



ONE DIMENSIONAL MODEL FOR RELATIVISTIC QUANTUM CHEMISTRY

Timothée AUDINET

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

Introduction

WHY ARE WE INTERESTED IN RELATIVISTIC QUANTUM CHEMISTRY?

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

² R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö and P. Zaleski-Ejgierd, Phys. Rev. Lett. 106, 018301 (2011)

³ K. Steenbergen, E. Pahl and P. Schwerdtfeger, J. Phys. Chem. Lett. 8, 1407 (2017)

Introduction

WHY ARE WE INTERESTED IN RELATIVISTIC QUANTUM CHEMISTRY?

- Important for fast-moving particles (e.g. electrons)

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

² R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö and P. Zaleski-Ejgierd, Phys. Rev. Lett. 106, 018301 (2011)

³ K. Steenbergen, E. Pahl and P. Schwerdtfeger, J. Phys. Chem. Lett. 8, 1407 (2017)

Introduction

WHY ARE WE INTERESTED IN RELATIVISTIC QUANTUM CHEMISTRY?

- Important for fast-moving particles (e.g. electrons)
- Explains some physical properties of heavy elements
 1. yellow color of gold ¹
 2. lead-acid battery electro-chemical potential ²
 3. liquid state of mercury at room temperature ³

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

² R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö and P. Zaleski-Ejgierd, Phys. Rev. Lett. 106, 018301 (2011)

³ K. Steenbergen, E. Pahl and P. Schwerdtfeger, J. Phys. Chem. Lett. 8, 1407 (2017)

Introduction

WHY ARE WE INTERESTED IN RELATIVISTIC QUANTUM CHEMISTRY?

- Important for fast-moving particles (e.g. electrons)
- Explains some physical properties of heavy elements
 1. yellow color of gold ¹
 2. lead-acid battery electro-chemical potential ²
 3. liquid state of mercury at room temperature ³
- Explains the electron spin and spin-orbit coupling

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

² R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö and P. Zaleski-Ejgierd, Phys. Rev. Lett. 106, 018301 (2011)

³ K. Steenbergen, E. Pahl and P. Schwerdtfeger, J. Phys. Chem. Lett. 8, 1407 (2017)

Yellow color of gold⁴

- 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 $5d$ and $6s$, from UV to yellow

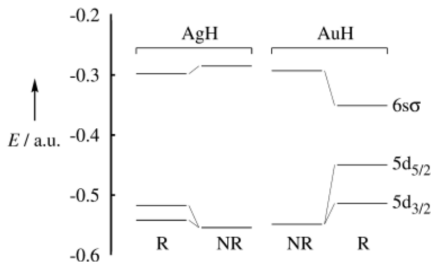


Figure 1: Orbitals diagram of Gold and Silver, with and without relativistic effects

⁴P. Pyykkö, Angew. Chem. Int. Ed. 43, 4412 (2004)

Relativistic energy

Relativistic energy

$$E^2 = m^2 c^4 + c^2 p^2 \Rightarrow E = \pm \sqrt{m^2 c^4 + p^2 c^2}, \quad (1)$$

- The energy can be negative!

Relativistic energy

Relativistic energy

$$E^2 = m^2 c^4 + c^2 p^2 \Rightarrow E = \pm \sqrt{m^2 c^4 + p^2 c^2}, \quad (1)$$

- The energy can be negative!

Link with non-relativistic energy

- Taylor expansion of the square root for the positive part

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

Dirac equation

Dirac operator

$$\mathcal{D}(x) = c (\vec{\alpha} \cdot \vec{p}) + \beta mc^2 + V(x), \quad (3)$$

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

Dirac equation

Dirac operator

$$\mathcal{D}(x) = c (\vec{\alpha} \cdot \vec{p}) + \beta mc^2 + V(x), \quad (3)$$

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

Dirac equation

$$\mathcal{D}(x)\psi(x) = \mathcal{E}\psi(x) \quad (4)$$

- $\psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$ 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

Hydrogenic spectrum

Non-relativistic spectrum

$$\mathcal{H}(x) = -\frac{\Delta}{2m} + V(x) \quad (5)$$

Spectrum:

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

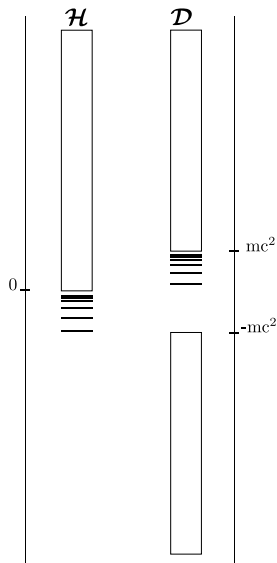
Relativistic spectrum

$$\mathcal{D}(x) = c (\vec{\alpha} \cdot \vec{p}) + \beta mc^2 + V(x) \quad (6)$$

Spectrum:

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

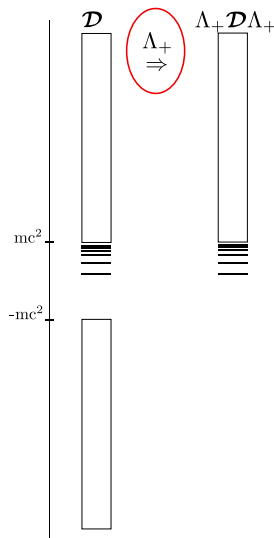
\Rightarrow Negative continuum spectrum



How to deal with the negative continuum

No-pair approximation

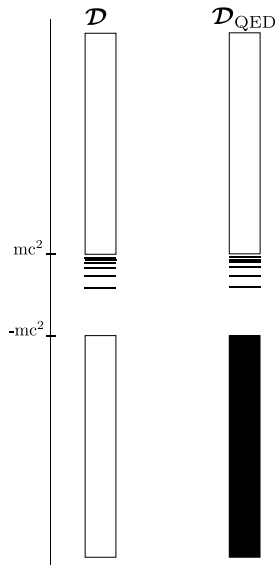
- Solving the Dirac equation
- Projecting it on the positive energy part



How to deal with the negative continuum

QED treatment of negative energy electrons

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



Relativistic calculations

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

⁵P. Schwerdtfeger *et al.*, Phys. Rev. Let. 118, 023002 (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)

⁵P. Schwerdtfeger *et al.*, Phys. Rev. Let. 118, 023002 (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)
- **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 2: IP and EA of gold with different levels of approximation⁵

⁵P. Schwerdtfeger *et al.*, *Phys. Rev. Let.* **118**, 023002 (2017)

Motivation

- Most of the relativistic calculation are done in the “no-pair” approximation
- Next challenge for RQC is to go beyond no-pair approximation!

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

Motivation

- Most of the relativistic calculation are done in the “no-pair” approximation
- Next challenge for RQC is to go beyond no-pair approximation!
- 3D RQC encounters heavy problems when looking at vacuum properties
- 1D model to understand the problem and offer a solution for these approximations
- 1D model to develop a relativistic functional based on a nice QED framework
- No-photon effective QED framework ⁶

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

From 3D to 1D⁷

Free 1D Dirac operator

$$\mathbf{D}_0(x) = -ic\sigma_x \frac{d}{dx} + \sigma_z mc^2 \quad (7)$$

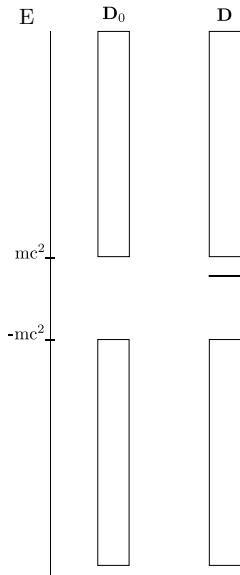
Dirac equations

$$\mathbf{D}_0(x)\psi_p^0(x) = \varepsilon_p\psi_p^0(x) \quad (8)$$

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

$$(\mathbf{D}_0(x) - Z\delta(x))\psi_p^Z(x) = \varepsilon_p\psi_p^Z(x) \quad (9)$$

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



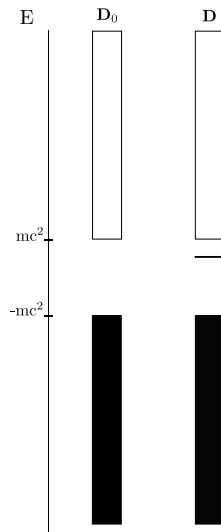
⁷ T. Audinet, J. Toulouse, J. Chem. Phys. 158, 244108 (2023)

