

A new definition of the Dirac-Fock ground state.

Éric SÉRÉ¹

December 26, 2022

¹ Université Paris Dauphine, PSL Research University, CNRS, UMR 7534, CEREMADE,
Place du Maréchal De Lattre De Tassigny, F-75775 Paris cedex 16, France
sere@ceremade.dauphine.fr

Abstract

The Dirac-Fock (DF) model replaces the Hartree-Fock (HF) approximation when relativistic effects cannot be neglected in atoms and molecules. Since the Dirac operator is not bounded from below, the notion of ground state is not obvious in this model, and several definitions have been proposed in the literature. We give a new definition for the ground state of the DF energy, inspired of Lieb's relaxed variational principle for HF. Our definition and existence proof are simpler and more natural than in previous works on DF, but remains more technical than in the nonrelativistic case. One first needs to construct a set of physically admissible density matrices that satisfy a certain nonlinear fixed-point equation: we do this by introducing an iterative procedure, described in an abstract context. Then the ground state is found as a minimizer of the DF energy on this set.

1 Introduction and notations.

The Hartree-Fock (HF) model is a mean-field approximation widely used in non-relativistic quantum chemistry and well understood mathematically (see [29], [30], [32], [1] and the references in these papers). The Hartree-Fock energy of a system of q electrons near a nucleus of atomic number Z can be defined on the set of projectors of rank q acting in the Hilbert space of one-body electronic states. The HF ground state is defined as a projector γ minimizing this energy. It satisfies the self-consistent equation $\gamma = \mathbf{1}_{(-\infty, \mu_{\gamma, q}]}(H_{\gamma})$ where H_{γ} is the mean-field Hamiltonian in the presence of the nucleus and of the electrons in the state γ , $\mu_{\gamma, i}$ being the i -th smallest eigenvalue of this Hamiltonian, counted with multiplicity (it was proved in [3] that for the ground state, $\mu_{\gamma, q} < \mu_{\gamma, q+1}$). In [29], Lieb gave an alternative formulation. He extended the Hartree-Fock functional to the closed convex envelope of the set of projectors and proved that for any operator in this envelope, there exists a projector having at most the same energy (see also [1] for a simpler proof of Lieb's result). Thanks to this principle, the existence of HF ground states is easily proved by weak lower semicontinuity arguments when $q \leq Z$. This relaxation of constraints also has applications to numerical quantum chemistry. Let us mention, in particular, the ODA algorithm of Cancès and Lebris [7] that has excellent stability properties.

The relativistic Dirac-Fock equations were first introduced by Swirles [37]. They are the relativistic analogue of the Hartree-Fock equations with the positive nonrelativistic Schrödinger Hamiltonian $-\Delta/2$ replaced by the free Dirac operator \mathcal{D} , a first order operator that is unbounded from below. The corresponding Dirac-Fock energy is also unbounded from below, contrary to the HF energy. This causes serious mathematical and numerical difficulties (see *e.g.* [13] and references therein). In particular, the Dirac-Fock equations can only be interpreted as stationarity equations of the DF energy. Despite this issue, the Dirac-Fock equations have been widely used in computational atomic physics and quantum chemistry to study atoms and molecules containing heavy nuclei. They provide results in good agreement with experimental data when the correlation between the electrons is not too strong (see *e.g.* [35] and references therein).

The free Dirac operator is defined as follows:

$$(1.1) \quad \mathcal{D} = -i \sum_{k=1}^3 \alpha_k \partial_k + \beta := -i \boldsymbol{\alpha} \cdot \nabla + \beta$$

where $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and

$$\beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix},$$

with

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Here we have taken units such that $\hbar = m = c = 1$ where m is the rest mass of the electron.

The operator \mathcal{D} , defined on the domain $H^1(\mathbb{R}^3, \mathbb{C}^4)$, is self-adjoint in the Hilbert space $\mathcal{H} := L^2(\mathbb{R}^3, \mathbb{C}^4)$. Its form-domain is $\mathcal{F} := H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, and we can also view \mathcal{D} as a bounded linear operator from \mathcal{F} to $\mathcal{F}^* = H^{-1/2}(\mathbb{R}^3, \mathbb{C}^4)$. The anticommutation relations satisfied by the matrices α_k and β ensure that

$$\mathcal{D}^2 = -\Delta + 1.$$

The spectrum of the self-adjoint operator \mathcal{D} is $\sigma(\mathcal{D}) = (-\infty, -1] \cup [1, \infty)$. In what follows, the projector associated with the negative (resp. positive) part of this spectrum will be denoted by Λ^- (resp. Λ^+):

$$\Lambda^- := \mathbb{1}_{(-\infty, 0)}(\mathcal{D}), \quad \Lambda^+ := \mathbb{1}_{(0, +\infty)}(\mathcal{D}).$$

