One dimensional model with delta-type interactions:

Dirac's equation with QED interactions

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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 approximation[3]

[1] P. Pyykkö, Angew. Chem. Int. Ed. 43, 4412 (2004)

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

[3] P. Schwerdtfeger *et al.*, Phys. Rev. Let. 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 framework[4]

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

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

3D Dirac's operator

Dirac operator

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

- $\vec{\boldsymbol{\alpha}} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$ 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 equation

$$\mathcal{D}\boldsymbol{\psi} = \mathcal{E}\boldsymbol{\psi} \tag{2}$$

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

Properties of the relativistic Hamiltonian

Non-relativistic spectrum

$$\mathcal{H} = -\frac{\Delta}{2m} + \mathrm{V} \tag{3}$$

Spectrum:

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

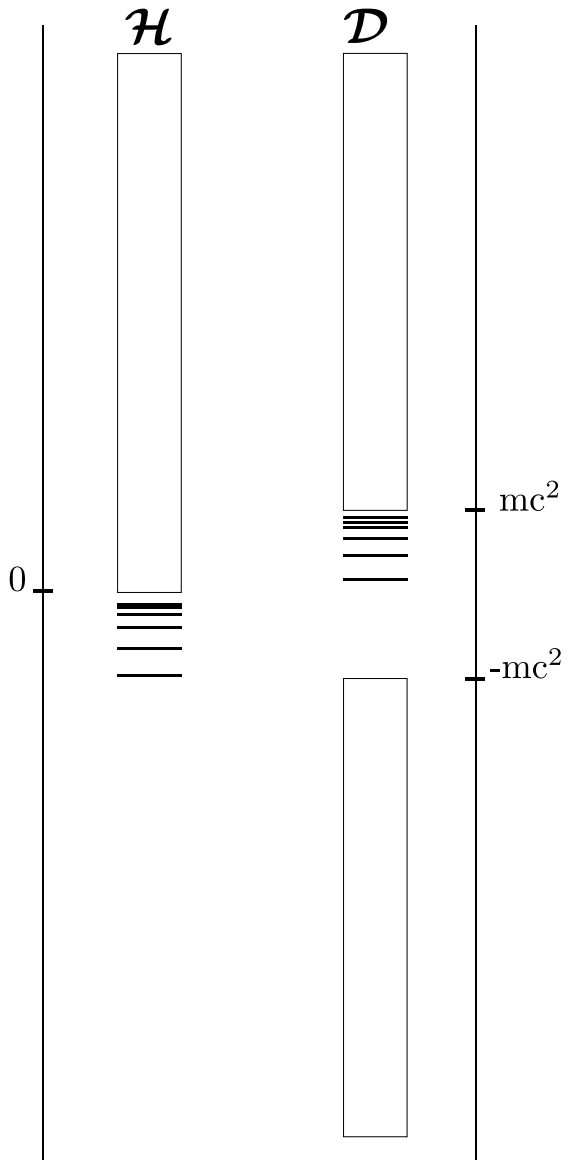
Relativistic spectrum

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

Spectrum:

