HAL open science

On the Hartree-Fock equations of the electron-positron field

Jean-Marie Barbaroux, Walter Farkas, Bernard Helffer, Heinz Siedentop

To cite this version:

Jean-Marie Barbaroux, Walter Farkas, Bernard Helffer, Heinz Siedentop. On the Hartree-Fock equations of the electron-positron field. Communications in Mathematical Physics, 2005, 255, pp.131-159. 10.1007/s00220-004-1156-x . hal-00008350

HAL Id: hal-00008350

https://hal.science/hal-00008350v1

Submitted on 11 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

arXiv:math-ph/0404009v1 2 Apr 2004

ON THE HARTREE-FOCK EQUATIONS OF THE ELECTRON-POSITRON FIELD

JEAN-MARIE BARBAROUX, WALTER FARKAS, BERNARD HELFFER, AND HEINZ SIEDENTOP

Abstract. We study the energy of relativistic electrons and positrons interacting via the second quantized Coulomb potential in the field of a nucleus of charge Z within the Hartree-Fock approximation. We show that the associated functional has a minimizer. In addition, all minimizers are purely electronic states, they are projections, and fulfill the no-pair Dirac-Fock equations.

1. Introduction

Heavy atoms should be described by relativistic quantum mechanics. It is commonly believed quantum electrodynamics (QED) yields such a description. Formally the Hamiltonian is given (Bjorken and Drell [7, Formula 15.28]) as

$$\begin{aligned} H &= \int dx : \psi^*(x) \left[\boldsymbol{\alpha} \cdot \left(\tfrac{1}{i}\nabla - \sqrt{\alpha}\mathbf{A}(x) \right) + m\beta - \tfrac{\alpha Z}{|\mathbf{x}|} \right] \psi(x) : \\ &\quad + \tfrac{\alpha}{2} \int dx \int dy \tfrac{:\psi^*(x)\psi(x)::\psi^*(y)\psi(y):}{|\mathbf{x}-\mathbf{y}|} + \tfrac{1}{8\pi} \int_{\mathbb{R}^3} : \mathbf{B}(\mathbf{x})^2 + \dot{\mathbf{A}}\,(\mathbf{x})^2 : \, d\mathbf{x} \,, \end{aligned} \tag{1}$$

where the normal ordering denoted by colons is with respect to a given choice of the one-electron space. However, it is not clear how this expression can be self-adjointly realized as a positive operator. To simplify matters we omit the energy of the transverse radiation field coupled to the current, i.e., we set $\mathbf{B} = \mathbf{0}$ and $\mathbf{A} = \mathbf{0}$ in the above expression. We will also regularize the Coulomb interaction of the electron-positron field by normal ordering it completely. Both assumptions are simplifications. The first one can be justified by the physical wisdom that the presence of self-generated magnetic field is physically known to be small compared to the relativistic effects in heavy atoms. Moreover, the inclusion poses serious technical problems that we presently cannot solve. The second assumption ignores the vacuum polarization effects which are also small comared to the relativistic effects and would contribute to the Lamb shift only.

Based on an interesting observation of Chaix, Iracane, and Lions [9, 10], Bach et al. [5, 4] showed positivity for the corresponding quadratic form without any constraints on the charge of the state, if the one-electron subspace is appropriately (Furry picture) chosen. In particular they showed that the vacuum state (particle number equal to zero) has energy zero.

Date: March 23, 2004.

Key words and phrases. Nopair atomic Dirac-Fock equations, electron-positron field, quasifree states, stability.

We thank K. Yajima for critical reading of a preliminary version of the manuscript and D. Hundertmark for useful and enjoyable discussions concerning various aspects of this paper. One of us, JMB, thanks B. Grébert for useful discussions concerning Section 3. Financial support of the Ministère de l'Education Nationale, de la Recherche et de la Technologie through ACI Blanche, of the Bayerisch-Französisches Hochschulzentrum, of the European Union through the IHP network "Analysis and Quantum", contract HPRN-CT-2002-00277, are gratefully acknowledged. Part of the work was done while three of us, JMB, BH, and HS, were visiting the Mittag-Leffler Institute, its support is also gratefully acknowledged.

In order to do so, they proved that the positivity of H on generalized Hartree-Fock states (quasifree states with finite free kinetic energy) is equivalent to the positivity of the Hartree-Fock functional (see the Definition given in (23)), a functional on density matrices γ, where the charge is given as tr γ, which thus is unrestricted.

For describing atoms one needs, however, to restrict to states with prescribed charge q. In order to implement this problem, we subtract from the energy the rest mass m, which – as we will see – will allow us to relax the constraint tr $\gamma = q$ to tr $\gamma \leq q$.

Given an electron space by the positive spectral subspace of a Dirac operator with a mean-field potential, we show that there exists a minimizer of the associated Hartree-Fock functional in a suitable set, if $q \leq Z$ (Theorem 3.9). Moreover, if q is a positive integer, all minimizers are projections of maximal rank. In particular, minimizers are purely electronic and are projections (Theorem 4.3). Finally, we show that the eigenfunctions of any minimizer γ fulfill the no-pair Dirac-Fock equations with the q first (positive) eigenvalues (Theorem 4.5).

According to Mittleman [17], the most stable, i.e., highest ground state energy is the physical ground state. Thus one should maximize among the allowed one-electron subspaces, yielding a max-min variational problem. The resulting Euler equation should, on a heuristic level, give the Dirac-Fock equations which were treated by Esteban, Séré, and Paturel [13, 19, 12]. There are indications that this latter question might be answered affirmatively only under additional hypotheses: In a recent work [6] an atom with total charge $q-Z \leq 0$ is considered. If the ground state of the noninteracting problem with $N = q$ electrons corresponds to a closed shell, then for small interaction maximizing over one-electron subspace yields the Dirac-Fock equations in the non-relativistic limit. However, if the noninteracting problem corresponds to an open shell, then, in the same limit, the max-min procedure does not yield a solution of the Dirac-Fock equations with self-consistent projector as considered by Esteban and Séré [13]. While this result is perturbative, it indicates on the one hand side that the Dirac-Fock equations and the Mittleman principle might agree in the case of filled shells whereas in the unfilled shell case it might give different results which raises the question which procedure is physically relevant, a problem that we have to leave open at this point.

We add a short guide through the paper for the orientation of the reader: Section 2 contains some basic material. We define the set of density matrices that will be allowed. There will be two types of density matrices, the charge density matrices γ for the electron-positron field and the density matrices δ giving the screening of the one-particle Dirac operator that defines the electron subspace. In addition this section contains some basic estimates on the direct and exchange energy. Section 3 contains the actual minimization. We first show that the elimination of positrons lowers the energy (Lemma 3.1); next we show that the density matrices can be restricted to finite rank (Lemma 3.3), and the minimization under the constraint tr $\gamma \leq q \leq Z$ gives a minimizer – if existing – with charge equal to q (Lemma 3.7). This allows us to show the existence of minimizers (Theorem 3.9). In Section 4 we investigate the minimizers. They turn out to be projections that fulfill the no-pair Dirac-Fock equations (Theorem 4.5). In the last section we give an outlook with respect to the above mentioned program of Mittleman. We derive the corresponding Euler equation (Theorem 5.1). However, we are not able to show that there is a maximizer.

2. Definition of the Problem

A single relativistic electron or positron in the field of a nucleus of charge Z can be described by the Coulomb-Dirac operator

$$D_Z := \boldsymbol{\alpha} \cdot \frac{1}{i}\nabla + m\beta - \alpha\frac{Z}{|\mathbf{x}|} \ , \tag{2}$$

where α is the Sommerfeld fine structure constant.

The operator D_Z is self-adjointly realized in $\mathfrak{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$ and essentially self-adjoint on $C_0^\infty(\mathbb{R}^3 \setminus \{0\}) \otimes \mathbb{C}^4$, if $\alpha Z \in (-\sqrt{3}/2, \sqrt{3}/2)$. Here, we will even assume

$$\alpha Z \in [0, \sqrt{3}/2) \quad \text{and} \quad \alpha \geq 0 \ , \tag{3}$$

throughout the paper. The domain of D_Z is $H^1(G)$ where

$$G := \mathbb{R}^3 \times \{1, 2, 3, 4\} \ .$$

(Landgren and Rejto [15], Theorem 2.1). For $Z = 0$, D_0 is just the free Dirac operator.

In the present paper, we consider a larger class of Dirac operators, namely Dirac-Fock operators. They are Hamiltonians for a relativistic particle 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 $X^{(\delta)}$ will be defined below.

For $p \in [1, \infty)$, we denote by $\mathfrak{S}_p(\mathfrak{H}) = \{A \in \mathcal{B}(\mathfrak{H}) \mid \operatorname{tr} |A|^p < \infty\}$, and by $\mathfrak{S}_\infty(\mathfrak{H})$ the space of compact operators on $\mathfrak{H}$.

Definition 2.1. *We denote by F the Banach space of all self-adjoint operators δ on $\mathfrak{H}$ such that the norm $\|\delta\|_F := \operatorname{tr}\left(|D_0|^{1/2} |\delta| \, |D_0|^{1/2} \right)$ is finite.*

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

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

(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

$$\varphi^{(\delta)}(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\rho_\delta(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \mathrm{d}\mathbf{y} \ , \tag{7}$$

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

$$\psi \mapsto \int \frac{\delta(x, y)\psi(y)}{|\mathbf{x} - \mathbf{y}|} \mathrm{d}y \ . \tag{8}$$

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

$$D^{(\delta)} := D_Z + \alpha W^{(\delta)} \ . \tag{9}$$

As shown in the Appendix A (Lemmata A.7 and A.8), the operator $W^{(\delta)}$ is bounded implying that $D^{(\delta)}$ is self-adjoint with the same domain as the Coulomb-Dirac operator D_Z which for $\alpha Z \in [0, \sqrt{3}/2)$ is identical with the domain of D_0. Moreover (see Lemma A.9), $W^{(\delta)}$ is relatively compact with respect to D_0 which implies

$$\sigma_{\rm ess}(D^{(\delta)}) = \sigma_{\rm ess}(D_0) = (-\infty, -m] \cup [m, \infty).$$

Finally, since $|D^{(\delta)}| \geq c_{\alpha,Z,m,\delta}|D_0|$ by definition of $c_{\alpha,Z,m,\delta}$ (Equation (87)) and since $|D_0| > 0$, the operator $D^{(\delta)}$ has a bounded inverse, as soon as $c_{\alpha,Z,m,\delta} > 0$.

The one-electron states are vectors in $\mathfrak{H}_+ = \Lambda_+\mathfrak{H}$ where Λ_+ is an orthogonal projection on $\mathfrak{H}$, whereas one-positron states are charge conjugated states in $\Lambda_-\mathfrak{H}$, where $\Lambda_- := 1 - \Lambda_+$ ([22]). We will take Λ_+ to be the projection $\Lambda_+^{(\delta)}$ onto the positive spectral subspace of the Dirac-Fock operator $D^{(\delta)}$, i.e.,

$$\Lambda_+ := \Lambda_+^{(\delta)} := \chi_{[0,\infty)}(D^{(\delta)}) \ , \tag{10}$$

where χ_I denotes the characteristic function of the set I. Thus, the choice of δ fixes the definition of the spaces of electrons and positrons.

The Coulomb scalar product is

$$D[\rho, \sigma] := \frac{1}{2}\int_{\mathbb{R}^3} {\rm d}\mathbf{x} \int_{\mathbb{R}^3} {\rm d}\mathbf{y} \frac{\overline{\rho(\mathbf{x})}\sigma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \ . \tag{11}$$

The exchange scalar product for $\gamma, \gamma' \in F$ is

$$E[\gamma, \gamma'] := \frac{1}{2}\int {\rm d}x \int {\rm d}y \frac{\overline{\gamma(x,y)}\gamma'(x,y)}{|\mathbf{x}-\mathbf{y}|} \ . \tag{12}$$

Lemma 2.2. *Assume that $\gamma, \gamma' \in F$. Then*

$$|D[\rho_\gamma, \rho_{\gamma'}]| \leq \frac{\pi}{4}\|\gamma\|_1 \, {\rm tr}\,(\sqrt{-\Delta}|\gamma'|) \ , \tag{13}$$

$$|E[\gamma, \gamma']| \leq D[\rho_{|\gamma|}, \rho_{|\gamma'|}] \ . \tag{14}$$

Proof. Expanding γ and γ' in their respective bases of eigenfunctions (see (5)), we get by the Cauchy-Schwarz inequality

$$\begin{aligned} &\left|\int\int \frac{\overline{\gamma(x,y)}\gamma'(x,y)}{|\mathbf{x}-\mathbf{y}|}{\rm d}x\,{\rm d}y\right| = \left|\int\int \sum_\mu \lambda_\mu \sum_\nu \lambda'_\nu \frac{\overline{\xi_\mu(x)}\xi_\mu(y)\xi'_\nu(x)\overline{\xi'_\nu(y)}}{|\mathbf{x}-\mathbf{y}|}{\rm d}x{\rm d}y\right| \\ &\leq \int\int \frac{\sum_\mu |\lambda_\mu||\xi_\mu(x)|^2 \sum_\nu |\lambda'_\nu||\xi'_\nu(y)|^2}{|\mathbf{x}-\mathbf{y}|}{\rm d}x{\rm d}y = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_{|\gamma|}(\mathbf{x})\rho_{|\gamma'|}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}{\rm d}\mathbf{x}\,{\rm d}\mathbf{y} \ , \end{aligned} \tag{15}$$

which shows that it suffices to prove (13).

To this end we remark that by Kato's inequality

$$\int dx|\xi_\mu(x)|^2 \int dy \frac{|\xi'_\nu(y)|^2}{|\mathbf{x}-\mathbf{y}|} \leq \frac{\pi}{2}(\xi'_\nu, |\nabla|\xi'_\nu) \ . \tag{16}$$

The claimed inequality follows now by multiplication with $|\lambda_\mu\lambda'_\nu|$ and summation over μ and ν. □

We will also need the following result of Bach et al ([5], Equation (30)) :

Lemma 2.3. *If $\gamma \in F$, then*

$$E[\gamma, \gamma] \leq \frac{\pi}{4}\ {\rm tr}\,\left(\gamma^* \sqrt{-\Delta}\,\gamma\right) \ .$$

Given an operator A on the Hilbert space $\mathfrak{H}$ the symbols $A_{++} = \Lambda_+^{(\delta)} A \Lambda_+^{(\delta)}$, $A_{+-} = \Lambda_+^{(\delta)} A \Lambda_-^{(\delta)}$, $A_{-+} = \Lambda_-^{(\delta)} A \Lambda_+^{(\delta)}$, and $A_{--} = \Lambda_-^{(\delta)} A \Lambda_-^{(\delta)}$ denote the matrix elements of the decomposition of A with respect to the splitting of the Hilbert space given by $\Lambda_+^{(\delta)}$ and $\Lambda_-^{(\delta)}$ (We assume that the operators $\Lambda_\pm^{(\delta)}$ leave the domain of A invariant).

