One dimensional model for Relativistic Quantum Chemistry

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Introduction

- Relativistic description of chemical systems is important, especially for heavy elements
- No-pair approximations is used: do not take into accounts the effects of the virtual electron-positron pairs

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Can we go beyond no-pair approximation?

- One-dimensional toy model to understand and explore quantum description beyond no-pair approximation
- Effective QED = no-photon QED

Free Dirac's equation

3D Dirac equation[1]

$$\mathbf{D}_{3D} = c\,(\vec{\boldsymbol{\alpha}} \cdot \vec{p}) + \boldsymbol{\beta}\, mc^2,$$

- $\vec{p} = -\mathrm{i}\vec{\nabla}$
- $\vec{\boldsymbol{\alpha}} = \left[\begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}; \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}; \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \right]$ and $\boldsymbol{\beta} = \begin{pmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{pmatrix}$
- 4×4 equation $\Rightarrow$ Eigenvectors: $\Psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$

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1D Dirac equation

$$\mathbf{D}_0(x) = -\mathrm{i}c \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2$$

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Dirac spectrum

Free Dirac equation

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Spectrum:

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

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Hydrogen-like Dirac equation

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

Spectrum:

- Bound State: $\tilde{\varepsilon}_b = mc^2 \frac{1-\lambda^2}{1+\lambda^2}$ with $\lambda = Z/2c$
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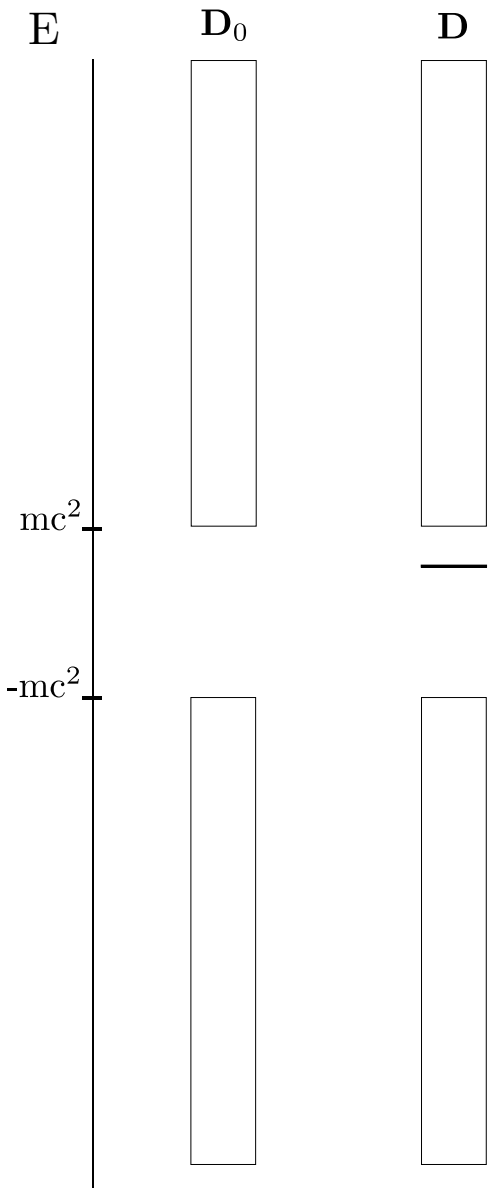
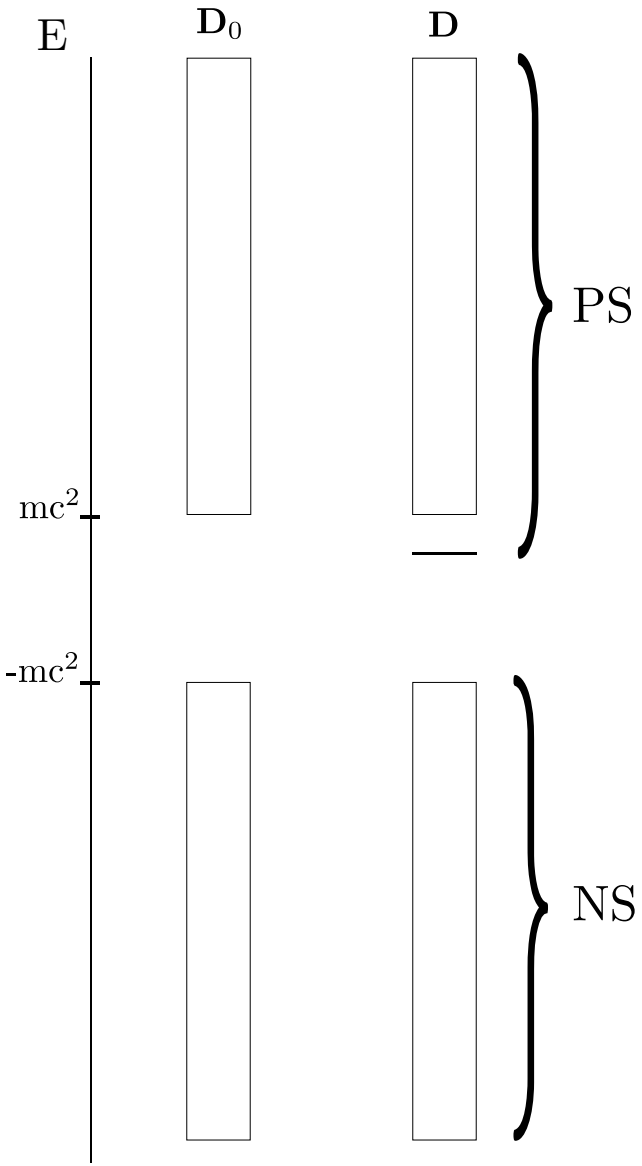


