Relativistic electronic-structure methods based on effective quantum electrodynamics

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Outline

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Importance of special relativity in quantum chemistry

- It is known that **special relativity effects** can strongly influence **chemical properties of heavy elements**.
  Pyykkö, Annu. Rev. Phys. Chem., 2012

- **A simple explanation:** the average electron velocity in hydrogen-like atoms

$$\sqrt{\langle \hat{v}^2 \rangle} = \frac{Z}{n}$$

  can be a significant fraction of the speed of light $c \approx 137$ a.u. for large Z.

- **Two striking examples:**
  - **Gold would not be yellow without relativity!**
    Relativity reduces the 5d $\rightarrow$ 6s excitation energy from 3.6 eV (UV) to 2 eV (Vis)
    Romaniello, de Boeij, JCP, 2005
  - **Lead-acid batteries would not work without relativity!**

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

    Relativity increases the electromotive force from 0.39 V to 2.13 V due to destabilization of PbO_2
    Ahuja, Blomqvist, Larsson, Pyykkö, Zaleski-Ejgierd, PRL, 2011

One-electron Dirac equation

- We start with the **one-electron Dirac equation** with a potential v:

$$(\mathbf{D}_0 + v(\vec{r}))\,\psi_p(\vec{r}) = \varepsilon_p \psi_p(\vec{r})$$

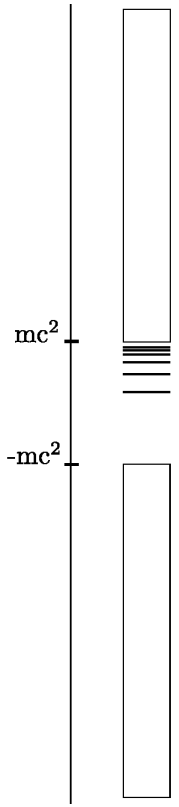
with the 4×4 **free Dirac Hamiltonian**

$$\mathbf{D}_0 = c\vec{\boldsymbol{\alpha}} \cdot \vec{p} + \boldsymbol{\beta} mc^2$$

where $\vec{p} = -\mathrm{i}\vec{\nabla}$ is the momentum operator, and $\vec{\boldsymbol{\alpha}} = (\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3)$ and $\boldsymbol{\beta}$ are the 4×4 Dirac matrices

$$\vec{\boldsymbol{\alpha}} = \begin{pmatrix} \mathbf{0}_2 & \vec{\boldsymbol{\sigma}} \\ \vec{\boldsymbol{\sigma}} & \mathbf{0}_2 \end{pmatrix} \text{ and } \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{I}_2 \end{pmatrix}$$

and $\vec{\boldsymbol{\sigma}} = (\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3)$ are the 2×2 Pauli matrices.



- The (4-component) eigenfunctions $\{\psi_p\}$ can be partitioned into
  - **positive-energy states (PS)** $\{\psi_p\}_{p\in\mathrm{PS}}$ $\longleftarrow$ **electrons**
  - **negative-energy states (NS)** $\{\psi_p\}_{p\in\mathrm{NS}}$ $\longleftarrow$ **positrons**

- Note: What we call "electrons" and "positrons" depend on the potential v!

No-pair many-electron Dirac-Coulomb-Breit (DCB) Hamiltonian

- In relativistic quantum chemistry, we normally neglect the negative-energy (positronic) states, which is called the **no-pair approximation**.
- Thus, we introduce the **Dirac electron field operator** (with only positive-energy states)

$$\hat{\psi}_+(\vec{r}) = \sum_{p \in \mathrm{PS}} \hat{b}_p \psi_p(\vec{r})$$

where $\{\hat{b}_p\}$ are electron annihilation operators.

