Laboratoire de Chimie Théorique

Development of a Relativistic One-Dimensional Model Including Quantum Electrodynamics Effects

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Thesis work with Julien Toulouse

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Introduction

Why are we interested in relativistic quantum chemistry?

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- Important for fast-moving particles: average electron velocity in hydrogen-like ground-state

$$v = (\alpha Z)\, c, \quad \text{with } \alpha \approx 1/137$$

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- Explains some physical properties of heavy elements

1. yellow color of gold

   P. Pyykkö, ACIE, (2004)
   P. Romaniello and P. L. de Boeij, JCP, (2005)

2. lead-acid battery electro-chemical potential

   R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö and P. Zaleski-Ejgierd, PRL, (2011)

3. liquid state of mercury at room temperature

   K. Steenbergen, E. Pahl and P. Schwerdtfeger, JPCL., (2017)

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- Includes the electron spin and spin-orbit coupling

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Free particle energy

- Non relativistic:

$$E = \frac{p^2}{2m} \Rightarrow E \in [0, +\infty),$$

- Relativistic:

$$E^2 = m^2c^4 + c^2p^2 \Rightarrow E \in (-\infty, -mc^2] \cup [mc^2, +\infty),$$

Free particle energy

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- Relativistic:

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Link between both

- Taylor expansion of the square root for the positive part

$$E = \underbrace{mc^2}_{\text{Rest mass}} + \underbrace{\frac{p^2}{2m}}_{\text{Kinetic energy}} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{1st order}} + \dots$$

From classical to quantum - Klein-Gordon equation

$$
\begin{aligned}
E^2 &= p^2c^2 + m^2c^4 \\
-\hbar^2\partial_t^2 &= -\hbar^2c^2\nabla^2 + m^2c^4
\end{aligned}
$$

- Negative energy solutions give negative probability...
- Does not include spin

Development of the equation

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$$

- Negative energy solutions give negative probability...
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From classical to quantum - Dirac equation

$$
\begin{aligned}
E &= \pm c\sqrt{p^2 + m^2c^2} \\
i\hbar\partial_t &= c\sqrt{p^2 + m^2c^2}
\end{aligned}
$$

- Expand the term under the square root as a perfect square:

$$
\begin{aligned}
p^2 + m^2c^2 &= (\vec{\boldsymbol{\alpha}} \cdot \vec{p} + \boldsymbol{\beta} mc)^2 \\
i\hbar\partial_t &= c\,\vec{\boldsymbol{\alpha}} \cdot \vec{p} + \boldsymbol{\beta} mc^2
\end{aligned}
$$

Dirac operator

$$\boldsymbol{D}_0(x) = c\,(\vec{\boldsymbol{\alpha}} \cdot \vec{p}) + \boldsymbol{\beta}\, mc^2, \tag{1}$$

- $\vec{\boldsymbol{\alpha}} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$ where $\vec{\sigma} = \{\sigma_x,\ \sigma_y,\ \sigma_z\}$ are the Pauli matrices
- $\boldsymbol{\beta} = \begin{pmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{pmatrix}$

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Dirac eigenvalue equation

$$(\boldsymbol{D}_0(x) + V(x))\,\boldsymbol{\psi}(x) = \mathscr{E}\boldsymbol{\psi}(x) \tag{2}$$

- $\boldsymbol{\psi} = \begin{pmatrix} \psi^{\mathrm{L}} \\ \psi^{\mathrm{S}} \end{pmatrix}$ where $\psi^{\mathrm{L/S}} = \begin{pmatrix} \psi_{\alpha}^{\mathrm{L/S}} \\ \psi_{\beta}^{\mathrm{L/S}} \end{pmatrix}$
- $\mathscr{E}$ is the energy of the state $\boldsymbol{\psi}$

Hydrogenic spectrum

Non-relativistic spectrum

$$\mathscr{H}(x) = -\frac{\Delta}{2m} + \mathrm{V}(x) \tag{3}$$

Spectrum:

- If $\mathscr{E} > 0$: continuum
- If $\mathscr{E} < 0$: bound states

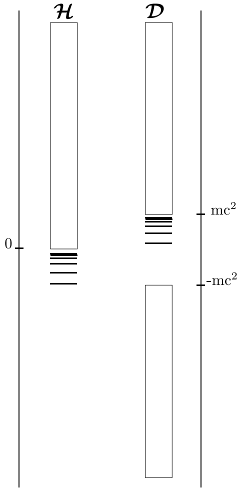
Relativistic spectrum

$$\boldsymbol{D}(x) = c\,(\vec{\boldsymbol{\alpha}} \cdot \vec{p}) + \boldsymbol{\beta}\; mc^2 + \mathrm{V}(x) \tag{4}$$