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

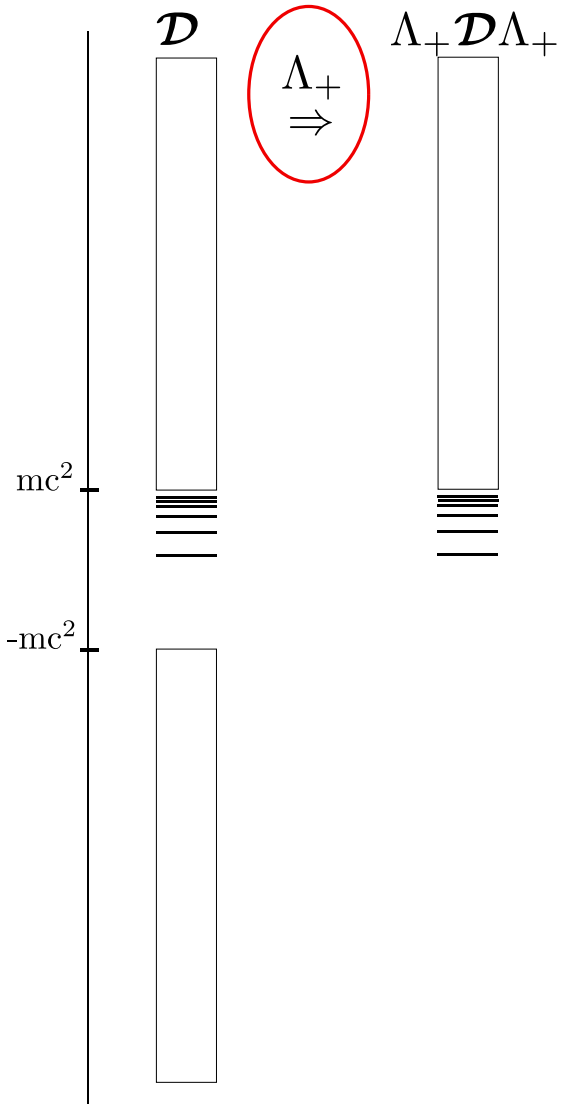
$\Rightarrow$ Negative continuum spectrum



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

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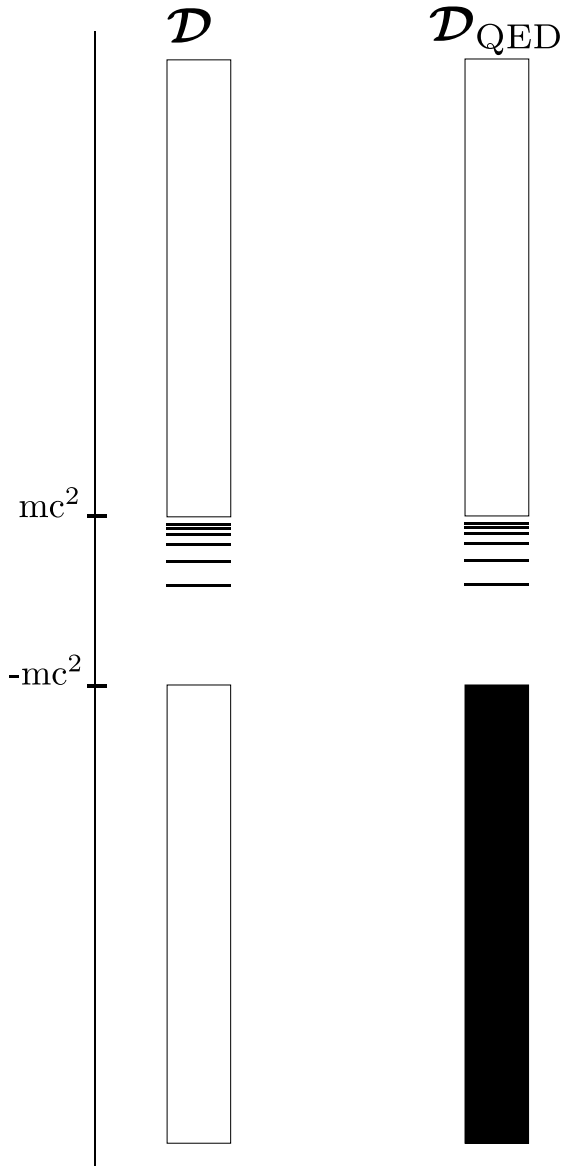
QED treatment of negative energy electrons

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



1D Dirac's operator[5]

Free Dirac operator

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

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

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

is a 2×2 operator!