- The **no-pair many-electron Dirac-Coulomb-Breit (DCB) Hamiltonian** is

$$\hat{H}^{\mathrm{np}} = \hat{T}^{\mathrm{np}} + \hat{V}^{\mathrm{np}} + \hat{W}^{\mathrm{np}}$$

with the **no-pair** free-electron and external potential operators

$$\hat{T}^{\mathrm{np}} = \int \hat{\psi}_+^\dagger(\vec{r}) \mathbf{D}_0 \hat{\psi}_+(\vec{r}) \mathrm{d}\vec{r} \quad \text{and} \quad \hat{V}^{\mathrm{np}} = \int \hat{\psi}_+^\dagger(\vec{r}) v(\vec{r}) \hat{\psi}_+(\vec{r}) \mathrm{d}\vec{r}$$

and the **no-pair** Coulomb-Breit two-electron interaction operator

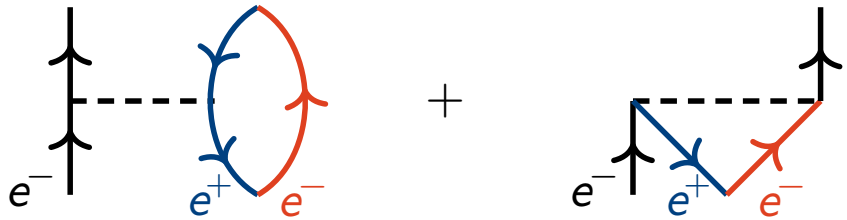
$$\hat{W}^{\mathrm{np}} = \frac{1}{2} \iint \hat{\psi}_+^\dagger(\vec{r}_1) \hat{\psi}_+^\dagger(\vec{r}_2) \mathbf{w}(\vec{r}_{12}) \hat{\psi}_+(\vec{r}_2) \hat{\psi}_+(\vec{r}_1) \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2$$

where

$$\mathbf{w}(\vec{r}_{12}) = \underbrace{\frac{1}{r_{12}}}_{\text{Coulomb}} \underbrace{-\frac{1}{2r_{12}} \left(\vec{\boldsymbol{\alpha}} \otimes \vec{\boldsymbol{\alpha}} + \frac{(\vec{\boldsymbol{\alpha}} \cdot \vec{r}_{12}) \otimes (\vec{\boldsymbol{\alpha}} \cdot \vec{r}_{12})}{r_{12}^2} \right)}_{\text{Breit}}$$

Beyond the no-pair approximation

- The next challenge in relativistic quantum chemistry is to go **beyond the no-pair approximation**, i.e. to include the **quantum-electrodynamics (QED) effect of vacuum polarization due to virtual electron-positron pairs**.



- This is necessary for high accuracy, but also to put relativistic quantum chemistry on firmer theoretical grounds.

- How to include QED effects in relativistic quantum chemistry?
  - Highly accurate QED calculations for very few electron systems
    E.g., Indelicato, Mohr, Book chapter, 2016
  - Model one-electron QED correction potentials for many-electron systems
    E.g., Sunaga, Salman, Saue, JCP, 2022

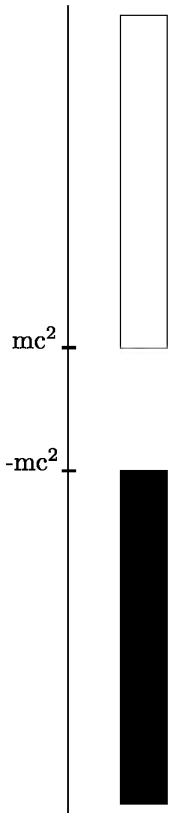
- Here, we explore an **effective QED theory**, i.e. without photons but with the static Coulomb-Breit two-particle interaction.

  Chaix, Iracane, JPB, 1989; Saue, Visscher, Book chapter, 2003;
  Hainzl, Lewin, Séré, Solovej, PRA, 2007; Kutzelnigg, CP, 2012; Liu, Lindgren, JCP, 2013;
  Toulouse, SciPost Chem., 2021.

Outline

Effective quantum electrodynamics (1/2)

- We start from the **free vacuum state** $|0\rangle$ where all the free negative-energy states are filled (called the "Dirac sea").