Spectrum:

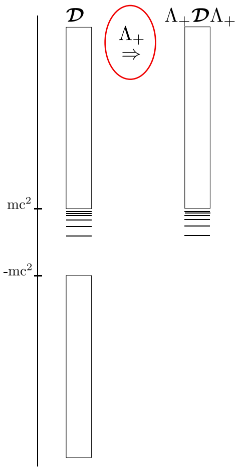
- If $\mathscr{E} \in (-\infty, -mc^2] \cup [mc^2, +\infty)$: continuum
- If $\mathscr{E} \in (-mc^2, mc^2)$: bound states

$\Rightarrow$ Negative continuum spectrum

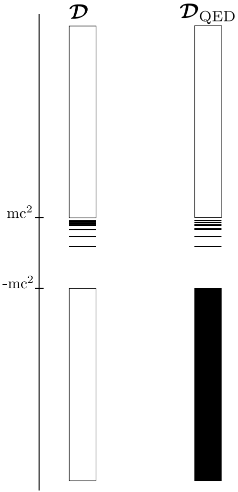


How to deal with the negative continuum

- No-pair approximation



- QED description



Is QED really important?

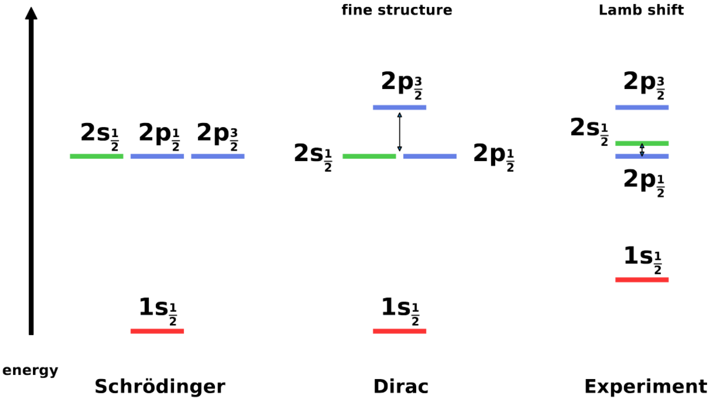


Figure 1: Lamb shift in hydrogen spectra[1]

[1] M. Salman, Ph.D. thesis (2022)

Motivations for the model

- We need accurate QED calculations for high precision spectroscopy
- So far, state-of-the-art relativistic quantum chemistry for many-electrons systems is based on no-pair approximation
- Next challenge in QC: can we go beyond the NPA?

Goal

Use a model system to understand how to develop new methods based on QED.

To do list:

- ☐ Study the 1D hydrogen and compute the QED effects.
- ☐ Study how to approximate these quantities in a finite basis set.
- ☐ Use our insight to solve the 3D problem.

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The 1D Operator

Free 1D Dirac operator

$$\mathbf{D}_0(x) = -\mathrm{i}c\sigma_x \frac{\mathrm{d}}{\mathrm{d}x} + \sigma_z mc^2 \quad (5)$$

Lapidus, AJP, (1983) ; T. Audinet, J. Toulouse, JCP, (2023)

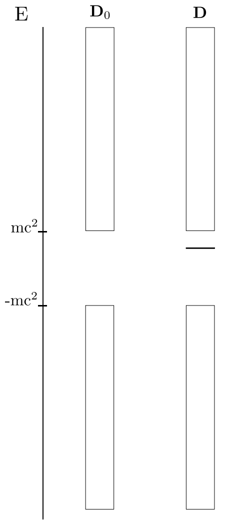
Dirac eigenvalue equations

$$\mathbf{D}_0(x)\psi_p^0(x) = \varepsilon_p \psi_p^0(x) \quad (6)$$

- Continuum: $\varepsilon_k = \pm\sqrt{m^2c^4 + k^2c^2}$

$$\left(\mathbf{D}_0(x) - Z\delta(x)\right)\psi_p^Z(x) = \varepsilon_p \psi_p^Z(x) \quad (7)$$

- Bound State: $\varepsilon_b < mc^2$
- Continuum: $\varepsilon_k = \pm\sqrt{m^2c^4 + k^2c^2}$

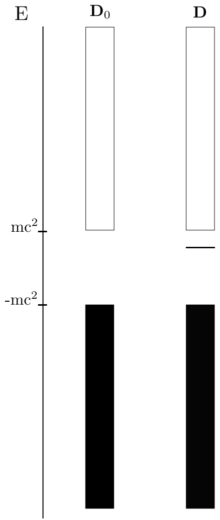


- Spontaneous creation of electron positron pairs due to the external potential
- Creates a charge density that will interact with the bound states through the two-electron interaction