Relativistic electrons and positrons are described by one-particle charge density matrices γ with certain additional properties reflecting the charge of the particle, and the fact that they are Fermions and thus obey the Pauli principle.

Definition 2.4. *Given $\delta \in F$ and $q \in \mathbb{R}_+$ we define the following sets of one-particle diagonal charge density matrices:*

$$S^{(\delta)} := \{\gamma \in F \mid -\Lambda_-^{(\delta)} \leq \gamma \leq \Lambda_+^{(\delta)}, \Lambda_-^{(\delta)} \gamma \Lambda_+^{(\delta)} = 0\} , \tag{17}$$

$$S_q^{(\delta)} := \{\gamma \in S^{(\delta)} \mid 0 \leq \operatorname{tr} \gamma \leq q\} , \tag{18}$$

$$S_{\partial q}^{(\delta)} := \{\gamma \in S^{(\delta)} \mid \operatorname{tr} \gamma = q\} . \tag{19}$$

We note that all sets are closed subsets of F. Furthermore, the first two are convex. Note also that for $\gamma \in S^{(\delta)}$ we have $\gamma_{++} \geq 0$ and $\gamma_{--} \leq 0$ which follows directly from the definition. We also observe that :

$$\gamma_{++}^2 \leq \gamma_{++} , \tag{20}$$

$$\gamma_{--}^2 \leq -\gamma_{--} , \tag{21}$$

which permits to get (in the case of diagonal density matrices)

$$\operatorname{tr}(|D^{(\delta)}||\gamma|) = \operatorname{tr}(D^{(\delta)}\gamma) \geq \operatorname{tr}(|D^{(\delta)}|\gamma^2) . \tag{22}$$

The elements of $S^{(\delta)}$ are the one-particle (renormalized) charge density matrices γ of the electron-positron field. The trace is its total charge. Since we are interested in describing atoms we want to fix the charge of the electron-positron field to be q and minimize the energy over the set $S_{\partial q}^{(\delta)}$. For technical reasons we will also use $S_q^{(\delta)}$.

We wish to point out that he derivation of the variational spaces of one-particle charge density matrices as done in [5] does not give the extra condition $\Lambda_-^{(\delta)} \gamma \Lambda_+^{(\delta)} = 0$ that appears in the definition of $S^{(\delta)}$. A formal calculation shows that if we do not assume that the one-particle density matrices have off diagonal terms equal zero, then in most cases, Lemma 3.1 and Theorem 4.3 and 4.5 do not hold. In particular, minimizers will contain electron-positron pairs.

The projections $\Lambda_-^{(\delta)}$ can be physically interpreted as the one-particle density matrix of the Dirac sea. In particular, $\Lambda_-^{(\delta)}$ is the Dirac sea under the influence of a nucleus of charge eZ and an electron-positron distribution given by δ.

For later purposes we also introduce (unrenormalized) density matrices as

$$\Gamma := \Lambda_-^{(\delta)} + \gamma ,$$

representing all electrons including those of the Dirac sea.

The unrenormalized density matrices are nonnegative expressing the fact that positrons occur in this picture only as 'holes' in the Dirac sea.

The energy of a system of electrons and positrons in Hartree-Fock approximation is given by the functional

$$\mathcal{E} : \begin{array}{lcl} S^{(\delta)} & \to & \mathbb{R} \\ \gamma & \mapsto & \operatorname{tr}(D_Z \gamma) + \alpha Q[\gamma, \gamma] , \end{array} \tag{23}$$

where

$$Q: \begin{array}{lll} S^{(\delta)} \times S^{(\delta)} & \to & \mathbb{R} \\ (\gamma, \gamma') & \mapsto & D[\rho_\gamma, \rho_{\gamma'}] - E[\gamma, \gamma'] \ . \end{array} \tag{24}$$

As explained above we are primarily interested in the infimum of $\mathcal{E}|_{S^{(\delta)}_{\partial q}}$; for technical reasons we will also consider, for $\mu \in \mathbb{R}$,

$$\mathcal{E}_\mu: \begin{array}{lll} S^{(\delta)} & \to & \mathbb{R} \\ \gamma & \mapsto & \mathcal{E}(\gamma) - \mu \operatorname{tr} \gamma \end{array} \tag{25}$$

Lemma 2.5. *For any $\mu \in \mathbb{R}$, the energy functional $\mathcal{E}_\mu$ is well defined and continuous in the $\|\cdot\|_F$ norm.*

Proof. The lemma is an immediate consequence of the definition of the norm, Lemma 2.3 together with the fact that $\gamma^2 \leq |\gamma|$ and Inequalities (13) and (14). □

3. Minimization of the Energy

3.1. Reduction to Electrons.

Lemma 3.1. *Assume $q > 0$, $\gamma \in S^{(\delta)}_{\partial q}$, $0 \leq \delta \in F$. Moreover, assume*

$$c_{\alpha,Z,m,\delta} > \pi\alpha(1/4 + \max\{\operatorname{tr} \delta, q\}) \ .$$

Then there exists a nonnegative $\gamma_e \in S^{(\delta)}_{\partial q}$ and $R \in S^{(\delta)}_{\partial 0}$ such that $\gamma = \gamma_e + R$ and $\mathcal{E}(\gamma_e) \leq \mathcal{E}(\gamma)$. In addition, equality can only occur if $0 \leq \gamma$.

Physically speaking this lemma says that it is favorable to have no positrons in the system and to restrict the minimization to electron states.

Proof. Using the spectral decomposition of γ, one can easily construct γ_e and R such that $\gamma_e \in S^{(\delta)}_{\partial q}$, $R \in S^{(\delta)}_{\partial 0}$ and $\gamma = \gamma_e + R$. We also note that we can pick $R \neq 0$, if $\gamma \not\geq 0$, and that we can pick $R = 0$, if $\gamma \geq 0$. We have

$$\begin{aligned} \mathcal{E}(\gamma_e) - \mathcal{E}(\gamma) &= -\operatorname{tr}(D_Z R) - \alpha Q[R,R] - 2\alpha \Re Q[R, \gamma_e] \\ &= -\operatorname{tr}(D^{(\delta)} R) - \alpha Q[R,R] - 2\alpha \Re Q[R, \gamma_e] + 2\alpha \Re Q[R, \delta] \\ &\leq -\operatorname{tr}(D^{(\delta)} R) + \alpha E[R,R] - 2\alpha \Re Q[R, \gamma_e] + 2\alpha \Re Q[R, \delta] \ , \end{aligned} \tag{26}$$

where in the last inequality, we used positivity of $D[\rho_R, \rho_R]$.

Let R_+ and R_- be respectively the positive and negative part of R, i.e.

$$R = R_+ - R_- \text{ with } R_\pm \geq 0 \ .$$

Using Lemma A.8 and the positivity of γ_e yields

$$\Re Q[R_+, \gamma_e] \geq 0 \text{ and thus } -\Re Q[R, \gamma_e] \leq \Re Q[R_-, \gamma_e] \ .$$

Similarly, we have $\Re Q[R, \delta] \leq \Re Q[R_+, \delta]$. Therefore, from Inequality (26) we obtain

$$\mathcal{E}(\gamma_e) - \mathcal{E}(\gamma) \leq -\operatorname{tr}(D^{(\delta)} R) + \alpha E[R,R] + 2\alpha \Re Q[R_-, \gamma_e] + 2\alpha \Re Q[R_+, \delta] \ . \tag{27}$$

From Lemma 2.3 and the definition of $c_{\alpha,Z,m,\delta}$ in (87), we get

$$E[R,R] \leq \frac{\pi}{4} \operatorname{tr}(|D_0| R^2) \leq \frac{\pi}{4 c_{\alpha,Z,m,\delta}} \operatorname{tr}(|D^{(\delta)}| R^2) \leq \frac{\pi}{4 c_{\alpha,Z,m,\delta}} \operatorname{tr}(D^{(\delta)} R) \ , \tag{28}$$

where the last inequality is a consequence of (22).

Using (14), (13), and, finally, the definition of $c_{\alpha,Z,m,\delta}$ in (87) we have

$$\begin{aligned} \Re Q[R_-, \gamma_e] &= D[\rho_{R_-}, \rho_{\gamma_e}] - \Re E[R_-, \gamma_e] \leq 2D[\rho_{R_-}, \rho_{\gamma_e}] \\ &\leq \frac{\pi}{2} \operatorname{tr} \gamma_e \operatorname{tr}(|p| R_-) \leq \frac{\pi \operatorname{tr} \gamma_e}{2 c_{\alpha,Z,m,\delta}} \operatorname{tr}(|D^{(\delta)}| R_-) \ . \end{aligned} \tag{29}$$

With exactly the same arguments as above, exchanging R_- by R_+ and γ_e by δ we get

$$\Re Q[R_+, \delta] \leq \frac{\pi \operatorname{tr} \delta}{2c_{\alpha,Z,m,\delta}} \operatorname{tr}(|D^{(\delta)}|R_+). \tag{30}$$

Since $\operatorname{tr}(|D^{(\delta)}||R|) = \operatorname{tr}(D^{(\delta)}R)$, we have, using (27)-(30)

$$\mathcal{E}(\gamma_e) - \mathcal{E}(\gamma) \leq \left(-1 + \frac{\pi\alpha}{4c_{\alpha,Z,m,\delta}} + \frac{\pi\alpha \max\{\operatorname{tr} \delta, q\}}{c_{\alpha,Z,m,\delta}}\right) \operatorname{tr}(D^{(\delta)}R) \leq 0\ , \tag{31}$$

under the hypothesis of the theorem. In addition we note that the last inequality is strict unless $R = 0$ or the prefactor vanishes. □

3.2. **Reduction to Density Matrices with Finite Spectrum.**

Lemma 3.2. *Assume $0 \leq q$, $0 \leq \delta \in F$ and $0 \leq \gamma \in S^{(\delta)}_{\partial q}$. Then there exists a sequence of finite rank density matrices $\gamma_K \in S^{(\delta)}_{\partial q}$ such that $\|\gamma_K - \gamma\|_F \to 0$ as $K \to \infty$.*

Proof. Let $(\xi_k)_{k\in\mathbb{N}}$ be a complete set of eigenfunctions in $H^1(G)$ of γ associated with the eigenvalues λ_k. Since $\gamma \geq 0$, we have $\gamma = \Lambda^{(\delta)}_+ \gamma \Lambda^{(\delta)}_+$ and, for all k, we have $\xi_k \in \Lambda^{(\delta)}_+ \mathfrak{H}$.

Assume that γ is not already of finite rank. Then, since γ is trace class, there exist infinitely many eigenvalues of γ in $(0, 1)$. Let us pick $\lambda_{n_0} \in (0, 1)$, one of these eigenvalues.

Set $\epsilon_K := q - \sum_{k=1}^K \lambda_k$. Then ϵ_K is a nonnegative monotone decreasing sequence tending to zero. Define $\gamma_K := \sum_{k=1}^K \lambda_k |\xi_k\rangle\langle\xi_k| + \epsilon_K |\xi_{n_0}\rangle\langle\xi_{n_0}|$.

We assume that K is chosen sufficiently large so that $K \geq n_0$ and $\lambda_{n_0} + \epsilon_K < 1$. Obviously each γ_K is nonnegative, belongs to $S^{(\delta)}_{\partial q}$ and has finite rank.

We now show that $\gamma_K \to \gamma$ in F-norm as $K \to \infty$. We have

$$\gamma - \gamma_K = \sum_{k=K+1}^{\infty} \lambda_k |\xi_k\rangle\langle\xi_k| - \epsilon_K |\xi_{n_0}\rangle\langle\xi_{n_0}|\ .$$

Thus,

$$\|\gamma - \gamma_K\|_F \leq \sum_{k=K+1}^{\infty} \lambda_k \operatorname{tr}(|D_0||\xi_k\rangle\langle\xi_k|) + \epsilon_K(\xi_{n_0}, |D_0|\xi_{n_0})\ . \tag{32}$$

The first in the right hand side tends to zero, since $|D_0||\gamma| \in \mathfrak{S}_1(\mathfrak{H})$, and the second tends to zero, since $\epsilon_K \to 0$. □

The following is an immediate consequence of the continuity of $\mathcal{E}$ in the F-norm and the preceding density result.

Lemma 3.3. *Assume that $q > 0$. Then*

$$\inf\{\mathcal{E}_\mu(\gamma) \mid 0 \leq \gamma \in S^{(\delta)}_{\partial q}\} = \inf\{\mathcal{E}_\mu(\gamma) \mid 0 \leq \gamma \in S^{(\delta)}_{\partial q}, \operatorname{rank}(\gamma) < \infty\}.$$

3.3. **Reduction to Projection.** Following an argument of Bach [3], we get

Lemma 3.4. *Assume $q \in \mathbb{N}$, $\delta \in F$, $0 \leq \gamma \in S^{(\delta)}_{\partial q}$ with finite rank. Then there exists a projection $P \in S^{(\delta)}_{\partial q}$ such that*

$$\mathcal{E}(P) \leq \mathcal{E}(\gamma)\ . \tag{33}$$

Equality in (33) *holds only if γ is already a projection.*

Proof. Suppose that γ is not a projection. Then γ has an eigenvalue $\lambda \in (0,1)$; we denote a corresponding normalized eigenvector by u and observe that it is in $H^1(G)$. Since $\operatorname{tr}(\gamma) \in \mathbb{N}$, there exists at least a second eigenvalue $\mu \in (0,1)$; we denote a corresponding normalized eigenvector by v. We set

$$\tilde{\gamma} := \gamma + \epsilon S \ , \tag{34}$$

where $S := |u\rangle\langle u| - |v\rangle\langle v|$. We get

$$\mathcal{E}(\tilde{\gamma}) - \mathcal{E}(\gamma) = \epsilon(\operatorname{tr}(D_Z S) + 2\Re Q[\gamma, S]) + \epsilon^2 Q[S,S] \ . \tag{35}$$

By explicit computation and use of the Cauchy-Schwarz inequality, one can show that :

$$Q[S,S] < 0 \ , \quad \text{if } S \text{ is a difference of two orthogonal rank one projections.} \tag{36}$$

Now – depending on the sign of the coefficient linear in ϵ – we lower the energy by increasing or decreasing ϵ from zero, until one of the constraints $0 \le \lambda + \epsilon, \mu - \epsilon \le 1$ forbids any further increase or decrease of ϵ. This process leaves all the eigenvalues of γ unchanged except for μ and λ, one of which becomes either 0 or 1.

