



Relativistic electronic-structure methods based on effective quantum electrodynamics

Julien Toulouse Laboratoire de Chimie Théorique Sorbonne Université and CNRS, Paris, France

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1 Relativistic electronic-structure theory



2 Effective quantum electrodynamics



3 1D model for effective quantum electrodynamics







Importance of special relativity in electronic-structure theory

It is known that special relativity effects can strongly influence physical and chemical properties of heavy elements.

Pyykkö, Annu. Rev. Phys. Chem., 2012

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

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

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!

 $\mathsf{Pb} + \mathsf{PbO}_2 + 2\mathsf{H}_2\mathsf{SO}_4 \longrightarrow 2\mathsf{PbSO}_4 + 2\mathsf{H}_2\mathsf{O}$

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*:

$$\left(\mathsf{D}_0 + \mathsf{v}(ec{r})
ight) \psi_{
ho}(ec{r}) = arepsilon_{
ho} \psi_{
ho}(ec{r})$$

on the Hilbert space $L^2(\mathbb{R}^3, \mathbb{C}^4)$ with the 4×4 free Dirac Hamiltonian

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

where $\vec{p} = -i\vec{\nabla}$ is the momentum operator, and $\vec{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and β are the 4 × 4 Dirac matrices

$$\vec{lpha} = \left(egin{array}{cc} \mathbf{0}_2 & \vec{\sigma} \\ \vec{\sigma} & \mathbf{0}_2 \end{array}
ight)$$
 and $\boldsymbol{eta} = \left(egin{array}{cc} \mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{I}_2 \end{array}
ight)$

and $ec{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ are the 2 imes 2 Pauli matrices.

We will work in a finite-dimensional Hilbert space with IR cutoff *L* and UV cutoff Λ : $h = \operatorname{span} \left(\mathbf{r} \in (-L/2, L/2)^3 \mapsto e^{i\mathbf{k}\cdot\mathbf{r}} \mid \mathbf{k} \in (2\pi\mathbb{Z}/L)^3, \ |\mathbf{k}| \le \Lambda \right) \otimes \mathbb{C}^4$

▶ The (4-component) eigenfunctions $\{\psi_p\}$ can be partitioned into

- positive-energy states (PS) $\{\psi_p\}_{p\in\mathsf{PS}}$ \leftarrow electrons
- negative-energy states (NS) $\{\psi_{
 ho}\}_{
 ho\in \mathsf{NS}}$ \longleftarrow positrons



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

- In relativistic electronic-structure theory, we normally neglect the negative-energy (positronic) states, which is called the **no-pair approximation**.
- ► We thus work in the Fock space generated by only the positive-energy states and we introduce the **Dirac electron field operator**

$$\hat{\psi}_+(ec{r}) = \sum_{
ho \in \mathsf{PS}} \hat{b}_{
ho} \psi_{
ho}(ec{r})$$

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

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

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

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

$$\hat{T}^{np} = \int \hat{\psi}^{\dagger}_{+}(\vec{r}) \mathsf{D}_{0} \hat{\psi}_{+}(\vec{r}) \mathsf{d}\vec{r} \text{ and } \hat{V}^{np} = \int \hat{\psi}^{\dagger}_{+}(\vec{r}) v(\vec{r}) \hat{\psi}_{+}(\vec{r}) \mathsf{d}\vec{r}$$

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

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

where

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

Beyond the no-pair approximation

The next challenge in relativistic electronic-structure theory 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 electronic-structure theory on firmer theoretical grounds.
- ▶ How to include QED effects in relativistic electronic-structure theory?
 - 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.



2 Effective quantum electrodynamics

Effective quantum electrodynamics (1/2)

- We start from the free vacuum state |0⟩ 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 $\{\psi_{p}^{o}\}$ is then:

$$\hat{\psi}(ec{r}) = \sum_{
ho\in\mathsf{PS}} \hat{b}_{
ho} \psi^0_{
ho}(ec{r}) + \sum_{
ho\in\mathsf{NS}} \hat{d}^\dagger_{
ho} \psi^0_{
ho}(ec{r})$$

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 $N = N_e - N_p$ is fixed.

