Laboratoire de Chimie Théorique

One dimensional model for Relativistic Quantum Chemistry

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Thesis work with Julien Toulouse

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- Explains some physical properties of heavy elements

1. yellow color of gold

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2. lead-acid battery electro-chemical potential

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- Includes the electron spin and spin-orbit coupling

Yellow color of gold[1]

- Fast-moving electrons in *s* and p orbitals
- Mass increases due to relativity
- Contraction of those orbitals
- Stronger screening of the nucleus
- Destabilize *d* and *f* orbitals
- Change the gap energy between 5*d* and 6*s*, from UV to yellow

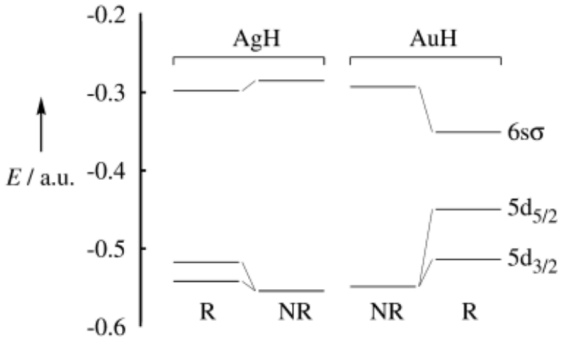

Figure 1: Orbitals diagram of Gold and Silver, with and without relativistic effects

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

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

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- Does not include spin

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 $\boldsymbol{\psi}$

Non-relativistic spectrum

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

Spectrum:

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

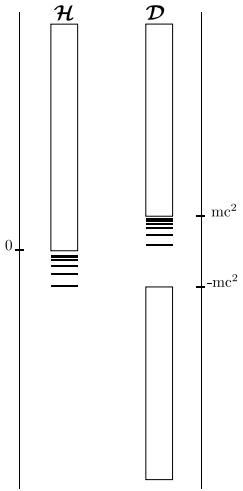
Relativistic spectrum

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

Spectrum:

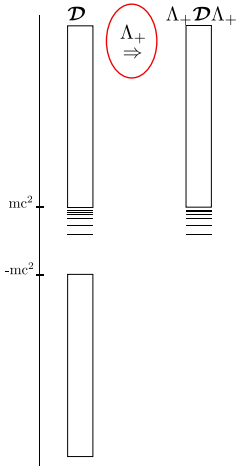
- If $\mathscr{E} \in (-\infty, -mc^2] \cup [mc^2, +\infty)$: continuum
- If $\mathscr{E} \in (-mc^2, mc^2)$: bound states

$\Rightarrow$ Negative continuum spectrum

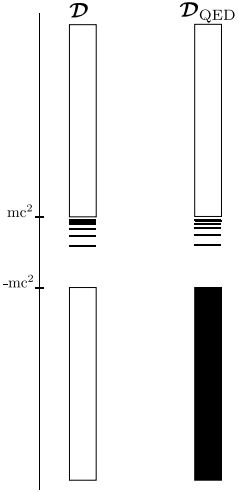


How to deal with the negative continuum

- No-pair approximation



- QED description



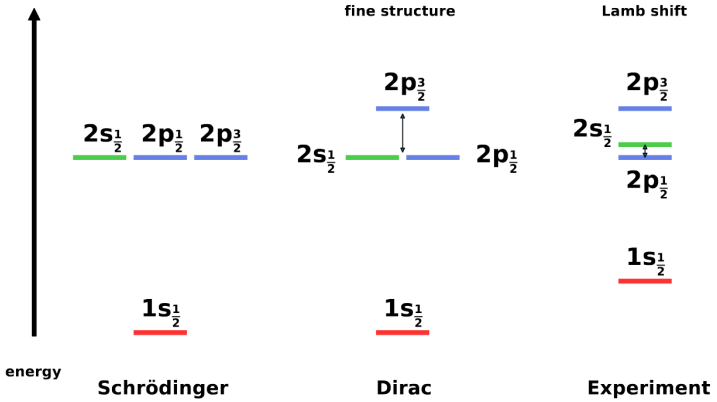


Figure 2: Lamb shift in hydrogen spectra[2]

