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Remarks on the Mittleman max–min variational method for the electron-positron field

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Abstract

Barbaroux, Esteban and Séré have investigated the relation between Mittleman's max–min principle and the solutions of the Dirac–Fock equations. Their comparison is valid in the non-relativistic limit, but it does not contain quantitative estimates. We generalize their result of non-agreement in the case of one electron and show that this non-agreement holds for the physical value of the fine structure constant if $Z < 42$ (molybdenum).

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1. Introduction

In this paper we would like to address several questions related to the connections between the Dirac–Fock equations and the Hartree–Fock equations of the electron–positron field (see, e.g., [1–3]).

We consider a system of relativistic electrons in the field of a nucleus of charge eZ. The energy describing the system is derived from a formal Hamiltonian in QED, in the Hartree–Fock approximation. The resulting functional energy $\mathcal{E}$ has been studied by Mittleman in [1]. Bach *et al* [4, 5] (see also [3]) consider the functional $\mathcal{E}$ taking into account that the vacuum—and therefore the meaning of electrons and positrons—will be changed by the nucleus and other charges. In particular, this requires the choice of a closed subspace $\mathfrak{H}_- \subset \mathfrak{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$. The orthogonal projection Λ_- onto $\mathfrak{H}_-$ represents the vacuum (in Hartree–Fock approximation). We write $\mathfrak{H}_+ := (\mathfrak{H}_-)^\perp$ and $\mathfrak{H}_\pm = \Lambda_\pm \mathfrak{H}$.

Mittleman [1] argued that for a system of total charge N with ground state energy $\mathfrak{e}$, the 'physical' projection Λ_+ yielding the one-electron states space $\mathfrak{H}_+$, the ground states γ and the ground state energy $\mathfrak{e}$ are given by the solutions of the max–min variational principle

$$\mathfrak{e} = \sup_{\Lambda_+} \inf_{\gamma \in S(\Lambda_+)} \mathcal{E}(\gamma), \tag{1}$$

where the set of allowed one-particle density matrices we consider is given by

$$S(\Lambda_+) = \{\gamma \in \mathcal{B}(\mathfrak{H}) | \gamma = \gamma^*,\ \mathrm{tr}|\gamma| < \infty, \mathrm{tr}\left(|D_0|^{\frac{1}{2}}|\gamma||D_0|^{\frac{1}{2}}\right) < \infty,$$
$$0 \leqslant \Lambda_- + \gamma \leqslant 1, \Lambda_- \gamma \Lambda_+ = 0, \mathrm{tr}\,\gamma = N\}.$$

This principle has already been partly discussed in [2]. In this context the following terminology is useful. A Slater determinant $\Psi = N!^{-1/2}\psi_1 \wedge \cdots \wedge \psi_N$—and in abuse of notation also its one-particle density matrix $\gamma_\Psi = \sum_{i=1}^N |\psi_i\rangle\langle\psi_i|$—is called an Esteban–Séré (ES) solution, if $\psi_1, \ldots, \psi_N$ fulfil the Dirac–Fock equations [6, 7]. We denote the lowest Dirac–Fock energy among the energies $\mathcal{E}^{\mathrm{DF}}(\Psi)$ of the solutions Ψ of the Dirac–Fock equations by E, i.e.,

$$E = \inf\{\mathcal{E}^{\mathrm{DF}}(\Psi) \mid \Psi = (\psi_1, \ldots, \psi_N) \text{ solution of the Dirac–Fock equations}\}. \tag{2}$$

Barbaroux *et al* [2] showed for fixed αZ in the nonrelativistic limit, i.e., $\alpha \ll 1$, that $\mathfrak{e} \leqslant E$. If additionally the interaction energy is small and the noninteracting system has an unfilled shell, e.g., the electron number is one, then they show: for any solution (Λ_+, γ) of the max–min principle (1), then—contrary to the Hellmann–Feynman theorem—when applied disregarding its hypothesis—at most one of the following two properties can be true.

Vacuum. Λ_- is the negative spectral projection of the Dirac–Fock operator associated with Ψ.
State. Ψ is a ES solution of the Dirac–Fock equations with $\mathcal{E}^{\mathrm{DF}}(\Psi) = E$.

We emphasize at this point that this result does not contradict the conjecture (1).

In the present paper, we wish to draw further consequences of Mittleman's conjecture and compare them with corresponding properties of the Dirac–Fock system.

We present here three different results, each one holding in the case of a system of electrons/positrons of total charge $-eN$, with $N = 1$, and a number of protons in the nucleus equals Z, i.e., the total physical charge of the atomic system is $e(Z - 1)$.

- The first result, proposition 3.1, states that the max–min variational principle (1) yields the correct ground state energy, which is in the case of an electronic system of charge $-e$ under consideration here, the first eigenvalue of the Coulomb–Dirac operator. We indeed prove that a solution of (1) is given by Λ_+, the projection onto the positive spectral subspace of the Coulomb–Dirac operator, and by $\gamma = |\psi\rangle\langle\psi|$ where ψ is a vector in the eigenspace associated with the lowest eigenvalue $\mu_{1,g}$ of the Coulomb–Dirac operator. This fully validates the Mittleman variational approach in the case $N = 1$.
- Our next important result, theorem 3.4 shows that Mittleman's variational principle forces a change of the max–min pair, if we allow for pair correlations, i.e., if we minimize over off-diagonal density matrices as well. More precisely, we prove that if we omit the condition $\Lambda_+ \gamma \Lambda_- = 0$ in the above definition of the set $S(\Lambda_+)$, the max–min variational principle is no longer realized by the same pair (Λ_+, γ) as above. Moreover the natural choice Λ_+ as the projection onto the positive spectral subspace of the Coulomb–Dirac operator (the so-called Furry picture), gives a minimizer γ in (1) which is not purely electronic and a ground state energy which is strictly smaller than E, contradicting thus the natural intuition.

- The third main result improves the work of Barbaroux, Esteban and Séré [4] mentioned above. We show, without requiring a nonrelativistic regime, that we obtain the right energy in the 'open shell case' $N = 1$, but—contrary to the intuition and to the closed shell case treated in [4]—the solutions can never fulfil simultaneously the above two properties denoted by *vacuum* and *state*. This result is a consequence of proposition 4.1, theorem 4.6 and theorem 4.9. In the case of theorem 4.9, the result holds for atomic number $2 < Z < 42$. This improvement of [4] completes the contributions of Huber [8] and Huber and Siedentop [9] who discuss the variational principle (1) and the properties *vacuum* and *state* in the closed shell case.

The collection of these above results leads to the conclusion that in the single electron case (or more precisely for $N = 1$), the variational principle (1) yields the correct approach to recover the ground state(s) and the ground state energy of a relativistic system of electrons in the field of a static point nucleus of charge eZ. It also supports the validity of this principle in more general open shell cases, although, for $N > 1$, we cannot offer an obvious choice for the physical projection Λ_+.

2. Definitions and notations

In this section, we introduce some useful notations. We define the Coulomb–Dirac operator

$$D_g := \boldsymbol{\alpha} \cdot \frac{1}{\mathrm{i}}\nabla + m\beta - g|\cdot|^{-1}. \tag{3}$$

Physically, $g = \alpha Z$ where $\alpha = e^2 \approx 1/137$ is the Sommerfeld fine structure constant, $-e$ is the charge of the electron and Z is the atomic number of the element considered.

The operator D_g is self-adjointly realized in $\mathfrak{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$ and essentially self-adjoint on $C_0^\infty(\mathbb{R}^3\backslash\{0\}) \otimes \mathbb{C}^4$, if $g \in (-\sqrt{3}/2, \sqrt{3}/2)$. The domain of D_g is $H^1(G)$ where $G := \mathbb{R}^3 \times \{1, 2, 3, 4\}$.