Vacuum Polarization Density

$$n^{\mathrm{vp}}(x) = \sum_{\varepsilon_p < 0} \psi_p^{Z\dagger}(x)\psi_p^{Z}(x) - \sum_{\varepsilon_p < 0} \psi_p^{0\dagger}(x)\psi_p^{0}(x)$$

- In 3D this quantity diverges, needs to be renormalized
- We want to have a better understanding of this quantity and its influence on the energy spectrum



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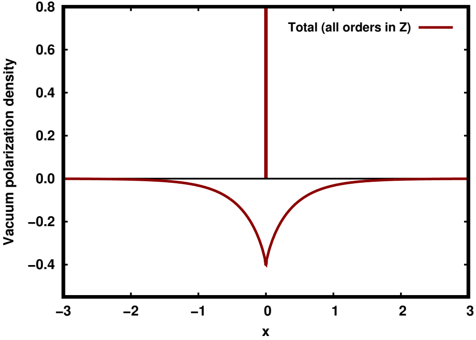
Vacuum Polarization Density

$$n^{\mathrm{vp}}(x) = \sum_{\varepsilon_p<0} \psi_p^{Z\dagger}(x)\psi_p^{Z}(x) - \sum_{\varepsilon_p<0} \psi_p^{0\dagger}(x)\psi_p^{0}(x) = \mathcal{N}_0^{\mathrm{vp}}\delta(x) + n_{\mathrm{reg}}^{\mathrm{vp}}(x) \quad (8)$$

Audinet, Morellini, Levitt, Toulouse, JPA, (2025)



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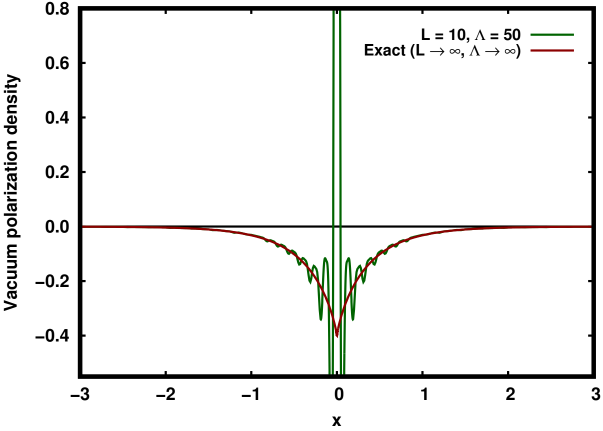
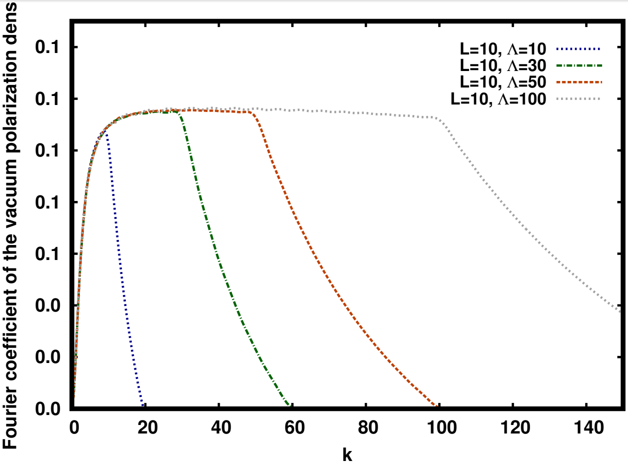
Plane waves basis

$$\forall\, x \in \mathbb{R}, k \in \frac{2\mathbb{Z}\pi}{L}, |k| \leq \Lambda, \quad \chi_k(x) = \frac{1}{\sqrt{L}} e^{ikx} \tag{9}$$



Regularization with Fourier Transform

$$n^{vp}_{reg}(x) = \mathscr{F}^{-1}\Big[\mathscr{F}[n^{vp}](k) - \mathscr{F}[n^{vp}](k_{max})\Big]\theta(k_{max} - k) \qquad (10)$$



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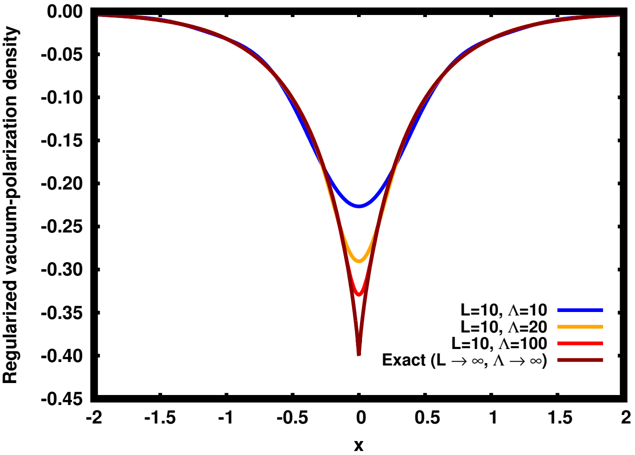