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

Relativistic calculations

- Different levels of relativistic corrections
- **Zeroth level:** Non-relativistic chemistry

[3] P. Schwerdtfeger *et al.*, PRL, (2017)

Relativistic calculations

- Different levels of relativistic corrections
- **Zeroth level:** Non-relativistic chemistry
- **First level:** Solving Dirac's equation or adding scalar-relativistic and spin-orbit correction to Schrödinger's equation (ZORA, DKHn, X2C)

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- Different levels of relativistic corrections
- **Zeroth level:** Non-relativistic chemistry
- **First level:** Solving Dirac's equation or adding scalar-relativistic and spin-orbit correction to Schrödinger's equation (ZORA, DKHn, X2C)
- **Second level:** Quantum electrodynamics (QED) effects (e.g. IP and EA of gold, Lamb shift in hydrogen)

	IP	Error	EA	Error
DC-HF	7.6892	−1.5363	0.6690	−1.6396
DC-CCSD	9.1164	−0.1092	2.1070	−0.2017
DC-CCSD(T)	9.2938	0.0683	2.3457	0.0371
DC-CCSDTQP	9.2701	0.0446	2.3278	0.0192
+Breit	9.2546	0.0290	2.3188	0.0102
+QED	9.2288	0.0032	2.3072	−0.0014
Experiment [31,32]	9.2256		2.3086	

Figure 3: IP and EA of gold with different levels of approximation[3]

[3] P. Schwerdtfeger *et al.*, PRL, (2017)

Motivations for the model

- We need accurate QED calculations for high precision spectroscopy
- Also studying core properties need to go into QED details
- So far, state of the art QED 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 the issue of developping new methods based on QED.

To do list:

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

Free Dirac operator

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

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

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

is a 2×2 operator!

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

Free 1D Dirac operator

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

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

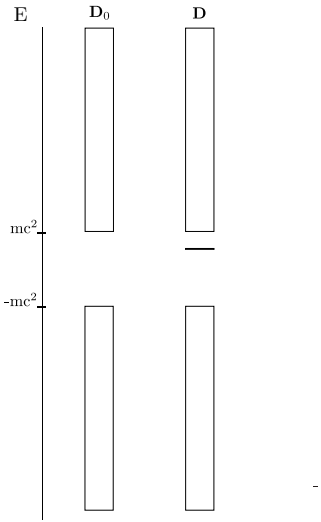
Dirac eigenvalue equations

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

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

$$(\mathbf{D}_0(x) - Z\delta(x))\,\psi_p^Z(x) = \varepsilon_p \psi_p^Z(x) \tag{7}$$

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



1D Schrödinger equation

$$\hat{H} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z\delta(x) \tag{8}$$

- follows from the generalization of $\hat{H}$ to arbitrary dimensions[5]
- recovers the energy, cusp and radial part of the 3D ground state of hydrogen[6]
- easily solvable model

1D Dirac equation

$$\hat{H} = -\mathrm{i}c\sigma_x\frac{\mathrm{d}}{\mathrm{d}x} + \sigma_z\, mc^2 - Z\delta(x) \tag{9}$$

- gives analytical QED results
- recovers the non-relativistic hydrogen 1D properties

[5] D. R. Herschbach, J. Chem. Phys., 84 (1986)

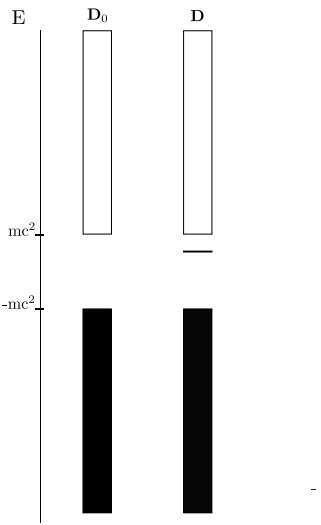
[6] D. Traore, E. Giner, J. Toulouse, J. Chem. Phys., 156 (2022)