Definition 2.1. *We denote by F the set of all self-adjoint operators δ on $\mathfrak{H}$ such that $|D_0|^{1/2}|\delta||D_0|^{1/2}$ is trace class.*

In the present paper, we consider a larger class of Dirac operators, namely Dirac–Fock operators. They are Hamiltonians for relativistic particles in a mean field created by other particles. For that purpose, we will consider operators with an additional mean field potential

$$W^{(\delta)} = \varphi^{(\delta)} - X^{(\delta)}, \tag{4}$$

where $\varphi^{(\delta)}$ and $X^{(\delta)}$ are the direct and exchange potentials defined below.

For $p \in [1, \infty)$, we denote by $\mathfrak{S}_p(\mathfrak{H}) = \{A \in \mathcal{B}(\mathfrak{H}) | \operatorname{tr}|A|^p < \infty\}$.

For a given element $\delta \in F$, we denote by (λ_n) the sequence of its eigenvalues and by (ξ_n) a corresponding orthonormal basis of eigenvectors; the associated integral kernel $\delta(x, y)$ is

$$\delta(x, y) := \sum_n \lambda_n \xi_n(x)\overline{\xi_n(y)}. \tag{5}$$

(It is convenient to introduce the notation $x = (\mathbf{x}, s)$ for an element of G and $\mathrm{d}x$ for the product of the Lebesgue measure $\mathrm{d}\mathbf{x}$ on $\mathbb{R}^3$ with the counting measure in $\{1, 2, 3, 4\}$.) Associated with δ is its one-particle density

$$\rho_\delta(\mathbf{x}) := \sum_{s=1}^{4} \sum_n \lambda_n |\xi_n(x)|^2, \tag{6}$$

its electric potential

$$\varphi^{(\delta)} = \rho_\delta * |\cdot|^{-1}, \tag{7}$$

and its exchange operator $X^{(\delta)}$ with integral kernel

$$X^{(\delta)}(x, y) := \delta(x, y)|\mathbf{x} - \mathbf{y}|^{-1}. \tag{8}$$

The difference of these two operators is the mean field potential $W^{(\delta)}$ defined in (4). Next, we define for the given δ the associated Dirac–Fock operator as

$$D^{(\delta)}_{g,\epsilon} := D_g + \epsilon W^{(\delta)}. \tag{9}$$

In our system of units, $\epsilon = \alpha$. However it is easier for the statements and proofs of the forthcoming results to consider it *a priori* as a distinct parameter. As shown in [2, appendix], the operator $W^{(\delta)}$ is bounded implying that $D^{(\delta)}_{g,\epsilon}$ is self-adjoint with the same domain as the Coulomb–Dirac operator D_g which for $g \in [0, \sqrt{3}/2)$ is identical with the domain of D_0.

The orthogonal projection onto the positive (respectively negative) spectral subspace of $D^{(\delta)}_{g,\epsilon}$ is $\Lambda^{(\delta)}_{g,\epsilon,+}$ (respectively $\Lambda^{(\delta)}_{g,\epsilon,-}$).

We also define the following variational sets:

$$T^{(\delta)}_{g,\epsilon} := \left\{\gamma \in F \;\middle|\; -\Lambda^{(\delta)}_{g,\epsilon,-} \leqslant \gamma \leqslant \Lambda^{(\delta)}_{g,\epsilon,+}\right\} \tag{10}$$

$$T^{(\delta)}_{g,\epsilon,\partial N} := \{\gamma \in T^{(\delta)}_{g,\epsilon} \mid \operatorname{tr}\gamma = N\} \tag{11}$$

$$S^{(\delta)}_{g,\epsilon} := \left\{\gamma \in F \;\middle|\; -\Lambda^{(\delta)}_{g,\epsilon,-} \leqslant \gamma \leqslant \Lambda^{(\delta)}_{g,\epsilon,+},\ \Lambda^{(\delta)}_{g,\epsilon,-}\gamma\Lambda^{(\delta)}_{g,\epsilon,+} = 0\right\}, \tag{12}$$

$$S^{(\delta)}_{g,\epsilon,\partial N} := \left\{\gamma \in S^{(\delta)}_{g,\epsilon} \middle|\, \operatorname{tr}\gamma = N\right\}. \tag{13}$$

The Hartree–Fock functional of a charge density matrix γ introduced in [4] is defined as

$$\mathcal{E}_{g,\epsilon}(\gamma) := \operatorname{tr}(D_g\gamma) + \epsilon Q[\gamma, \gamma], \tag{14}$$

where $Q[\gamma, \gamma] = D[\rho_\gamma, \rho_\gamma] - E[\gamma, \gamma]$, D is the Coulomb scalar product on $L^2(\mathbb{R}^3)$

$$D[\rho, \sigma] := \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{x} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{y}\, \overline{\rho(\mathbf{x})}\sigma(\mathbf{y})|\mathbf{x} - \mathbf{y}|^{-1}, \tag{15}$$

and E is the exchange scalar product, i.e., for $\gamma, \gamma' \in F$,

$$E[\gamma, \gamma'] := \frac{1}{2}\int \mathrm{d}x \int \mathrm{d}y\, \overline{\gamma(x, y)}\gamma'(x, y)|\mathbf{x} - \mathbf{y}|^{-1}. \tag{16}$$

The quantity $\operatorname{tr}\gamma$ denotes the charge of a system in the state γ, which in our system of units corresponds to an electric charge $-\sqrt{\alpha}\operatorname{tr}\gamma$.

We denote by $\mu_{1,g}$ the lowest positive eigenvalue of D_g. We know that the corresponding eigenspace $\operatorname{Ker}(D_g - \mu_{1,g})$ is two-dimensional (Darwin [10] and Gordon [11]). For sake of completeness, we remind some basic facts concerning this eigenspace in appendix A.

In this paper, we shall denote by $\psi_{1,g}$ and $\psi_{2,g}$ two orthogonal and normalized vectors in $\operatorname{Ker}(D_g - \mu_{1,g})$. These spinors are necessarily already orthogonal pointwise when taking the scalar product in $\mathbb{C}^4$ only, i.e., we have pointwise $\sum_{\sigma=1}^4 \overline{\psi_{1,g}(\mathbf{x}, \sigma)}\psi_{2,g}(\mathbf{x}, \sigma) = 0$ (see e.g. appendix A). For a sake of simplicity, when there is no possible confusion we will omit the index g in $\mu_{1,g}$, $\psi_{1,g}$ and $\psi_{2,g}$. Throughout this paper, we will use the following notations for the Hartree–Fock potential W of the orbital $\psi_{2,g}$,

$$W := W^{|\psi_{2,g}\rangle\langle\psi_{2,g}|} = \varphi - X, \tag{17}$$

$$\varphi := \varphi^{|\psi_{2,g}\rangle\langle\psi_{2,g}|} = |\cdot|^{-1} * |\psi_{2,g}|^2, \tag{18}$$

$$X(x, y) := X^{|\psi_{2,g}\rangle\langle\psi_{2,g}|}(x, y) = \psi_{2,g}(x)\overline{\psi_{2,g}(y)}/|\mathbf{x} - \mathbf{y}|, \tag{19}$$

where, as usual, we use the same notation for the function φ and the associated operator of multiplication by φ.

Furthermore, we denote by $\Lambda_g := \chi_{(0,\infty)}(D_g)$ the positive spectral projection of the Coulomb-Dirac operator, and by $\Lambda_g^\perp := 1 - \Lambda_g$ its orthogonal complement. Note that according to definition (9) for the Dirac–Fock operator, in absence of Dirac–Fock potential, i.e. for $\delta = 0$, we recover the Coulomb–Dirac operator D_g. Therefore, we have $D_g = D_{g,\epsilon}^{(0)}$ and $\Lambda_g = \Lambda_{g,\epsilon,+}^{(0)}$.