Negative electronic sea



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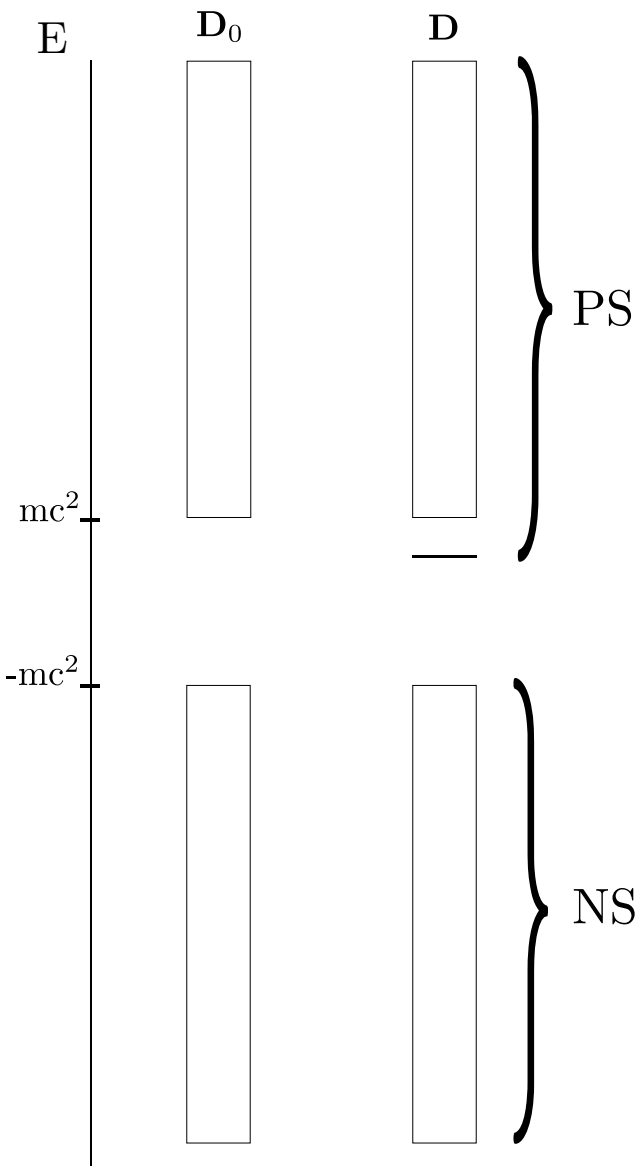
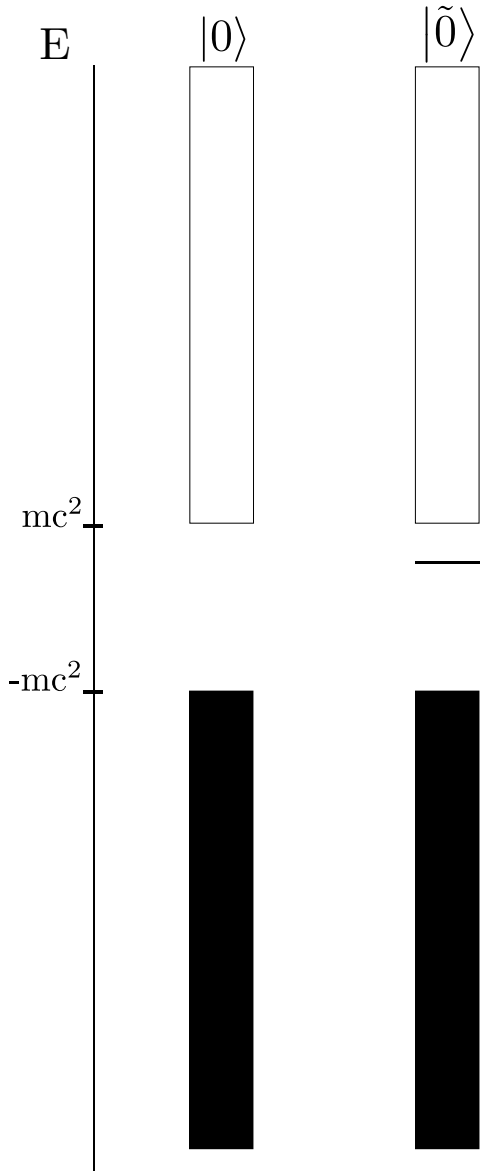


