

ONE DIMENSIONAL MODEL WITH DELTA-TYPE
INTERACTIONS:
DIRAC'S EQUATION WITH QED INTERACTIONS

Timothée AUDINET, Julien TOULOUSE

*Laboratoire de Chimie Théorique, Sorbonne Université and CNRS, F-75005
Paris, France*

Introduction: Relativity

- Relativity has explained some physical properties
 1. yellow color of gold ¹
 2. liquid state of mercury at room temperature ²
- Encounters some heavy problems when facing the quantum electrodynamics (QED) interactions in 3D

| | IP | Error |
|--------------------|--------|---------|
| DC-HF | 7.6892 | -1.5363 |
| DC-CCSD | 9.1164 | -0.1092 |
| DC-CCSD(T) | 9.2938 | 0.0683 |
| DC-CCSDTQP | 9.2701 | 0.0446 |
| +Breit | 9.2546 | 0.0290 |
| +QED | 9.2288 | 0.0032 |
| Experiment [31,32] | 9.2256 | |

Figure 1: IP of gold with different levels of approximation³

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² K. Steenbergen, E. Pahl and P. Schwerdtfeger, *J. Phys. Chem. Lett.* 8, 1407 (2017)

³ P. Schwerdtfeger *et al.*, *Phys. Rev. Lett.* 118, 023002 (2017)

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Why don't we look at a 1D model to have a better understanding?

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Introduction: 1D Model

- 1D model have been shown pretty efficient in understanding a non-relativistic problem ([Diata's talk](#))
- Most of the actual calculation are done with the “no-pair” approximation
- Develop a no-photon effective QED framework⁴

Purposes

- ☐ To develop an analytical solution of the 1D problem
- ☐ To have a better understanding of the physical issues of QED interactions
- ☐ To develop this problem in a finite basis set

⁴P. Chaix and D. Iracane, J. Phys. B 22, 3791 (1989)

3D Dirac's operator

Dirac operator

$$\mathcal{D} = c (\vec{\alpha} \cdot \vec{p}) + \beta mc^2 + V, \quad (1)$$

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

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Dirac equation

$$\mathcal{D}\psi = \mathcal{E}\psi \quad (2)$$

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

Properties of the relativistic Hamiltonian

Non-relativistic spectrum

$$\mathcal{H} = -\frac{\Delta}{2m} + V \quad (3)$$

Spectrum:

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

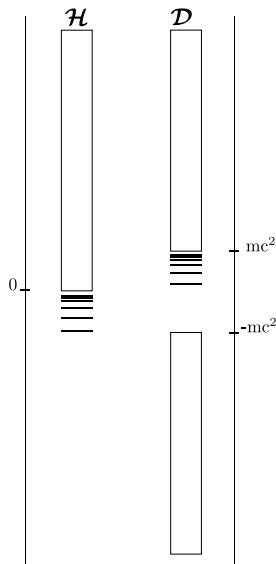
Relativistic spectrum

$$\mathcal{D} = c (\vec{\alpha} \cdot \vec{p}) + \beta mc^2 + V \quad (4)$$

Spectrum:

- If $\mathcal{E} \in (-\infty, -mc^2] \cup [mc^2, +\infty)$: continuum
- If $\mathcal{E} \in (0, mc^2)$: bound states

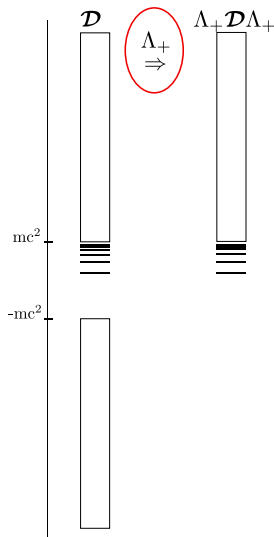
\Rightarrow Negative continuum spectrum



How to deal with the negative continuum

No-pair approximation

- Solving the Dirac equation
- Projecting it on the positive energy part



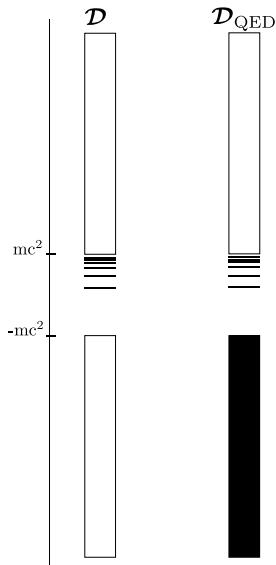
How to deal with the negative continuum

No-pair approximation

- Solving the Dirac equation
- Projecting it on the positive energy part

QED treatment of negative energy electrons

- Solving the Dirac equation
- Filling the negative part with electrons
- QED description of the system