Eventually, we define the Dirac–Fock ground state energy as the lowest energy of the solutions of the Dirac–Fock equations (see also [2, 12])

$$E_{g,\epsilon} := \inf \left\{ \mathcal{E}_{g,\epsilon}(\gamma_\Psi) \,\middle|\, D_{g,\epsilon}^{(\gamma_\Psi)} \psi_i = \lambda_i \psi_i,\ \psi_i \in H^1(G),\ \lambda_i \in (0, m), \right.$$
$$\left. (\psi_i, \psi_k) = \delta_{ik},\ i, k = 1, \ldots, N \right\}. \tag{20}$$

3. *W* is off-diagonal

In this section we first show in proposition 3.1 that for a system of charge one, the energy given by Mittleman's max–min variational principle equals both the ground state energy $E_{g,\epsilon}$ defined in (20) by means of the Dirac–Fock equations and the lowest bound state energy $\mu_{1,g}$ of the Dirac–Coulomb operator. Then we show in theorem 3.4 that the max–min variational principle is drastically changed, if we allow pair correlations in the set of admissible one-particle density matrices, i.e., if we replace $S_{\partial 1}^{(\delta)}$ by $T_{\partial 1}^{(\delta)}$ in (21).

The proof of proposition 3.1 is partly based on [3, section 3] which uses the results of Morozov [13]. Thus, for the statement of the proposition, we need to introduce some constants defined in [13]: for $C_{g,0} := (-4g + \sqrt{4g^2 + 9})/3$, let $\nu_{g,0}$ be the maximal value of ν satisfying the two inequalities

$$\nu + \frac{C_{g,0}^2 g^2}{\left(C_{g,0}^2 - \nu\right)} \leqslant 1 \qquad \text{and} \qquad 0 \leqslant \nu \leqslant C_{g,0}^2.$$

(the value $\nu_{g,0}$ is always defined under our assumption on g).

Proposition 3.1. *Assume that $\epsilon \geqslant 0$ and $g \geqslant 0$ fulfil $\sqrt{\nu_{g,0}} \geqslant \epsilon(4 + 5\pi/4)$. Then for $N = 1$, we have*

$$\sup_{\{\delta \in F \mid \delta \geqslant 0, \operatorname{tr} \delta \leqslant 1\}} \inf_{\{\gamma \in S_{g,\epsilon,\partial 1}^{(\delta)}\}} \mathcal{E}_{g,\epsilon}(\gamma) = \mu_{1,g} = E_{g,\epsilon}. \tag{21}$$

Moreover, the sup inf *on the left-hand side of (21) is attained by the pair $(\delta, \gamma) = (0, |\psi\rangle\langle\psi|)$ where ψ is any normalized vector in* $\operatorname{Ker}(D_g - \mu_{1,g})$.

Proof. From [3, section 3], the assumptions on g and ϵ, and the fact that for a rank one projection $|\xi\rangle\langle\xi|$ we have $\mathcal{E}_{g,\epsilon}(|\xi\rangle\langle\xi|) = (\xi, D_g \xi)$, we infer

$$\inf \left\{ \mathcal{E}_{g,\epsilon}(\gamma) \,\middle|\, \gamma \in S_{\partial 1}^{(\delta)} \right\} = \inf \left\{ (\xi, D_g \xi) \,\middle|\, \Lambda_{g,\epsilon,+}^{(\delta)} \xi = \xi,\ \|\xi\| = 1,\ \xi \in H^{\frac{1}{2}}(G) \right\}. \tag{22}$$

In particular, for $\delta = 0$, it yields

$$\inf \left\{ \mathcal{E}_{g,\epsilon}(\gamma) \,\middle|\, \gamma \in S_{g,\epsilon,\partial 1}^{(0)} \right\} = \mu_{1,g}. \tag{23}$$

Now, the operator $W^{(\delta)}$ is bounded, for all non-negative $\delta \in F$, because of [2, lemma A7-A8]. Thus, we get $\mathfrak{D}(D_g + \epsilon W^{(\delta)}) = \mathfrak{D}(D_g) = H^1(G)$. Moreover, by [3, lemma A8], we have $W^{(\delta)} \geqslant 0$ whenever $\delta \geqslant 0$ and $\delta \in F$. Therefore, we can apply [14, theorem 3 i)] (see also appendix B): for a given $\delta \in F, \delta \geqslant 0$, if we pick, using the notations of [14], $A = D_g$, $\Lambda_\pm = \Lambda_{g,\epsilon,\pm}^{(\delta)}$, $P_+ = \chi_{(0,\infty)}(D_g)$, and $\mathfrak{Q} = \mathfrak{D}(A)$, we

obtain $\mathfrak{D}(A) = \mathfrak{Q} \subset \mathfrak{Q}(A)$, $\Lambda_\pm \mathfrak{D}(A) \subset \mathfrak{Q}$ and for $\mathfrak{Q}_\pm = \mathfrak{Q} \cap \Lambda_\pm \mathfrak{H}$, we have: $\forall \xi \in \mathfrak{Q}_-$, $(\xi, A\xi) = (\xi, D_g\xi) = (\xi, (D_g + \epsilon W)\xi) - \epsilon(\xi, W\xi) \leqslant 0$. Thus, [14, theorem 3 (i)] yields

$$\inf_{\substack{\psi \in (\Lambda^{(\delta)}_{g,\epsilon,+}\mathfrak{H}) \cap H^1(G) \\ \psi \neq 0}} \sup_{\substack{\xi \in \mathrm{Span}\{\psi\} \oplus \Lambda^{(\delta)}_{g,\epsilon,-}\mathfrak{H} \\ \|\xi\|=1}} (\xi, D_g\xi) \leqslant \mu_{1,g}(\chi_{(0,\infty)}(D_g)D_g),$$

where $\mu_1(\chi_{(0,\infty)}(D_g)D_g)$ denotes the lowest eigenvalue of $\chi_{(0,\infty)}(D_g)D_g$, which is equal to $\mu_{1,g}$. Using (22) it implies for all $\delta \in F$, $\delta \geqslant 0$,

$$\inf \left\{ \mathcal{E}_{g,\epsilon}(\gamma) \,\middle|\, \gamma \in S^{(\delta)}_{g,\epsilon,\partial 1} \right\} \leqslant \mu_{1,g}. \tag{24}$$

Equality (23) together with (24) concludes the proof of the first equality in (21).

For $E_{g,\epsilon}$ defined by (20), the proof of the equality $E_{g,\epsilon} = \mu_{1,g}$ is an obvious fact since in the case $N = 1$, there is no self-consistent potential in the Dirac–Fock equations, and the problem is purely linear. □

We have the following results.

Lemma 3.2. *Assume $g \in (0, \sqrt{3}/2)$ and φ as defined in (18). Then $\varphi \in W^{1,\infty}(\mathbb{R}^3)$.*

Proof. Let $\psi_{2,g} \in \mathrm{Ker}(D_g - \mu_{1,g})$. From [2, lemma A7], we know that $\varphi \in L^\infty(\mathbb{R}^3)$. Moreover, for almost every $\mathbf{x}$

$$|\nabla\varphi(\mathbf{x})| = |\nabla[|\psi_{2,g}|^2 * |\cdot|^{-1}](\mathbf{x})| \leqslant \int |\psi_{2,g}(y)|^2/|\mathbf{x} - \mathbf{y}|^2 \,\mathrm{d}y. \tag{25}$$

We have $|\psi_{2,g}|^2 = cr^{2(\sqrt{1-g^2}-1)} \exp(-mgr)$ for some constant c (see appendix A). Since $g < \sqrt{3}/2$, the right-hand side of (25) is finite which concludes the proof. □

Proposition 3.3. *Assume $g \in (0, \sqrt{3}/2)$. The Hartree–Fock mean field operator W given by (17) is off-diagonal with respect to Λ_g, that is $\Lambda_g^\perp W \Lambda_g \neq 0$. Moreover, $\Lambda_g^\perp W \psi_{1,g} \neq 0$.*

Proof. For simplicity, we shall drop the index g for $\psi_{1,g}$, $\psi_{2,g}$ and $\mu_{1,g}$.

