtain the same non-relativistic limit as in the first matching condition.

4. Link with the article of Guilarte *et al.*

From the wave functions derived in the second matching conditions, Eq. (A5)(A6), one can recover and show that we obtain the same results as in the article of 2019, Guilarte *et al.* [12]. They determined the eigenfunctions of the continuum for the electronic and positronic eigenfunctions of the one-dimensional hydrogen with delta interactions. Using a scattering approach, they obtained the following eigenfunctions

$$\Psi^R(x,k)=\begin{cases}u_+(k)e^{\mathrm{i}kx}+\rho_R(k)\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}, & x>0\\ \sigma_R(k)u_+(k)e^{\mathrm{i}kx}, & x<0\end{cases};\ \text{and}\quad \Psi^L(x,k)=\begin{cases}\sigma_L(k)\boldsymbol{\sigma^3}u_+(k)e^{-\mathrm{i}kx}, & x>0\\ \rho_L(k)u_+(k)e^{\mathrm{i}kx}+\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}, & x<0\end{cases}.$$

with R for the "right" eigenfunction, the one scattering from the $x>0$ half-line and L for the "left" eigenfunction, the one scattering from the $x<0$ half-line. The quantities introduced are

$$u_+(k) = \begin{pmatrix}1\\ \frac{kc}{\varepsilon_k+mc^2}\end{pmatrix} \tag{A19}$$

$$\sigma_R(k)=\sigma_L(k) = \frac{kc}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)} \tag{A20}$$

$$\rho_R(k)=\rho_L(k) = -\frac{\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)}. \tag{A21}$$

Then by taking the sum and the difference of these two functions one can rederive the wave function that we build with our method

$$\begin{aligned}\tilde{\psi}^g_{+,k}(x) &= \Psi^R(x,k)+\Psi^L(x,k)\\ &= \left[u_+(k)e^{\mathrm{i}kx}+\Big[\rho_R(k)+\sigma_L(k)\Big]\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(x)+\left[\Big[\sigma_R(k)+\rho_L(k)\Big]u_+(k)e^{\mathrm{i}kx}+\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(-x)\\ &= \left[u_+(k)e^{\mathrm{i}kx}+\frac{kc-\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)}\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(x)+\left[\frac{kc-\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)}u_+(k)e^{\mathrm{i}kx}+\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(-x),\end{aligned}$$

for the *gerade* electronic wave function and

$$\begin{aligned}\tilde{\psi}^u_{+,k}(x) &= \Psi^L(x,k)-\Psi^R(x,k)\\ &= \left[-u_+(k)e^{\mathrm{i}kx}+\Big[\sigma_L(k)-\rho_R(k)\Big]\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(x)+\left[\Big[\rho_L(k)-\sigma_R(k)\Big]u_+(k)e^{\mathrm{i}kx}+\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(-x)\\ &= \left[-u_+(k)e^{\mathrm{i}kx}+\frac{kc+\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)}\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(x)+\left[-\frac{kc+\mathrm{i}mc^2\sin(2\lambda)}{kc\cos(2\lambda)+\mathrm{i}\varepsilon_k\sin(2\lambda)}u_+(k)e^{\mathrm{i}kx}+\boldsymbol{\sigma}_z u_+(k)e^{-\mathrm{i}kx}\right]\theta(-x).\end{aligned}$$

for the *ungerade* wave function.

And the same linear combination can be done in order to recover our positronic wave function from theirs.

Appendix B: Derivation of the vacuum polarization density for the commutator definition

Because the vacuum polarization density is even with respect to the spatial symmetry $x \to -x$, we can calculate it on the half-line $x \in \mathbb{R}^+$. We will use the wave functions defined in Eq. (47)-(48) for the electronic orbitals and Eq. (56)-(57) for the positronic ones. In this subspace the electronic *gerade* and *ungerade* orbitals have the form,

$$\tilde{\psi}^g_{+,k}(x) = A\left[\begin{pmatrix}1\\a\end{pmatrix}e^{ikx} + \zeta^g_{+,k}\begin{pmatrix}1\\-a\end{pmatrix}e^{-ikx}\right] \quad ; \quad \tilde{\psi}^u_{+,k}(x) = A\left[\begin{pmatrix}-1\\-a\end{pmatrix}e^{ikx} + \zeta^u_{+,k}\begin{pmatrix}1\\-a\end{pmatrix}e^{-ikx}\right]$$

with

$$a = \frac{kc}{\tilde{\varepsilon}_k + mc^2}. \tag{B1}$$

We can then calculate the second term in the Eq. (91),

$$\sum_{p\in \mathrm{PS}} \tilde{\psi}^\dagger_p(x)\tilde{\psi}_p(x) = \tilde{\psi}^\dagger_0(x)\tilde{\psi}_0(x) + \sum_{p\in\{p\in\mathrm{PS}|\varepsilon_p\geqslant mc^2\}} \tilde{\psi}^\dagger_p(x)\tilde{\psi}_p(x) \tag{B2}$$

the first term is the bound state term due to the presence of the Dirac potential,

$$\begin{aligned}\tilde{\psi}^\dagger_0(x)\tilde{\psi}_0(x) &= \frac{\kappa}{1+\lambda^2}(1+\lambda^2)e^{-2\kappa x}\\ &= \kappa e^{-2\kappa x}.\end{aligned} \tag{B3}$$