1D Dirac's operator⁵

Free Dirac operator

$$\mathcal{D}_{0,x} = c \boldsymbol{\alpha}_x p_x + \boldsymbol{\beta} mc^2, \quad (5)$$

- From this 1D operator we can make an unitary transformation

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

- Define a new operator $\mathcal{D}'_{0,x} = \mathbf{U} \mathcal{D}_{0,x} \mathbf{U}^{-1} = \begin{pmatrix} \mathbf{D}_0 & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{D}_0 \end{pmatrix}$
- Where

$$\mathbf{D}_0 = c \boldsymbol{\sigma}_x p_x + \boldsymbol{\sigma}_z mc^2$$

is a 2×2 operator!

⁵T. Audinet, J. Toulouse, J. Chem. Phys. 158, 244108 (2023)

1D Dirac's equation

1D Free Dirac operator

$$\mathbf{D}_0 = c \boldsymbol{\sigma}_x p_x + \boldsymbol{\sigma}_z mc^2, \quad (6)$$

- with domain: $\text{Dom}(\mathbf{D}_0) = H^1(\mathbb{R}, \mathbb{C}) \otimes \mathbb{C}^2$
- where: $H^1(\mathbb{R}, \mathbb{C}) = \{\psi \in L^2(\mathbb{R}, \mathbb{C}) | d\psi/dx \in L^2(\mathbb{R}, \mathbb{C})\}$ is the first-order Sobolev space

1D Free Dirac equation

$$\mathbf{D}_0 \psi = \mathcal{E} \psi, \quad (7)$$

- $\mathcal{E}_k = \sqrt{k^2 c^2 + m^2 c^4}$
- $\mathcal{E}_k = -\sqrt{k^2 c^2 + m^2 c^4}$

$$\psi_{+,k}^g(x) = A_k \begin{pmatrix} \cos(kx) \\ i s_k \sin(kx) \end{pmatrix}$$

$$\psi_{-,k}^g(x) = A_k \begin{pmatrix} i s_k \cos(kx) \\ \sin(kx) \end{pmatrix}$$

- where s_k goes to zero when $c \rightarrow \infty$

Hydrogen-like Dirac operator

$$\mathbf{D} = \mathbf{D}_0 - Z\delta(x)\mathbb{I}_2, \quad (8)$$

- Ambiguity on the action of a delta distribution on discontinuous functions
- The action of \mathbf{D} is defined such that $\mathbf{D}\psi = \mathbf{D}_0\psi$, $\forall x \neq 0$
- with domain

$$\text{Dom}(\mathbf{D}) = \{\tilde{\psi} \in H^1(\mathbb{R} \setminus \{0\}, \mathbb{C}) \otimes \mathbb{C}^2 \mid \tilde{\psi}(0^+) = \mathcal{M}\tilde{\psi}(0^-)\}$$

- where \mathcal{M} enforces the continuity of the density $\tilde{\psi}^\dagger \tilde{\psi}$ at $x = 0$

$$\mathcal{M} = \begin{pmatrix} \cos \theta & i \sin \theta \\ i \sin \theta & \cos \theta \end{pmatrix} ; \text{ with } \theta = 2 \arctan(Z/2c) \quad (9)$$

Hydrogen-like Dirac equation

$$\mathbf{D}\tilde{\psi} = \tilde{\mathcal{E}}\tilde{\psi}, \quad (10)$$

- This Hamiltonian has a single bound state

$$\tilde{\psi}_1(x) = A \begin{pmatrix} 1 \\ i\lambda \operatorname{sgn}(x) \end{pmatrix} e^{-\kappa|x|} \quad (11)$$

- with energy $\tilde{\mathcal{E}}_1 = mc^2 \frac{1-\lambda^2}{1+\lambda^2}$, with $\lambda = \frac{Z}{2c}$
- Non-relativistic limit of the bound-state eigenfunction

$$\lim_{c \rightarrow \infty} \tilde{\psi}_1(x) = \sqrt{mZ} \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-mZ|x|} \quad (12)$$