We then have

$$\begin{aligned} \mathcal{D}\Lambda^- &= \Lambda^- \mathcal{D} = -\sqrt{1 - \Delta} \Lambda^- = -\Lambda^- \sqrt{1 - \Delta}, \\ \mathcal{D}\Lambda^+ &= \Lambda^+ \mathcal{D} = \sqrt{1 - \Delta} \Lambda^+ = \Lambda^+ \sqrt{1 - \Delta}. \end{aligned}$$

We endow the form-domain \mathcal{F} with the Hilbert-space norm $\|\psi\|_{\mathcal{F}} := (\psi, |\mathcal{D}|\psi)^{1/2}$.

In the whole paper, $\mathcal{B}(E_1, E_2)$ is the space of bounded linear maps from the Banach space E_1 to the Banach space E_2 ; the corresponding norm is $\|\cdot\|_{\mathcal{B}(E_1, E_2)}$. We note $\mathcal{B}(E) := \mathcal{B}(E, E)$. When E is a Hilbert space we also consider the space $\sigma_1(E)$ of trace-class operators on E . The associated norm and trace are denoted by $\|\cdot\|_{\sigma_1(E)}$ and tr_E .

Let

$$(1.2) \quad X = \{\gamma \in \mathcal{B}(\mathcal{H}) : \gamma = \gamma^*, (1 - \Delta)^{1/4} \gamma (1 - \Delta)^{1/4} \in \sigma_1(\mathcal{H})\}.$$

We endow X with the Banach-space norm

$$(1.3) \quad \|\gamma\|_X := \|(1 - \Delta)^{1/4} \gamma (1 - \Delta)^{1/4}\|_{\sigma_1(\mathcal{H})}.$$

Now, to each positive integer q we associate the set of projectors

$$\mathcal{P}_q := \{\gamma \in X : \gamma^2 = \gamma, \operatorname{tr}_{\mathcal{H}}(\gamma) = q\}.$$

The elements of \mathcal{P}_q are of the form $\gamma = \sum_{k=1}^q |\psi_k\rangle\langle\psi_k|$ with $\psi_k \in H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$ and $(\psi_k, \psi_l)_{L^2} = \delta_{kl}$. They are the one-body density operators of the pure q -electronic Dirac-Fock states $\Psi = \frac{1}{\sqrt{N}} \psi_1 \wedge \cdots \wedge \psi_q$, and we refer to them as *pure Dirac-Fock density operators*.

We also associate to any nonnegative real number q , the sets

$$\Gamma_q := \{\gamma \in X : 0 \leq \gamma \leq id_{\mathcal{H}} \text{ and } \operatorname{tr}_{\mathcal{H}}(\gamma) = q\}, \quad \Gamma_{\leq q} := \bigcup_{0 \leq q' \leq q} \Gamma_{q'}.$$

The elements of Γ_q are the one-body density operators of quasi-free states with particle number q [29], and we refer to them as *mixed Dirac-Fock density operators*. The set $\Gamma_{\leq q}$ is convex and closed for the weak-* topology of X . When q is a positive integer, $\Gamma_{\leq q}$ is the weak-* closed convex envelope of \mathcal{P}_q in X and the projectors of rank q are its extremal points. Here, the weak-* topology of X is the smallest topology such that for any compact operator $Q : \mathcal{H} \rightarrow \mathcal{H}$, the linear form $\ell_Q : \gamma \in X \rightarrow \operatorname{tr}_{\mathcal{H}}(Q(1 - \Delta)^{1/4} \gamma (1 - \Delta)^{1/4})$ is continuous.

The electrons are submitted to an external Coulomb field $V = -\alpha \mathbf{n} * \frac{1}{|x|}$ generated by a nonnegative nuclear charge distribution $\mathbf{n} \in \mathcal{M}_+(\mathbb{R}^3)$ with finite number of protons $Z := \int_{\mathbb{R}^3} d\mathbf{n}$. In our system of units, $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$ is a dimensionless constant. Its physical value is approximately 1/137.