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

$$\mathbf{n}_1^{\text{vp}}(x, x') = \sum_{\varepsilon_p < 0} \psi_p^Z(x) \psi_p^{Z+}(x') - \sum_{\varepsilon_p < 0} \psi_p^0(x) \psi_p^{0+}(x')$$

- 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

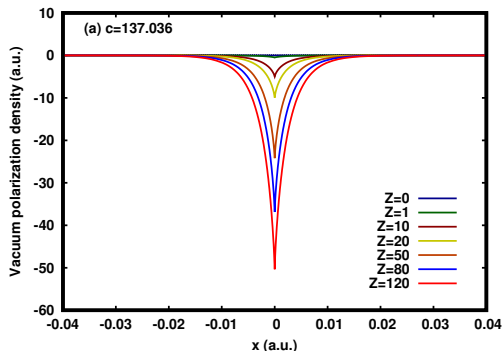


Vacuum Polarization

Vacuum Polarization Density

$$n^{\text{vp}}(x) = \text{tr} [\mathbf{n}_1^{\text{vp}}(x, x)] \quad (10)$$

$$= \sum_{\varepsilon_p < 0} \psi_p^{Z+}(x) \psi_p^Z(x') - \sum_{\varepsilon_p < 0} \psi_p^{0+}(x) \psi_p^0(x') \quad (11)$$



In a basis... convergence issues?

Plane waves basis

$$\forall x \in \mathbb{R}, k \in \frac{2\mathbb{Z}\pi}{L}, |k| \leq \Lambda, \quad \zeta_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \quad (12)$$

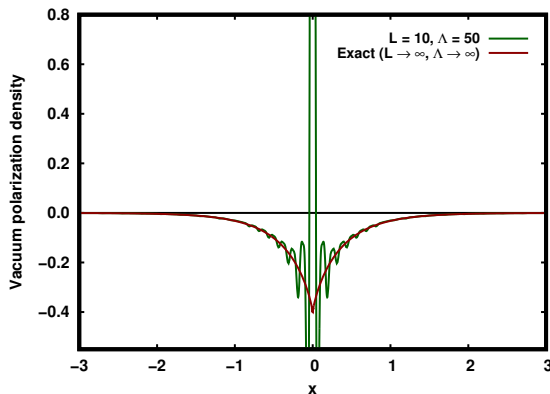


Figure 3: Vacuum polarization density $n^{\text{vp}}(x)$ as a function of x for $c = 1$.

Using Green's functions

Direct Fourier transform

$$\mathcal{F}[n^{\text{vp}}](k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} n^{\text{vp}}(x) e^{-ikx} dx \quad (13)$$

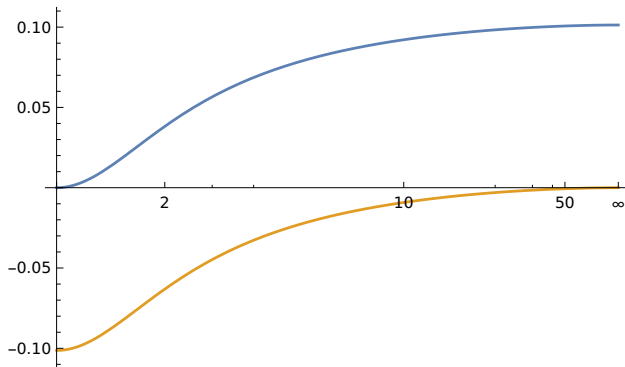
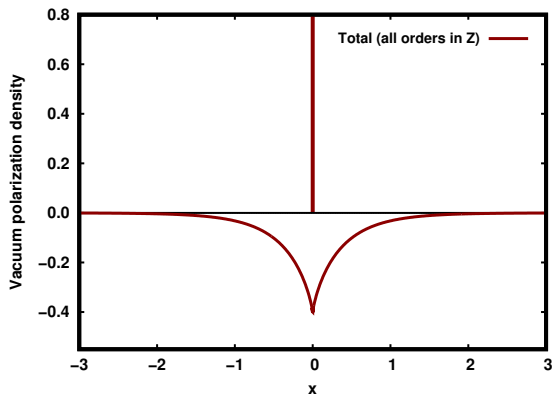