We assume by contradiction that $\Lambda_g^\perp W\psi_1 = 0$. By the pointwise orthogonality of ψ_1 and ψ_2, we get $X\psi_1 = 0$, and thus

$$\Lambda_g^\perp \varphi \psi_1 = 0. \tag{26}$$

Using consecutively $X\psi_1 = 0$ and $W\psi_2 = 0$ yields

$$(\varphi\psi_1, \psi_2) = (W\psi_1, \psi_2) = (\psi_1, W\psi_2) = 0. \tag{27}$$

If $\varphi\psi_1 = \lambda\psi_1$ for a given $\lambda \neq 0$, then it implies that $\varphi = \lambda$ almost everywhere on the union of the supports of each component of the 4-vector ψ_1, which is a contradiction to the fact that $\varphi \in L^4(\mathbb{R}^3)$ (see, e.g., [2, appendix]), and that the support of at least one component of the 4-vector ψ_1 is all of $\mathbb{R}^3$ (see, e.g., appendix A). Thus,

$$\varphi\psi_1 \notin \mathrm{Span}\{\psi_1\}. \tag{28}$$

Thus, (27) and (28) yield

$$\varphi\psi_1 \notin \mathrm{Span}\{\psi_1, \psi_2\} = \mathrm{Ker}(D_g - \mu_1) \subset \mathrm{Ker}(\Lambda_g(D_g - \mu_1)\Lambda_g). \tag{29}$$

Since ψ_1 is an eigenfunction of D_g, we get $\psi_1 \in H^1(G)$, as already shown for ψ_2 in the proof of lemma 3.2. Therefore, since φ is bounded, $\varphi\partial_{\mathbf{x}_i}\psi_1 \in \mathfrak{H}$ $(i = 1, 2, 3)$ which yields, together with lemma 3.2 that $\varphi\psi_1 \in H^1(G) = \mathfrak{D}(D_g)$. Thus, using (26), (29), and the positivity of $\Lambda_g(D_g - \mu_1)\Lambda_g$ imply

$$(\psi_1, \varphi(D_g - \mu_1)\varphi\psi_1) = (\psi_1, \varphi\Lambda_g(D_g - \mu_1)\Lambda_g\varphi\psi_1) > 0. \tag{30}$$

On the other hand, $(\psi_1, \varphi(D_g - \mu_1)\varphi\psi_1)$ is real and by the product rule we have

$$(D_g - \mu_1)\varphi\psi_1 = \varphi(D_g - \mu_1)\psi_1 + \frac{1}{\mathrm{i}}\sum_{n=1}^{3}\partial_n\varphi\alpha_n\psi_1.$$

Thus we obtain, observing that the α_n satisfy $\alpha_n^* = \alpha_n$ and that φ is real,

$$(\psi_1, \varphi(\mathrm{d}z - \mu_1)\varphi\psi_1) = -\sum_{n=1}^{3}\Re\left[\mathrm{i}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{x}\varphi(\mathbf{x})\partial_n\varphi(\mathbf{x})\psi_1^*(\mathbf{x})\circ\alpha_n\circ\psi_1(\mathbf{x})\right] = 0 \tag{31}$$

which contradicts (30). □

Theorem 3.4. *In the one-particle case $N = 1$, for $\delta = 0$, i.e., if we pick $\Lambda_+ := \Lambda_+^{(0)} = \chi_{(0,+\infty)}(D_g)$, assuming that $\epsilon > 0$, and $g \geqslant 0$ fulfil $\sqrt{\nu_{g,0}} \geqslant \epsilon 5\pi/4$, we have*

$$\inf\left\{\mathcal{E}_{g,\epsilon}(\gamma) \,\middle|\, \gamma \in T^{(0)}_{g,\epsilon,\partial 1}\right\} < \inf\left\{\mathcal{E}_{g,\epsilon}(\gamma) \,\middle|\, \gamma \in S^{(0)}_{g,\epsilon,\partial 1}\right\}.$$

In particular, if we replace $S^{(\delta)}_{g,\epsilon,\partial 1}$ by $T^{(\delta)}_{g,\epsilon,\partial 1}$ on the right-hand side of (21), then for any eigenfunction ψ in $\mathrm{Ker}(D_g - \mu_{1,g})$, *the* sup inf *is not attained by the couple* $(0, |\psi\rangle\langle\psi|)$.

Proof. From [2], denoting $\chi_{(0,\infty)}(D_g)$ by Λ_g, we obtain

$$\begin{aligned}\inf\{\mathcal{E}_{g,\epsilon}(\gamma) \mid \gamma \in S_{g,\epsilon,\partial 1}\} &= \inf\{\mathcal{E}_{g,\epsilon}(\gamma_f) \mid \gamma_f = |f\rangle\langle f|,\ f \in H^{\frac{1}{2}}(G),\ \Lambda_g f = f\}\\ &= \inf\{(f, D_g f) \mid f \in H^{1/2}(G),\ \Lambda_g f = f\} = \mu_{1,g}.\end{aligned}$$

Pick ψ a normalized eigenfunction in $\mathrm{Ker}(D_g - \mu_{1,g})$. Let ψ_1 be a normalized vectors in the eigenspace of D_g associated with $\mu_{1,g}$, orthogonal to ψ. Then, for $u \in \Lambda_g^{\perp}\mathfrak{H}$ and $-1 \leqslant \kappa < 1$, if we define

$$\gamma_\kappa := |\psi\rangle\langle\psi| + \kappa^2(|\psi_1\rangle\langle\psi_1| - |u\rangle\langle u|) + \kappa(1-\kappa^2)^{1/2}(|\psi_1\rangle\langle u| + |u\rangle\langle\psi_1|),$$

we have $\gamma_\kappa \in T^{(\delta)}{}_{\partial 1}$ and

$$\begin{aligned}\mathcal{E}_{g,\epsilon}(\gamma_\kappa) - \mathcal{E}_{g,\epsilon}(|\psi\rangle\langle\psi|) &= 2\epsilon\kappa\Re Q[|\psi_1\rangle\langle u| + |u\rangle\langle\psi_1|, |\psi\rangle\langle\psi|] + \mathcal{O}(\kappa^2)\\ &= \epsilon\kappa\Re(u, W\psi_1) + \mathcal{O}(\kappa^2),\end{aligned}$$

where $W := W^{|\psi\rangle\langle\psi|}$. By using proposition 3.3, picking κ with the correct sign and small enough, and for some $u \in \Lambda_g^{\perp}\mathfrak{H}$ we find

$$\mathcal{E}_{g,\epsilon}(\gamma_\kappa) < \mathcal{E}_{g,\epsilon}(|\psi\rangle\langle\psi|) = \mu_{1,g}$$

which completes the proof. □

4. The positive spectral projection of the Dirac–Fock operator and the maximizer of mittleman's max–min principle are different: towards a non-perturbative proof

4.1. The Barbaroux–Esteban–Séré result for one electron

If $N = 1$, then any ψ in the eigenspace of D_g associated with the first eigenvalue $\mu_{1,g}$, is a solution of the Dirac–Fock equation; moreover, $|\psi\rangle\langle\psi|$ minimizes the Dirac–Fock energy functional $\mathcal{E}_{g,\epsilon}$ among all ES solutions of the Dirac–Fock equations.