Since there are only finitely many eigenvalues of γ strictly between zero and one (even if they are counted according to their multiplicity), iterating this process eliminates all eigenvalues that are strictly between 0 and 1, i.e., we have found a density matrix P such that $P^2 = P$. □

Remark 3.5. *Following the same method in the case of $q \ge 0$, not necessarily integer, we can show that, given $0 \le \gamma \in S^{(\delta)}_{\partial q}$, there exists $\tilde{P}$ equals a projection plus a rank one operator such that $\operatorname{tr} \tilde{P} = \operatorname{tr} \gamma$, $\tilde{P} \ge 0$ and $\mathcal{E}(\tilde{P}) \le \mathcal{E}(\gamma)$, with equality only if γ is already a projection plus a rank one operator.*

3.4. **Lower Bound on the Energy.** In this subsection, we show that for sufficiently small fine structure constant α and atomic number Z, the energy is bounded from below.

Theorem 3.6. *Assume $0 \le \delta \in F$, and $c_{\alpha,Z,m,\delta} \ge \pi\alpha(1/4 + \max\{\operatorname{tr} \delta, q\}) > 0$. Then, for all $\gamma \in S^{(\delta)}_q$, $\mathcal{E}(\gamma) \ge 0$.*

Proof. By Lemma 3.1 we need to consider only positive γ's. In this case, (14) implies $Q[\gamma,\gamma] \ge 0$. Now, for $f \in \Lambda^{(\delta)}_+ \mathfrak{H}$, using the definition (87) of $c_{\alpha,Z,m,\delta}$, Inequality (13) and the positivity of $E^{(\delta)}$, we obtain

$$(f, D_Z f) = (f, |D^{(\delta)}| f) - \alpha(f, W^{(\delta)} f) \ge c_{\alpha,Z,m,\delta}(f, |p| f) - \frac{\pi}{4}\alpha \operatorname{tr} \delta(f, |p| f) \ge 0 \ .$$

Thus, under our hypotheses, $\mathcal{E}(\gamma) \ge \operatorname{tr}(D_Z \gamma) \ge 0$. □

3.5. **Reduction to Density Matrices of Maximal Charge.**

Lemma 3.7. *Assume $0 \le q$, $0 \le \delta \in F$ and suppose that, for all $0 \le p < q$ and all $0 \le \gamma \in S^{(\delta)}_p$, the operator $\Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+$ has infinitely many eigenvalues in $(0,m)$. Then*

$$\inf\left\{\mathcal{E}_m(\gamma) | \gamma \in S^{(\delta)}_{\partial q}, \gamma \ge 0\right\} = \inf\left\{\mathcal{E}_m(\gamma) | \gamma \in S^{(\delta)}_q, \gamma \ge 0\right\} \ .$$

If in addition $0 \le \tilde{\gamma}$ is a minimizer of $\mathcal{E}_m$ in $S^{(\delta)}_q$, it follows that $\operatorname{tr} \tilde{\gamma} = q$.

Proof. That the left side bounds the right side from above is obvious. To prove the converse inequality, we assume $0 \le \gamma \in S^{(\delta)}_q$, with $\operatorname{tr} \gamma < q$. By Lemma 3.4 and Remark 3.5 we can assume that γ is a projection plus a rank one operator; in particular its range is finite dimensional. Since by assumption the discrete spectral

subspace $\mathfrak{X}$ of $\Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)}$ is infinite dimensional we can find $u \in \mathfrak{H}_+ \cap \mathfrak{X} \cap \gamma(\mathfrak{H})^\perp$ with $0 < \|u\| \leq 1$ and define $\tilde{\gamma} := \gamma + A$ with $A := |u >< u|$. We then get

$$\mathcal{E}_m(\gamma + A) - \mathcal{E}_m(\gamma) = \operatorname{tr}(D_Z A) + 2\Re Q(\gamma, A) - m\|u\|^2 = \langle u, (D^{(\gamma)} - m)u\rangle < 0 \ .$$

Thus, this construction yields a density matrix $\tilde{\gamma}$ with strictly smaller energy and a trace that can be made bigger by $\min\{1, q - \operatorname{tr}\gamma\}$. Iteration of the construction yields the desired result. This proves both claims. □

3.6. **Existence of a Minimizer.** We wish to show the existence of a minimizer by weak lower semi-continuity of the functional on a minimizing sequence and weak compactness. However, we are faced with the problem that we are minimizing on charge density matrices and the fact that the Coulomb potential is not relatively compact with respect to the relativistic energy $|p|$. The first problem has been addressed by Solovej [21] in the non-relativistic context. To handle the second problem we will decompose the one-particle part of the energy.

Theorem 3.8. *Assume $0 < c_{\alpha,Z,m,\delta}$, $0 \leq \delta \in F$ and $q \in \mathbb{N}$. Furthermore, suppose that $\mathcal{E}_m$ is bounded below on $S_{\partial q}^{(\delta)}$ and*

$$\inf\{\mathcal{E}_m(\gamma) \mid \gamma \in S_q^{(\delta)}\} = \inf\{\mathcal{E}_m(\gamma) \mid \gamma \in S_{\partial q}^{(\delta)}, \gamma^2 = \gamma\} \ .$$

Then the energy functional $\mathcal{E}_m|_{S_q^{(\delta)}}$ has a minimizer.

Proof. Let γ_n be a minimizing sequence of orthogonal projections in $S_{\partial q}^{(\delta)}$.

Step 1. Weak Limit of the Minimizing Sequence: Since $\mathcal{E}_m(\gamma_n)$ and $\varphi^{(\delta)}$ are bounded (Lemma A.7) (and thus also $X^{(\delta)}$, by Lemma A.8, and $W^{(\delta)}$) there exists a constant C such that, for any $p \geq 1$

$$\begin{aligned} C \geq \mathcal{E}_m(\gamma_n) + \alpha q \|W^{(\delta)}\| \geq \operatorname{tr}(|D^{(\delta)}|\gamma_n) \geq c_{\alpha,Z,m,\delta} \operatorname{tr}(|D_0|\gamma_n) = c_{\alpha,Z,m,\delta}\|\gamma_n\|_F \\ \geq c_{\alpha,Z,m,\delta}\||D_0|^{1/2}\gamma_n|D_0|^{1/2}\|_p \ . \end{aligned}$$

Thus, according to Banach and Alaoglu, there exists, for all $p > 1$, γ_∞ with $\||D_0|^{1/2}\gamma_\infty|D_0|^{1/2}\|_p < \infty$ and a subsequence of γ_n – also denoted by γ_n – such that for all B with $\|B\|_q < \infty$,

$$\operatorname{tr}(B|D_0|^{1/2}\gamma_n|D_0|^{1/2}) \to \operatorname{tr}(B|D_0|^{1/2}\gamma_\infty|D_0|^{1/2}) \ , \tag{37}$$

where $1/p + 1/q = 1$.

We denote $\|\gamma_n\|_{F,p} := \||D_0|^{1/2}\gamma_n|D_0|^{1/2}\|_p$. Given $p_1 \geq p_2 \geq 1$, it is always possible to extract a subsequence of γ_n – again denoted by γ_n –, such that it converges weakly in $(F, \|.\|_{F,p_1})$ and $(F, \|.\|_{F,p_2})$. Denote the weak limits respectively by $\gamma_\infty^{(p_1)}$ and $\gamma_\infty^{(p_2)}$. Then for all $B \in \mathfrak{S}_{q_1}(\mathfrak{H})$ we have $B \in \mathfrak{S}_{q_2}(\mathfrak{H})$ and

$$\operatorname{tr}(B|D_0|^{1/2}\gamma_\infty^{(p_1)}|D_0|^{1/2}) = \lim_{n\to\infty} \operatorname{tr}(B|D_0|^{1/2}\gamma_n|D_0|^{1/2}) = \operatorname{tr}(B|D_0|^{1/2}\gamma_\infty^{(p_2)}|D_0|^{1/2}) \ .$$

Thus, for all $B \in \mathfrak{S}_{q_1}(\mathfrak{H})$, we have

$$\operatorname{tr}(B|D_0|^{1/2}(\gamma_\infty^{(p_1)} - \gamma_\infty^{(p_2)})|D_0|^{1/2}) = 0 \ .$$

This yields $\gamma_\infty^{(p_1)} = \gamma_\infty^{(p_2)}$.

Therefore, in the other parts of this proof, we will always assume we have chosen a subsequence of γ_n such that, for the considered p, the weak-limits in $(F, \|.\|_{F,p})$ exist and coincide.

Step 2. Lower Semi-Continuity: We will now prove that taking the limit decreases the energy, i.e. $\liminf_{n\to\infty} \mathcal{E}_m(\gamma_n) \geq \mathcal{E}_m(\gamma_\infty)$. We define $\Lambda_m := \chi_{[0,m]}(D^{(\delta)})$

and $\Lambda'_m := \Lambda_+^{(\delta)} - \Lambda_m$ and split the energy functional. We treat the various terms separately

$$\begin{aligned}\mathcal{E}_m(\gamma_n) =& T_1(\gamma_n) + T_2(\gamma_n) + T_3(\gamma_n) + T_4(\gamma_n) + T_5(\gamma_n)\\ :=& \operatorname{tr}(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m\gamma_n) + \operatorname{tr}(\Lambda_m(D^{(\delta)} - m)\Lambda_m\gamma_n) - \alpha\operatorname{tr}(\varphi^{(\delta)}\gamma_n)\\ &+ \alpha\operatorname{tr}(X^{(\delta)}\gamma_n) + \alpha Q(\gamma_n,\gamma_n)\ .\end{aligned}$$

Step 2.1. Fix a basis $(e_\ell)_{\ell\in\mathbb{N}}$ of $\mathfrak{H}_+$, each element being in $H^1(G)$. Then

$$\begin{aligned}T_1(\gamma_n) &:= \operatorname{tr}\Big(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m\gamma_n\Big)\\ &= \operatorname{tr}\Big((\Lambda'_m(D^{(\delta)} - m)\Lambda'_m)^{1/2}\gamma_n(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m)^{1/2}\Big)\\ &= \sum_k (e_k, (\Lambda'_m(D^{(\delta)} - m)\Lambda'_m)^{1/2}\gamma_n \underbrace{(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m)^{1/2}e_k)}_{f_k:=}\\ &= \sum_k \operatorname{tr}\Big(\underbrace{|\,|D_0|^{-1/2}f_k\rangle\langle|D_0|^{-1/2}f_k\,|}_{H_k:=}|D_0|^{1/2}\gamma_n|D_0|^{1/2}\Big)\ .\end{aligned}$$

Obviously, H_k is a non-negative Hilbert-Schmidt operator. Thus, applying first Fatou's lemma and then using (37), we get

(38)
$$\begin{aligned}\liminf_{n\to\infty}\operatorname{tr}\Big(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m\gamma_n\Big) &= \liminf_{n\to\infty}\textstyle\sum_k \operatorname{tr}(H_k|D_0|^{1/2}\gamma_n|D_0|^{1/2})\\ &\geq \textstyle\sum_k \liminf_{n\to\infty}\operatorname{tr}(H_k|D_0|^{1/2}\gamma_n|D_0|^{1/2})\\ &= \textstyle\sum_k \operatorname{tr}(H_k|D_0|^{1/2}\gamma_\infty|D_0|^{1/2})\\ &= \operatorname{tr}\Big(\Lambda'_m(D^{(\delta)} - m)\Lambda'_m\gamma_\infty\Big)\ ,\end{aligned}$$

which proves $\liminf_{n\to\infty} T_1(\gamma_n) \geq T_1(\gamma_\infty)$.

Step 2.2. Because T_2 is continuous in the $\|\cdot\|_{F,2}$-norm (Lemma A.13) the claim follows for T_2.

Step 2.3. Since $\varphi^{(\delta)} \in L^4(\mathbb{R}^3)$ (Lemma A.7), we have, by [20, Theorem 4.1], that $|D_0|^{-1/2}\varphi^{(\delta)}|D_0|^{-1/2} \in \mathfrak{S}_4(\mathfrak{H})$. By Hölder inequality, this implies that T_3 is continuous in the $\|\cdot\|_{F,4/3}$-norm, and $\lim_{n\to+\infty} T_3(\gamma_n) = T_3(\gamma)$.

Step 2.4. We would like to prove

$$\liminf_{n\to\infty} Q[\gamma_n,\gamma_n] \geq Q[\gamma_\infty,\gamma_\infty]\ . \tag{39}$$

To that end, we will first show

$$\lim_{n\to\infty}\gamma_n(x,y) = \gamma_\infty(x,y)\ , \tag{40}$$

for a.e. $(x,y) \in G^2$, and

$$\lim_{n\to\infty}\gamma_n(x,x) = \gamma_\infty(x,x)\ , \tag{41}$$

for a.e. $x \in G$.

Now, (γ_n) is a bounded sequence in $\mathfrak{S}_2(\mathfrak{H})$. Again, we can extract a subsequence such that γ_n converges weakly to $\tilde{\gamma}_\infty$ in $\mathfrak{S}_2(\mathfrak{H})$. Using (37), we get for all $B \in \mathfrak{S}_2(\mathfrak{H})$

$$\begin{aligned}\operatorname{tr}(B\tilde{\gamma}_\infty) &= \lim_{n\to\infty}\operatorname{tr}(B\gamma_n) = \lim_{n\to\infty}\operatorname{tr}\Big(\underbrace{|D_0|^{-\frac{1}{2}}B|D_0|^{-\frac{1}{2}}}_{\in\mathfrak{S}_2(\mathfrak{H})}|D_0|^{\frac{1}{2}}\gamma_n|D_0|^{\frac{1}{2}}\Big)\\ &= \operatorname{tr}\Big(|D_0|^{-\frac{1}{2}}B|D_0|^{-\frac{1}{2}}|D_0|^{\frac{1}{2}}\gamma_\infty|D_0|^{\frac{1}{2}}\Big) = \operatorname{tr}(B\gamma_\infty)\ .\end{aligned}$$

Thus $\tilde{\gamma}_\infty = \gamma_\infty$. In particular we have

$$\gamma_n(\cdot,\cdot) \to \gamma_\infty(\cdot,\cdot)\ , \tag{42}$$

weakly in $L^2(G\times G)$.