$\Rightarrow$



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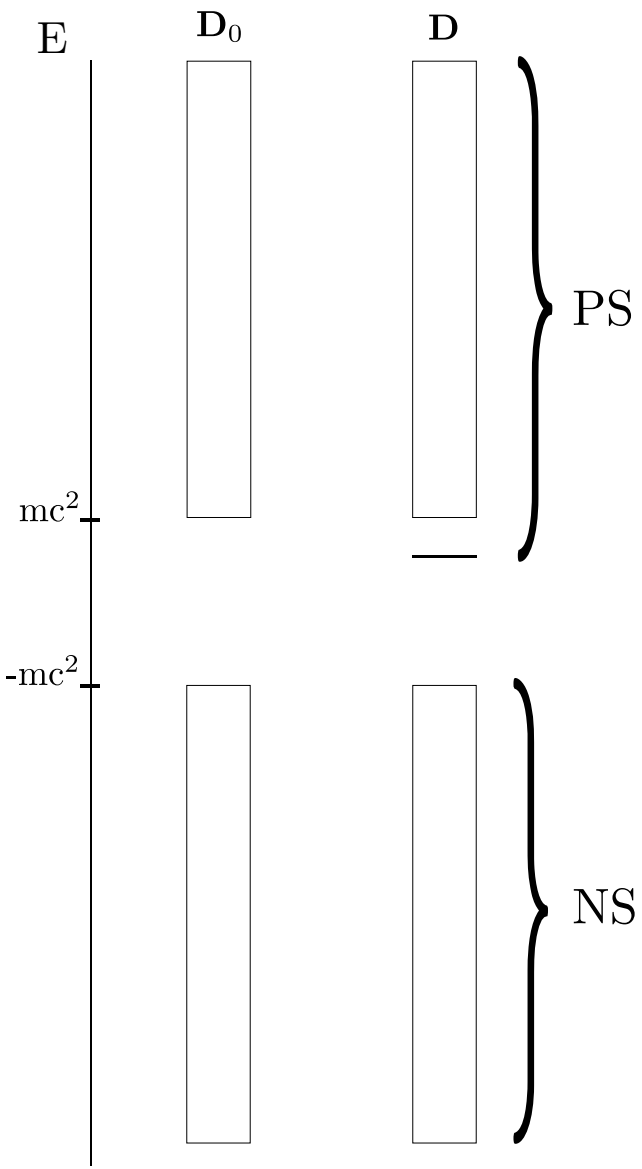

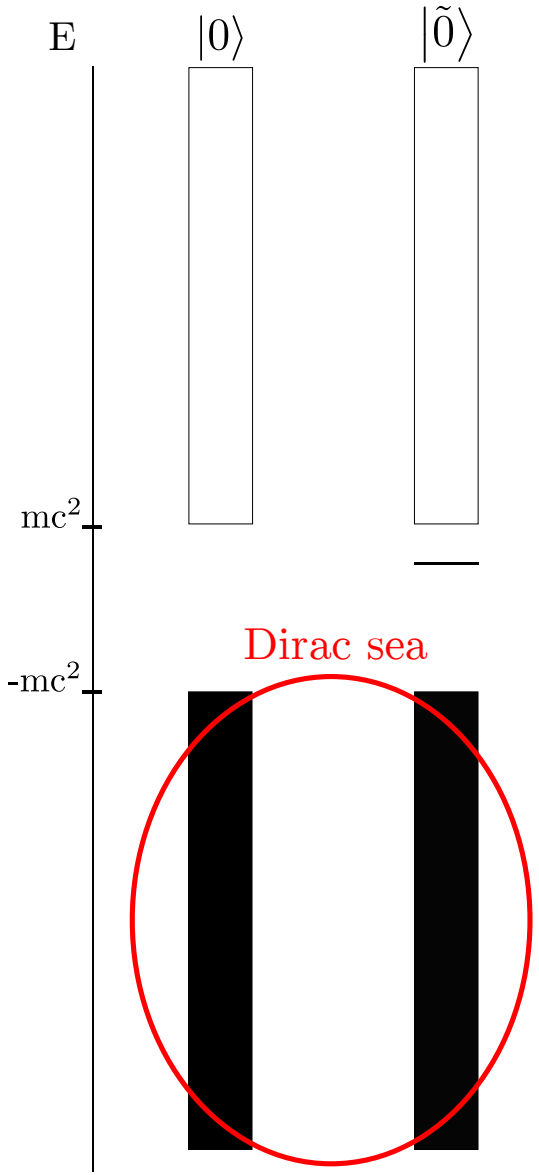

Second quantization

Fock space

$$\mathcal{F} = \bigoplus_{(n,m)=(0,0)}^{(\infty,\infty)} \mathcal{H}^{(n,m)} = \bigoplus_{q=-\infty}^{\infty} \mathcal{F}_q$$

- Electron and positron anihilation operator: $\hat{b}_p$, $\hat{d}_p$
- Fermionic Fock space: $\left\{\hat{b}_p, \hat{b}_q^\dagger\right\} = \delta_{pq}$ and $\left\{\hat{d}_p, \hat{d}_q^\dagger\right\} = \delta_{pq}$
- Dirac field operator: $\hat{\psi}(x) = \sum_{p\in \mathrm{PS}} \psi_p(x)\hat{b}_p + \sum_{p\in \mathrm{NS}} \psi_p(x)\hat{d}_p^\dagger$

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Second quantized Dirac operator

$$\hat{\mathbf{D}}_0 = \int \mathrm{tr}\left[\mathbf{D}_0(x)\hat{\boldsymbol{\rho}}_1(x,x')\right]_{x'=x} \mathrm{d}x$$

$$\hat{\mathbf{D}} = \int \mathrm{tr}\left[\mathbf{D}(x)\hat{\boldsymbol{\rho}}_1(x,x')\right]_{x'=x} \mathrm{d}x$$

- One-particle density-matrix operator: $\hat{\boldsymbol{\rho}}_1(x,x') = \hat{\boldsymbol{\psi}}^\dagger(x') \otimes \hat{\boldsymbol{\psi}}(x)$