Figure 4: Fourier coefficient of Uehling density with both FT and PT

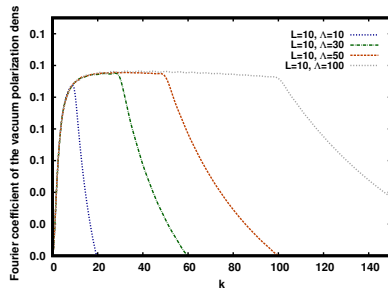
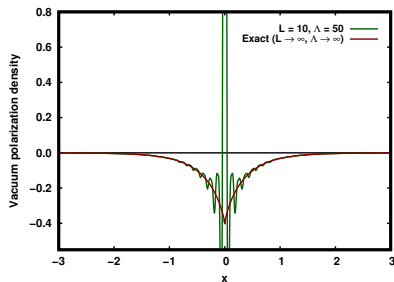
Finding the delta

Vacuum polarization density

$$n^{\text{vp}}(x) = \mathcal{N}_0^{\text{vp}} \delta(x) + n_{\text{reg}}^{\text{vp}}(x) \quad (14)$$



The Fourier coefficients



Regularization

$$n_{\text{reg}}^{\text{vp}}(x) = \mathcal{F}^{-1} \left[\mathcal{F}[n^{\text{vp}}](k) \theta(k_{\text{max}} - k) - \mathcal{F}[n^{\text{vp}}](k_{\text{max}}) \right] \quad (15)$$

Regularization of vacuum polarization density

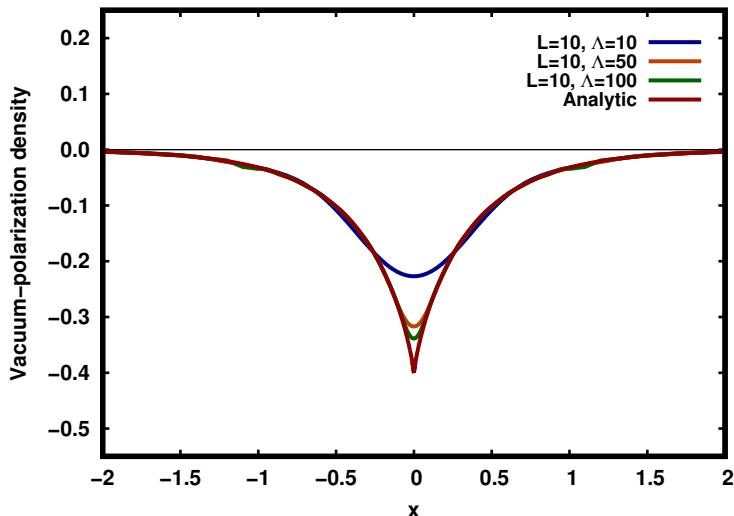


Figure 5: Convergence of the regular part of the vacuum polarization density

Lamb Shift calculation

Lamb shift

$$\begin{aligned}\mathcal{E}_{\text{Lamb}} &= \iint \text{Tr} \left[\mathbf{w} \mathbf{n}^{\text{el}} \otimes \mathbf{n}^{\text{vp}} \right] d1d2 \\ &= \iint \text{Tr} \left[\mathbf{w} \mathbf{n}^{\text{el}} \otimes \mathbf{n}_{\text{reg}}^{\text{vp}} \right] d1d2 + \mathcal{N}_0^{\text{vp}} n^{\text{el}}(0)\end{aligned}\quad (16)$$

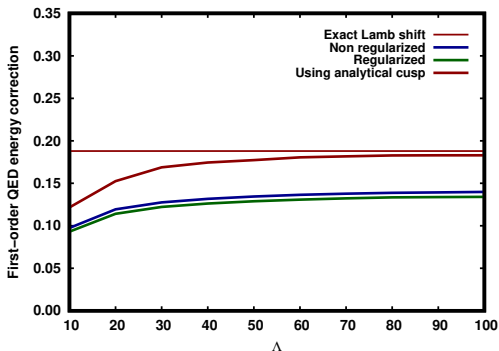


Figure 6: Convergence of the Lamb shift in a basis

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

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

Perspectives

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