In the case of open shells for the noninteracting model, the result of Barbaroux, Esteban and Séré [2] states: if γ_Ψ is an ES solution, the pair $(\gamma_\Psi, \gamma_\Psi)$ cannot be a solution of the sup inf problem (21) in the nonrelativistic limit, i.e., in our system of unit, for αZ fixed and $\alpha \ll 1$.

We would like to consider the simplest case, namely $N = 1$, but without performing the nonrelativistic limit.

Proposition 4.1. *Let $N = 1$, $g \in (0, \sqrt{3}/2)$, and $\epsilon > 0$. Let us assume that for some vector ψ in* $\mathrm{Ker}(D_g - \mu_{1,g})$,

$$\Lambda^{\perp}(\mathrm{Ker}(D_g - \mu_{1,g})) \neq \{0\} \qquad \textit{with} \qquad \Lambda = \Lambda_{g,\epsilon}^{(|\psi\rangle\langle\psi|)}. \tag{32}$$

Then $(|\psi\rangle\langle\psi|, |\psi\rangle\langle\psi|)$ is not a solution of the sup inf *(21). Moreover we have*

$$\inf\{\mathcal{E}(|\vartheta\rangle\langle\vartheta|)|\Lambda\vartheta = \vartheta, \qquad \vartheta \in H^{\frac{1}{2}}(G), \quad \|\vartheta\| = 1\} < \mu_{1,g}. \tag{33}$$

Proof. In this proof, we will use the notations $\mu_1 = \mu_{1,g}$. Let ψ_1 be a normalized eigenfunction of D_g associated with μ_1. Then

$$(\Lambda\psi_1, D_g\Lambda\psi_1) = \mu_1\|\Lambda\psi_1\|^2 + (\Lambda^{\perp}\psi_1, (D_g - \mu_1)\Lambda^{\perp}\psi_1).$$

Since $\epsilon W^{(|\psi\rangle\langle\psi|)} \geqslant 0$, we have

$$\begin{aligned}(\Lambda^{\perp}\psi_1, (D_g - \mu_1)\Lambda^{\perp}\psi_1) &\leqslant (\Lambda^{\perp}\psi_1, (D_g + \epsilon W^{(|\psi\rangle\langle\psi|)})\Lambda^{\perp}\psi_1) - \mu_1\|\Lambda^{\perp}\psi_1\|^2 \\ &\leqslant -\mu_1\|\Lambda^{\perp}\psi_1\|^2.\end{aligned}$$

Consequently, we obtain

$$(\Lambda\psi_1, D_g\Lambda\psi_1) < \mu_1\|\Lambda\psi_1\|^2,$$

if $\mu_1 > 0$ and $\Lambda^{\perp}\psi_1 \neq 0$. Therefore, for $\vartheta = \|\Lambda\psi_1\|^{-2}|\Lambda\psi_1\rangle\langle\Lambda\psi_1|$, we obtain $Q[\vartheta, \vartheta] = 0$, since ϑ is rank one, and

$$\mathcal{E}(\vartheta) = \|\Lambda\psi_1\|^{-2}(\Lambda\psi_1, D_g\Lambda\psi_1) < \mu_1.$$

□

Because $\Lambda^{\perp}\psi = 0$, we can and will assume that ψ_1 is orthogonal to ψ. So, since $\mathrm{Ker}(D_g - \mu_{1,g})$ is of dimension 2, the condition (32) reads more simply

$$\Lambda^{\perp}\psi_1 \neq 0 \tag{34}$$

for a normalized ψ_1 orthogonal to ψ.

4.2. The first eigenspace of the Dirac hydrogen operator contains dressed positrons: analyticity argument

In this subsection we discuss condition (32). It is important to see, if it is reasonable, i.e., that it is satisfied for positive α up to $1/137$.

Barbaroux *et al* [2] show the validity of (32) (see property (P) therein) in certain cases. However, they do not give any quantitative estimate on the range of allowed fine structure constants. Here, we will give a partially different proof yielding a definite estimate on the maximal α that is physically satisfactory.

We first fix $g = \alpha Z$ and treat $\epsilon W^{|\psi\rangle\langle\psi|}$ as a perturbation of D_g. We consider $\Lambda_\epsilon := \chi_{(0,\infty)}(D_g + \epsilon W^{(|\psi\rangle\langle\psi|)})$ and choose ψ and ψ_1 as two orthonormal vectors in $\mathrm{Ker}(D_g - \mu_{1,g})$. We will show the

Proposition 4.2. *For any $g \in (0, \sqrt{3}/2)$, there exists an $\epsilon_0 > 0$, such that for all $\epsilon \in (0, \epsilon_0)$, condition (32) is satisfied.*

Proof. We consider

$$h(\epsilon) := 1 - (\psi_1, \Lambda^{\epsilon}\psi_1).$$

If $h(\epsilon) > 0$, it is clear that $(\Lambda^{\epsilon})^{\perp}\psi_1$ is not identically 0, implying that (32) is fulfilled. We have of course $h(0) = 0$ and, h being necessarily nonnegative, we also get $h'(0) = 0$.

$$h'(\epsilon) = \frac{1}{2\pi}\left(\psi_1, \int_{-\infty}^{\infty} \mathrm{d}\eta (H_\epsilon + \mathrm{i}\eta)^{-1} W (H_\epsilon + \mathrm{i}\eta)^{-1}\psi_1\right), \tag{35}$$

with $H_\epsilon = D_g + \epsilon W^{(|\psi\rangle\langle\psi|)}$. Here we have used the identities

$$\Lambda^\epsilon = \frac{1}{2} + \frac{1}{2\pi} \lim_{A\to+\infty} \int_{-A}^{+A} (H_\epsilon + \mathrm{i}\eta)^{-1}\, \mathrm{d}\eta$$

and

$$\frac{\partial}{\partial\epsilon}(H_\epsilon + \mathrm{i}\eta)^{-1} = -(H_\epsilon + \mathrm{i}\eta)^{-1} W (H_\epsilon + \mathrm{i}\eta)^{-1}.$$

By differentiation of (35), we obtain

$$h''(\epsilon) = -\frac{1}{\pi}\Re(\psi_1, \int_{-\infty}^{\infty} \mathrm{d}\eta (H_\epsilon + \mathrm{i}\eta)^{-1} W (H_\epsilon + \mathrm{i}\eta)^{-1} W (H_\epsilon + \mathrm{i}\eta)^{-1}\psi_1). \tag{36}$$

Let us compute $h''(0)$. We know *a priori* that $h''(0) \geqslant 0$, but we are going for strict positivity. Using the spectral decomposition, we get

$$\begin{aligned} h''(0)/2 &= -\Re\left(\psi_1, \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}\eta \frac{1}{(\mu_1 + \mathrm{i}\eta)} W \frac{1}{(D_g + \mathrm{i}\eta)} W \frac{1}{(\mu_1 + \mathrm{i}\eta)}\psi_1\right) \\ &= -\frac{1}{2\pi}\Re\left(W\psi_1, \int_{-\infty}^{+\infty} \mathrm{d}\eta \int \mathrm{d}P_\mu \frac{1}{(\mu_1 + \mathrm{i}\eta)^2}\frac{1}{\mu + \mathrm{i}\eta} W\psi_1\right), \end{aligned} \tag{37}$$

where $P_\mu = \chi_{(-\infty,\mu)}(D_g)$ is the spectral family associated with D_g. The η integration in (37) gives zero for positive values of μ, since μ_1 is also positive. Moreover,

$$\int_{-\infty}^{+\infty} \frac{1}{(\mu_1 + \mathrm{i}\eta)^2}\frac{1}{\mu + \mathrm{i}\eta}\,\mathrm{d}\eta = \frac{1}{\mathrm{i}}\int_{-\infty}^{+\infty} \frac{1/(\mu_1 + \mathrm{i}\eta)^2}{\eta - \mathrm{i}\mu}\,\mathrm{d}\eta = -\frac{2\pi}{(\mu_1 + \mathrm{i}(\mathrm{i}\mu))^2}.$$