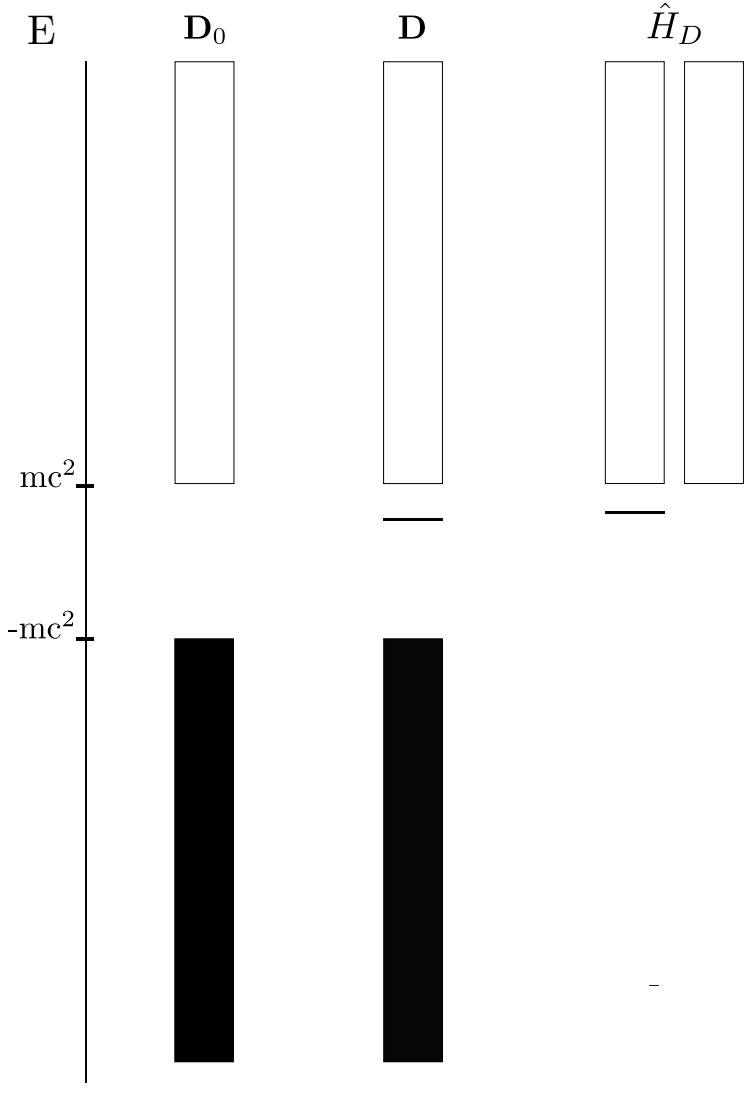
Normal ordering[2]

- Energy of the $|0\rangle$ state: $\langle 0|\,\hat{\mathbf{D}}_0\,|0\rangle \to -\infty$

Normal ordering

$$\begin{aligned}\hat{H}_D &= \mathcal{N}\left[\hat{\mathbf{D}}\right] \\ &= \hat{\mathbf{D}} - \langle 0|\,\hat{\mathbf{D}}\,|0\rangle\end{aligned}$$

- Energy of the $|0\rangle$ state: $\langle 0|\,\hat{H}_D\,|0\rangle = 0$
- $\hat{H}_D$ is bounded from below: minimization principle



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

Second Quantization

Normal ordered density operator[2]

$$\hat{\mathbf{n}}_1(x,x') = \hat{\boldsymbol{\rho}}_1(x,x') - \langle 0|\, \hat{\boldsymbol{\rho}}_1(x,x')\, |0\rangle$$

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Normal-ordered second quantized full Hamiltonian[2]

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

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

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

Hartree-Fock approximation

Energy of a N electrons state

$$E_N = \min_{|\Psi\rangle \in \mathcal{F}_N \mid \langle\Psi|\Psi\rangle = 1} \langle\Psi| \hat{H} |\Psi\rangle$$

Hartree-Fock energy

$$E_N^{\mathrm{HF}} = \min_{|\Phi\rangle \in \mathcal{S}_N} \langle\Phi| \hat{H} |\Phi\rangle$$

Hartree-Fock equations

$$(\mathbf{D}(x) + \mathbf{v}_{\mathrm{H}}(x))\phi_p(x) + \int \mathbf{v}_{\mathrm{X}}(x, x')\phi_p(x')\mathrm{d}x' = \varepsilon_p \phi_p(x)$$

- HF equations cannot be solved exactly
- Perturbation theory with respect to $\mathbf{w}$

First-order perturbation theory with respect to **w**

Zeroth-order orbitals

$$\mathbf{D}_0(x)\psi_p(x) = \varepsilon_p\psi_p(x)$$

$$\mathbf{D}(x)\tilde{\psi}_p(x) = \tilde{\varepsilon}_p\tilde{\psi}_p(x)$$

One-electron density-matrix

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

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

Pair density-matrix

$$\mathbf{n}_2(x_1,x_2) = \mathbf{n}_1(x_1,x_1)\otimes\mathbf{n}_1(x_2,x_2) - \mathbf{X}\left(\mathbf{n}_1(x_2,x_1)\otimes\mathbf{n}_1(x_1,x_2)\right)$$