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

1D Dirac's equation

1D Free Dirac operator

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

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

1D Free Dirac equation

$$\mathbf{D}_0\boldsymbol{\psi} = \mathcal{E}\boldsymbol{\psi}, \tag{7}$$

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

$$\boldsymbol{\psi}^g_{+,k}(x) = A_k \begin{pmatrix} \cos(kx) \\ \mathrm{i}s_k \sin(kx) \end{pmatrix}$$

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

$$\boldsymbol{\psi}^g_{-,k}(x) = A_k \begin{pmatrix} \mathrm{i}s_k \cos(kx) \\ \sin(kx) \end{pmatrix}$$

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

Hydrogen-like Dirac operator

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

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

$$\mathrm{Dom}(\mathbf{D}) = \{\tilde{\boldsymbol{\psi}} \in H^1(\mathbb{R}\backslash\{0\}, \mathbb{C}) \otimes \mathbb{C}^2 |\ \tilde{\boldsymbol{\psi}}(0^+) = \mathcal{M}\tilde{\boldsymbol{\psi}}(0^-)\}$$

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

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

Hydrogen-like Dirac equation

$$\mathbf{D}\tilde{\boldsymbol{\psi}} = \tilde{\mathcal{E}}\tilde{\boldsymbol{\psi}}, \tag{10}$$

- This Hamiltonian has a single bound state

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

- 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

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

Summary: Solving the one-electron 1D Dirac equation

Free Dirac equation

$$\mathbf{D}_0 \boldsymbol{\psi}_p = \mathcal{E}_p \boldsymbol{\psi}_p \tag{13}$$

Spectrum:

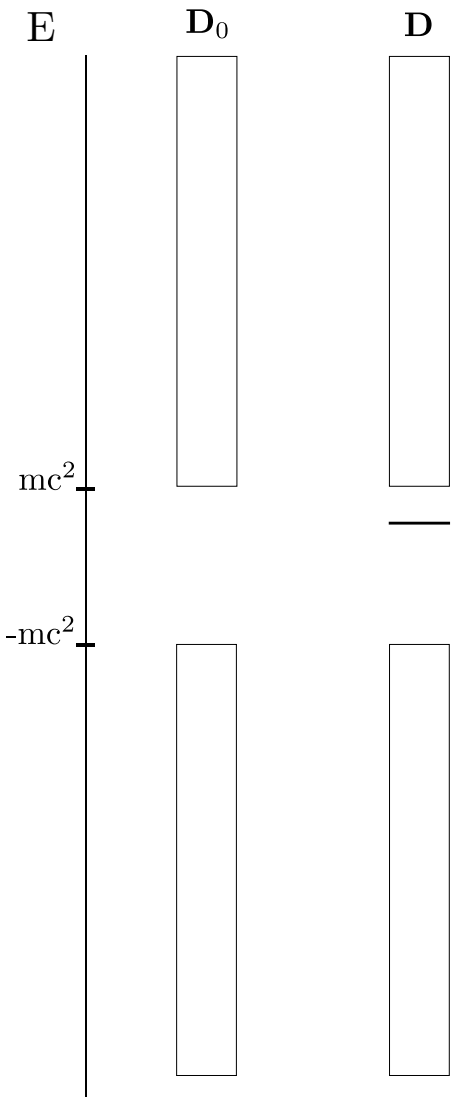
- Continuum: $\mathcal{E}_k = \pm\sqrt{m^2c^4 + k^2c^2}$

Hydrogen-like Dirac equation

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

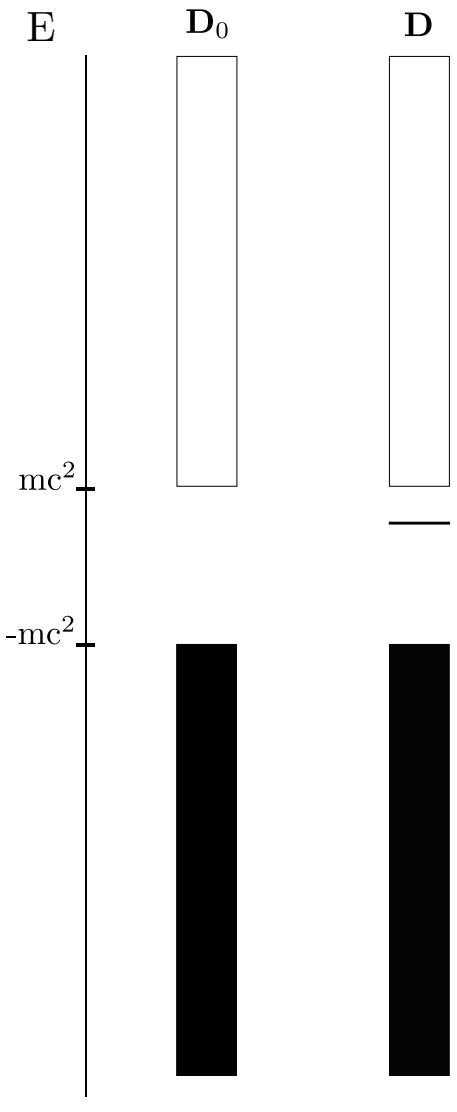
Spectrum:

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



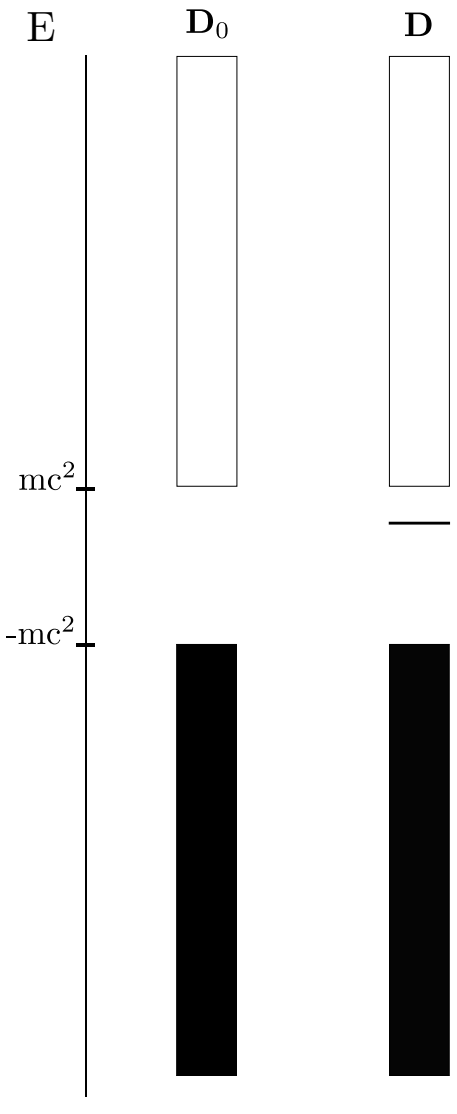
QED Effects

- 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

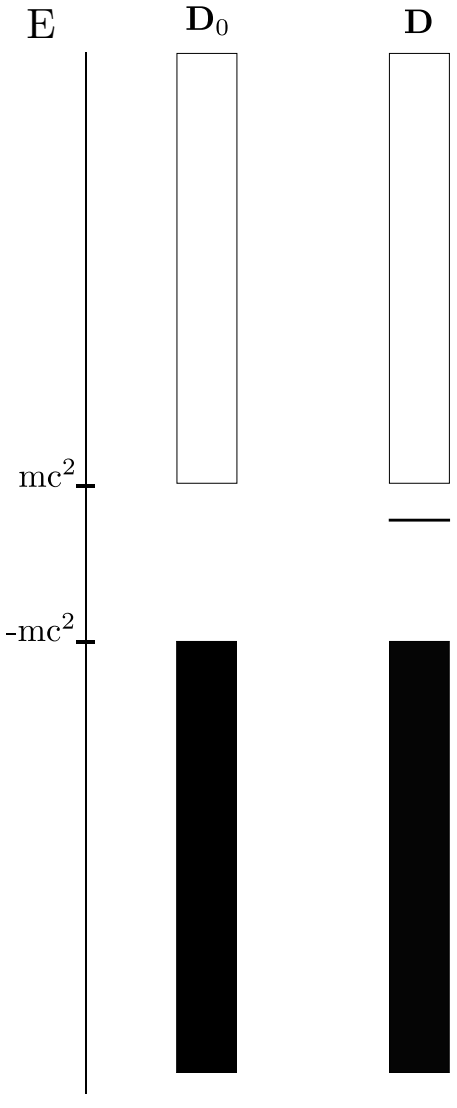


Vacuum Polarization

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

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

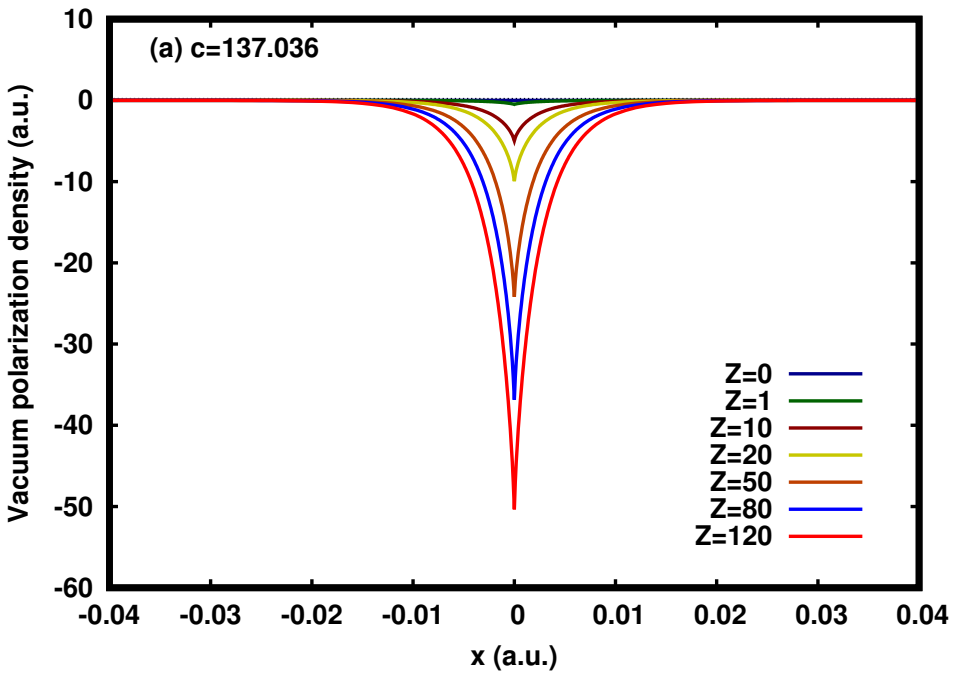
- In 3D this quantity diverges, needs to be renormalized
- We want to have a better understanding of this quantity and its influence on the energy spectrum



Vacuum Polarization Density – Analytical form

Analytical expression

$$
\begin{aligned}
n^{\mathrm{vp}}(x) &= \mathrm{tr}\left[\mathbf{n}_1^{\mathrm{vp}}(x,x)\right] = \sum_{\tilde{\mathcal{E}}_p<0} \tilde{\psi}_p^{\dagger}(x)\tilde{\psi}_p(x) - \sum_{\mathcal{E}_p<0} \psi_p^{\dagger}(x)\psi_p(x) \\
&= -\int_0^{\infty} \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2} \left(\kappa \cos(2k|x|) - \frac{\tilde{\mathcal{E}}_b}{\mathcal{E}_k} \sin(2k|x|) \right)
\end{aligned}
$$