Given $\gamma \in X$ we define

$$\mathcal{D}_{V,\gamma} := \mathcal{D} + V + \alpha W_{\gamma}$$

where

$$W_{\gamma}\psi(x) = (\rho_{\gamma} * \frac{1}{|x|})\psi(x) - \int_{\mathbb{R}^3} \frac{\gamma(x,y)\psi(y)}{|x-y|} dy$$

and $\rho_{\gamma}(x) = \operatorname{tr}_{\mathbb{C}^4} \gamma(x, x)$. Here, $\gamma(x, y)$ is the integral kernel of the trace-class operator γ . If $\|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} < 1$, the operator $\mathcal{D}_{V,\gamma}$ is self-adjoint in \mathcal{H} , with same domain, form-domain and essential spectrum as \mathcal{D} . Note that by Hardy's inequality, a sufficient condition for the inequality $\|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} < 1$ is $2\alpha Z < 1$. For larger values of αZ this inequality does not necessarily hold, but one can still say that $\mathcal{D}_{V,\gamma}$ is self-adjoint with domain $H^1(\mathbb{R}^3, \mathbb{C}^4)$ if $\alpha Z < \frac{\sqrt{3}}{2}$, while for $\frac{\sqrt{3}}{2} \leq Z < 1$ one can say that this operator has a distinguished self-adjoint realization in \mathcal{H} whose domain is a subspace of $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$ (see e.g. [39, 14] and references therein). From the point of view of physics, the operator $\mathcal{D}_{V,\gamma}$ represents the Hamiltonian of an electron in the mean field created by the one-body operator γ . This Hamiltonian is not bounded from below and contains the infinite interval of negative energies $(-\infty, -1]$. To address this difficulty, we introduce the spectral projectors

$$P_{V,\gamma}^{\pm} := \mathbb{1}_{\mathbb{R}^{\pm}}(\mathcal{D}_{V,\gamma}).$$

With this notation, $P_{V,0}^{\pm} = \mathbb{1}_{\mathbb{R}^{\pm}}(\mathcal{D} + V)$ and $P_{0,0}^{\pm} = \Lambda^{\pm}$.

The negative spectral subspace $P_{V,\gamma}^- \mathcal{H}$ is the Dirac sea in the presence of the nuclei and electrons. According to Dirac's interpretation of negative energy states, physical electrons should be orthogonal to their own Dirac sea. This leads us to define, for $q \in \mathbb{Z}_+$, the set of *admissible* pure Dirac-Fock density operators

$$\mathcal{P}_q^+ := \{\gamma \in \mathcal{P}_q : P_{V,\gamma}^+ \gamma = \gamma\},$$

and, for $q \in \mathbb{R}_+$, the sets of admissible mixed Dirac-Fock density operators

$$\Gamma_q^+ := \{\gamma \in \Gamma_q : P_{V,\gamma}^+ \gamma = \gamma\}, \quad \Gamma_{\leq q}^+ := \bigcup_{0 \leq q' \leq q} \Gamma_{q'}^+.$$

The Dirac-Fock equations take the form

$$[D_{V,\gamma}, \gamma] = 0, \quad \gamma \in \mathcal{P}_q^+.$$

In relativistic quantum chemistry, one is particularly interested in ground state solutions. By analogy with the nonrelativistic theory, a possible definition of such states (for $q \in \mathbb{Z}_+$) is that

$$\gamma = \mathbf{1}_{(0,\mu]}(D_{V,\gamma}) \text{ for some } \mu \text{ such that } \text{tr}_{\mathcal{H}}(\gamma) = q.$$

In order to give a more accurate definition, one should introduce the Dirac-Fock energy functional

$$\mathcal{E}_{DF}(\gamma) = \text{tr}((\mathcal{D} + V)\gamma) + \frac{\alpha}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y) - \text{tr}_{\mathbb{C}^4}(\gamma(x,y)\gamma(y,x))}{|x - y|} dx dy.$$

The relation between \mathcal{E}_{DF} and $\mathcal{D}_{V,\gamma}$ is the following: if γ and $\gamma + h$ are in $\Gamma_{\leq q}$ then the right derivative of $f(t) = \mathcal{E}_{DF}(\gamma + th)$ at $t = 0$ is $\text{tr}(\mathcal{D}_{V,\gamma}h)$. Note that in general, for γ in X , $(\mathcal{D} + V)\gamma$ does not make sense as a trace-class operator in \mathcal{H} , so the expression $\text{tr}((\mathcal{D} + V)\gamma)$ should be interpreted as $\text{tr}_{\mathcal{H}}(|\mathcal{D}|^{1/2}\gamma|\mathcal{D}|^{1/2}\text{sign}(\mathcal{D})) + \alpha \int_{\mathbb{R}^3} V \rho_\gamma$. A similar interpretation should be made for $\text{tr}(\mathcal{D}_{V,\gamma}h)$. Such an abuse of notation is common in the mathematical literature on Hartree-Fock theory (see *e.g.* [36], Remark 2.2) and we make it throughout the paper.