Using the spectral decomposition of the γ_n's, we may write each $\gamma_n(x,y)$ as

$$\gamma_n(x,y) = \sum_{i=1}^{q} u_i^{(n)}(x)\overline{u_i^{(n)}(y)} \ ,$$

where each sequence $(u_i^{(n)})_{n\in\mathbb{N}}$ $(i=1,\dots,q)$ is an orthonormal family in $\in H^{1/2}(G)\cap \Lambda_+^{(\delta)}\mathfrak{H}$. Since the sequence $(\mathrm{tr}\,(|p|\gamma_n))_{n\in\mathbb{N}}$ is bounded, it follows that, for each $i\in\{1,\dots,q\}$, the sequence $(u_i^{(n)})_{n\in\mathbb{N}}$ is bounded in $H^{1/2}(G)$.

Therefore, applying [16, Theorem 16.1], for all $\chi\in C_0^\infty(\mathbb{R}^3)$ and $i\in\{1,\dots,q\}$, there exists a subsequence of $(u_i^{(n)})_{n\in\mathbb{N}}$ – also denoted $(u_i^{(n)})_{n\in\mathbb{N}}$ – such that $(\chi u_i^{(n)})$ converges strongly in $L^2(G)$.

Thus, after extraction of a subsequence of $\left(u_1^{(n)},u_2^{(n)},\dots,u_q^{(n)}\right)_{n\in\mathbb{N}}$, denoted again by $\left(u_1^{(n)},u_2^{(n)},\dots,u_q^{(n)}\right)_{n\in\mathbb{N}}$, we obtain, for all $i=1,\dots,q$ and for almost every $x\in G$,

$$u_i^{(n)}(x)\to u_i^{(\infty)}(x)\ . \tag{43}$$

Consequently, we obtain

$$\gamma_n(x,y)\to\beta(x,y):=\sum_{i=1}^{q} u_i^{(\infty)}(x)\,\overline{u_i^{(\infty)}(y)}\ , \tag{44}$$

almost everywhere in G^2. Now from (42) and (44) it follows by standard arguments that $\gamma_\infty(x,y)=\beta(x,y)$ almost everywhere in $G\times G$. Thus $\gamma_n(x,y)$ converges almost everywhere to $\gamma_\infty(x,y)$. This together with (44) implies (40).

The above also immediately implies that

$$\gamma_\infty=\sum_{i=1}^{q}|u_i^{(\infty)}\rangle\langle u_i^{(\infty)}|\ , \tag{45}$$

proving (41).

Applying Fatou's lemma to the pointwise positive functions $(x,y)\mapsto\gamma_n(x,x)\gamma_n(y,y)-|\gamma_n(x,y)|^2$ and using in addition (40) and (41) yields

$$\begin{aligned}\liminf_{n\to\infty} Q[\gamma_n,\gamma_n] &\geq \int \liminf_{n\to\infty}\frac{\gamma_n(x,x)\gamma_n(y,y)-|\gamma_n(x,y)|^2}{|\mathbf{x}-\mathbf{y}|}\mathrm{d}x\,\mathrm{d}y\\ &= \int\frac{\gamma_\infty(x,x)\gamma_\infty(y,y)-|\gamma_\infty(x,y)|^2}{|\mathbf{x}-\mathbf{y}|}\mathrm{d}x\,\mathrm{d}y = Q[\gamma_\infty,\gamma_\infty]\ ,\end{aligned}$$

which proves (39).

Step 2.5. Since $\varphi^{(\delta)}\in L^4(\mathbb{R}^3)$ (Lemma A.7) and $X^{(\delta)}\leq\varphi^{(\delta)}$ (by Lemma A.8 and the positivity of $X^{(\delta)}$ and δ), we have $|D^{(\delta)}|^{-1/2}X^{(\delta)}|D^{(\delta)}|^{-1/2}\in\mathfrak{S}_4$. Thus T_5 is continuous in the $\|\cdot\|_{F,4/3}$-norm (by Hölder inequality). Therefore

$$\lim_{n\to+\infty}T_5(\gamma_n)=T_5(\gamma_\infty)\ .$$

This concludes the proof of Theorem 3.8. □

Theorem 3.9. *Assume* $0\leq\delta\in F$, $q\in\mathbb{N}$, $q\leq Z$ *and*

$$\pi\alpha(1/4+\max\{\mathrm{tr}\ \delta,q\})<(d-4\alpha\,\mathrm{tr}\ \delta).$$

Then the functional $\mathcal{E}|_{S_{\partial q}^{(\delta)}}$ *(see the Definition* (23) *and* (19)*) has a minimizer.*

Proof. Using lemma A.6 and the assumptions, we obtain

$$\pi\alpha(\frac{1}{4}+\max\{\mathrm{tr}\ \delta,q\})<c_{\alpha,Z,m,\delta}. \tag{46}$$

Therefore, by Theorem 3.6, the functional $\mathcal{E}_m$ is bounded below on $S_q^{(\delta)}$.

Lemmata 3.1, 3.3 and 3.4 together with Remark 3.5 imply that it suffices to minimize over positive γ's in $S_q^{(\delta)}$ that can be written as a sum of a projection and a rank one operator. Moreover, Inequality (46) and Lemma A.12 permit to apply Lemma 3.7, which, together with the above and the fact that q is an integer yields

$$\inf\{\mathcal{E}_m(\gamma)|\gamma \in S_q^{(\delta)}\} = \inf\{\mathcal{E}_m(\gamma)|\gamma \in S_{\partial q}^{(\delta)}, \gamma^2 = \gamma\}. \tag{47}$$

Thus, applying Theorem 3.8 and again Lemma 3.7 shows that $\mathcal{E}_m|_{S_q^{(\delta)}}$ has a minimizer in $S_{\partial q}^{(\delta)}$. Therefore the functional $\mathcal{E}|_{S_{\partial q}^{(\delta)}}$ also has a minimizer. □

4. Properties of the Minimizers: No-Pair Dirac-Fock Equations

4.1. **Infinitesimal Perturbations of Projections.** In this section, we will prove that all minimizers γ fulfill a no-pair Dirac-Fock equation. We first need to state preliminary results. The first was already used in the adiabatic theory (see Nenciu [18] and references therein).

Lemma 4.1 (Nenciu)**.** *Given an orthogonal projection P_0, its orthogonal complement $P_0^\perp = 1 - P_0$, a bounded operator A, and $\epsilon \in \mathbb{R}$, with $4|\epsilon|\,\|A\| < 1$, there exists an operator B_ϵ with $\|B_\epsilon\| \leq 4\,\|A\|^2$ such that*

$$P_\epsilon = P_0 + \epsilon\left(P_0 A P_0^\perp + P_0^\perp A^* P_0\right) + \epsilon^2 B_\epsilon \tag{48}$$

is an orthogonal projection.

Proof. We set

$$P_\epsilon := \frac{1}{2\pi i}\oint_{|z-1|=\frac{1}{2}} \frac{1}{z - P_0 - \epsilon a}\mathrm{d}z, \tag{49}$$

where

$$a := P_0 A P_0^\perp + P_0^\perp A^* P_0\ .$$

We observe that $\|a\| \leq \|A\|$. Therefore under the assumption $4\epsilon\|A\| < 1$, we obtain that $\sigma(P_0 + \epsilon a) \subset (-1/4, 1/4) \cup (3/4, 5/4)$. Thus, by the holomorphic functional calculus, P_ϵ is the projector onto the eigenspace of $(P_0 + \epsilon a)$ corresponding to $(3/4, 5/4)$.

$$\begin{aligned} P_\epsilon = P_0 &+ \frac{\epsilon}{2\pi i}\oint_{|z-1|=\frac{1}{2}} \frac{1}{z - P_0} a \frac{1}{z - P_0}\,\mathrm{d}z \\ &- \frac{\epsilon^2}{2\pi i}\oint_{|z-1|=\frac{1}{2}} \frac{1}{z - P_0} a \frac{1}{z - P_0 - \epsilon a} a \frac{1}{z - P_0}\,\mathrm{d}z\ . \end{aligned} \tag{50}$$

Since P_0 is an orthogonal projection, there exists a basis $(e_j)_{j\in\mathbb{N}}$ of $\mathfrak{H}$ and $I \subset \mathbb{N}$ such that

$$P_0 = \sum_{j\in I} |e_j\rangle\langle e_j|.$$

Note also for later purpose that

$$\frac{1}{z - P_0} = \frac{1}{z-1}\sum_{j\in I}|e_j\rangle\langle e_j| + \frac{1}{z}\sum_{j\in\mathbb{N}\setminus I}|e_j\rangle\langle e_j| = \frac{1}{z-1}P_0 + \frac{1}{z}P_0^\perp\ . \tag{51}$$

Using Cauchy's residue Theorem and (51), we obtain

$$\begin{aligned} \frac{1}{2i\pi}\oint_{|z-1|=\frac{1}{2}} \frac{1}{z - P_0} a \frac{1}{z - P_0}\mathrm{d}z &= \frac{1}{2i\pi}\oint_{|z-1|=\frac{1}{2}} \left(P_0^\perp a P_0 + P_0 a P_0^\perp\right)\frac{\mathrm{d}z}{z(z-1)} \\ &= P_0^\perp a P_0 + P_0 a P_0^\perp = a\ . \end{aligned} \tag{52}$$

This proves that the second summand in the right hand side of (50) is equal to ϵa. This leads us to introduce :

$$B_\varepsilon := -\frac{1}{2\pi i}\oint_{|z-1|=\frac{1}{2}} \frac{1}{z-P_0} a \frac{1}{z-P_0-\epsilon a} a \frac{1}{z-P_0}\,\mathrm{d}z\ . \tag{53}$$

Since $\|a\| \leq \|A\|$ and $\sigma(P_0+\epsilon a) \subset (-1/4, 1/4) \cup (3/4, 5/4)$, we have

$$\begin{aligned} &\left\| \oint_{|z-1|=\frac{1}{2}} \frac{1}{z-P_0} a \frac{1}{z-P_0-\epsilon a} a \frac{1}{z-P_0}\,\mathrm{d}z \right\| \\ &\leq \pi\|a\|^2 \sup_{|z-1|=\frac{1}{2}} \|\frac{1}{z-P_0}\|^2 \sup_{|z-1|=\frac{1}{2}} \|\frac{1}{z-P_0-\epsilon a}\| \leq 16\pi\|A\|^2. \end{aligned} \tag{54}$$

This, together with (50) and (52), proves Lemma 4.1. □

In the case when γ is an orthogonal projection with range in $\mathfrak{H}_+$, we apply Lemma 4.1 with $P_0 = \gamma$, $P_\epsilon = \gamma_\epsilon$ (given by (48)).

Lemma 4.2. *Assume $0 \leq \delta \in F$ and γ an orthogonal projection in $S^{(\delta)}_{\partial q}$, $q \in \mathbb{N}$. Then, for operators A such that $\Lambda^{(\delta)}_+ A \Lambda^{(\delta)}_+ = A$, $|D_0|A \in \mathfrak{S}_1(\mathfrak{H})$ and ϵ sufficiently close to zero, γ_ϵ is again an orthogonal projection in $S^{(\delta)}_{\partial q}$.*

Proof. By construction, since $\Lambda^{(\delta)}_+ A \Lambda^{(\delta)}_+ = A$, we have

$$\Lambda^{(\delta)}_- \gamma_\epsilon \Lambda^{(\delta)}_- = \Lambda^{(\delta)}_+ \gamma_\epsilon \Lambda^{(\delta)}_- = \Lambda^{(\delta)}_- \gamma_\epsilon \Lambda^{(\delta)}_+ = 0\ .$$

Moreover, $\gamma_\epsilon^2 = \gamma_\epsilon$, thus $-\Lambda^{(\delta)}_- \leq \gamma_\epsilon \leq \Lambda^{(\delta)}_+$ and $\Lambda^{(\delta)}_- \gamma_\epsilon \Lambda^{(\delta)}_+ = 0$.

The trace condition is obviously fulfilled since tr γ_ϵ depends continuously on the parameter ϵ. That $D_0\gamma_\epsilon$ is trace class follows immediately from the explicit expressions for the difference $\gamma_\epsilon - \gamma$ in (50), from (51) and the assumptions on A. □

4.2. **Minimizers are Projections.**

Theorem 4.3. *Assume that $0 \leq \delta \in F$, $q \in \mathbb{N}$, and*

$$0 < \pi\alpha(1/4 + \max\{\mathrm{tr}\ \delta, q\}) < c_{\alpha,Z,m,\delta}\ .$$

If γ is a minimizer of $\mathcal{E}|_{S^{(\delta)}_{\partial q}}$, then $\gamma = \gamma^* = \gamma^2 = \Lambda^{(\delta)}_+ \gamma \Lambda^{(\delta)}_+$.

Proof. The proof of $\Lambda^{(\delta)}_+ \gamma \Lambda^{(\delta)}_+ = \gamma$ is a consequence of Lemma 3.1. The proof of $\gamma^2 = \gamma$ follows exactly the lines of Lemma 3.4 except that the iteration of the process is superfluous here. □

4.3. **Minimizers Fulfill the No-Pair Dirac-Fock Equations.** Eventually we derive the Euler equations for the minimizer of the energy.