- The **Dirac field operator** in terms of free electron and positron states $\{\psi_p^0\}$ is then:

$$\hat{\psi}(\vec{r}) = \sum_{p \in \mathrm{PS}} \hat{b}_p \psi_p^0(\vec{r}) + \sum_{p \in \mathrm{NS}} \hat{d}_p^\dagger \psi_p^0(\vec{r})$$

where $\{\hat{b}_p\}$ are electron annihilation operators and $\{\hat{d}_p^\dagger\}$ are positron creation operators such that $\hat{b}_p|0\rangle = \hat{d}_p|0\rangle = 0$.

- We work in the **electron-positron Fock space** which can be decomposed into charge sectors:

$$\mathcal{F} = \bigoplus_N \mathcal{F}_N$$

where $\mathcal{F}_N$ is the Fock space for N negative charges.

- In $\mathcal{F}_N$, the number of electrons N_e and the number of positrons N_p **are not fixed**, but only the net (opposite) charge $N = N_\mathrm{e} - N_\mathrm{p}$ is fixed.

Effective quantum electrodynamics (2/2)

- The **effective QED Hamiltonian** is defined as

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

with the **normal-ordered** free-particle and external potential operators

$$\hat{T} = \int \mathcal{N}_0 \left[\hat{\psi}^\dagger(\vec{r}) \mathbf{D}_0 \hat{\psi}(\vec{r}) \right] \mathrm{d}\vec{r} \quad \text{and} \quad \hat{V} = \int \mathcal{N}_0 \left[\hat{\psi}^\dagger(\vec{r}) v(\vec{r}) \hat{\psi}(\vec{r}) \right] \mathrm{d}\vec{r}$$

and the **normal-ordered** Coulomb-Breit two-particle interaction operator

$$\hat{W} = \frac{1}{2} \iint \mathcal{N}_0 \left[\hat{\psi}^\dagger(\vec{r}_1) \hat{\psi}^\dagger(\vec{r}_2) \mathbf{w}(\vec{r}_{12}) \hat{\psi}(\vec{r}_2) \hat{\psi}(\vec{r}_1) \right] \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2$$

- The **normal ordering** $\mathcal{N}_0[...]$ is taken **with respect to the free vacuum state** $|0\rangle$:
  - the annihilation electron and positron operators $\hat{b}_p$ and $\hat{d}_p$ are put to the right of the creation electron and positron operators $\hat{b}_p^\dagger$ and $\hat{d}_p^\dagger$
  - the energy is calculated with respect to the free vacuum state, i.e. $\langle 0|\hat{H}|0\rangle = 0$
  - the Hamiltonian correctly has charge-conjugation symmetry: $\hat{C}\hat{H}[v]\hat{C}^\dagger = \hat{H}[-v]$

Relativistic DFT based on effective QED (1/2)

- We can formulate a **relativistic density-functional theory (DFT) based on effective QED** in a very similar way to non-relativistic DFT.
  Toulouse, SciPost Chem., 2021.

- In effective QED, the **ground-state energy for N negative charges** is

$$E_N = \min_{|\Psi\rangle \in \mathcal{W}_N} \langle \Psi | \hat{T} + \hat{W} + \hat{V} | \Psi \rangle$$

  where $\mathcal{W}_N = \{|\Psi\rangle \in \mathcal{F}_N \mid \langle \Psi | \Psi \rangle = 1\}$.

- Thus, we define the corresponding **Levy-Lieb universal density functional** as

$$F[n] = \min_{\substack{|\Psi\rangle \in \mathcal{W}_N \\ |\Psi\rangle \rightsquigarrow n}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

  where n is the **opposite charge density** associated with the **normal-ordered density operator** $\hat{n}(\vec{r}) = \mathcal{N}_0 \left[\hat{\psi}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \right]$.

- The **exact ground-state energy for N negative charges** can then be expressed as

$$E_N = \min_{n \in \mathcal{D}_N} \left(F[n] + \int v(\vec{r}) n(\vec{r}) \mathrm{d}\vec{r} \right)$$

  where $\mathcal{D}_N = \{n \mid \exists\, |\Psi\rangle \in \mathcal{W}_N \text{ s.t. } |\Psi\rangle \rightsquigarrow n\}$ is the set of N-representable densities.