Therefore, together with (36) and (37), this implies

$$h''(0) = 2\left(W\psi_1, \int_{-\infty}^{0} \mathrm{d}P_\mu (\mu_1 - \mu)^{-2} W\psi_1\right). \tag{38}$$

So $h''(0) > 0$ if $(1 - \Lambda^0)W\psi_1 \neq 0$ which is the content of proposition 3.3. □

Lemma 4.3. *Assume $\epsilon > 0$, $g \in (0, \sqrt{3}/2)$, and pick two orthonormal vectors ψ and ψ_1 in* $\mathrm{Ker}(D_g - \mu_{1,g})$ *and $\Lambda^\epsilon = \chi_{(0,+\infty)}(D_g + \epsilon W^{(|\psi\rangle\langle\psi|)})$. Then*

$$(\Lambda^\epsilon)^\perp\psi_1 = 0 \quad \Leftrightarrow \quad (\Lambda^\epsilon)^\perp W^{(|\psi\rangle\langle\psi|)}\psi_1 = 0.$$

Proof. We denote here $\Lambda = \Lambda^\epsilon$, and $H_\epsilon = D_g + \epsilon W^{(|\psi\rangle\langle\psi|)}$. If $\Lambda^\perp\psi_1 = 0$, we have on the one hand $\Lambda^\perp H_\epsilon\psi_1 = H_\epsilon\Lambda^\perp\psi_1 = 0$ and, on the other hand $\Lambda^\perp H_\epsilon\psi_1 = \mu_1\Lambda^\perp\psi_1 + \epsilon\Lambda^\perp W\psi_1 = \epsilon\Lambda^\perp W\psi_1$. This shows that $\Lambda^\perp W\psi_1 = 0$, if $\Lambda^\perp\psi_1$ and $\epsilon \neq 0$.

Conversely, if $\Lambda^\perp W\psi_1 = 0$, we get $\Lambda^\perp H_\epsilon\psi_1 = \mu_1\Lambda^\perp\psi_1 = H_\epsilon\Lambda^\perp\psi_1$. But $\Lambda^\perp\psi_1$ cannot be an eigenfunction of H_ϵ with eigenvalue $\mu_1 > 0$, since it is in the negative spectral subspace of H_ϵ. Therefore, $\Lambda^\perp\psi_1 = 0$. □

Let g_c be the unique zero of $(0, \infty) \to \mathbb{R}$, $g \mapsto 1 - g\sqrt{1 + 2g}/(1 - 2g)$. The numerical value is about 0.3059 which corresponds to Z up to 41 (niobium) included.

Lemma 4.4. *Let ψ be a normalized vector in* $\mathrm{Ker}(D_g - \mu_{1,g})$. *Then for all $\epsilon \leqslant g < g_c$*

$$\sigma(D_g + \epsilon W^{(|\psi\rangle\langle\psi|)}) \cap (-m, \mu_{1,g}) = \emptyset. \tag{39}$$

Proof. We first note that the density $\sum_{\sigma=1}^4 |\psi(\mathbf{y}, \sigma)|^2$ of ψ is spherically symmetric (see, e.g., appendix A). For all $f \in H^1(G)$,

$$0 \leqslant (f, Wf) \leqslant 2D(|f|^2, |\psi|^2) \leqslant \int |f(x)|^2 |\mathbf{x}|^{-1} \, \mathrm{d}x, \tag{40}$$

where we used Newton's theorem [15] and the spherical symmetry of the density of ψ.

For $A := D_g + m$, $W := W^{(|\psi\rangle\langle\psi|)}$ and $B := A + \epsilon W$, we have $A \leqslant B$, since $W \geqslant 0$. Set $\mathfrak{H}_+ := \chi_{(0,+\infty)}(D_0)$. By Tix's inequality [16, 17] we have $(\psi, A\psi) > 0$ for all non-vanishing $\psi \in \mathcal{D}(D_g) \cap \mathfrak{H}_+$. Since $g < g_c$ we have $\| |D_0|^{1/2} \chi_{(0,\infty)}(D_0) \chi_{(-\infty,0)}(D_g) |D_0|^{-1/2} \| < 1$ (see [18, corollary 1]). Thus the hypotheses of the min–max principle [18, theorem 1] are fulfilled, for $g \leqslant g_c$ and we can estimate the lowest eigenvalue $\mu_1 + m$ of A as

$$\begin{aligned} \mu_1 + m &\leqslant \inf_{M \subset \mathfrak{H}_+, \dim(M)=1} \sup_{\psi \in \mathfrak{H}_- \oplus M, \|\psi\|=1} (\psi, A\psi) \\ &\leqslant \inf_{M \subset \mathfrak{H}_+, \dim(M)=1} \sup_{\psi \in \mathfrak{H}_- \oplus M, \|\psi\|=1} (\psi, B\psi). \end{aligned} \tag{41}$$

Since W is bounded, $\mathcal{D}(A) = \mathcal{D}(B)$. The operator inequality $A \leqslant B$ implies immediately $\forall \psi \in \mathfrak{H}_+, 0 < (\psi, B\psi)$. Moreover, for all $\psi \in \mathfrak{H}_-$, using (40)

$$(\psi, B\psi) = (\psi, (D_{\alpha Z} + m + \epsilon W)\psi) \leqslant (\psi, (D_{\alpha Z - \epsilon} + m)\psi) \leqslant (\psi, (D_0 + m)\psi) \leqslant 0. \tag{42}$$

Therefore, by again applying the min–max principle—this time in the simpler form [14]—to the right-hand side of (41), we obtain that the lowest positive eigenvalue of B is greater than or equal to $\mu_1 + m$, i.e., that $D_g + \epsilon W$ has its lowest eigenvalue greater than or equal to μ_1.□

Proposition 4.5. *Pick two orthonormal vectors $\psi, \psi_1 \in \mathrm{Ker}(D_g - \mu_{1,g})$ and assume $g \in (0, g_c)$. Then there exists a finite set M of real numbers, such that for all $\epsilon \in (0, g) \backslash M$*

$$\Lambda^{(|\psi\rangle\langle\psi|)}_{g,\epsilon,-} \psi_1 \neq 0.$$

Proof. For all $\epsilon \in \{z \in \mathbb{C}; \mathrm{Re}\, z \in (0, 1)\}$, we define with $H_\epsilon = D_g + \epsilon W^{(|\psi\rangle\langle\psi|)}$

$$h(\epsilon) = \left(\psi_1, \left[\frac{1}{2} + \frac{1}{2\pi} \int_{-\infty}^{+\infty} (H_\epsilon + \mathrm{i}\eta)^{-1} \, \mathrm{d}\eta \right] \psi_1 \right).$$

For ϵ real, $h(\epsilon) = \left(\psi_1, \Lambda^{(|\psi\rangle\langle\psi|)}_{g,\epsilon,-} \psi_1\right)$. Let $\epsilon_0 \in \mathcal{T} := \{\epsilon \in \mathbb{C} \mid \mathrm{Re}(\epsilon) \in (0, g), |\mathrm{Im}(\epsilon)| < \mu_{1,g}/(2\|W\|)\}$. For $\epsilon = \epsilon_0 + a$, $a \in \mathbb{C}$ and $|a| \ll 1$ we have

$$\begin{aligned} 2\pi \frac{h(\epsilon) - h(\epsilon_0)}{\epsilon - \epsilon_0} &= -\left(\psi_1, \int \frac{1}{H_\epsilon + \mathrm{i}\eta} W \frac{1}{H_{\epsilon_0} + \mathrm{i}\eta} \, \mathrm{d}\eta \psi_1 \right) \\ &= \left(\psi_1, \int \frac{-1}{H_{\epsilon_0} + \mathrm{i}\eta} W \frac{1}{H_{\epsilon_0} + \mathrm{i}\eta} + a \frac{1}{H_{\epsilon_0} + \mathrm{i}\eta} W \frac{1}{H_\epsilon + \mathrm{i}\eta} W \frac{1}{H_{\epsilon_0} + \mathrm{i}\eta} \, \mathrm{d}\eta \psi_1 \right). \end{aligned} \tag{43}$$