Summary: Solving the one-electron 1D Dirac equation

Free Dirac equation

$$\mathbf{D}_0 \psi_p = \mathcal{E}_p \psi_p \quad (13)$$

Spectrum:

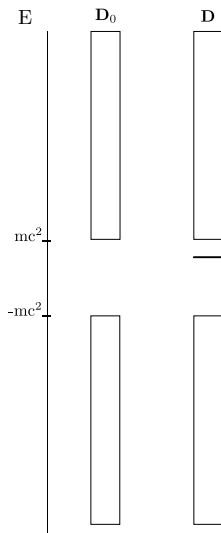
- Continuum: $\mathcal{E}_k = \pm \sqrt{m^2 c^4 + k^2 c^2}$

Hydrogen-like Dirac equation

$$\begin{aligned} \mathbf{D} \tilde{\psi}_p &= (\mathbf{D}_0 - Z\delta(x)) \tilde{\psi}_p \\ &= \tilde{\mathcal{E}}_p \tilde{\psi}_p \end{aligned} \quad (14)$$

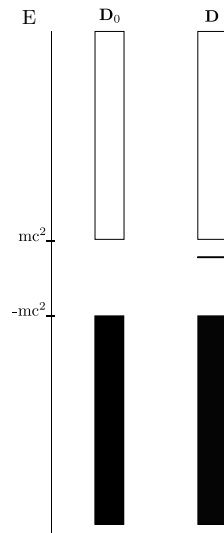
Spectrum:

- Bound State: $\tilde{\mathcal{E}}_b = mc^2 \frac{1-\lambda^2}{1+\lambda^2}$ with $\lambda = Z/2c$
- Continuum: $\tilde{\mathcal{E}}_k = \pm \sqrt{m^2 c^4 + k^2 c^2}$



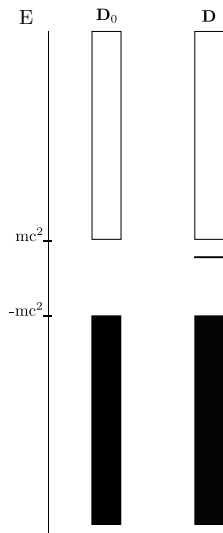
QED Effects

- Need to describe an infinite number of particles
- Need to take into account the two-electron interaction



QED Effects

- Need to describe an infinite number of particles
- Need to take into account the two-electron interaction
- How to compute the energy of an infinite amount of particles? It diverges
- Define a reference \rightarrow the free vacuum

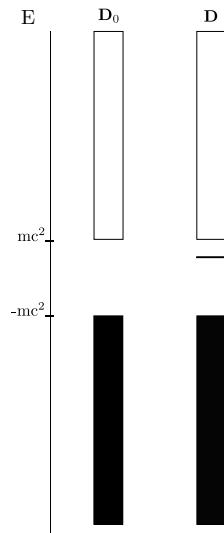


Vacuum Polarization

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

$$\mathbf{n}_1^{\text{vp}}(x, x') = \sum_{\tilde{\mathcal{E}}_p < 0} \tilde{\psi}_p(x) \tilde{\psi}_p^\dagger(x') - \sum_{\mathcal{E}_p < 0} \psi_p(x) \psi_p^\dagger(x')$$

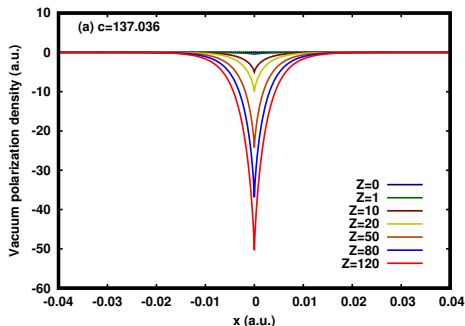
- In 3D this quantity diverges, needs to be renormalized
- We want to have a better understanding of this quantity and its influence on the energy spectrum



Vacuum Polarization Density – Analytical form

Analytical expression

$$\begin{aligned} n^{\text{vp}}(x) &= \text{tr} [n_1^{\text{vp}}(x, x)] = \sum_{\tilde{\mathcal{E}}_p < 0} \tilde{\psi}_p^\dagger(x) \tilde{\psi}_p(x) - \sum_{\mathcal{E}_p < 0} \psi_p^\dagger(x) \psi_p(x) \\ &= - \int_0^\infty \frac{dk}{\pi} \frac{\kappa}{k^2 + \kappa^2} \left(\kappa \cos(2k|x|) - \frac{\tilde{\mathcal{E}}_b}{\mathcal{E}_k} \sin(2k|x|) \right) \end{aligned}$$