Relativistic DFT based on effective QED (2/2)

- We can set up a **Kohn-Sham DFT scheme** by decomposing the universal functional as

$$F[n] = \min_{\substack{|\Phi\rangle \in \mathcal{S}_N \\ |\Phi\rangle \rightsquigarrow n}} \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathrm{Hxc}}[n]$$

where $\mathcal{S}_N$ is the set of all N-electron Slater determinant states and $E_{\mathrm{Hxc}}[n]$ is a Hartree-exchange-correlation density functional.

- The **exact ground-state energy for N negative charges** can then be expressed as

$$E_N = \min_{|\Phi\rangle \in \mathcal{S}_N} \left(\langle \Phi | \hat{T} + \hat{V} | \Phi \rangle + E_{\mathrm{Hxc}}[n_{|\Phi\rangle}] \right)$$

- The corresponding **Kohn-Sham equations** are

$$\left(\mathbf{D}_0 + v(\vec{r}) + v_{\mathrm{Hxc}}(\vec{r})\right) \psi_p(\vec{r}) = \varepsilon_p \psi_p(\vec{r})$$

where $v_{\mathrm{Hxc}}(\vec{r}) = \delta E_{\mathrm{Hxc}}[n]/\delta n(\vec{r})$ and the density is written as

$$n(\vec{r}) = \sum_{i=1}^{N} \psi_i^\dagger(\vec{r}) \psi_i(\vec{r}) + n^{\mathrm{vp}}(\vec{r})$$

where $n^{\mathrm{vp}}(\vec{r})$ is the **vacuum-polarization density**

$$n^{\mathrm{vp}}(\vec{r}) = \sum_{p \in \mathrm{NS}} \psi_p^\dagger(\vec{r}) \psi_p(\vec{r}) - \sum_{p \in \mathrm{NS}} \psi_p^{0\dagger}(\vec{r}) \psi_p^0(\vec{r})$$

How to implement effective QED in practice?

- Effective QED, like standard QED, suffers from **singularities**.
- In particular, in the complete-basis limit, the **vacuum-polarization density diverges!**
- In standard QED, this divergence can be regularized with a UV cutoff and the dependence on the cutoff is absorbed into a redefinition of the elementary charge. This is called **charge renormalization**.
- In effective QED, **charge renormalization** can also be performed in the complete-basis limit.
  Hainzl, Lewin, Séré, Solovej, PRA, 2007
- **But we do not know yet how to handle the situation in a finite basis!**
- To progress toward a practical implementation in a finite basis, we will now study a **1D effective QED model**.
  Audinet, Toulouse, JCP, 2023

Outline

1D hydrogen-like Dirac equation

- We consider a **1D hydrogen-like Dirac equation** with a **delta potential**:

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

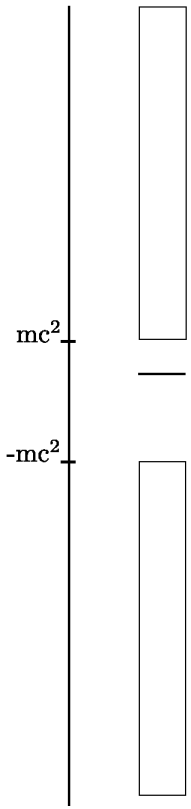
with the **1D** 2×2 **free Dirac Hamiltonian**

$$\mathbf{D}_0 = c\boldsymbol{\sigma}_1\, p_x + \boldsymbol{\sigma}_3 mc^2$$

where $p_x = -\mathrm{i}\,\mathrm{d}/\mathrm{d}x$ is the momentum operator, and $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_3$ are the Pauli matrices

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{ and } \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Lapidus, AJP, 1983



- **The delta potential simulates the Coulomb interaction in 1D.**
  Herrick, Stillinger, PRA, 1975
- The **bound and continuum eigenfunctions** can be calculated **analytically**.
  Nogami, Beachey, EL, 1986
- There are subtilities on the mathematical interpretation of the delta potential.
  Audinet, Morellini, Levitt, Toulouse, in preparation