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

Vacuum Polarization Density

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

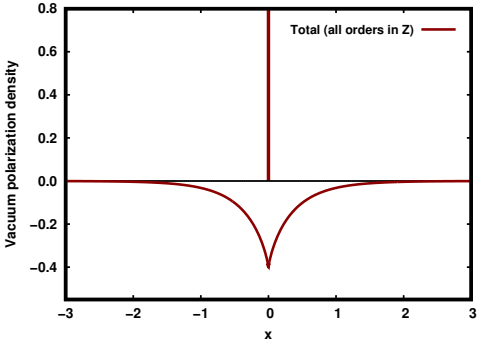
- In 3D this quantity diverges, needs to be renormalized
- We want to have a better understanding of this quantity and its influence on the energy spectrum



Vacuum Polarization Density

$$n^{\mathrm{vp}}(x) = \sum_{\varepsilon_p<0} \psi_p^{Z\dagger}(x)\psi_p^{Z}(x) - \sum_{\varepsilon_p<0} \psi_p^{0\dagger}(x)\psi_p^{0}(x) = \mathcal{N}_0^{\mathrm{vp}}\,\delta(x) + n_{\mathrm{reg}}^{\mathrm{vp}}(x) \tag{10}$$

Audinet, Morellini, Levitt, Toulouse, in preparation

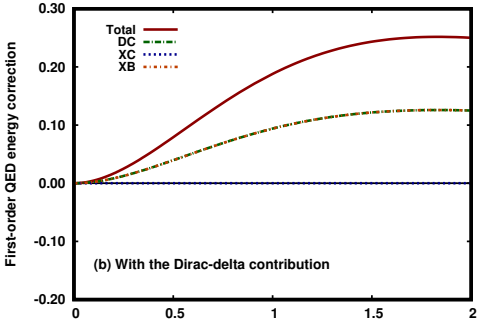


Lamb shift

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

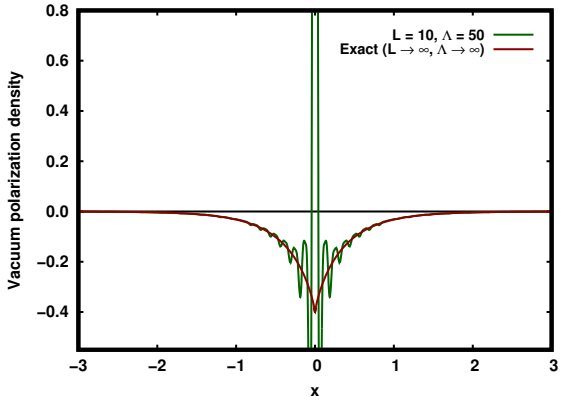
$$\mathscr{E}^{\mathrm{D}}_{\mathrm{Lamb}} = \int n_{1\mathrm{s}}(x) n^{\mathrm{vp}}(x) \mathrm{d}x$$