Vacuum Polarization Density – Convergence test

Hermite-Gaussian functions

$$\forall x \in \mathbb{R}, f_n^\alpha(x) = N_n^\alpha H_n(\sqrt{2\alpha}x) e^{-\alpha x^2} \quad (15)$$

- Orthonormal basis set of $L^2(\mathbb{R}, \mathbb{C})$ in the limit $n \rightarrow \infty$

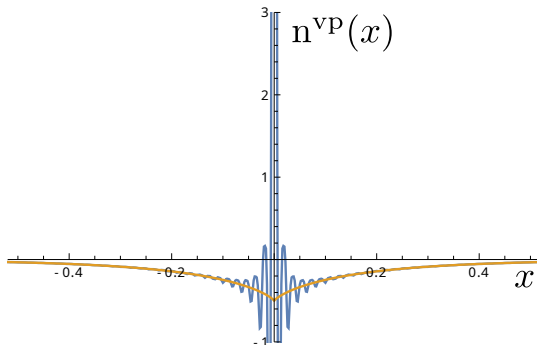
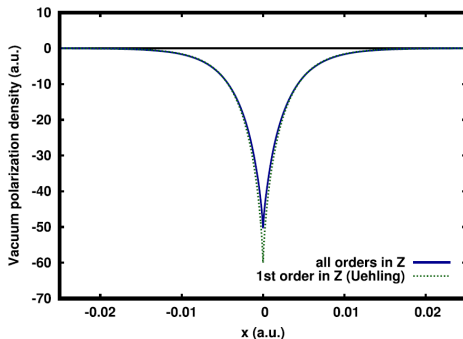


Figure 2: Vacuum polarization density $n^{\text{vp}}(x)$ as a function of x for $c = 1$ and $n_{\text{max}} = 800$.

Uehling Density

First-order vacuum polarization density in Z

$$n^{\text{vp},(1)}(x) = -\frac{Zm}{\pi} \int_1^\infty dt \frac{e^{-2mc|x|t}}{t\sqrt{t^2-1}} \quad (16)$$



First-order correction energy

One-body density matrix for any system

$$\mathbf{n}_1(x, x') = \mathbf{n}_1^{\text{el}}(x, x') + \mathbf{n}_1^{\text{vp}}(x, x') \quad (17)$$

- $\mathbf{n}_1^{\text{el}}(x, x') = \sum_{i=1}^N \tilde{\psi}_i(x) \tilde{\psi}_i^\dagger(x')$
- $\mathbf{n}_1^{\text{vp}}(x, x') = \sum_{\tilde{\epsilon}_p < 0} \tilde{\psi}_p(x) \tilde{\psi}_p^\dagger(x') - \sum_{\epsilon_p < 0} \psi_p(x) \psi_p^\dagger(x')$
- Through the two-electron interaction \rightarrow interaction between the electronic density and the vacuum-polarization density
- Direct contribution: $\mathcal{E}_N^{(1),D} = \int n^{\text{el}}(x) n^{\text{vp}}(x) dx$
- Exchange contribution: $\mathcal{E}_N^{(1),X} = - \int \text{tr}[\mathbf{n}_1^{\text{el}}(x) \mathbf{n}_1^{\text{vp}}(x)] dx$

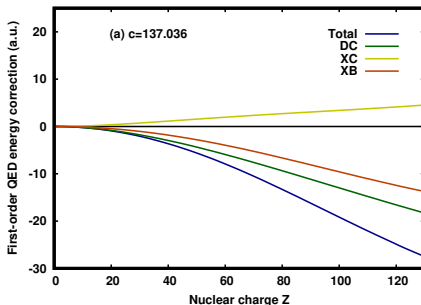
Lamb shift

Lamb shift

Correction to the 1s orbital energy of the hydrogen spectrum due to the interaction between the electrons and the vacuum polarization density

$$\mathcal{E}_{\text{Lamb}}^{\text{D}} = \int n_{1s}(x) n^{\text{vp}}(x) dx$$

$$\mathcal{E}_{\text{Lamb}}^{\text{X}} = - \int \text{tr} [\mathbf{n}_{1s}(x) \mathbf{n}^{\text{vp}}(x)] dx$$