Vacuum-polarization density in a *complete* basis

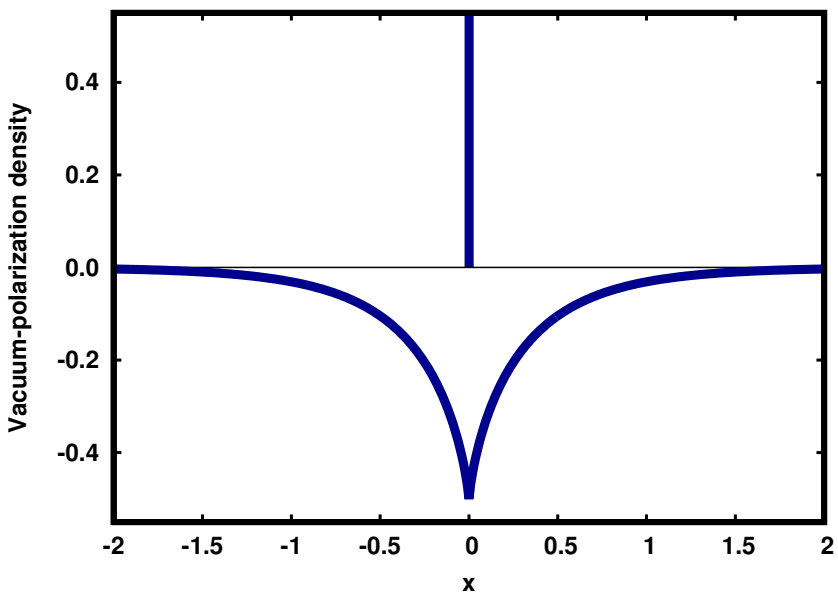
- At first order in Z, the **(Uehling) vacuum-polarization density** is

$$n^{\text{vp}}(x) = \frac{Z}{\pi c}\delta(x) + n^{\text{vp}}_{\text{reg}}(x)$$

where the regular part is $n^{\text{vp}}_{\text{reg}}(x) = -\dfrac{Zm}{\pi}\displaystyle\int_1^\infty \frac{e^{-2mc|x|t}}{t\sqrt{t^2-1}}\mathrm{d}t.$

- The vacuum-polarization density has a **singular delta contribution at the nucleus**, similarly to the 3D case, but with a **finite coefficient**.

- Vacuum-polarization density $n^{\text{vp}}(x)$ for $Z = c = m = 1$:



Audinet, Toulouse, JCP, 2023; Audinet, Morellini, Levitt, Toulouse, in preparation

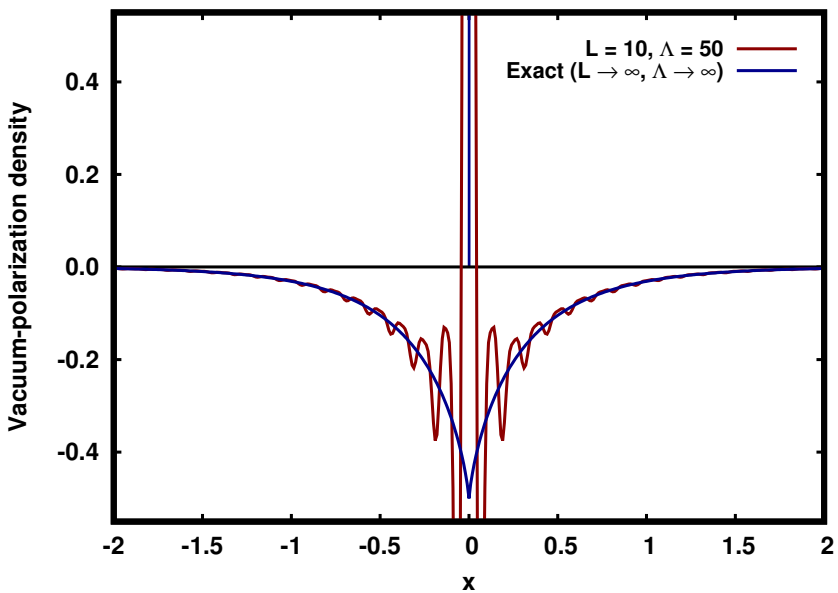
Vacuum-polarization density in a *finite* basis

- We use a **finite plane-wave basis** $\left\{e^{ikx}, k = \frac{2\pi\mathbb{Z}}{L}, |k| \leq \Lambda\right\}$ on the interval $[-L/2, L/2]$.