Vacuum Polarization Density – Convergence test

Hermite-Gaussian functions

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

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

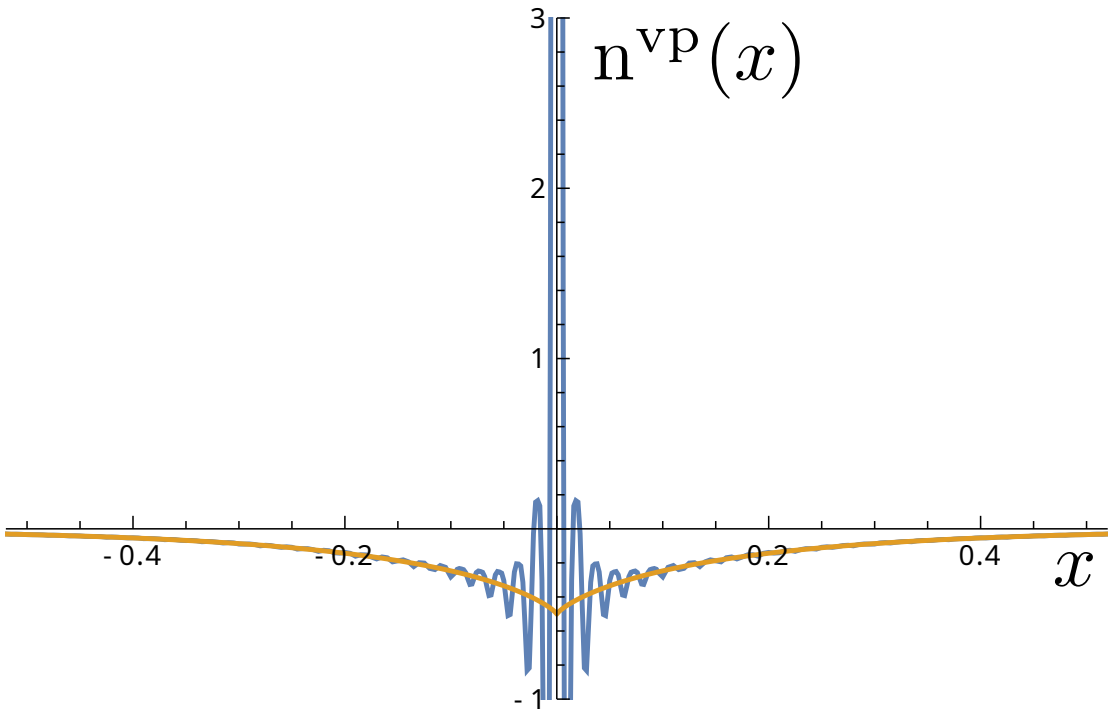
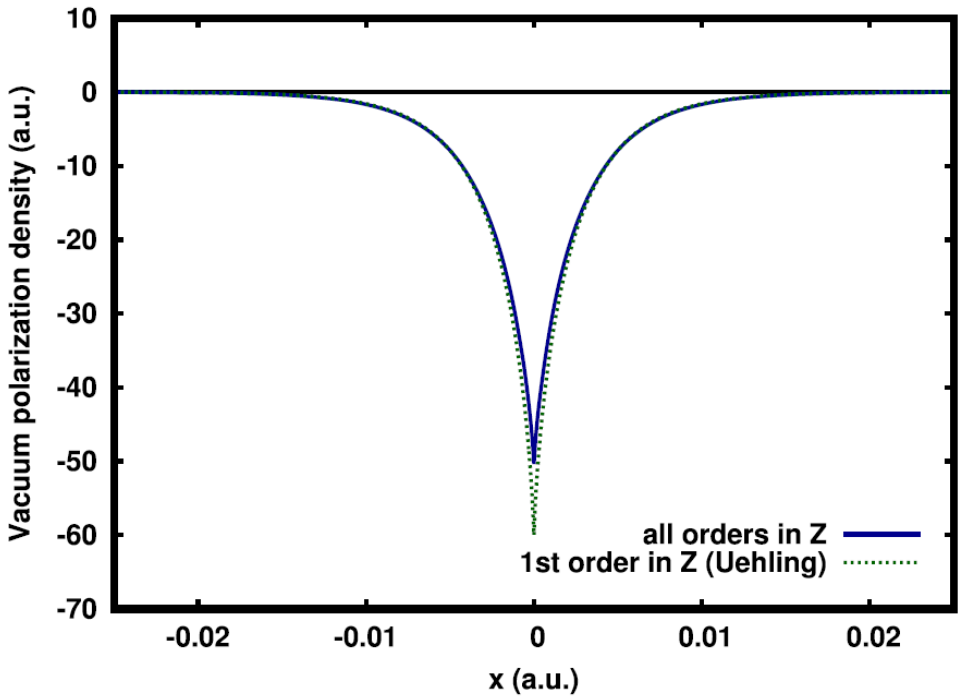


Figure 2: Vacuum polarization density $n^{vp}(x)$ as a function of x for $c = 1$ and $n_{max} = 800$.

