One dimensional model for Relativistic Quantum Chemistry

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Introduction

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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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  3. liquid state of mercury at room temperature

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- Explains the electron spin and spin-orbit coupling

Relativistic energy

Free particle energy

- Non relativistic:

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

- Relativistic:

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

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Link between both

- Taylor expansion of the square root for the positive part

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

Dirac equation

Dirac operator

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

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

$$\left(\mathcal{D}_0(x) + \mathrm{V}(x)\right) \boldsymbol{\psi}(x) = \mathcal{E}\boldsymbol{\psi}(x) \tag{2}$$

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

Hydrogenic spectrum

Non-relativistic spectrum

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

Spectrum:

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

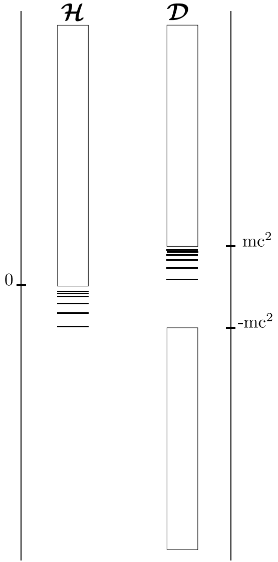
Relativistic spectrum

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

Spectrum:

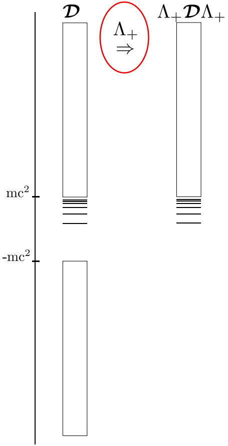
- If $\mathcal{E} \in (-\infty, -mc^2] \cup [mc^2, +\infty)$: continuum
- If $\mathcal{E} \in (-mc^2, mc^2)$: bound states

$\Rightarrow$ Negative continuum spectrum

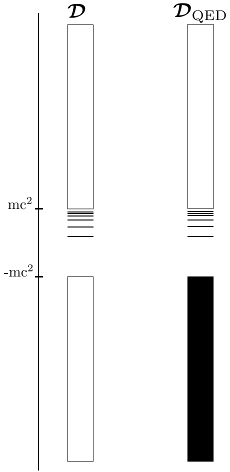


How to deal with the negative continuum

- No-pair approximation



- QED description



Relativistic calculations

- Different levels of relativistic corrections
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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)
- **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 1: IP and EA of gold with different levels of approximation

P. Schwerdtfeger *et al.*, PRL, (2017)

From 3D to 1D

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)

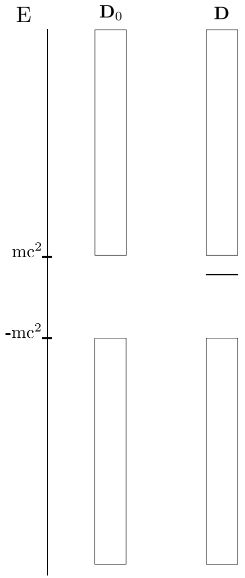
Dirac eigenvalue equations

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

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

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

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

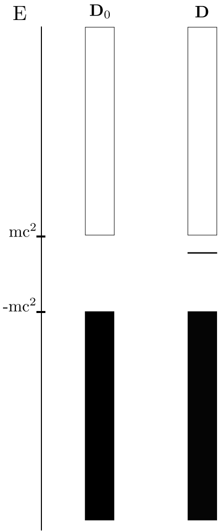


Vacuum Polarization

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

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

- 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



Plotting the vacuum polarization

Vacuum Polarization Density

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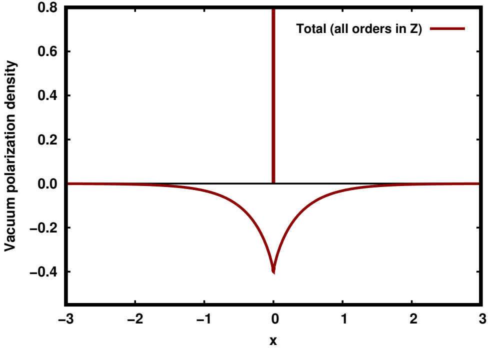
$$= \mathcal{N}_0^{\mathrm{vp}}\delta(x) + n_{\mathrm{reg}}^{\mathrm{vp}}(x) \tag{9}$$

Audinet, Morellini, Levitt, Toulouse, in preparation



In a basis... convergence issues?

- Plane wave basis: $\forall\ x \in \mathbb{R}, k \in \frac{2\mathbb{Z}\pi}{L}, |k| \leq \Lambda, \quad \xi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$
- Regularization process to clean oscillations

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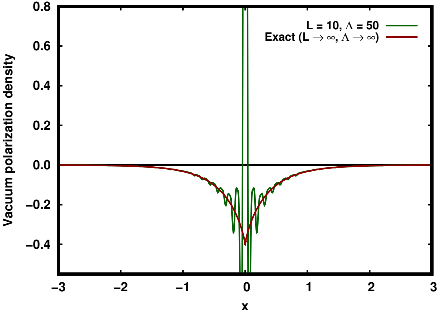

Figure 2: Non-regularized plot

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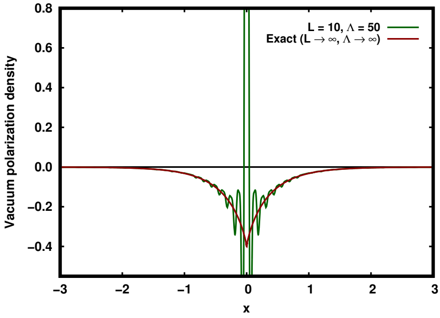

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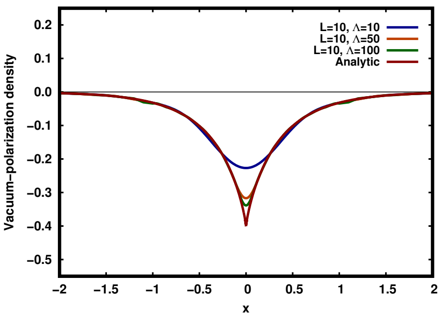

Figure 3: Regularized plot

Conclusion

- Effective QED theory including electron-positron pairs
- QED effects are the next challenge of relativistic quantum chemistry
- QED quantities are very troublesome in 3D
- Some singularities appears in a finite basis
- This 1D model help us to understand this problem

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Perspectives

- Develop relativistic functional beyond the no-pair approximation for molecules
- Generalize the problem to 3D