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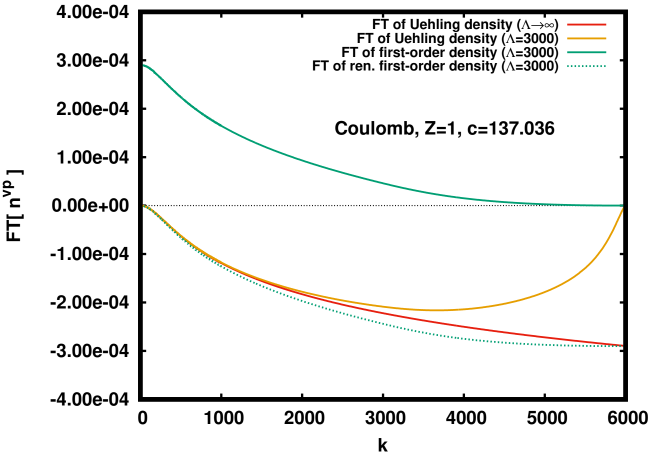
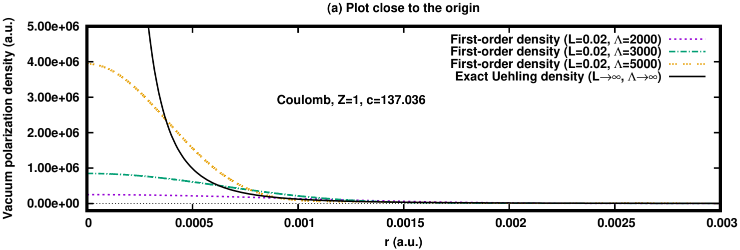
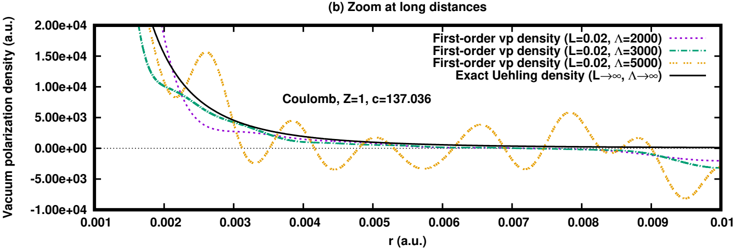
The truncated first-order vacuum-polarization density

$$\hat{n}_{\Lambda}^{\mathrm{vp},(1)}(\mathbf{k}) = \hat{n}_{\Lambda}^{\mathrm{vp},\mathrm{U}}(\mathbf{k}) + \hat{n}_{\Lambda}^{\mathrm{vp},\mathrm{renorm}}(\mathbf{k}) \qquad (12)$$

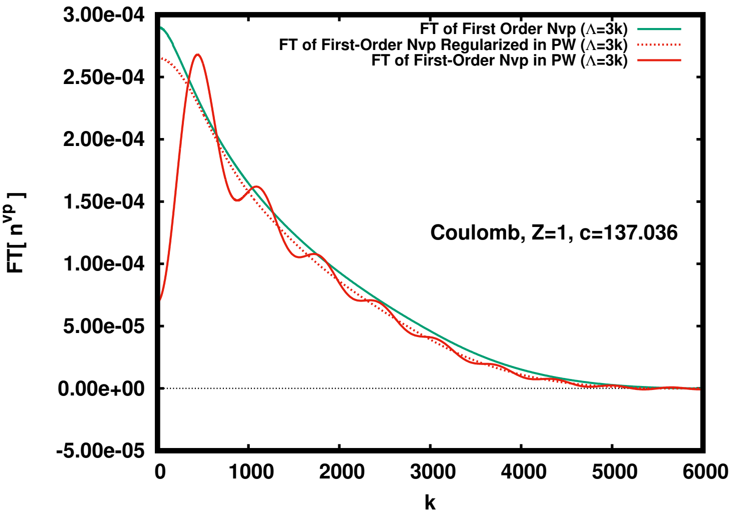


Plane-wave implementation – Real space





Plane-wave implementation – Regularization



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To do list:

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- ✓ Study how to approximate these quantities in a finite basis set.
- ⊟ Use our insight to solve the 3D problem (in progress).

- We developed an effective QED theory including electron-positron pairs.
- Some singularities appears in a finite basis.
- This 1D model help us to understand this problem.
- Promising results for the 3D but limited by the size of the basis.