Theorem 4.4. *Assume $q \in \mathbb{N}_0$ and γ is an orthogonal projection minimizing $\mathcal{E}$ in $S^{(\delta)}_{\partial q}$. Then γ commutes with the no-pair Dirac-Fock operator $\Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+$, i.e.,*

$$\left[\gamma, \Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+\right] = 0. \tag{55}$$

Proof. Let $A \in \mathcal{B}(\mathfrak{H})$ such that

$$D^{(\delta)} A^* \in \mathcal{B}(\mathfrak{H})\ . \tag{56}$$

Then, for ϵ sufficiently close to zero, the projector

$$\gamma_\epsilon := \gamma + \epsilon a + \epsilon^2 B_\epsilon\ , \tag{57}$$

with

$$a = \gamma\Lambda_+^{(\delta)} A \Lambda_+^{(\delta)} \gamma^\perp + \gamma^\perp \Lambda_+^{(\delta)} A^* \Lambda_+^{(\delta)} \gamma \ , \tag{58}$$

and B_ϵ given by (53) (with P_0 replaced by γ), belongs to $S_{\partial q}^{(\delta)}$. Moreover

$$\begin{aligned} &\mathcal{E}(\gamma_\epsilon) - \mathcal{E}(\gamma) \\ &= \epsilon\{\mathrm{tr}\,(D_Z a) + 2\alpha \Re Q[\gamma, a]\} + \epsilon^2\{\mathrm{tr}\,(D_Z B_\epsilon) + 2\alpha\Re Q[\gamma, B_\epsilon] + \alpha Q[a+\epsilon B_\epsilon, a+\epsilon B_\epsilon]\}. \end{aligned} \tag{59}$$

We want to show that the last term is $o(\epsilon)$. By (13), (14) and Lemmata A.7 and A.8, it is sufficient to show that there exists a constant $\mathrm{c} < \infty$ such that, for all $\epsilon \in (-1, 1)$,

$$\max\{\|B_\epsilon\|_1, \|a\|_1, \|D^{(\delta)} B_\epsilon\|_1, \|D^{(\delta)} a\|_1\} < c \ . \tag{60}$$

We first have

$$\begin{aligned} \|D^{(\delta)} a\|_1 &\leq \|D^{(\delta)} \gamma \Lambda_+^{(\delta)} A \Lambda_+^{(\delta)} \gamma^\perp\|_1 + \|D^{(\delta)} \gamma^\perp \Lambda_+^{(\delta)} A^* \Lambda_+^{(\delta)} \gamma\|_1 \\ &\leq \|D^{(\delta)}\gamma\|_1 \, \|A\| + \|D^{(\delta)}\gamma\| \, \|A^*\| \, \|\gamma\|_1 + \|D^{(\delta)} A^*\| \, \|\gamma\|_1 < \mathrm{c} \ , \end{aligned} \tag{61}$$

since $\gamma \in F$ and (56) is assumed. We also have

$$\begin{aligned} \|D^{(\delta)} B_\epsilon\|_1 &= \frac{1}{2\pi} \| \oint_{|z-1|=\frac{1}{2}} D^{(\delta)} \frac{1}{z-\gamma} a \frac{1}{z-\gamma-\epsilon a} a \frac{1}{z-\gamma} \mathrm{d}z \|_1 \\ &\leq \frac{1}{2\pi} \int_0^{2\pi} \|D^{(\delta)} \frac{1}{1+\frac{1}{2}e^{i\varphi}-\gamma} a\|_1 \, \| \frac{1}{1+\frac{1}{2}e^{i\varphi}-\gamma-\epsilon a} a \frac{1}{1+\frac{1}{2}e^{i\varphi}-\gamma} \| \, \mathrm{d}\varphi \\ &\leq \mathrm{c}_1 \, ||a|| \int_0^{2\pi} \|D^{(\delta)} \left(\frac{1}{1+\frac{1}{2}e^{i\varphi}-1} \gamma + \frac{1}{1+\frac{1}{2}e^{i\varphi}} (1-\gamma) \right) a\|_1 \mathrm{d}\varphi \\ &\leq \mathrm{c}_2 \, ||a|| \, \left(\|D^{(\delta)}\gamma\|_1 \|a\| + \|D^{(\delta)} a\|_1 \right) \ , \end{aligned}$$

where the constant c_2 is uniform in ϵ for ϵ close to zero. We also have used (51). Using (61), and $\gamma \in F$ yields

$$\|D^{(\delta)} B_\epsilon\| < \mathrm{c} \ . \tag{62}$$

Similarly to the above, we show

$$\|a\|_1 < \mathrm{c} \quad \text{and} \quad \|B_\epsilon\|_1 < \mathrm{c} \ . \tag{63}$$

Inequalities (61), (62) and (63) yield (60).

Since $\mathcal{E}(\gamma_\epsilon) - \mathcal{E}(\gamma) \geq 0$, whatever the sign of ϵ is, we conclude that the term linear in ϵ in (59) has to vanish

$$\mathrm{tr}\,(D_Z a) + 2\alpha\Re Q[\gamma, a] = \mathrm{tr}\,(D^{(\gamma)} a) = 0 \ . \tag{64}$$

Thus, for all A satisfying (56), equalities (58) and (64) and the fact that $[\Lambda_+^{(\delta)}, \gamma] = 0$ (since γ is an orthonormal projection in $S_{\partial q}^{(\delta)}$) yield

$$\mathrm{tr}\,(\gamma^\perp \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma A) + \mathrm{tr}\,(\gamma \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma^\perp A^*) = 0 \ .$$

Replacing A by iA, we first obtain :

$$\mathrm{tr}\,(\gamma^\perp \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma A) = \mathrm{tr}\,(\gamma \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma^\perp A^*) = 0 \ .$$

Since A can be taken in the set of rank one operators of the form $|u\rangle\langle v|$, with u and v in $C_0^\infty(\mathbb{R}^3) \otimes \mathbb{C}^4$, we obtain

$$\gamma^\perp \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma = \gamma \Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)} \gamma^\perp = 0 \ ,$$

which yields (55). □

This result can be also written as follows

Theorem 4.5. *Assume that γ is an orthogonal projection minimizing $\mathcal{E}$ in $S^{(\delta)}_{\partial q}$. Then there exist q normalized spinors $\psi_1, ..., \psi_q \in \Lambda^{(\delta)}_+(\mathfrak{H}) \cap \mathfrak{D}(D_Z)$ such that*

$$\gamma = \sum_{i=1}^{q} |\psi_i\rangle \langle\psi_i| \ , \tag{65}$$

and

$$\Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+ \psi_i = \epsilon_i \psi_i, \quad \text{for } i = 1, \ldots, q \ , \tag{66}$$

with $\epsilon_1, ..., \epsilon_q \in [0, 1]$.

Proof. The proof is immediate since the range of γ is finite dimensional reducing it to the simultaneous diagonalization of two commuting Hermitian matrices. □

One may characterize the eigenvalues $\epsilon_1, \ldots, \epsilon_q$ more precisely following Bach et al [2]:

Theorem 4.6. *[There are no unfilled shells in no-pair Dirac-Fock theory] Under the same assumptions of Theorem 4.5, $\epsilon_1, ..., \epsilon_q$ are the q lowest eigenvalues of $\Lambda^{(\delta)}_+ D^{(\delta)} \Lambda^{(\delta)}_+$. Moreover, if ϵ_{q+1} denotes the $(q+1)$-th eigenvalue (counting multiplicities) of the no-pair Dirac-Fock operator $\Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+$, we have, for all $i = 1, \cdots, q$, the strict inequality $\epsilon_i < \epsilon_{q+1}$.*

Proof. Assume by contradiction that there exists a normalized eigenspinor v of $\Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+$ with eigenvalue ϵ such that $\epsilon \leq \max\{\epsilon_1, ..., \epsilon_q\}$ and not in the range of γ. Then, for a normalized eigenvector u of γ with $\langle u, \Lambda^{(\delta)}_+ D^{(\gamma)} \Lambda^{(\delta)}_+ u\rangle \geq \epsilon$ and for $\gamma' := \gamma - |u\rangle\langle u| + |v\rangle\langle v|$, we have

$$\begin{aligned}
&\mathcal{E}^{(\delta)}(\gamma') - \mathcal{E}^{(\delta)}(\gamma) \\
&= \langle v, D_Z v\rangle - \langle u, D_Z u\rangle + 2\alpha \Re Q\left[\gamma, |v\rangle\langle v| - |u\rangle\langle u|\right] \\
&\quad + Q\left[|v\rangle\langle v| - |u\rangle\langle u|, |v\rangle\langle v| - |u\rangle\langle u|\right] \\
&< \langle v, D^{(\gamma)} v\rangle - \langle u, D^{(\gamma)} u\rangle \leq 0,
\end{aligned}$$

where – as in the proof of Lemma 3.4 – we used (36), with $S = |v\rangle\langle v| - |u\rangle\langle u|$. This gives a contradiction to the property that γ is the minimizer. □

5. Outlook

In this final section, we first express the energy as a functional of the unrenormalized density matrix Γ and the Dirac sea Λ_-. This has the advantage that the dependence of the energy on Λ_- becomes explicit and that the constraining condition $-\Lambda_- \leq \gamma \leq \Lambda_+$ becomes $0 \leq \Gamma \leq 1$, i.e. independent of Λ_-. Throughout this section we will use the notation $\Lambda := \Lambda_-$.

For a given $q \in \mathbb{N}$, let us define the set

$$\begin{aligned}
\Upsilon_q \ := \ & \Big\{(\Gamma, \Lambda) \in \mathfrak{B}(\mathfrak{H})^2 \mid \Gamma, \Lambda \text{ orth. proj.}, (\Gamma - \Lambda) \in \mathfrak{S}_1, \text{tr } (\Gamma - \Lambda) = q, \\
& D_Z(\Gamma - \Lambda) \in \mathfrak{S}_1, [D_Z, \Lambda] \in \mathcal{B}(\mathfrak{H}), [D_Z, \Gamma] \in \mathcal{B}(\mathfrak{H})\Big\}
\end{aligned}$$

and the following functional on Υ_q:

$$\mathfrak{E}(\Gamma, \Lambda) := \text{tr } ((D_Z - m)(\Gamma - \Lambda)) + \alpha Q[\Gamma - \Lambda, \Gamma - \Lambda] \ ,$$

where $Q[\cdot, \cdot]$ is defined in (24). Note that if $\Lambda = \Lambda^{(\delta)}_-$ for some $\delta \in F$, and if $(\Gamma - \Lambda) \in S^{(\delta)}$, then we have $\mathfrak{E}(\Gamma, \Lambda) = \mathcal{E}(\Gamma - \Lambda)$.

Theorem 5.1. *Assume that* $(\Gamma, \Lambda) \in \Upsilon_q$ *is a critical point of* $\mathfrak{E}$. *Then, with* $\gamma := \Gamma - \Lambda$,

$$[D^{(\gamma)}, \Gamma] = [D^{(\gamma)}, \Lambda] = 0. \tag{67}$$

Proof. For all $\epsilon \in \mathbb{R}$ and $A \in \mathfrak{S}_1(\mathfrak{H})$ such that :

$$D_Z A \in \mathfrak{S}_1(\mathfrak{H})\,,\ D_Z A^* \in \mathfrak{S}_1(\mathfrak{H})\,,\ 4|\epsilon|\|A\| < 1\,,\ 8q\epsilon^2\|A\|^2 < 1 \text{ and } \epsilon^2\|A\|_1 < 1\,, \tag{68}$$

we define (see Lemma 4.1) the orthogonal projector :

$$\Lambda_\epsilon = \frac{1}{2\pi i} \oint_{|z-1|=\frac{1}{2}} \frac{1}{z - \Lambda - \epsilon a}\, \mathrm{d}z\,, \tag{69}$$

where $a = \Lambda A \Lambda^\perp + \Lambda^\perp A^* \Lambda$. From Lemma 4.1, we get the decomposition

$$\Lambda_\epsilon = \Lambda + \epsilon a + \epsilon^2 B_\epsilon\,, \tag{70}$$

with P_0 replaced by Λ.
Let us prove that $(\Gamma, \Lambda_\epsilon)$ belongs to Υ_q.

We first show $\Gamma - \Lambda_\epsilon \in \mathfrak{S}_1(\mathfrak{H})$. We have

$$\|a\|_1 \leq 2\|A\|_1 < \infty\,, \tag{71}$$

and, as in the proof of (54), we get

$$\|B_\epsilon\|_1 \leq 16\pi\|A\|\,\|A\|_1\,. \tag{72}$$

Therefore, $\Gamma - \Lambda_\epsilon = \Gamma - \Lambda + \epsilon a + \epsilon^2 B_\epsilon \in \mathfrak{S}_1(\mathfrak{H})$.

We next establish $D_Z \Lambda_\epsilon \in \mathfrak{S}_1(\mathfrak{H})$. Since $(\Gamma, \Lambda) \in \Upsilon_q$, $[D_Z, \Lambda]$ is a bounded operator and A, $D_Z A \in \mathfrak{S}_1(\mathfrak{H})$. Thus

$$\begin{aligned} \|D_Z \Lambda A \Lambda^\perp\|_1 &\leq \|\Lambda D_Z A \Lambda^\perp\|_1 + \|\,[\,D_Z\,,\,\Lambda\,] A \Lambda^\perp\|_1 \\ &\leq \|D_Z A\|_1 + \|\,[\,D_Z\,,\,\Lambda\,]\,\|\ \|A\|_1 < \infty\,. \end{aligned} \tag{73}$$

Similarly, we can prove

$$\|D_Z \Lambda^\perp A^* \Lambda\|_1 \ \leq \|D_Z A^*\|_1 + \|\,[\,D_Z\,,\,\Lambda^\perp\,]\,\|\ \|A^*\|_1 < \infty\,, \tag{74}$$

which implies, together with (73) that there exists a constant c such that

$$\|D_Z a\|_1 < c\,. \tag{75}$$

Using again that $[\,D_Z\,,\,\Lambda\,]$ is bounded and Formula (51), valid with Λ instead of P_0 and $\Lambda^\perp$ instead of $P_0^\perp$, we get the existence of a constant c such that for all ϵ small enough

$$\|D_Z B_\epsilon\|_1 < c\,. \tag{76}$$

Inequalities (75) and (76) yield $D_Z \Lambda_\epsilon \in \mathfrak{S}_1(\mathfrak{H})$.

Now, from (75), (76) and $[D_Z, \Lambda_\epsilon] = [D_Z, \Lambda] + [D_Z, \epsilon a + \epsilon^2 B_\epsilon]$, we obtain $[\,D_Z\,,\,\Lambda_\epsilon\,] \in \mathcal{B}(\mathfrak{H})$.

We finally prove that $\mathrm{tr}\,(\Gamma - \Lambda_\epsilon) = q$. For that purpose, we first note that, due to Effros [11] (see also Avron et al [1, Theorem 4.1]), and since from the above $\Gamma - \Lambda_\epsilon \in \mathfrak{S}_1(\mathfrak{H})$, and both Γ and Λ_ϵ are projections, we have $\mathrm{tr}\,(\Gamma - \Lambda_\epsilon) \in \mathbb{Z}$. Furthermore, from (70), (71) and (72) we get

$$\|(\Gamma - \Lambda) - (\Gamma - \Lambda_\epsilon)\|_1 = \mathcal{O}(\epsilon)\,.$$

Since $\mathrm{tr}\,(\Gamma - \Lambda_\epsilon)$ is an integer and $\mathrm{tr}\,(\Gamma - \Lambda) = q$, this yields, for ϵ small enough, $\mathrm{tr}\,(\Gamma - \Lambda_\epsilon) = q$. This concludes the proof that $(\Gamma, \Lambda_\epsilon) \in \Upsilon_q$.