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



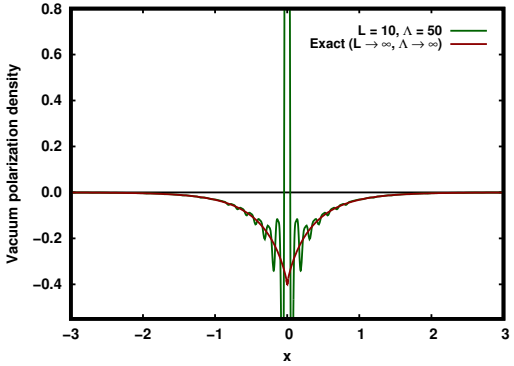
Plane waves basis

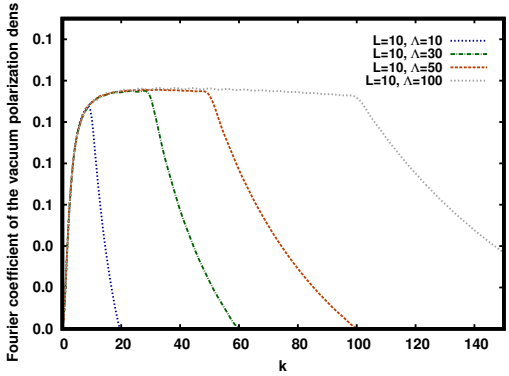
$$\forall\, x \in \mathbb{R}, k \in \frac{2\mathbb{Z}\pi}{L}, |k| \leq \Lambda, \quad \chi_k(x) = \frac{1}{\sqrt{L}} e^{ikx} \tag{11}$$



Regularization with Fourier Transform

$$n^{\mathrm{vp}}_{\mathrm{reg}}(x) = \mathscr{F}^{-1}\Big[\mathscr{F}[n^{\mathrm{vp}}](k)\theta(k_{\max}-k) - \mathscr{F}[n^{\mathrm{vp}}](k_{\max})\Big] \tag{12}$$





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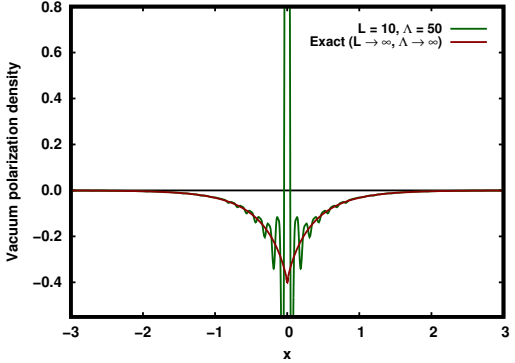
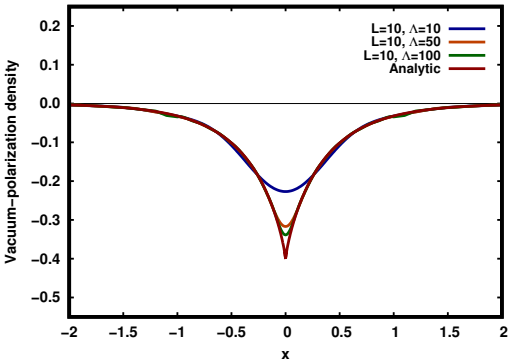
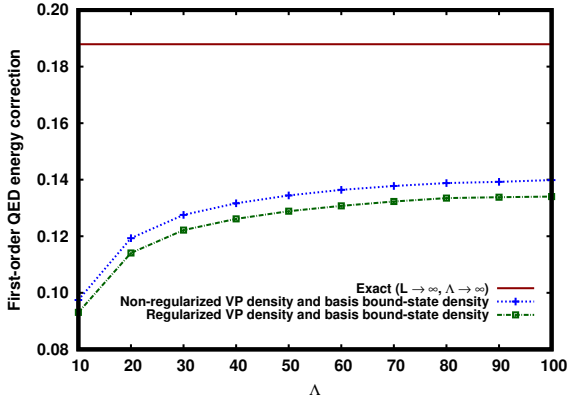