Summary: QED effects

- Developed a nice QED model
- Developed and found an analytical expression of the vacuum polarization density
- Found a reasonable approximation to compare it to 3D
- We have been able to compute its interaction with the electrons of the system

Purposes

- ✓ To develop an analytical solution of the 1D problem
- ✓ To have a better understanding of the physical issues of QED interactions
- ✗ To develop this problem in a finite basis set

Conclusion

- QED effects are the next challenge of relativistic quantum chemistry
- Nowadays some codes offer such calculations but only for atoms and with some approximations
- This 1D model help us to understand this problem
- Develop a code to reproduce the analytic results and overcome most of the difficulties

Conclusion

- QED effects are the next challenge of relativistic quantum chemistry
- Nowadays some codes offer such calculations but only for atoms and with some approximations
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Perspectives

- Add correlation to the code
- Generalize the problem to molecules
- Develop relativistic functional beyond the no-pair approximation for molecules

Fermionic Fock space

- Fock space:

$$\mathcal{F} = \bigoplus_{(n,m)=(0,0)}^{(M_{PS}, M_{NS})} \mathcal{H}^{(n,m)} = \bigoplus_{q=-M_{NS}}^{M_{PS}} \mathcal{F}_q \quad (18)$$

- with: $\mathcal{F}_q = \mathcal{H}^{(q,0)} \oplus \mathcal{H}^{(q+1,1)} \oplus \dots \oplus \mathcal{H}^{(M_{PS}, M_{NS}-q)}$
- Fermionic

$$\forall p, q \in PS, \{\hat{b}_p, \hat{b}_q^\dagger\} = \delta_{pq} \text{ and } \forall p, q \in NS, \{\hat{d}_p, \hat{d}_q^\dagger\} = \delta_{pq}$$

- Dirac field operator⁶

$$\hat{\psi}(x) = \sum_{p \in PS} \psi_p(x) \hat{b}_p + \sum_{p \in NS} \psi_p(x) \hat{d}_p^\dagger \quad (19)$$

⁶ P. Chaix and D. Iracane, J. Phys. B 22, 3791 (1989)

Second Quantization⁷

Normal ordered density operator

$$\hat{\mathbf{n}}_1(x, x') = \hat{\boldsymbol{\psi}}^\dagger(x') \otimes \hat{\boldsymbol{\psi}}(x) - \langle 0 | \hat{\boldsymbol{\psi}}^\dagger(x') \otimes \hat{\boldsymbol{\psi}}(x) | 0 \rangle \quad (20)$$

Normal-ordered second quantized full Hamiltonian

$$\hat{H} = \int \text{tr}[\mathbf{D}(x)\hat{\mathbf{n}}_1(x, x')]_{x'=x} dx + \frac{1}{2} \iint \text{Tr}[\mathbf{w}(x_1, x_2)\hat{\mathbf{n}}_2(x_1, x_2)] dx_1 dx_2$$

- $\mathbf{w}(x_1, x_2) = \delta(x_1 - x_2) (\mathbb{I}_2 \otimes \mathbb{I}_2 - \sigma_1 \otimes \sigma_1)$
- Normal-ordered pair density-matrix operator: $\hat{\mathbf{n}}_2(x, x')$
- tr and Tr designate the trace for 2×2 and 4×4 matrices

⁷ P. Chaix and D. Iracane, J. Phys. B 22, 3791 (1989)

Vacuum polarization origin

Vacuum Polarization

The vacuum polarization is the expectation value of the normal ordered density on the polarized vacuum $|\tilde{0}\rangle$

$$\begin{aligned}
 \mathbf{n}_1^{\text{vp}}(x, x') &= \langle \tilde{0} | \hat{\mathbf{n}}_1(x, x') | \tilde{0} \rangle \quad (21) \\
 &= \langle \tilde{0} | \hat{\boldsymbol{\psi}}^\dagger(x') \otimes \hat{\boldsymbol{\psi}}(x) | \tilde{0} \rangle \\
 &\quad - \langle 0 | \hat{\boldsymbol{\psi}}^\dagger(x') \otimes \hat{\boldsymbol{\psi}}(x) | 0 \rangle \\
 &= \sum_{\tilde{\varepsilon}_p < 0} \tilde{\psi}_p(x) \tilde{\psi}_p^\dagger(x') \\
 &\quad - \sum_{\varepsilon_p < 0} \psi_p(x) \psi_p^\dagger(x')
 \end{aligned}$$