Now, using lemma 4.4 we get the bound $\left\| \left(H_{\mathrm{Re}(\epsilon_0)} + \mathrm{i}\eta\right)^{-1} \right\| \leqslant \left(\mu_{1,g}^2 + \eta^2\right)^{-1/2}$. Since $\epsilon_0 \in \mathcal{T}$ we get $\|(H_{\mathrm{Re}(\epsilon_0)} + \mathrm{i}\eta)^{-1} \, \mathrm{Im}(\epsilon_0) W\| \leqslant 1/2$ and thus, using the resolvent equation

$$\left(H_{\epsilon_0} + \mathrm{i}\eta\right)^{-1} = (1 - \mathrm{i}\,\mathrm{Im}(\epsilon_0)(H_{\mathrm{Re}(\epsilon_0)} + \mathrm{i}\eta)^{-1} W)^{-1} (H_{\mathrm{Re}(\epsilon_0)} + \mathrm{i}\eta)^{-1}. \tag{44}$$

Therefore,

$$\left\| \left(H_{\epsilon_0} + \mathrm{i}\eta\right)^{-1} \right\| \leqslant 2\left(\mu_{1,g}^2 + \eta^2\right)^{-1/2}. \tag{45}$$

Similarly, for $|a| < \min(\epsilon_0, g - \epsilon_0)$ we obtain $\|(H_\epsilon + \mathrm{i}\eta)^{-1}\| \leqslant 2\mu_{1,g}^{-1}$, which yields, together with (45)

$$\left| \left(\psi_1, \int \left(H_{\epsilon_0} + \mathrm{i}\eta\right)^{-1} W (H_\epsilon + \mathrm{i}\eta)^{-1} W \left(H_{\epsilon_0} + \mathrm{i}\eta\right)^{-1} \mathrm{d}\eta \psi_1 \right) \right| \leqslant \frac{8\|W\|^2}{\mu_{1,g}} \int \frac{\mathrm{d}\eta}{\mu_{1,g}^2 + \eta^2}.$$

Together with (43), this implies

$$\lim_{\epsilon\to\epsilon_0}\frac{h(\epsilon)-h(\epsilon_0)}{\epsilon-\epsilon_0}=-\frac{1}{2\pi}\left(\psi_1,\int\left(H_{\epsilon_0}+\mathrm{i}\eta\right)^{-1}W\left(H_{\epsilon_0}+\mathrm{i}\eta\right)^{-1}\mathrm{d}\eta\psi_1\right),$$

and thus $h(\epsilon)$ is analytic in $\mathcal{T}$. Thus, it is either a constant in this interval or takes any given value at most finitely many times. However, by proposition 4.2 it cannot vanish identically. This concludes the proof. □

Theorem 4.6. *Assume $g\in(0,g_c),\epsilon>0$ fulfilling $\sqrt{\nu_{g,0}}>\epsilon(4+5\pi/4)$. Pick a normalized $\psi\in\mathrm{Ker}(D_g-\mu_{1,g})$. Then there exists a finite set M of real numbers such that for all $\epsilon\in(0,g)\backslash M$, we have*

$$\inf\{\mathcal{E}_{g,\epsilon}(\gamma)\mid\gamma\in F,0\leqslant\Lambda_{g,\epsilon,-}^{(|\psi\rangle\langle\psi|)}+\gamma\leqslant 1,\Lambda_{g,\epsilon,-}^{(|\psi\rangle\langle\psi|)}\gamma\Lambda_{g,\epsilon,+}^{(|\psi\rangle\langle\psi|)}=0,\mathrm{tr}\,\gamma=1\}<E.$$

Proof. This is a consequence of proposition 4.1, proposition 4.5 and [3, theorem 3.8]. □

Remark 4.7. Note that is sufficient to prove the weaker condition $\mu_{1,g}>\inf\sigma\left(\Lambda_{g,\epsilon,+}^{(|\psi\rangle\langle\psi|)}D_g\Lambda_{g,\epsilon,+}^{(|\psi\rangle\langle\psi|)}\right)$. This leaves room for other approaches.

4.3. The first eigenspace of the Dirac hydrogen operator contains dressed positrons: a direct proof

In the following we will denote by $\mu_{2,g}$ the second eigenvalue of D_g, the third counting multiplicity.

Proposition 4.8. *Assume $g\in(0,g_c),\epsilon\geqslant 0$ and pick two orthonormal vectors $\psi,\psi_1\in\mathrm{Ker}(D_g-\mu_{1,g})$. If $\epsilon\|\varphi^{(|\psi\rangle\langle\psi|)}\|<\mu_{2,g}-\mu_{1,g}$, then*

$$\Lambda_{g,\epsilon,-}^{(|\psi\rangle\langle\psi|)}\psi_1\neq 0.$$

Proof. For simplicity, we abbreviate again: $\Lambda=\Lambda_{g,\epsilon,+}^{(|\psi\rangle\langle\psi|)}$, $W=W^{(|\psi\rangle\langle\psi|)}$, $\varphi=\varphi^{(|\psi\rangle\langle\psi|)}$, $\mu_1=\mu_{1,g}$ and $\mu_2=\mu_{2,g}$.

Assume by contradiction that $\Lambda\psi_1=\psi_1$. By lemma 4.3, we also have $\Lambda W\psi_1=W\psi_1$. Moreover, $W\psi_1=\varphi\psi_1$. As already shown in the proof of proposition 3.3, $\varphi\psi_1\notin\mathrm{Span}\{\psi_1,\psi\}$, thus $\dim(\mathrm{Span}\{\psi_1,\psi,\varphi\psi_1\})=3$ and by lemma 3.2 and the contradiction assumption, we get $\mathrm{Span}\{\psi_1,\psi,\varphi\psi_1\}\subset\Lambda\mathfrak{H}$. Therefore, denoting by $\lambda_j(\epsilon)$ the jth eigenvalue of $H_\epsilon:=D_g+\epsilon W$, counting multiplicity, using the fact that H_ϵ has no negative eigenvalues by lemma 4.4, and using the Courant min–max principle yields

$$\lambda_3(\epsilon)\leqslant\tilde{\mu}:=\sup\{(f,H_\epsilon f)\mid f\in\mathrm{Span}\{\psi_1,\psi,\varphi\psi_1\},\|f\|=1\}. \tag{46}$$

We now provide an upper bound for $\tilde{\mu}$: let $f\in\mathrm{Span}\{\psi_1,\varphi\psi_1,\psi_2\}$ with $\|f\|=1$. Then, a straightforward calculation, using $(\psi_1,\psi)=0$, $\psi_1,\psi\in\mathrm{Ker}(D_g-\mu_1)$, $W\psi=0$, $(\psi,\varphi\psi_1)=(\psi,W\psi_1)=0$, and equation (31) yield

$$(f,D_gf)=\mu_1. \tag{47}$$

Since $0\leqslant W\leqslant\varphi\leqslant\|\varphi\|$, we get $(f,H_\epsilon f)\leqslant\mu_1+\epsilon\|\varphi\|$. Since the eigenvalues $\lambda_j(\epsilon)$ increase with ϵ and since H_ϵ has no negative eigenvalues (lemma 4.4), we obtain $\mu_2\leqslant\lambda_3(\epsilon)$, which contradicts (46) if $\epsilon\|\varphi\|<\mu_2-\mu_1$. □