Uehling Density

First-order vacuum polarization density in Z

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



First-order correction energy

One-body density matrix for any system

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

- $\mathbf{n}_1^{\mathrm{el}}(x,x') = \sum_{i=1}^{N} \tilde{\psi}_i(x)\tilde{\psi}_i^{\dagger}(x')$
- $\mathbf{n}_1^{\mathrm{vp}}(x,x') = \sum_{\tilde{\varepsilon}_p<0} \tilde{\psi}_p(x)\tilde{\psi}_p^{\dagger}(x') - \sum_{\varepsilon_p<0} \psi_p(x)\psi_p^{\dagger}(x')$

- Through the two-electron interaction $\rightarrow$ interaction between the electronic density and the vacuum-polarization density
- Direct contribution: $\mathcal{E}_N^{(1),\mathrm{D}} = \int n^{\mathrm{el}}(x) n^{\mathrm{vp}}(x) \mathrm{d}x$
- Exchange contribution: $\mathcal{E}_N^{(1),\mathrm{X}} = -\int \mathrm{tr}\left[\mathbf{n}_1^{\mathrm{el}}(x)\mathbf{n}_1^{\mathrm{vp}}(x)\right] \mathrm{d}x$

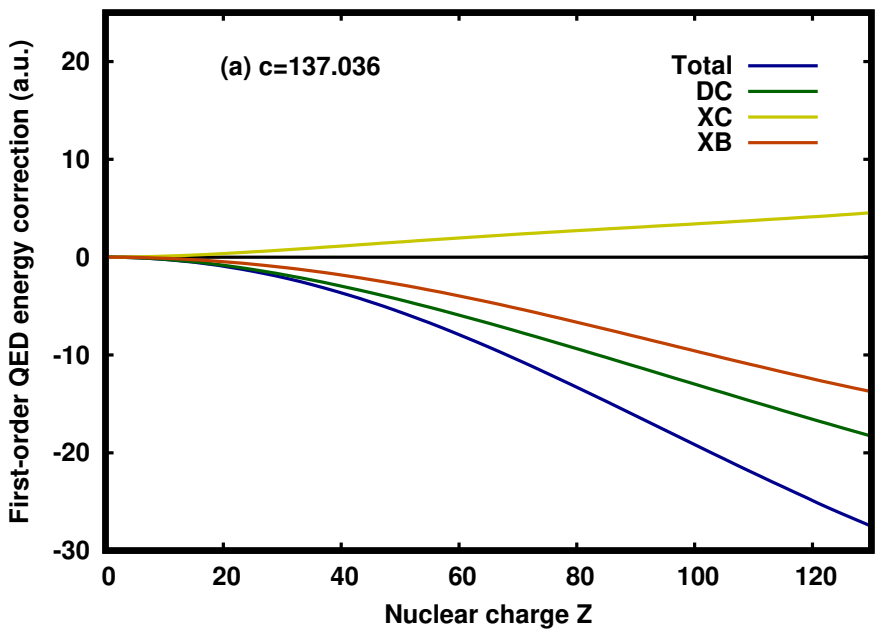
Lamb shift

Lamb shift

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

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

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



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
- This 1D model help us to understand this problem
- Develop a code to reproduce the analytic results and overcome most of the difficulties

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:

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

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

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

- Dirac field operator[6]

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

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

Second Quantization[7]

Normal ordered density operator

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

Normal-ordered second quantized full Hamiltonian

$$\hat{H} = \int \mathrm{tr}\left[\mathbf{D}(x)\hat{\mathbf{n}}_1(x,x')\right]_{x'=x} \mathrm{d}x + \frac{1}{2}\iint \mathrm{Tr}[\mathbf{w}(x_1,x_2)\hat{\mathbf{n}}_2(x_1,x_2)]\mathrm{d}x_1\mathrm{d}x_2$$

- $\mathbf{w}(x_1,x_2) = \delta(x_1-x_2)\left(\mathbb{I}_2 \otimes \mathbb{I}_2 - \sigma_1 \otimes \sigma_1\right)$
- 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 $\left|\tilde{0}\right\rangle$

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