First-order perturbation theory

Zeroth-order energy

- Total energy: $E_N^{(0)} = \int \mathrm{tr}\left[\mathbf{D}(x)\mathbf{n}_1(x,x')\right]$
- Relative energy: $\mathcal{E}_N^{(0)} = E_N^{(0)} - E_0^{(0)} = \int \mathrm{tr}\left[\mathbf{D}(x)\mathbf{n}_1^{\mathrm{el}}(x,x')\right]$
- where: $\mathbf{n}_1^{\mathrm{el}}(x,x') = \mathbf{n}_1(x,x') - \mathbf{n}_1^{\mathrm{vp}}(x,x')$

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First-order energy correction

- Total energy: $E_N^{(1)} = \frac{1}{2}\int\int \mathrm{Tr}\left[\mathbf{w}(x_1,x_2)\mathbf{n}_2(x_1,x_2)\right]$
- Relative energy: $\mathcal{E}_N^{(1)} = \frac{1}{2}\int\int \mathrm{Tr}\left[\mathbf{w}(x_1,x_2)\Delta\mathbf{n}_2(x_1,x_2)\right]$
- where: $\Delta\mathbf{n}_2(x_1,x_2) = \mathbf{n}_2(x_1,x_2) - \mathbf{n}_2^{\mathrm{vp}}(x_1,x_2)$

First-orer perturbation theory

First-order relative energy correction

- 2 contributions: $\mathcal{E}_N^{(1)} = \mathcal{E}_N^{\mathrm{el},(1)} + \mathcal{E}_N^{\mathrm{vp},(1)}$
- Two-body interaction: $\mathbf{w}(x_1, x_2) = \delta(x_1 - x_2)\left(\mathbb{I}_2 \otimes \mathbb{I}_2 - \sigma_1 \otimes \sigma_1\right)$

$$\mathcal{E}_N^{\mathrm{vp},(1)} = \mathcal{E}_N^{\mathrm{vp},(1),\mathrm{DC}} + \mathcal{E}_N^{\mathrm{vp},(1),\mathrm{XC}} + \mathcal{E}_N^{\mathrm{vp},(1),\mathrm{DB}} + \mathcal{E}_N^{\mathrm{vp},(1),\mathrm{XB}}$$

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where

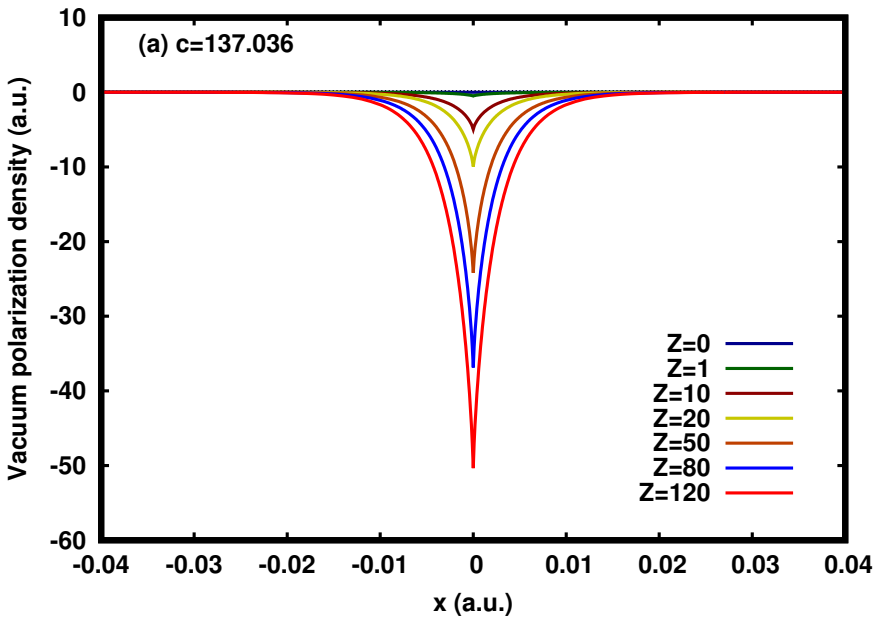
- $\mathcal{E}_N^{\mathrm{vp},(1),\mathrm{DC}} = \int n^{\mathrm{el}}(x) n^{\mathrm{vp}}(x) \mathrm{d}x$
- $\mathcal{E}_N^{\mathrm{vp},(1),\mathrm{XC}} = -\int \mathrm{tr}\left[\mathbf{n}_1^{\mathrm{el}}(x)\mathbf{n}_1^{\mathrm{vp}}(x)\right]\mathrm{d}x$
- $\mathcal{E}_N^{\mathrm{vp},(1),\mathrm{DB}} = -\frac{1}{c^2}\int j^{\mathrm{el}}(x) j^{\mathrm{vp}}(x)\mathrm{d}x$
- $\mathcal{E}_N^{\mathrm{vp},(1),\mathrm{XB}} = \frac{1}{c^2}\int \mathrm{tr}\left[\mathbf{j}_1^{\mathrm{el}}(x)\mathbf{j}_1^{\mathrm{vp}}(x)\right]\mathrm{d}x$
- $\mathbf{j}_1^{\mathrm{vp}}(x) = c\sigma_1 \mathbf{n}_1^{\mathrm{vp}}(x)$