> PS

NS

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

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

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

$$\hat{W} = \frac{1}{2} \iint \mathcal{N}_{0} \Big[\hat{\psi}^{\dagger}(\vec{r}_{1}) \hat{\psi}^{\dagger}(\vec{r}_{2}) \mathbf{w}(\vec{r}_{12}) \hat{\psi}(\vec{r}_{2}) \hat{\psi}(\vec{r}_{1}) \Big] \mathrm{d}\vec{r}_{1} \mathrm{d}\vec{r}_{2}$$

• 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. $\langle 0|\hat{H}|0
 angle=0$
- the Hamiltonian correctly has charge-conjugation symmetry: $\hat{C}\hat{H}[v]\hat{C}^{\dagger}=\hat{H}[-v]$
- ▶ \hat{H} conserves **charge**, not electron/positron numbers $N_{\rm e}$ and $N_{\rm p}$

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 $\mathcal{D}_N = \{n \mid \exists \mid \Psi \rangle \in \mathcal{W}_N \text{ s.t. } |\Psi \rangle \rightsquigarrow n\}$ 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

$$F[n] = \min_{\substack{|\Phi\rangle \in S_N \\ |\Phi\rangle \rightsquigarrow n}} \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathsf{Hxc}}[n]$$

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

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

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

The corresponding Kohn-Sham equations are

$$\left(\mathsf{D}_0 + v(ec{r}) + v_{\mathsf{Hxc}}(ec{r})
ight) \psi_{
ho}(ec{r}) = arepsilon_{
ho} \psi_{
ho}(ec{r})$$

where $v_{Hxc}(\vec{r}) = \delta E_{Hxc}[n] / \delta n(\vec{r})$ 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 $n^{vp}(\vec{r})$ is the vacuum-polarization density

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

How to implement effective QED in practice?

- ► Effective QED, like standard QED, suffers from singularities.
- ▶ In particular, the vacuum-polarization density diverges in the UV limit $\Lambda \rightarrow \infty$.
- In standard QED, this divergence can be regularized by using a finite UV cutoff Λ and the dependence on the cutoff Λ 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 infinite-dimensional setting.
 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; Audinet, Morellini, Levitt, Toulouse, JPA, 2025





3 1D model for effective quantum electrodynamics

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

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

on the Hilbert space $L^2(\mathbb{R}, \mathbb{C}^2)$ with the 1D 2 × 2 free Dirac Hamiltonian

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

where $\rho_x=-i\,d/dx$ is the momentum operator, and σ_1 and σ_3 are the Pauli matrices

$$\sigma_1=\left(egin{array}{cc} 0 & 1 \ 1 & 0 \end{array}
ight)$$
 and $\sigma_3=\left(egin{array}{cc} 1 & 0 \ 0 & -1 \end{array}
ight)$

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, JPA, 2025

mc²

-mc²

Vacuum-polarization density in a complete basis

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

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

where the regular part is $n_{\rm reg}^{\rm vp}(x) = -\frac{Zm}{\pi} \int_1^\infty \frac{e^{-2mc|x|t}}{t\sqrt{t^2-1}} {\rm d}t.$

- 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 $n^{vp}(x)$ for Z = c = m = 1:



Audinet, Toulouse, JCP, 2023; Audinet, Morellini, Levitt, Toulouse, JPA, 2025

Vacuum-polarization density in a finite basis

► We use a finite plane-wave basis $\left\{x \in (-L/2, L/2) \mapsto e^{ikx} \mid k \in 2\pi \mathbb{Z}/L, |k| \leq \Lambda \right\}$.

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

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

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



Audinet, Morellini, Levitt, Toulouse, JPA, 2025

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:

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

for some $k_{\max} \approx \Lambda$ depending on the basis.

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



Audinet, Morellini, Levitt, Toulouse, JPA, 2025

QED correction to the bound-state energy (Lamb shift)

The vacuum-polarization density matrix creates a shift of the bound-state energy through the 1D analog of the Coulomb-Breit two-particle interaction

$$\mathbf{w}(x_1, x_2) = \delta(x_1 - x_2) \left(\mathbf{I}_2 \otimes \mathbf{I}_2 - \boldsymbol{\sigma}_1 \otimes \boldsymbol{\sigma}_1 \right)$$

First-order QED correction using the regularized vacuum-polarization density matrix in the finite basis (Z = c = m = 1):



Audinet, Morellini, Levitt, Toulouse, JPA, 2025

Summary:

- Effective QED includes electron-positron pairs without photons
- ▶ More tractable alternative to standard QED for electronic-structure calculations
- Relativistic DFT can be formulated based on this effective QED
- Need to handle singularities in a finite basis for a practical implementation
- Our 1D model suggests that it can be done

Outlook:

- Extension to real 3D systems
- Development of approximate relativistic density functionals