Let us now prove that for $\gamma := \Gamma - \Lambda$ we have

$$[D^{(\gamma)}, \Lambda] = 0\,. \tag{77}$$

Since (Γ,Λ) is a critical point of $\mathfrak{E}$, for all $A\in\mathfrak{S}_1(\mathfrak{H})$ satisfying (68), we have

$$\frac{\partial\mathfrak{E}(\Gamma,\Lambda_\epsilon)}{\partial\epsilon}\Big|_{\epsilon=0}=0\ , \tag{78}$$

where Λ_ϵ is defined by (70). On the other hand, we have

(79)
$$\begin{aligned}\mathfrak{E}(\Gamma,\Lambda_\epsilon)=\mathrm{tr}\ ((D_Z-m)\gamma)+\alpha Q[\gamma,\gamma]-\epsilon\Big\{\mathrm{tr}\ ((D_Z-m)a)+2\alpha\Re Q[a,\gamma]\Big\}\\ +\epsilon^2\Big\{\mathrm{tr}\ ((D_Z-m)B_\epsilon)+\alpha Q[a+\epsilon B_\epsilon,a+\epsilon B_\epsilon]-2\alpha\Re Q[\gamma,B_\epsilon]\Big\}\ .\end{aligned}$$

Inequalities (72) and (76) imply that there exists a constant c_1 such that for all ϵ small enough

$$|\mathrm{tr}\ ((D_Z-m)B_\epsilon)|<c_1\ . \tag{80}$$

Furthermore, using Lemma A.1, we have

$$\begin{aligned}\mathrm{tr}\,(|D_0|^{1/2}|a+\epsilon B_\epsilon|\,|D_0|^{1/2}) &= \mathrm{tr}\,(|a+\epsilon B_\epsilon|^{1/2}|D_0||a+\epsilon B_\epsilon|^{1/2})\\ &\le \frac{1}{d}\,\mathrm{tr}\,(|a+\epsilon B_\epsilon|^{1/2}|D_Z||a+\epsilon B_\epsilon|^{1/2})\\ &\le \frac{1}{d}\||D_Z|\,|a+\epsilon B_\epsilon|\|_1=\frac{1}{d}\|D_Z(a+\epsilon B_\epsilon)\|_1\ ,\end{aligned}$$

which yields, together with (75) and (76), $a+\epsilon B_\epsilon\in F$. Thus Lemma 2.2 implies

(81)
$$\begin{aligned}|Q[a+\epsilon B_\epsilon,a+\epsilon B_\epsilon]|\le 2D[a+\epsilon B_\epsilon,a+\epsilon B_\epsilon]&\le\frac{\pi}{2}\|a+\epsilon B_\epsilon\|_1\,\mathrm{tr}\ (|D_0||a+\epsilon B_\epsilon|)\\ &\le\frac{\pi}{2d}\|a+\epsilon B_\epsilon\|_1\,\mathrm{tr}\ (|D_Z||a+\epsilon B_\epsilon|)\\ &\le\frac{\pi}{2d}\|a+\epsilon B_\epsilon\|_1\|D_Z(a+\epsilon B_\epsilon)\|_1\end{aligned}$$

According to (75) and (76), we conclude from (81) that there exists a constant c_2 such that for all ϵ small enough

$$|Q[a+\epsilon B_\epsilon,a+\epsilon B_\epsilon]|<c_2\ . \tag{82}$$

Now we prove that there exists c_3 such that for all ϵ small enough

$$|Q[\gamma,B_\epsilon]|<c_3\ . \tag{83}$$

We have, for $W^{(B_\epsilon)}$ being the mean field potential associated with $B_\epsilon\in F$, as defined in (4)

$$|Q[\gamma,B_\epsilon]|=|\,\mathrm{tr}\,(W^{(B_\epsilon)}\gamma)|\ .$$

Moreover

$$|\,\mathrm{tr}\,(W^{(B_\epsilon)}\gamma)|\le\|W^{(B_\epsilon)}\gamma\|_1\le\|W^{(B_\epsilon)}(D_0)^{-1}\|\ \|D_0(D_Z)^{-1}\|\ \|D_Z\gamma\|_1\ . \tag{84}$$

Using Lemmata A.3 and A.4 with B_ϵ instead of δ implies

$$\|W^{(B_\epsilon)}(D_0)^{-1}\|\le 4\|B_\epsilon\|_1\ . \tag{85}$$

Since $D_0(D_Z)^{-1}$ is bounded, by using Inequalities (84), (85) and the fact that $(\Gamma,\Lambda)\in\Upsilon_q$, we obtain (83).

Collecting (80), (82), and (83) yields, together with (79),

$$\begin{aligned}\mathfrak{E}(\Gamma,\Lambda_\epsilon)&=\mathrm{tr}\,((D_Z-m)\gamma)+\alpha Q[\gamma,\gamma]-\epsilon\Big\{\mathrm{tr}\,((D_Z-m)a)+2\alpha\Re Q[a,\gamma]\Big\}+\mathcal{O}(\epsilon^2)\\ &=\mathfrak{E}(\Gamma,\Lambda)-\epsilon\,\mathrm{tr}\,((D^{(\gamma)}-m)a)+\mathcal{O}(\epsilon^2)\\ &=\mathfrak{E}(\Gamma,\Lambda)-\epsilon\,\mathrm{tr}\,(\Lambda^\perp(D^{(\gamma)}-m)\Lambda A)-\epsilon\,\mathrm{tr}\,(\Lambda(D^{(\gamma)}-m)\Lambda^\perp A^*)+\mathcal{O}(\epsilon^2)\ .\end{aligned}$$

For A fixed as above, this result remains true for all ϵ small enough. Therefore, (78) implies

$$\operatorname{tr}\left(\Lambda^{\perp}(D^{(\gamma)}-m)\Lambda A\right)+\operatorname{tr}\left(\Lambda(D^{(\gamma)}-m)\Lambda^{\perp}A^{*}\right)=0\,.$$

As at the end of the proof of Theorem 4.4, we obtain $[D^{(\gamma)},\,\Lambda]=0$.

Finally, exchanging the roles of Γ and Λ in the above proof yields $[D^{(\gamma)},\,\Gamma]$. □

Appendix A. Some Spectral Properties of Screened Coulomb-Dirac Operators

We recall the following result:

Lemma A.1 (Brummelhuis et al [8])**.** *Let*

$$d:=(1/3)(1-(\alpha Z)^2)^{1/2}((4(\alpha Z)^2+9)^{1/2}-4\alpha Z)$$

and assume $0\le\alpha Z<\sqrt{3}/2$. *Then*

$$|D_Z|^2\ge d^2|D_0|^2 \text{ and } |D_Z|\ge d|D_0|. \tag{86}$$

We would like to compare $|D_0|$ and $|D^{(\delta)}|$.

Definition A.2. *Given positive* α, Z, *and* m *and* $\delta\in F$, *we define*

$$c_{\alpha,Z,m,\delta}:=\sup\{c\in\mathbb{R}\,|\,|D^{(\delta)}|\ge c|D_0|\}\,. \tag{87}$$

Lemma A.3. *If* $\delta\in F$, *then, for all* $u\in H^1(\mathbb{R}^3)\otimes\mathbb{C}^4$, *we have*

$$\|X^{(\delta)}u\|\le 2\,\|\delta\|_1\,\|\nabla u\|\,.$$

Proof. Using the spectral decomposition of δ, we have

$$\begin{aligned}
\|X^{(\delta)}u\|^2=&\int\frac{\delta(x,z)\,\overline{\delta(x,y)}\,u(z)\overline{u(y)}}{|\mathbf{x}-\mathbf{z}||\mathbf{x}-\mathbf{y}|}\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\\
=&\sum_{i,\,j}\lambda_i\,\lambda_j\int\frac{\xi_i(x)\overline{\xi_i(z)}\,\overline{\xi_j(x)}\xi_j(y)u(z)\overline{u(y)}}{|\mathbf{x}-\mathbf{z}||\mathbf{x}-\mathbf{y}|}\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\\
=&\sum_{i,\,j}\lambda_i\,\lambda_j\int\xi_i(x)\overline{\xi}_j(x)\left(\int\frac{\xi_j(y)\overline{u(y)}}{|\mathbf{x}-\mathbf{y}|}\mathrm{d}y\int\frac{\overline{\xi_i(z)}u(z)}{|\mathbf{x}-\mathbf{z}|}\mathrm{d}z\right)\mathrm{d}x\\
\le&\sum_{i,\,j}\int|\lambda_i|\,|\lambda_j|\,|\xi_i(x)|\,|\xi_j(x)|\left[\left(\int|\xi_j(y)|^2\mathrm{d}y\right)\left(\int\frac{|u(y)|^2}{|\mathbf{x}-\mathbf{y}|^2}\mathrm{d}y\right)\right]\mathrm{d}x\\
\le&4\sum_{i,\,j}\int|\lambda_i|\,|\lambda_j|\,|\xi_i(x)|\,|\xi_j(x)|\,\|\nabla u\|^2\,\mathrm{d}x\\
\le&4\,\|\delta\|_1^2\,\|\nabla u\|^2\,,
\end{aligned}$$

where we used the Cauchy-Schwarz inequality, the Hardy inequality, and the identity $\sum_i|\lambda_i|=||\delta||_1$. □

Similar estimates can be found for the direct part,

Lemma A.4. *If* $\delta\in F$, *then* $\|\varphi^{(\delta)}u\|\le 2\,\|\delta\|_1\|\nabla u\|$, *for all* $u\in H^1(\mathbb{R}^3)\otimes\mathbb{C}^4$.

Proof. We have successively

$$\begin{aligned}
\|\varphi^{(\delta)}u\|^2 &= \int |u(y)|^2 \frac{\delta(x,x)\delta(z,z)}{|\mathbf{x}-\mathbf{y}|\,|\mathbf{z}-\mathbf{y}|}\mathrm{d}x\mathrm{d}y\mathrm{d}z \\
&= \int \delta(x,x)\delta(z,z)\left(\int \frac{|u(y)|^2}{|\mathbf{x}-\mathbf{y}|\,|\mathbf{z}-\mathbf{y}|}\mathrm{d}y\right)\mathrm{d}x\mathrm{d}z \\
&\leq \frac{1}{2}\int |\delta(x,x)|\,|\delta(z,z)|\left(\int \frac{|u(y)|^2}{|\mathbf{x}-\mathbf{y}|^2}\mathrm{d}y + \int \frac{|u(y)|^2}{|\mathbf{z}-\mathbf{y}|^2}\mathrm{d}y\right)\mathrm{d}x\mathrm{d}z \\
&\leq 4\int |\delta(x,x)|\mathrm{d}x \int |\delta(z,z)|\mathrm{d}z\, \|\nabla u\|^2 \leq 4\,\|\delta\|_1^2\,\|\nabla u\|^2\,, \qquad (88)
\end{aligned}$$

where we used Hardy's inequality in (88). □

A direct consequence of Lemma A.4 and the fact that square root is operator monotone is

Lemma A.5. *If $\delta \in F$, then $|\varphi^{(\delta)}| \leq 2\|\delta\|_1 |D_0|$.*

Lemma A.6. *If $\delta \in F$ and $\alpha Z \leq \sqrt{3}/2$, the following operator inequality holds*

$$c_{\alpha,Z,m,\delta} \geq (d - 4\alpha\|\delta\|_1)\,. \qquad (89)$$

Proof. This is a direct consequence of Lemmata A.3 and A.4, since we have for all u in $\mathfrak{D}(D^{(\delta)})$

$$\begin{aligned}
\|D^{(\delta)}u\| &= \|\left(D_Z + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)}\right)u\| \\
&\geq \|D_Z u\| - \alpha\|\varphi^{(\delta)}u\| - \alpha\|X^{(\delta)}u\| \\
&\geq (d - 4\alpha\|\delta\|_1)\|D_0 u\|\,.
\end{aligned} \qquad (90)$$

Therefore $|D^{(\delta)}|^2 \geq (d-4\alpha\|\delta\|_1)^2|D_0|^2$, which concludes the proof since the square root is operator monotone. □

Lemma A.7. *Assume $\delta \in F$ and $\epsilon > 0$, then $\varphi^{(\delta)}, \varphi^{(|\delta|)} \in L^{3+\epsilon}(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$.*

Proof. As before we denote by $(\lambda_n)_{n\in\mathbb{N}}$ the eigenvalues of δ and by (ξ_n) a corresponding orthonormal basis of eigenfunctions. Since $|\varphi^{(\delta)}|(\mathbf{x})| \leq \varphi^{(|\delta|)}(\mathbf{x})$, it is sufficient to prove the result for $\varphi^{(|\delta|)}$.
We first prove that $\varphi^{(|\delta|)} \in L^{3+\epsilon}(\mathbb{R}^3)$. We write χ_R for the characteristic function of the ball with center 0 and radius R, and set $\chi_{\bar{R}} := 1 - \chi_R$. We get

$$\begin{aligned}
\|\,|\xi_n|^2 * |\cdot|^{-1}\|_{3+\epsilon} &\leq \|\,|\xi_n|^2\|_{\frac{3}{2}}\,\|\,\chi_R\,|\cdot|^{-1}\,\|_{3/(2+\epsilon)} + \|\,\chi_{\bar{R}}\,|\cdot|^{-1}\,\|_{3+\epsilon} \\
&\leq \mathrm{c}[\langle \xi_n\,,\,|\mathbf{p}|\,\xi_n\rangle + 1]\,,
\end{aligned}$$

where we used the Hausdorff-Young inequality and the Sobolev inequality. Multiplication by $|\lambda_n|$, summation over n, and the triangular inequality yields the result.

$$\|\varphi^{(|\delta|)}\|_{3+\epsilon} \leq \mathrm{c}\sum_n |\lambda_n|[\langle \xi_n\,,\,|\nabla|\,\xi_n\rangle + 1] \leq \mathrm{c}\|\delta\|_F\,.$$

Next we estimate $\|\varphi^{(|\delta|)}\|_\infty$. Using Kato's inequality, we get

$$|\varphi^{(|\delta|)}(\mathbf{x})| \leq \sum_n |\lambda_n| \int dy\,|\xi_n(y)|^2/|\mathbf{x}-\mathbf{y}| \leq \frac{\pi}{2}\sum_n |\lambda_n|\,\langle \xi_n\,,\,|\mathbf{p}|\,\xi_n\rangle \leq \frac{\pi}{2}\,\|\delta\|_F\,.$$

□

Lemma A.8. *If $\delta \in F$, then $|X^{(\delta)}| \leq \varphi^{(|\delta|)}$.*

Proof. This is a straightforward consequence of the spectral decomposition of δ and the Cauchy-Schwarz inequality. □

Lemma A.9. *If $\delta \in F$, then $W^{(\delta)}$ is relatively compact with respect to D_0.*

Proof. Since $\varphi^{(\delta)} \in L^4(\mathbb{R}^3)$ by Lemma A.7, using an inequality of Seiler and Simon [20, Theorem 4.1], we have

$$\|\varphi^{(\delta)}(-\Delta+m^2)^{-1/2}\|_4 \leq \|\varphi^{(\delta)}(\cdot)\|_4 \, \|(|\cdot|^2+m^2)^{-1/2}\|_4 < \infty \,, \tag{91}$$

implying $D_0^{-1}\varphi^{(\delta)} \in \mathfrak{S}_\infty$.