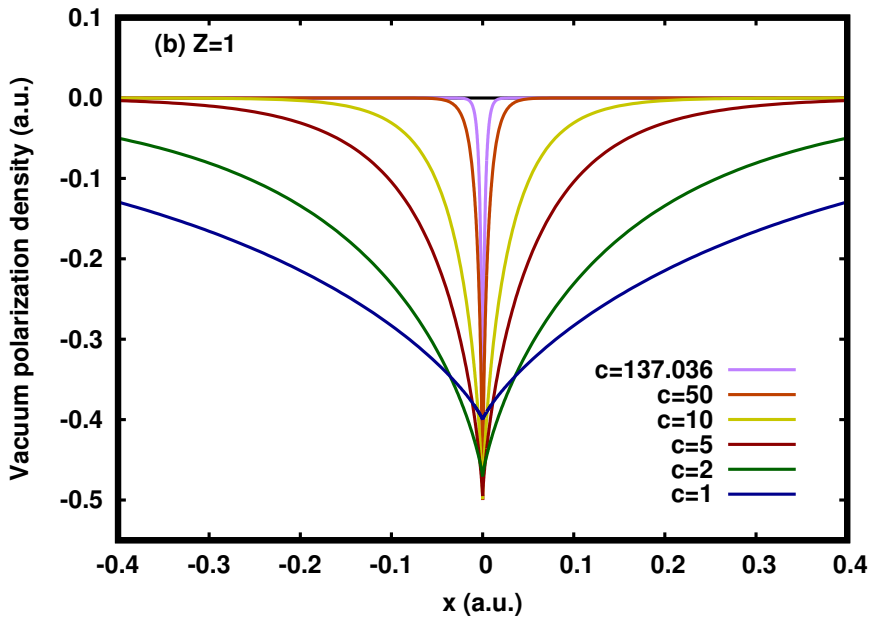
Vacuum polarization density

Vacuum Polarization Density

Spontaneous creation of electron positron pairs due to the potential

$$\begin{aligned} n^{\mathrm{vp}}(x) &= \mathrm{tr}\left[\mathbf{n}_1^{\mathrm{vp}}(x,x)\right] \\ &= \sum_{p\in \mathrm{NS}} \tilde{\psi}_p^\dagger(x)\tilde{\psi}_p(x) - \sum_{p\in \mathrm{NS}} \psi_p^\dagger(x)\psi_p(x) \end{aligned}$$





Vacuum polarization density

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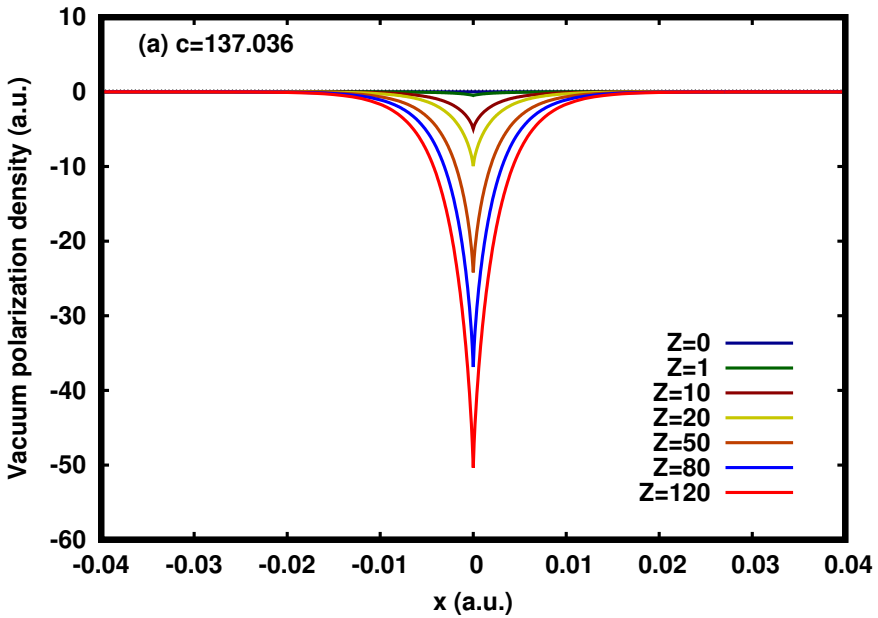
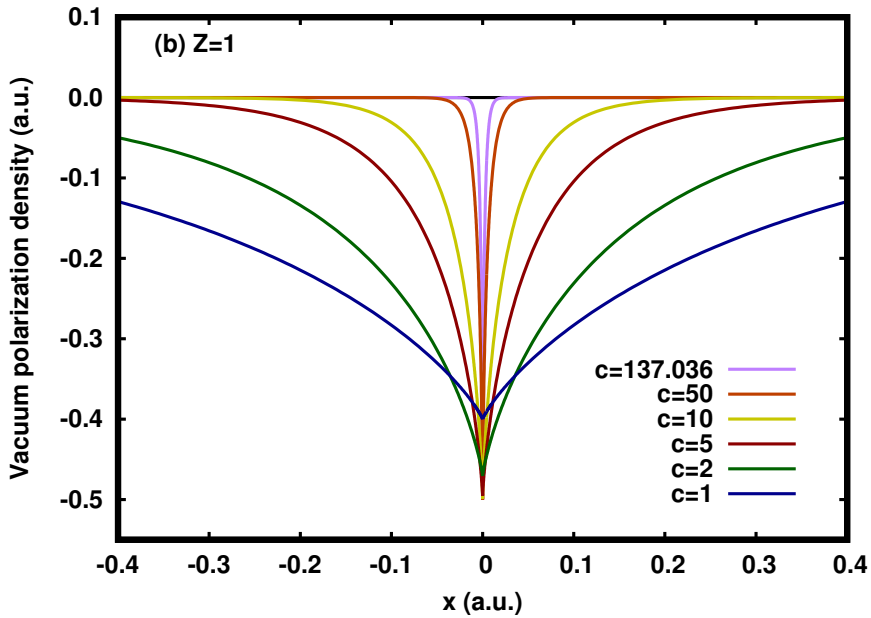
Spontaneous creation of electron positron pairs due to the potential