- The vacuum-polarization density is calculated from the eigenfunctions at Z and $Z = 0$:

$$n^{\text{vp}}(x) = \sum_{p\in\text{NS}} \psi_p^{Z\dagger}(x)\psi_p^{Z}(x) - \sum_{p\in\text{NS}} \psi_p^{0\dagger}(x)\psi_p^{0}(x)$$

- Vacuum-polarization density $n^{\text{vp}}(x)$ for $Z = c = m = 1$ in the **finite basis**:



Audinet, Morellini, Levitt, Toulouse, in preparation

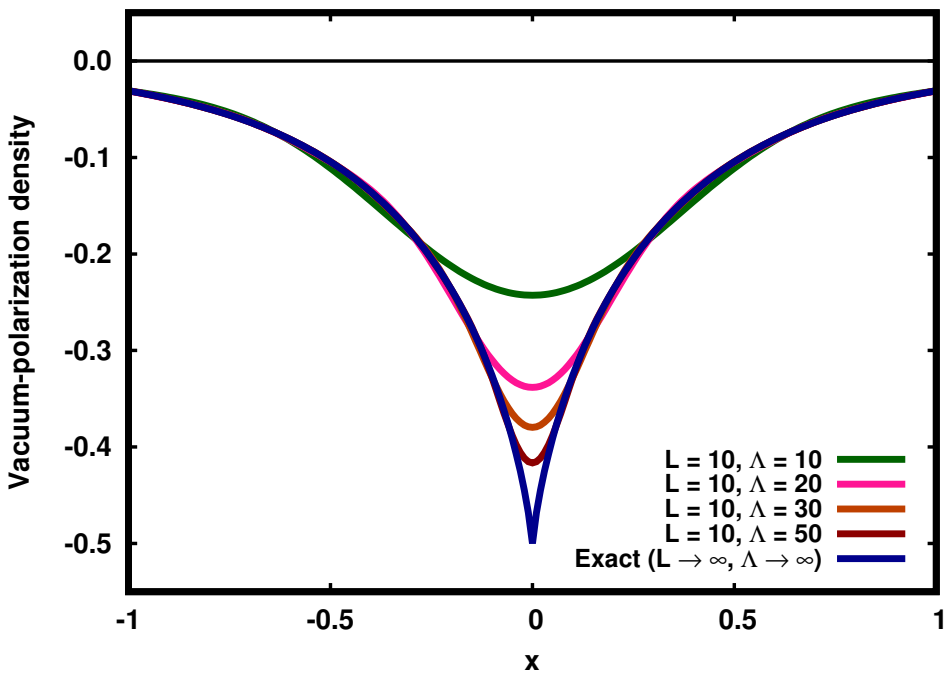
Regularized vacuum-polarization density in a finite basis

- The vacuum-polarization density calculated in the finite basis is **regularized in Fourier space by removing the large-momentum contributions**:

$$n^{\mathrm{vp}}_{\mathrm{regularized}}(x) = F^{-1}\Big[\, F\left[n^{\mathrm{vp}}\right](k)\, \theta(k_{\mathrm{max}} - k) - F\left[n^{\mathrm{vp}}\right](k_{\mathrm{max}})\Big]$$

for some k_{max} depending on the basis.

- **Regularized** vacuum-polarization density $n^{\mathrm{vp}}(x)$ for $Z = c = m = 1$ in the finite basis:



Audinet, Morellini, Levitt, Toulouse, in preparation

Conclusions

- **Summary:**
  - Effective QED includes electron-positron pairs without photons
  - More tractable alternative to standard QED for electronic-structure calculations
  - Need to handle singularities in a finite basis for a practical implementation
  - Our 1D model suggests that it can be done

- **Outlook:**
  - Develop relativistic DFT for the 1D effective QED model
  - Extension to real 3D systems

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