We next prove that $X^{(\delta)}$ is relatively compact with respect to D_0. Let us denote by δ_+ (respectively δ_-) the positive part (respectively the negative part) of δ: $\delta = \delta_+ - \delta_-$, $\delta_\pm \geq 0$.

We have, using $\delta_\pm(x,y) = \overline{\delta_\pm(y,x)}$,

$$\begin{aligned}\langle u, (X^{(\delta_\pm)})^2 u\rangle &= \int \overline{u(x)} \left(\int \frac{\delta_\pm(x,y)\delta_\pm(y,z)}{|\mathbf{x}-\mathbf{y}|\;|\mathbf{y}-\mathbf{z}|} u(z) \mathrm{d}y \mathrm{d}z \right) \mathrm{d}x \\ &\leq \int \frac{h(x)}{h(z)} G(x,z)^{\frac{1}{2}} G(z,x)^{\frac{1}{2}} \frac{h(z)}{h(x)} \mathrm{d}x\mathrm{d}z,\end{aligned}$$

where $G(x,z) := \left| \int \frac{\delta_\pm(x,y)\delta_\pm(y,z)}{|\mathbf{x}-\mathbf{y}|\;|\mathbf{y}-\mathbf{z}|} \mathrm{d}y \right| |u(x)|^2$ and h is positive and measurable. Applying the Cauchy-Schwarz inequality and $|\delta_\pm(x,y)|^2 \leq \delta_\pm(x,x)\delta_\pm(y,y)$ yield

$$\begin{aligned}\langle u, (X^{(\delta_\pm)})^2 u\rangle &\leq \int \frac{h(x)^2}{h(z)^2} \left| \int \frac{\delta_\pm(x,y)\delta_\pm(y,z)}{|\mathbf{x}-\mathbf{y}|\;|\mathbf{y}-\mathbf{z}|} \mathrm{d}y \right| |u(x)|^2 \mathrm{d}x\mathrm{d}z \\ &\leq \int |u(x)|^2 \frac{h(x)^2}{h(z)^2} \left(\int \frac{\sqrt{\delta_\pm(x,x)}\delta_\pm(y,y)\sqrt{\delta_\pm(z,z)}}{|\mathbf{x}-\mathbf{y}|\;|\mathbf{y}-\mathbf{z}|} \mathrm{d}y \right) \mathrm{d}x\mathrm{d}z.\end{aligned}$$

Picking $h(x) = \delta_\pm(x,x)^{-1/4}$ implies

$$\begin{aligned}\langle u, (X^{(\delta_\pm)})^2 u\rangle &\leq \int |u(x|^2 \left(\int \frac{\delta_\pm(y,y)\delta_\pm(z,z)}{|\mathbf{x}-\mathbf{y}|\;|\mathbf{y}-\mathbf{z}|} \mathrm{d}y \right) \mathrm{d}x\mathrm{d}z \\ &= \int |u(x|^2 \left(\int \varphi^{(\delta_\pm)}(\mathbf{y}) \frac{\delta_\pm(y,y)}{|\mathbf{x}-\mathbf{y}|} \mathrm{d}y \right) \mathrm{d}x \leq \|\varphi^{(\delta_\pm)}\|_\infty \langle u, \varphi^{(\delta_\pm)} u\rangle \,.\end{aligned} \tag{92}$$

Now, similarly to (91), we have $\|\varphi^{(\delta_\pm)}(-\Delta+m^2)^{-1/2}\|_4 < \infty$. Thus, since D_0^{-1} is bounded, we obtain $D_0^{-1}\varphi^{(\delta_\pm)}D_0^{-1} \in \mathfrak{S}_4(\mathfrak{H})$. Moreover, by Lemma A.7 we have $\|\varphi^{(\delta_\pm)}\|_\infty < \infty$. Therefore, using (92), we get $D_0^{-1}(X^{(\delta_\pm)})^2 D_0^{-1} \in \mathfrak{S}_4(\mathfrak{H})$ and thus $X^{(\delta_\pm)}D_0^{-1} \in \mathfrak{S}_8(\mathfrak{H}) \subset \mathfrak{S}_\infty(\mathfrak{H})$, which implies $X^{(\delta)}D_0^{-1}$ compact. Using this, and the fact that $\varphi^{(\delta)}$ is relatively D_0 compact conclude the proof. □

Lemma A.9, the Kato-Rellich Theorem, and Weyl's theorem imply

Lemma A.10. *Let $Z > 0$ such that $\alpha Z \leq 1$ and let $\delta \in F$. Then the operator $D^{(\delta)} = D_Z + \alpha(\varphi^{(\delta)} - X^{(\delta)})$ is self-adjoint with domain $\mathfrak{D}(D^{(\delta)}) = \mathfrak{D}(D_Z)$. Moreover*

$$\sigma_{\mathrm{ess}}\left(D^{(\delta)}\right) = \sigma_{\mathrm{ess}}\left(D_Z\right) = (-\infty, -m] \cup [m, +\infty) \,.$$

If δ is a positive density matrix of q electrons with $q < Z+1$, then the potential of the nucleus prevails giving an attractive Coulomb tail at infinity. This leads us to expect that $D^{(\delta)}$ has infinitely many bound states in the gap accumulating at m. The following theorem expresses this expectation formally.

Theorem A.11. *Assume $0 \leq \delta \in F$ and $\operatorname{tr}\delta < Z$. Then the operator $D^{(\delta)}$ has infinitely many eigenvalues in $(0,m)$ accumulating at the point m.*

Proof. Pick a function $f \in C_0^\infty(\mathbb{R}^3)$, normalized in $L^2(\mathbb{R}^3)$, which is also spherically symmetric. We also define, for all $R > 1$, the functions

$$f_R(x) := R^{-3/2} f(x/R) \text{ and } \psi_R = (f_R, 0, 0, 0) \,.$$

Straightforward calculations using scaling arguments and the specific form of ψ_R give

(93)
$$
\begin{aligned}
&\| \left(D_0 - \frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R \|^2 \\
&= \|\boldsymbol{\alpha} \cdot \frac{1}{i}\nabla\psi_R\|^2 + \|m\beta\psi_R\|^2 + \| \left(-\frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R \|^2 \\
&\quad + 2\Re \left\langle m\beta\psi_R,\, \boldsymbol{\alpha} \cdot \frac{1}{i}\nabla\psi_R \right\rangle + 2\Re \left\langle \left(-\frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R,\, \boldsymbol{\alpha} \cdot \frac{1}{i}\nabla\psi_R \right\rangle \\
&\quad + 2\Re \left\langle m\beta\psi_R,\, \left(-\frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R \right\rangle \\
&= \|\nabla\psi_R\|^2 + m^2 + \alpha^2 \| \left(-\frac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)} \right) \psi_R \|^2 \\
&\quad + 2m\alpha \left\langle \psi_R, \left(-\frac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)} \right) \psi_R \right\rangle \\
&\leq \frac{1}{R^2}\|\nabla f\|^2 + m^2 + \frac{2\alpha^2}{R^2} \left(\|\frac{Z}{|\mathbf{x}|} f\|^2 + 8(q')^2 \|\nabla f\|^2 \right) \\
&\quad + 2m \left\langle \psi_R, \left(-\frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R \right\rangle \\
&\leq m^2 + \frac{c_1}{R^2} + 2m \left\langle \psi_R, \left(-\frac{\alpha Z}{|\mathbf{x}|} + \alpha\varphi^{(\delta)} - \alpha X^{(\delta)} \right) \psi_R \right\rangle \ ,
\end{aligned}
$$

where c_1 is a constant independent of R. Note that we have used Lemmata A.3 and A.4 for getting an upper bound of $\|(\phi^{(\delta)} - X^{(\delta)})\psi_R\|^2$.

Now, since f is spherically symmetric, using Riesz's rearrangement inequality and Newton's Theorem, we obtain

$$
\begin{aligned}
\left\langle \psi_R,\, \varphi^{(\delta)}\psi_R \right\rangle &= \int \frac{|f_R(\mathbf{x})|^2 \rho_\delta(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{y} \leq \int \frac{|f_R(\mathbf{x})|^2 \rho_\delta^*(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{y} \\
&\leq \int \frac{|f_R(\mathbf{x})|^2}{|\mathbf{x}|}\, \mathrm{d}\mathbf{x} \int \rho_\delta^*(\mathbf{y})\, \mathrm{d}\mathbf{y} \leq q' \int \frac{|f_R(\mathbf{x})|^2}{|\mathbf{x}|}\, \mathrm{d}\mathbf{x} \ ,
\end{aligned}
$$

where we used, since $\rho_\delta(\mathbf{y}) = \sum_{s=1}^4 \delta(y,\, y)$ is positive, that

$$
\int \rho_\delta^*(\mathbf{y})\, \mathrm{d}\mathbf{y} = \|\rho_\delta^*\|_1 = \|\rho_\delta\|_1 = q' \ .
$$

Note also that $\langle \psi_R, X^{(\delta)}\psi_R \rangle \geq 0$ and

$$
\left\langle \psi_R,\, \frac{1}{|\mathbf{x}|}\psi_R \right\rangle = \frac{1}{R}\langle f, \frac{1}{|\mathbf{x}|} f \rangle = \frac{c_2}{R} \ ,
$$

with $c_2 := \langle f, \frac{1}{|\mathbf{x}|} f \rangle > 0$. Thus, we have

$$
\left\langle \psi_R,\, \left(-\frac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)} \right) \psi_R \right\rangle \leq -\frac{c_2\,(Z - q')}{R} \ . \tag{94}
$$

Now (93) and (94) imply

$$\begin{aligned}\| \left[D^{(\delta)} - E\right] \psi_R\|^2 &= \|D^{(\delta)}\psi_R\|^2 + E^2 - 2E\left\langle \psi_R, D^{(\delta)}\psi_R\right\rangle \\ &\leq m^2 + \tfrac{c_1}{R^2} + 2m\langle \psi_R, \alpha\left(-\tfrac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)}\right)\psi_R\rangle + E^2 \\ &\quad -2E\langle \psi_R, \alpha\left(-\tfrac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)}\right)\psi_R\rangle - 2E\langle \psi_R, D_0\psi_R\rangle \\ &\leq m^2 + \tfrac{c_1}{R^2} + 2(m-E)\langle \psi_R, \alpha\left(-\tfrac{Z}{|\mathbf{x}|} + \varphi^{(\delta)} - X^{(\delta)}\right)\psi_R\rangle \\ &\quad +E^2 + \tfrac{c_1}{R^2} - 2mE \\ &= (m-E)^2 + 2\tfrac{c_1}{R^2} - 2(m-E)\alpha\tfrac{c_2(Z-q')}{R}\ .\end{aligned}$$

Therefore, if R is large enough, we get the inequality

$$\| \left(D^{(\delta)} - E\right)\psi_R\| < |m-E|\ ,$$

which implies, by taking $E = m/2$, that $D^{(\delta)}$ has at least one eigenvalue λ_1 in $(0, m)$.

Now by taking $E = (m + \lambda_1)/2$, by the same argument as above, one gets a second eigenvalue $\lambda_2 \in (\lambda_1, m)$. The iteration of this procedure yields an infinite sequence of eigenvalues (λ_n) of $D^{(\delta)}$ in $(0, m)$ tending to m. □

A similar result holds for the no-pair Dirac-Fock operator.

Lemma A.12. *Assume that δ and γ are two positive definite finite rank density matrices. Assume, in addition, that γ is purely electronic having particle number not exceeding Z, i.e., we have*

$$\delta \in F\ ,\ \delta \geq 0\ ,\ \gamma \in F \cap S^\delta\ ,\ \Lambda_+^{(\delta)}\gamma\Lambda_+^{(\delta)} = \gamma \text{ and } \operatorname{tr}\gamma < Z\ .$$

Moreover we assume

$$d - 2\alpha(2\operatorname{tr}\delta + \operatorname{tr}\gamma) \geq 0\ .$$

Then the no-pair Dirac-Fock Hamiltonian $\Lambda_+^{(\delta)}D^{(\gamma)}\Lambda_+^{(\delta)}$ has infinitely many eigenvalues in $(0, m)$.

Proof. We first prove that

$$\sigma_{\text{ess}}(\Lambda_+^{(\delta)}D^{(\gamma)}\Lambda_+^{(\delta)}) = [m, +\infty) \tag{95}$$

Lemma A.9 implies that $W^{(\delta)}D_0^{-1}$ and $W^{(\gamma)}D_0^{-1}$ are compact. By assumption, we have $(d - 4\alpha\|\delta\|_1) > 0$; thus (90) implies that $D_0(D^{(\delta)})^{-1}$ is bounded. This yields

$$(W^{(\gamma)} - W^{(\delta)})(D^{(\delta)})^{-1} = W^{(\gamma)}D_0^{-1}D_0(D^{(\delta)})^{-1} - W^{(\delta)}D_0^{-1}D_0(D^{(\delta)})^{-1} \in \mathfrak{S}_\infty(\mathfrak{H})\ ,$$

and

$$\Lambda_+^{(\delta)}(W^{(\gamma)} - W^{(\delta)})\Lambda_+^{(\delta)}(\Lambda_+^{(\delta)}D^{(\delta)}\Lambda_+^{(\delta)})^{-1} \in \mathfrak{S}_\infty(\mathfrak{H})\ .$$

Using the Kato-Rellich Theorem, this implies

$$\sigma_{\text{ess}}(\Lambda_+^{(\delta)}D^{(\gamma)}\Lambda_+^{(\delta)}) = \sigma_{\text{ess}}(\Lambda_+^{(\delta)}(D^{(\delta)} + W^{(\gamma)} - W^{(\delta)})\Lambda_+^{(\delta)}) = \sigma_{\text{ess}}(\Lambda_+^{(\delta)}D^{(\delta)}\Lambda_+^{(\delta)})\ .$$

Together with Lemma A.10, this proves (95).