$$n^{\mathrm{vp}}(x) = -\int \frac{\mathrm{d}k}{\pi} \frac{\kappa}{k^2+\kappa^2} \left(\kappa \cos(2k|x|) - \frac{\tilde{\varepsilon}_b}{\varepsilon_k} \sin(2k|x|) \right)$$





Vacuum charge

- Is the vacuum charged?
- $Q^{\text{vac}} = -\int n^{\text{vp}}(x)\mathrm{d}x \neq 0$!

Vacuum charge

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- $Q^{\mathrm{vac}} = -\int n^{\mathrm{vp}}(x)\mathrm{d}x \neq 0$!
- The one-particle density matrix operator is not trace class![3]

Vacuum charge

$$Q^{\mathrm{vac}} = -\left(N_e^{\mathrm{vac}} - N_p^{\mathrm{vac}}\right)$$

- $N_e^{\mathrm{vac}} = \iint \mathrm{tr}\left[\mathbf{P}_+^0(x',x)\mathbf{n}_1^{\mathrm{vp}}(x,x')\right]\mathrm{d}x\mathrm{d}x'$
- $N_p^{\mathrm{vac}} = -\iint \mathrm{tr}\left[\mathbf{P}_-^0(x',x)\mathbf{n}_1^{\mathrm{vp}}(x,x')\right]\mathrm{d}x\mathrm{d}x'$
- Then, $Q^{\mathrm{vac}} = 0$

[3] C. Hainzl, M. Lewin, E. Séré and J. P. Solovej, Phys. Rev. A 76, 052104 (2007)

First-order for the hydrogen-like atom

Zeroth-order energy: Bound state energy

$$\mathcal{E}_1^{(0)} = E_1^{(0)} - E_0^{(0)} = \tilde{\varepsilon}_b$$

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Zeroth-order energy: Bound state energy

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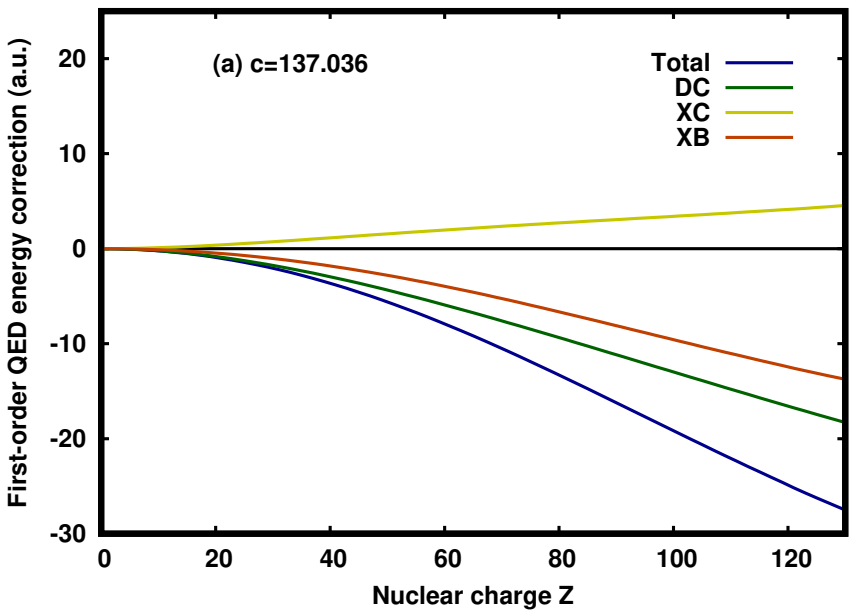
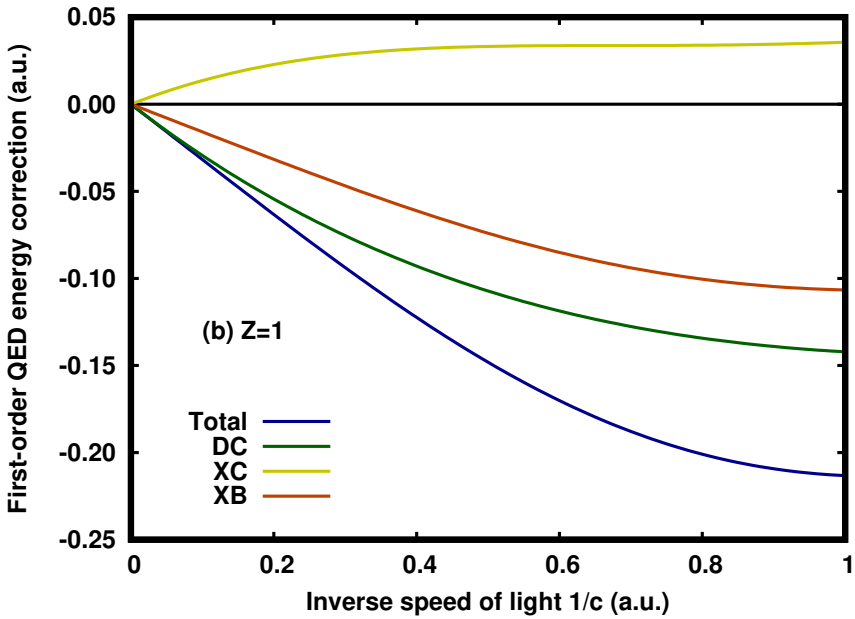
First-order energy correction: Lamb shift correction