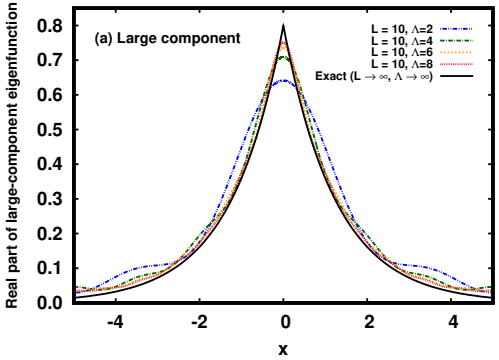
Computing the Lamb shift

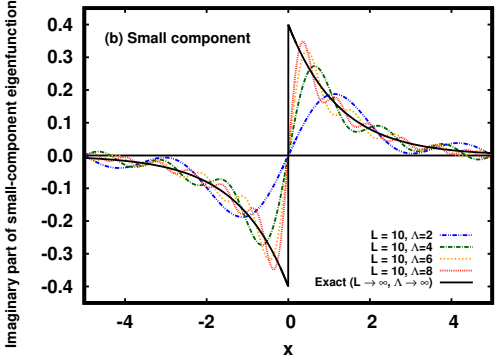
- Non-regularized: $\mathscr{E}_{\text{Lamb}} = \int n_{1s}(x) n^{\text{vp}}(x) \mathrm{d}x$
- Regularized: $\mathscr{E}^{\text{reg}}_{\text{Lamb}} = \int n_{1s}(x) n^{\text{vp}}_{\text{reg}}(x) \mathrm{d}x + \mathscr{N}_0^{\text{vp}} n_{1s}(0)$



Value at $x = 0$

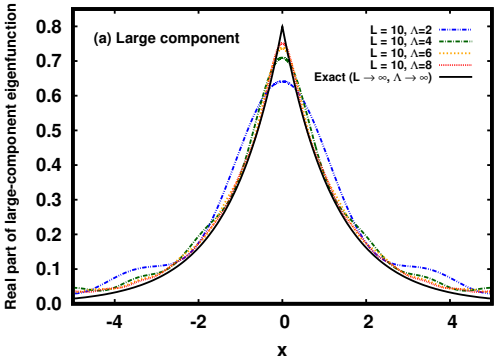
$$n_{1s}(x=0) = |\psi^{\mathrm{L}}_{1s}(0)|^2 + |\psi^{\mathrm{S}}_{1s}(0)|^2 \tag{14}$$

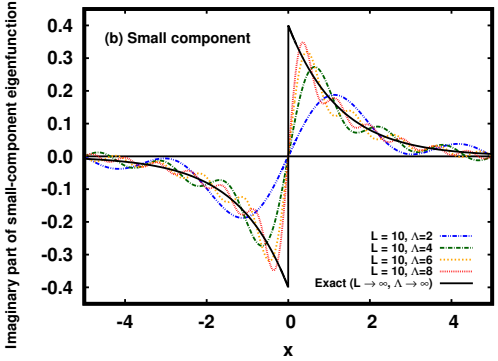




Value at $x = 0$

$$n_{1s}^{\text{improved}}(x=0) = |\psi_{1s}^{\text{L}}(0)|^2 + \max_{x\in\mathbb{R}}(|\psi_{1s}^{\text{S}}(x)|^2) \tag{15}$$





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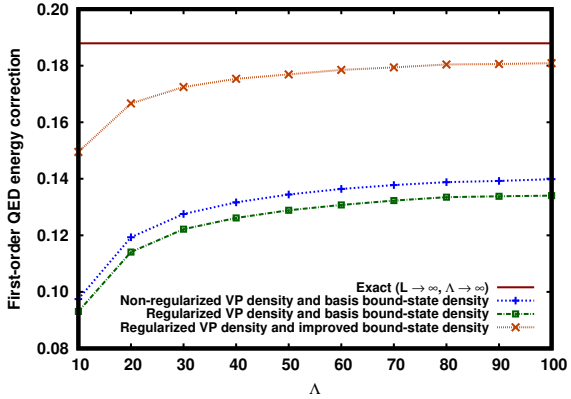

Goal

Use a model system to understand the issue of developping new methods based on QED.

To do list:

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

- We developped an effective QED theory including electron-positron pairs.
- Some singularities appears in a finite basis.
- This 1D model help us to understand this problem.