Set $q' := \operatorname{tr}\delta$ and $q := \operatorname{tr}\gamma$. We denote by $\varphi^{(\gamma)}$ and $X^{(\gamma)}$ respectively the direct and exchange operators associated to γ, defined by replacing δ with γ in (7) and (8). For all $u \in \Lambda_-^{(\delta)}\left(H^1(\mathbb{R}^3) \otimes \mathbb{C}^4\right)$, we have

$$\begin{aligned}\langle u,\, D^{(\gamma)}u\rangle &= \langle u, D^{(\delta)}u\rangle + \alpha\langle u, \varphi^{(\gamma)}u\rangle - \alpha\langle u, X^{(\gamma)}u\rangle - \alpha\langle u, \varphi^{(\delta)}u\rangle + \alpha\langle u, X^{(\delta)}u\rangle \\ &\leq -\langle u, |D^{(\delta)}|u\rangle + \alpha\langle u, \varphi^{(\gamma)}u\rangle\ , \qquad (96)\end{aligned}$$

where, in Inequality (96), we used Lemma A.8 and the fact that $X^{(\gamma)} \geq 0$. Now, from Lemmata A.5 and A.6 we obtain

$$\langle u,\, D^{(\gamma)}u\rangle \leq (-(d - 4\alpha q') + 2\alpha q)\,\langle u,\, |D_0|u\rangle\ .$$

Since $-(d-4\alpha q')+2\alpha q<0$, we have

$$\Lambda_-^{(\delta)} D^{(\gamma)} \Lambda_-^{(\delta)} \leq 0 \,. \tag{97}$$

Now, thanks to (97), one can apply [14, Theorem 3]. With their notations, since $\mathfrak{D}(D^{(\delta)})=\mathfrak{D}(D^{(\gamma)})$, we first define $\mathfrak{Q}_\pm := \left(\mathfrak{D}(D^{(\gamma)})\right)\cap \Lambda_\pm^{(\delta)}\mathfrak{H}$. Then, denoting by $\mu_n(A)$ the nth lowest eigenvalue of the operator A, we obtain

$$m > \mu_n\left(D^{(\gamma)}|_{\Lambda_+{}^{(\gamma)}\mathfrak{H}}\right) \quad \geq \quad \inf_{\substack{M_+\subset\mathfrak{Q}_+\\ \dim(M_+)=n}} \sup_{\substack{\zeta\in M_+\oplus\mathfrak{Q}_-\\ \|\zeta\|=1}} \langle \zeta,\, D^{(\gamma)}\zeta\rangle \,.$$

Moreover,

$$\inf_{\substack{M_+\subset\mathfrak{Q}_+\\ \dim(M_+)=n}} \sup_{\substack{\zeta\in M_+\oplus\mathfrak{Q}_-\\ \|\zeta\|=1}} \langle \zeta,\, D^{(\gamma)}\zeta\rangle \geq \inf_{\substack{M_+\subset\mathfrak{Q}_+\\ \dim(M_+)=n}} \sup_{\substack{\zeta\in M_+\\ \|\zeta\|=1}} \langle \zeta,\, D^{(\gamma)}\zeta\rangle = \mu_n\left(\Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)}\right) \,.$$

Therefore

$$m > \mu_n\left(D^{(\gamma)}|_{\Lambda_+^{(\gamma)}\mathfrak{H}}\right) \geq \mu_n\left(\Lambda_+^{(\delta)} D^{(\gamma)} \Lambda_+^{(\delta)}\right) \,.$$

Since from Theorem A.11 the operator $D^{(\gamma)}$ has infinitely many eigenvalues in $(0,\, m)$, using (95), we finally get the expected result. □

If we have a non-negative spherical symmetric density ρ with

$$q := \int \rho(\mathbf{y}) d\mathbf{y} \leq Z \,,$$

then

$$-Z/|\cdot| + \rho * |\cdot|^{-1} \geq 0 \,.$$

This implies that the n-th eigenvalue of $D_Z+\varphi$ can be estimated from below by the n-th eigenvalue of D_{Z-q}. For a non-spherical symmetric potential this situation for the positive eigenvalues is disturbed only slightly.

Lemma A.13. *Assume $0\leq\delta\in F$. Then $\chi_{(0,m)}(D^{(\delta)})(D^{(\delta)}-m)$ is a Hilbert-Schmidt operator.*

Proof. Since $\delta\in F$, by writing $W^{(\delta)}D_Z^{-1} = W^{(\delta)}D_0^{-1}D_0D_z^{-1}$, Lemmata A.1 and A.9 imply that $W^{(\delta)}$ is relatively compact with respect to D_Z. Moreover, since $\delta\geq 0$, we have $W^{(\delta)}\geq 0$ (see lemma A.8).

Let $\lambda_0(0)\leq\lambda_1(0)\leq\ldots$ be the ordered positive eigenvalues of D_Z, including multiplicity. We first prove that for all $\epsilon\in[0,1]$, there exist $N_+(\epsilon)$ and $N_-(\epsilon)$ in $\{-\infty\}\cup\mathbb{Z}\cup\{+\infty\}$, with $N_-(\epsilon)\leq N_+(\epsilon)$, and $(\lambda_k(\epsilon))_{k\in\{N_-(\epsilon),\ldots,N_+(\epsilon)\}}$ such that

i) $\sigma\left(D_Z+\epsilon\alpha W^{(\delta)}\right)\cap(-m,m)=\{\lambda_{N_-(\epsilon)}(\epsilon),\lambda_{N_-(\epsilon)+1}(\epsilon),\ldots,\lambda_{N_+(\epsilon)}(\epsilon)\}$

ii) $\lambda_{N_-(\epsilon)}(\epsilon)\leq\lambda_{N_-(\epsilon)+1}(\epsilon)\leq\ldots\leq\lambda_{N_+(\epsilon)}(\epsilon)$

iii) For all $k\in\{N_-(\epsilon),\ldots,N_+(\epsilon)\}$ the functions $\lambda_k(\epsilon)$ are continuous, monotone increasing.

Using Kato's perturbation theory for isolated eigenvalues and numbering the eigenvalues that are crossing with respect to their ordering – namely the largest after crossing gets the highest index –, yields i) and ii). Continuity is also a consequence of perturbation theory for eigenvalues. The asserted monotonicity is a consequence of positivity of $W^{(\delta)}$.

We next show that the number M of eigenvalues $\lambda_k(\epsilon)$ that crosses zero when ϵ increases from 0 to 1 is finite. By the Birman-Schwinger principle,

$$M = \#\{\lambda\in[1,\infty)\,|\,\lambda \text{ eigenvalue of } R\} \,,$$

where $R = -(W^{(\delta)})^{1/2} D_Z^{-1} (W^{(\delta)})^{1/2}$ is the Birman-Schwinger kernel with energy 0. Thus, since we count only the eigenvalues of R larger than 1, we have, using the notation $W := W^{(\delta)}$ and $\varphi := \varphi^{(\delta)}$,

$$\begin{aligned} M &\leq \|R\|_4^4 \leq \|W^{\frac{1}{2}} \varphi^{-\frac{1}{2}} \varphi^{\frac{1}{2}} |D_0|^{-\frac{1}{2}} |D_0|^{\frac{1}{2}} D_Z^{-1} |D_0|^{\frac{1}{2}} |D_0|^{-\frac{1}{2}} \varphi^{\frac{1}{2}} \varphi^{-\frac{1}{2}} W^{\frac{1}{2}}\|_4^4 \\ &\leq \|W^{\frac{1}{2}} \varphi^{-\frac{1}{2}}\|^8 \, \| \, |D_0|^{\frac{1}{2}} D_Z^{-\frac{1}{2}}\|^8 \, \|\varphi^{\frac{1}{2}} |D_0|^{-\frac{1}{2}}\|_8^8 \end{aligned} \tag{98}$$

Since $0 \leq W^{(\delta)} = \varphi^{(\delta)} - X^{(\delta)} \leq \varphi^{(\delta)}$, we get

$$\|(W^{(\delta)})^{1/2} (\varphi^{(\delta)})^{-1/2}\| \leq 1. \tag{99}$$

Lemma A.1 yields

$$\||D_0|^{1/2} D_Z^{-1/2}\| \leq d^{-1} < \infty. \tag{100}$$

Using (86) and [20, Theorem 4.1] as for Inequality (91) in the proof of Lemma A.9 yields

$$\|(\varphi^{(\delta)})^{1/2} |D_0|^{-1/2}\|_8 \leq \|\varphi^{(\delta)}(\cdot)\|_4^{1/2} \|\sqrt{|\cdot|^2 + m^2}\|_4^{1/2} < \infty. \tag{101}$$

Collecting (98)-(101) proves $M < \infty$.

Therefore, apart from the eigenvalues $\lambda_0(1), \lambda_1(1), \ldots$, the operator $D^{(\delta)}$ has only finitely many other eigenvalues in $[0, m]$. Thus, $\chi_{(0,m)}(D^{(\delta)})(D^{(\delta)} - m) \in \mathfrak{S}_2(\mathfrak{H})$ follows if the series $\sum_{k \geq 0} (\lambda_k(1) - m)^2 \leq \sum_{k \geq 0} (\lambda_k(0) - m)^2$ is convergent. At this point we remind the reader that the relativistic hydrogen eigenvalues $\lambda_k(0)$ can be grouped into "multiplets" of $2n^2$ eigenvalues corresponding to one non-relativistic eigenvalue $m - Z^2\alpha^2/n^2$. Each element of such a multiplet can be bounded from below by the previous non-relativistic eigenvalue $m - Z^2\alpha^2/(n-1)^2$. Thus, up to an unessential multiplicative constant, $\sum_{n \geq 2} n^2/(n-1)^4$ is a convergent majorant. This proves the claim. □

References

[1] J. Avron, R. Seiler, and B. Simon. The index of a pair of projections. *J. Funct. Anal.*, 120(1):220–237, 1994.

[2] V. Bach, E. H. Lieb, and J. P. Solovej. Generalized Hartree-Fock theory and the Hubbard model. *J. Stat. Phys.*, 76(1&2):3–89, 1994.

[3] Volker Bach. Error bound for the Hartree-Fock energy of atoms and molecules. *Comm. Math. Phys.*, 147:527–548, 1992.

[4] Volker Bach, Jean-Marie Barbaroux, Bernard Helffer, and Heinz Siedentop. Stability of matter for the Hartree-Fock functional of the relativistic electron-positron field. *Doc. Math.*, 3:353–364 (electronic), 1998.

[5] Volker Bach, Jean-Marie Barbaroux, Bernard Helffer, and Heinz Siedentop. On the stability of the relativistic electron-positron field. *Comm. Math. Phys.*, 201:445–460, 1999.

[6] Jean-Marie Barbaroux, Maria J. Esteban, and Eric Séré. Some connections between Dirac-Fock and electron-positron Hartree-Fock. *arXiv:math-ph*, (0402058), March 2004. http://xxx.lanl.gov/ps/math-ph/0402058.

[7] James D. Bjorken and Sidney D. Drell. *Relativistic Quantum Fields*. International Series in Pure and Applied Physics. McGraw-Hill, New York, 1 edition, 1965.

[8] Raymond Brummelhuis, Norbert Röhrl, and Heinz Siedentop. Stability of the relativistic electron-positron field of atoms in Hartree-Fock approximation: Heavy elements. *Doc. Math., J. DMV*, 6:1–8, 2001.

[9] P. Chaix and D. Iracane. From quantum electrodynamics to mean-field theory: I. The Bogoliubov-Dirac-Fock formalism. *J. Phys. B.*, 22(23):3791–3814, December 1989.

[10] P. Chaix, D. Iracane, and P. L. Lions. From quantum electrodynamics to mean-field theory: II. Variational stability of the vacuum of quantum electrodynamics in the mean-field approximation. *J. Phys. B.*, 22(23):3815–3828, December 1989.

[11] Edward G. Effros. Why the circle is connected: an introduction to quantized topology. *Math. Intelligencer*, 11(1):27–34, 1989.

[12] M. J. Esteban and E. Séré. Nonrelativistic limit of the Dirac-Fock equations. *Ann. Henri Poincaré*, 2(5):941–961, 2001.

[13] Maria J. Esteban and Eric Séré. Solutions of the Dirac-Fock equations for atoms and molecules. *Comm. Math. Phys.*, 203(3):499–530, 1999.

[14] Marcel Griesemer and Heinz Siedentop. A minimax principle for the eigenvalues in spectral gaps. *J. London Math. Soc. (2)*, 60(2):490–500, 1999.

[15] J. J. Landgren and P. A. Rejto. An application of the maximum principle to the study of essential selfadjointness of Dirac operators. I. *J. Math. Phys.*, 20(11):2204–2211, 1979.

[16] J.-L. Lions and E. Magenes. *Non-homogeneous boundary value problems and applications. Vol. I.* Springer-Verlag, New York, 1972. Translated from the French by P. Kenneth, Die Grundlehren der mathematischen Wissenschaften, Band 181.

[17] Marvin H. Mittleman. Theory of relativistic effects on atoms: Configuration-space Hamiltonian. *Phys. Rev. A*, 24(3):1167–1175, September 1981.

[18] G. Nenciu. On asymptotic perturbation theory for quantum mechanics: almost invariant subspaces and gauge invariant magnetic perturbation theory. *J. Math. Phys.*, 43(3):1273–1298, 2002.

[19] Eric Paturel. Solutions of the Dirac-Fock equations without projector. *Ann. Henri Poincaré*, 1(6):1123–1157, 2000.

[20] Barry Simon. *Trace Ideals and their Applications*, volume 35 of *London Mathematical Society Lecture Note Series*. Cambridge University Press, Cambridge, 1979.

[21] Jan Philip Solovej. Proof of the ionization conjecture in a reduced Hartree-Fock model. *Inventiones Math.*, 104(2):291–311, 1991.

[22] Bernd Thaller. *The Dirac Equation*. Texts and Monographs in Physics. Springer-Verlag, Berlin, 1 edition, 1992.

Département de Mathématiques, Université du Sud Toulon-Var, Avenue de l'Université, BP 132, 83957 La Garde Cedex, France
E-mail address: barbarou@univ-tln.fr

Swiss Banking Institute, Universität Zürich, Plattenstr. 14, 8032 Zürich, Switzerland
E-mail address: farkas@math.ethz.ch

Département de Mathématiques, Bâtiment 425, Université Paris Sud, 91405 Orsay Cédex, France
E-mail address: Bernard.Helffer@math.u-psud.fr

Mathematisches Institut, LMU, Theresienstr. 39, 80333 München, Germany
E-mail address: h.s@lmu.de