Then the continuum must be calculated as an integral over all $k \in \mathbb{R}^+$ for the *gerade* part,

$$\begin{aligned}\sum_{p\in\{p\in\mathrm{PS}|\varepsilon_p\geqslant mc^2\}} \tilde{\psi}^{\dagger,g}_p(x)\tilde{\psi}^g_p(x) &= \int_0^{+\infty} \mathrm{d}k A^2\left((1+a^2)(1+|\zeta^g_{+,k}|^2) + (1-a^2)\left[\zeta^g_{+,k}e^{-2ikx} + \zeta^{g,*}_{+,k}e^{2ikx}\right]\right)\\ &= \int_0^{+\infty}\mathrm{d}k\frac{1}{4\pi}\left(2 + \frac{1-a^2}{1+a^2}\left[\zeta^g_{+,k}e^{-2ikx} + \zeta^{g,*}_{+,k}e^{2ikx}\right]\right)\\ &= \int_0^{+\infty}\mathrm{d}k\frac{1}{4\pi}\left(2 + \frac{mc^2}{\varepsilon_k}\left[\zeta^g_{+,k}e^{-2ikx} + \zeta^{g,*}_{+,k}e^{2ikx}\right]\right)\end{aligned} \tag{B4}$$

and the *ungerade* part,

$$\sum_{p\in\{p\in\mathrm{PS}|\varepsilon_p\geqslant mc^2\}} \tilde{\psi}^{\dagger,u}_p(x)\tilde{\psi}^u_p(x) = \int_0^{+\infty}\mathrm{d}k\frac{1}{4\pi}\left(2 - \frac{mc^2}{\varepsilon_k}\left[\zeta^u_{+,k}e^{-2ikx} + \zeta^{u,*}_{+,k}e^{2ikx}\right]\right). \tag{B5}$$

The positive continuum can then be derived as,

$$\begin{aligned}\sum_{p\in\mathrm{PS}} \tilde{\psi}^\dagger_p(x)\tilde{\psi}_p(x) &= \kappa e^{-2\kappa x} + \int_0^{+\infty}\mathrm{d}k\frac{1}{4\pi}\left(4 + \frac{mc^2}{\varepsilon_k}\left[(\zeta^g_{+,k} - \zeta^u_{+,k})e^{-2ikx} + (\zeta^{g,*}_{+,k} - \zeta^{u,*}_{+,k})e^{2ikx}\right]\right)\\ &= \kappa e^{-2\kappa x} + \int_0^{+\infty}\mathrm{d}k\frac{1}{\pi}\left(1 + \mathrm{i}\frac{mc^2}{2\varepsilon_k}\left[\frac{e^{2ikx}2mc^2\lambda}{kc(1-\lambda^2) - 2\mathrm{i}\varepsilon_k\lambda} - \frac{e^{-2ikx}2mc^2\lambda}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\right]\right).\end{aligned} \tag{B6}$$

We need then to derive the negative continuum density in the $\mathbb{R}^+$ subspace. We have already done this calculation right above with the positive continuum density. It gives,

$$\sum_{p\in\mathrm{NS}} \tilde{\psi}^\dagger_p(x)\tilde{\psi}_p(x) = \int_0^{+\infty}\mathrm{d}k\frac{1}{\pi}\left(1 - 2\mathrm{i}mc^2\lambda\frac{mc^2}{2\varepsilon_k}\left[\frac{e^{-2ikx}}{kc(1-\lambda^2) - 2\mathrm{i}\varepsilon_k\lambda} - \frac{e^{2ikx}}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\right]\right), \tag{B7}$$

The total density is now assembled by doing the difference of the negative continuum and the positive one,

$$\begin{aligned}\tilde{n}^{c,vp}(x) &= -\frac{\kappa}{2}e^{-2\kappa x} + \frac{1}{2}\int_0^{+\infty}\mathrm{d}k\frac{\mathrm{i}mc^2}{2\pi\varepsilon_k}2mc^2\lambda\left[\frac{e^{-2ikx} - e^{2ikx}}{kc(1-\lambda^2) - 2\mathrm{i}\varepsilon_k\lambda} - \frac{e^{2ikx} - e^{-2ikx}}{kc(1-\lambda^2)+2\mathrm{i}\varepsilon_k\lambda}\right]\\ &= -\frac{\kappa}{2}e^{-2\kappa x} + \frac{1}{2}\int_0^{+\infty}\mathrm{d}k\frac{\mathrm{i}mc^2}{2\pi\varepsilon_k}2mc^2\lambda\frac{2kc(1-\lambda^2)}{[kc(1-\lambda^2)]^2 + [2\varepsilon_k\lambda]^2}\left(e^{-2ikx} - e^{2ikx}\right)\\ &= -\frac{\kappa}{2}e^{-2\kappa|x|} + \int_0^{+\infty}\frac{\mathrm{d}k}{\pi}\frac{\kappa}{k^2+\kappa^2}\frac{\varepsilon_0}{\varepsilon_k}k\sin(2k|x|).\end{aligned} \tag{B8}$$