$$\begin{aligned} \mathcal{E}_1^{(1)} &= 0 + \mathcal{E}_1^{\mathrm{vp},(1)} \\ &= \mathcal{E}_1^{\mathrm{vp},(1),\mathrm{DC}} + \mathcal{E}_1^{\mathrm{vp},(1),\mathrm{XC}} + 0 + \mathcal{E}_1^{\mathrm{vp},(1),\mathrm{XB}} \end{aligned}$$

First-order for the hydrogen-like atom





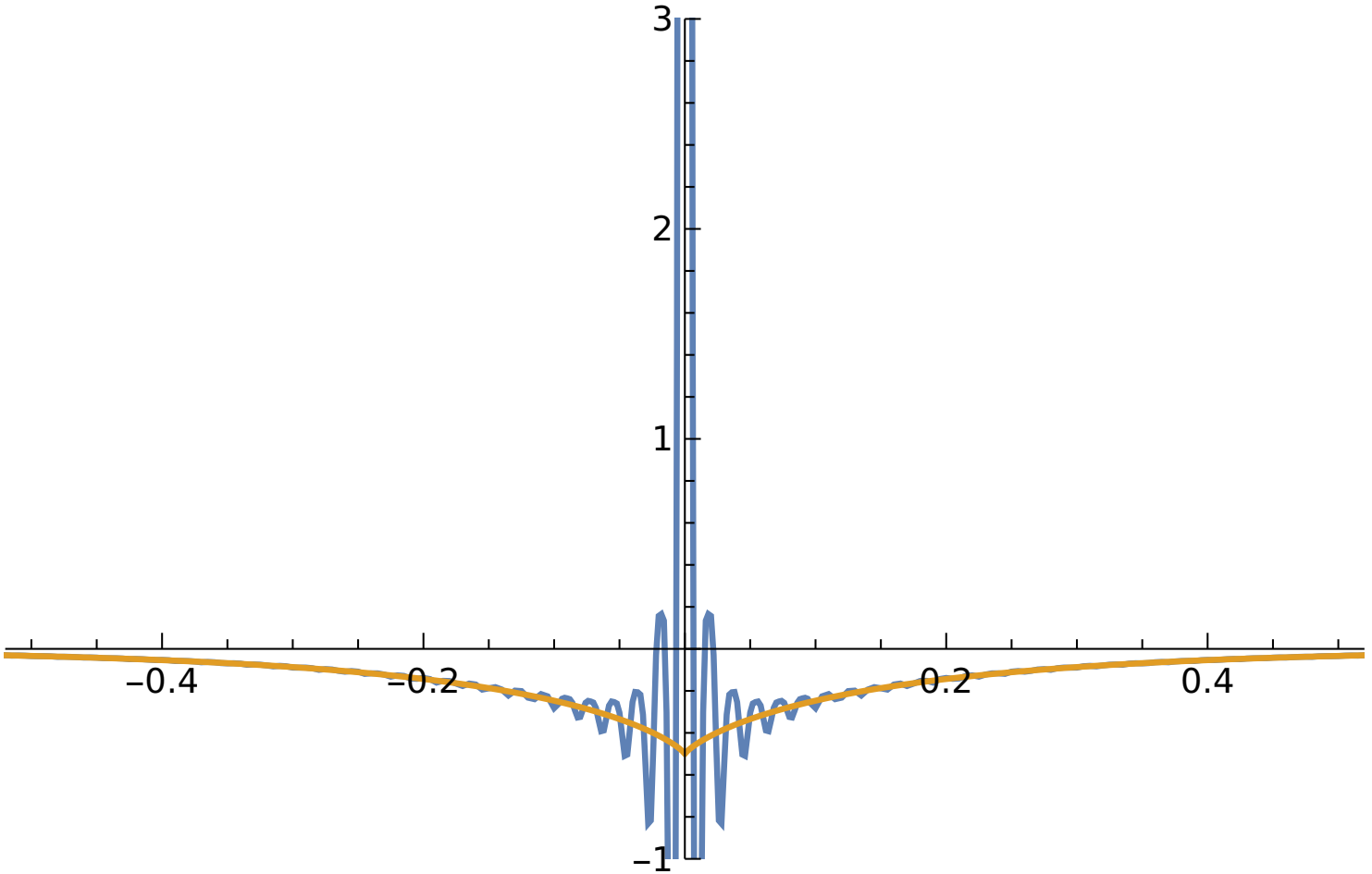
- Recover all terms and their signs compared to 3D
- Terms do not have the same amplitude as in 3D

Conclusion

- QED effects have some importance in quantum calculations: even for the Hydrogen atom
- Need to take into account the negative energy solutions of the Dirac equation
- Even an Hydrogen calculation need a FCI calculation
- 1D toy model allows a better comprehension of the QED effects

Perspective: Basis Expansion

- Implementation in a code
- Convergence of such quantities in basis sets



3D to 1D

Wave function

Pair density matrix operator