Theorem 4.9. *Assume $g\in(0,g_c)$ fulfilling $\sqrt{\nu_{g,0}}>\epsilon(4+5\pi/4)$, and*

$$\epsilon<g^{-1}\left(\sqrt{1+\sqrt{1-g^2}}\sqrt{1-g^2}/\sqrt{2}-1+g^2\right).$$

Then

$$\inf\left\{\mathcal{E}_{g,\epsilon}(\gamma)\,\middle|\,\gamma\in F, 0\leqslant \Lambda_{g,\epsilon,-}^{(|\psi\rangle\langle\psi|)}+\gamma\leqslant 1, \Lambda_{g,\epsilon,-}^{(|\psi\rangle\langle\psi|)}\gamma\Lambda_{g,\epsilon,+}^{(|\psi\rangle\langle\psi|)}=0, \operatorname{tr}\gamma=1\right\}<E.$$

We note that the hypothesis is fulfilled, if $\epsilon=\alpha\approx 1/137$ and $2<Z<42$. Of course, we do not claim that this is the optimal range of atomic numbers.

Proof. From the explicit expression (A.1) we get the density ρ of any normalized eigenfunction of D_g in its first eigenspace

$$\rho(\mathbf{x})=\frac{2g^3}{\pi}\frac{1}{\Gamma(1+2\upsilon)}(2g|\mathbf{x}|)^{2\upsilon-2}\,\mathrm{e}^{-2g|\mathbf{x}|}.$$

We note that $0\leqslant\varphi(\mathbf{x})=\rho*|\cdot|^{-1}(\mathbf{x})\leqslant\varphi(0)$. Thus it suffices to compute

$$\begin{aligned}\int_0^\infty \mathrm{d}r\,4\pi r^2\frac{(2g)^3}{4\pi}\frac{1}{\Gamma(1+2\upsilon)}(2gr)^{2\upsilon-2}\,\mathrm{e}^{-2gr}/r&=\frac{2g}{\Gamma(1+2\upsilon)}\int_0^\infty \mathrm{d}r\,r^{2\upsilon-1}\,\mathrm{e}^{-r}\\&=2g\Gamma(2\upsilon)/\Gamma(1+2\upsilon)=g/\upsilon=g/\sqrt{1-g^2}.\end{aligned}\tag{48}$$

Moreover, $\mu_{2,g}-\mu_{1,g}=[1+(1-g^2)^{1/2}]^{1/2}/\sqrt{2}-(1-g^2)^{1/2}$ which combined with (48) and proposition 4.8 shows the result. □

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Appendix A. Some properties of the eigenspace associated with the ground state energy of the Coulomb–Dirac operator

For the reader's convenience we collect some basic useful facts on eigenvalues and eigenfunctions of Dirac operators.

A.1. Eigenspaces have even dimension (spin degeneracy)

First, we remark that any eigenvalues of an electric Dirac operator has even dimension. To see this we follow Parisse [19, proof of theorem 2.4] and Balslev and Helffer [20]. According to Kramer's theorem (see Balslev–Helffer in this context) there exists an anti-linear operator with $K^2=-1$ commuting with the Dirac operator. This operator is

$$K=\begin{pmatrix}\sigma_2 & 0\\ 0 & \sigma_2\end{pmatrix}\Gamma,$$

where Γ is the complex conjugation. If u is an eigenvector, then u and Ku are linearly independent. Otherwise, we would have—for some complex λ—$Ku=\lambda u$ and consequently

$$-u=K^2u=K(Ku)=K(\lambda u)=\bar{\lambda}Ku=|\lambda|^2u$$

which gives a contradiction.

Note also that if u is an eigenvector, then $u+Ku$ and $u-Ku$ are pointwise orthogonal. Note that no special assumption on the potential are required.

A.2. Eigenfunctions and eigenvalues of the Coulomb–Dirac operator

The hydrogen problem was already solved by Darwin [10] and Gordon [11] and has reached textbook dissemination. The eigenspace associated with the lowest positive eigenvalue $\mu_{1,g}$ of the Dirac–Coulomb operator D_g is of dimension 2, as is well known, and a basis is given by the following two 4-vectors, given in spherical coordinates (see, e.g., Itzykson and Zuber [21, formulae (2.94)]

$$f(r)\begin{pmatrix} 1 \\ 0 \\ \mathrm{i}(1-\upsilon)g^{-1}\cos\theta \\ \mathrm{i}(1-\upsilon)g^{-1}\sin\theta\exp(\mathrm{i}\varphi) \end{pmatrix}, f(r)\begin{pmatrix} 0 \\ 1 \\ \mathrm{i}(1-\upsilon)g^{-1}\sin\theta\exp(-\mathrm{i}\varphi) \\ -\mathrm{i}(1-\upsilon)g^{-1}\cos\theta, \end{pmatrix} \tag{A.1}$$

where f is the real radial function

$$f(r) = \frac{(2g)^{3/2}}{(4\pi)^{1/2}}\left(\frac{1+\upsilon}{2\Gamma(1+2\upsilon)}\right)^{1/2}(2gr)^{\upsilon-1}\,\mathrm{e}^{-gr}$$

and $\upsilon = \sqrt{1-g^2}$. Obviously, we can also explicitly verify that the $\mathbb{C}^4$ scalar product of these 2 vectors equals zero, as stated in generality above, i.e., we have pointwise orthogonality. It is easy to check that the same also holds, if you pick any two orthonormal eigenfunctions in the space generated by these 2 vectors.

Appendix B. Griesemer–Siedentop minimax principle

We reproduce here a theorem due to Griesemer and Siedentop [14, theorem 3 (i)] on a minimax principle for eigenvalues in a spectral gaps.

In the following, for A being a self-adjoint operator, $\mathfrak{D}(A)$ and $\mathfrak{Q}(A)$ denote respectively the domain and the form domain of A, P_+ is the projection onto the positive spectral subspace of A, and $\mu_n(A \restriction P_+\mathfrak{h})$ is the nth eigenvalue (counting from below and counting multiplicity) of P_+A or, if P_+A has less than n eigenvalues below the bottom of the spectrum of P_+A, $\mu_n(A \restriction P_+\mathfrak{h})$ is the bottom of the essential spectrum.

Theorem B.1. *Suppose that A is a self-adjoint operator in a Hilbert space $\mathfrak{h} = \mathfrak{h}_+ \oplus \mathfrak{h}_-$ where $\mathfrak{h}_+ \perp \mathfrak{h}_-$. Let $\Lambda_\pm$ be the orthogonal projections onto $\mathfrak{h}_\pm$ and let $\mathfrak{Q}$ be a subspace with $\mathfrak{D}(A) \subset \mathfrak{Q} \subset \mathfrak{Q}(A)$ and $\Lambda_\pm\mathfrak{D}(A) \subset \mathfrak{Q}$. Let $P_+ := P_{(0,\infty)}(A)$, $P_- := P_{(-\infty,0]}(A)$, $\mathfrak{Q}_\pm := \mathfrak{Q} \cap \mathfrak{h}_\pm$, and*

$$\lambda_n(A) := \inf_{\substack{M_+\subset\mathfrak{Q}_+ \\ \dim(M_+)=n}} \sup_{\substack{\xi\in M_+\oplus\mathfrak{Q}_- \\ \|\xi\|=1}} (\xi, A\xi).$$

If $(\xi, A\xi) \leqslant 0$ for all $\xi \in \mathfrak{Q}_-$, then $\lambda_n(A) \leqslant \mu_n(A \restriction P_+\mathfrak{h})$.

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