In the physical literature, the DF functional is usually defined on the set \mathcal{P}_q of pure densities (for $q \in \mathbb{Z}_+^*$) and is written as a function of an orthonormal sequence of mono-electronic states $\Psi = (\psi_1, \dots, \psi_q)$ that generates the range of γ . This point of view was adopted in the mathematical works [15] and [34] where solutions of the Dirac-Fock equations were found as min-max critical points of the energy $\mathcal{E}_{DF}(\Psi)$. The property $\gamma \in \mathcal{P}_q^+$ was not imposed as an *a priori* constraint, it was an *a posteriori* consequence of the min-max method in which the constraints $(\psi_k, \psi_l)_{L^2} = \delta_{kl}$ were replaced by a penalization. There was no direct way of defining a ground state in this framework, since there was no minimization principle at hand, except in the weakly relativistic regime [16],[17] that is, when α is very small. Note that in [16],[17], the conditions on α were not made explicit. This would have been possible in principle, but the result would certainly have been very far from the physical value 1/137. An alternative approach was introduced by Huber and Siedentop in [26] and provided existence of a ground state in the regime of weak interaction between electrons, obtained by a fixed-point procedure for an explicit range of (small) values of α . The physical value 1/137 was not in this range, but not by far in the case of highly ionized atoms. Another work where a simple definition of the ground state is given and its existence proved, is the paper [11] by Coti Zelati and Nolasco where a one-electron atom with self-generated electromagnetic field is considered. A concavity argument allows these authors to define a reduced energy

functional that is bounded from below. However it does not seem easy to extend their elegant construction to multi-electronic problems.

A physical derivation of the DF model as a mean-field approximation of QED was proposed by Mittleman [33]. This derivation leads to a max-min definition of the ground state. One first considers an infinite-rank projector, and one minimizes the Dirac-Fock energy on a corresponding set of projected states. Then, in a second step, one maximizes the resulting minimum by varying the projector. Unfortunately, such a procedure does not always give solutions of the DF equations: a rigorous justification of the first step (minimization among projected states) has been given in [5], but negative results on the second step (maximization among projectors) for $q > 1$ can be found in [4],[6]. Another approach was initiated by Chaix and Iracane [9], who derived from QED the Bogoliubov-Dirac-Fock mean-field approximation that takes into account the polarization of the Dirac sea, neglected by Mittleman. From the point of view of mathematics, the main advantage of BDF over DF is that the energy is bounded from below when defined in a suitable functional framework (see [10],[2],[21],[22],[24],[25]) so the definition of a ground state becomes straightforward and general existence results can be obtained for positive ions and neutral molecules [23],[19] thanks to Lieb's variational principle. But the BDF ground state is not trace-class, an ultraviolet regularization is necessary in order to define its energy and a charge renormalization is needed to interpret correctly the Euler-Lagrange equation.

Our new definition of a DF ground state avoids the delicate min-max procedure of [15],[34] as well as the complicated functional framework of BDF, and the associated existence result has a domain of validity much larger than [16],[17],[26],[11], that includes the physical value of α and multi-electronic atoms.

Definition 1.1. *To any nonnegative real number q we associate the energy*

$$E_q := \min_{\gamma \in \Gamma_{\leq q}^+} (\mathcal{E}_{DF}(\gamma) - \text{tr}_{\mathcal{H}} \gamma).$$

We call Dirac-Fock ground state of charge number q in the external field V , any $\gamma_ \in \Gamma_q^+$ such that $\mathcal{E}_{DF}(\gamma_*) = q + E_q$.*

The main result of this paper is the existence of a Dirac-Fock ground state of charge number q for positive ions and neutral molecules, under a smallness assumption on V and αq :

Theorem 1.2 (Existence of a ground state). *Let us introduce the constants*

$$\kappa := \|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha q \quad \text{and} \quad \lambda_0 := 1 - \alpha \max(q, Z).$$

Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$, and that the following condition is satisfied:

$$(1.4) \quad \alpha \max(q, Z) < \frac{2}{\pi/2 + 2/\pi} \quad \text{and} \quad \pi\alpha q < 2(1 - \kappa)^{\frac{1}{2}} \lambda_0^{\frac{1}{2}} \left(1 - \kappa - \frac{\pi}{4}\alpha q\right)^{\frac{1}{2}}.$$

Then:

- *There exists an admissible mixed Dirac-Fock density operator $\gamma_* \in \Gamma_{\leq q}^+$ such that*

$$\mathcal{E}_{DF}(\gamma_*) - \text{tr}(\gamma_*) = E_q.$$

- *For any such minimizer, there is an energy level $\mu \in (0, 1]$ such that*

$$(1.5) \quad \gamma_* = \mathbb{1}_{(0, \mu)}(\mathcal{D}_{V, \gamma_*}) + \delta \quad \text{with} \quad 0 \leq \delta \leq \mathbb{1}_{\{\mu\}}(\mathcal{D}_{V, \gamma_*}).$$

- If $q < Z$ then $\mu < 1$.
- If $q \leq Z$ then $\text{tr}(\gamma_*) = q$ and the following strict binding inequalities hold:

$$(1.6) \quad \forall r \in (0, q), \quad E_q < E_r.$$

Remark 1.3. Hardy's inequality immediately implies that $\kappa \leq 2\alpha(Z + q)$: see (2.7). Using this estimate and taking $\alpha \approx \frac{1}{137}$ we find that the smallness assumption (1.4) is satisfied by neutral atoms up to $Z = 22$. When $q = 2$ one can take any $2 \leq Z \leq 63$. Condition (1.4) comes from technical estimates in the proof. It would be interesting to improve these estimates in order to extend our method to higher values of Z and q .

Remark 1.4. In the case $q > Z$, it follows from our proof that if (1.4) and (1.6) hold then $\text{tr}(\gamma_*) = q$ (see Proposition 3.7). However we are not even able to prove (1.6) for $q = Z + \varepsilon$ with ε positive and small.

Remark 1.5. The scalar $\mu - 1$ is the Lagrange multiplier associated with the constraint $\text{tr}(\gamma) \leq q$. Contrary to the HF situation [29, 3], we are not able to prove that the highest occupied energy level μ of the mean-field operator $\mathcal{D}_{V, \gamma_*}$ is full and that the one-body density matrix γ_* is pure. The main difficulty is that the projector $P_{V, \gamma}^+$ depends on γ in a complicated way and the set $\Gamma_{\leq q}^+$ on which we minimize does not seem to be convex.

In order to prove that our minimizer satisfies the Euler-Lagrange equation (1.5), we will need some informations on $\Gamma_{\leq q}^+$. A fundamental tool will be a map that we denote θ , which is a retraction of a certain closed subset F of $\Gamma_{\leq q}$ onto $F \cap \Gamma_{\leq q}^+$. The set F will be large enough to contain the “ground state” of the Dirac-Fock functional. The construction of θ will be iterative: for $\gamma \in F$, taking $\gamma_0 = \gamma$ and $\gamma_{p+1} = P_{V, \gamma_p}^+ \gamma_p P_{V, \gamma_p}^+$, $\theta(\gamma)$ will be the limit of the sequence (γ_p) for the topology of X .

The paper is organized as follows. In Section 2, the existence and regularity properties of θ are studied by first constructing this retraction in an abstract context under general assumptions, then checking these assumptions in the case of the Dirac-Fock problem. In Section 3, Theorem 1.2 and Proposition 3.3 are proved thanks to the construction of the preceding section.

An unpublished version of the present paper is mentioned in [18] where our new definition of the ground state is used. Moreover, in the recent work [8], the existence of solutions of the Dirac-Fock equations in crystals is proved by adapting the arguments of the present paper. This long-standing problem could not be solved using the critical point approach.

Acknowledgement.

The author wishes to thank Isabelle Catto and Long Meng for carefully reading a preliminary version of this manuscript and making very useful remarks. In particular, Long Meng suggested an improvement of estimate (2.15) that increased the domain of validity of the method for neutral atoms (from $Z \leq 18$ to $Z \leq 22$) as well as for positive ions.

2 The retraction θ .

2.1 An abstract construction.

We start with an abstract construction valid in any complete metric space.

Proposition 2.1. *Let (F, d) be a complete metric space and $T : F \rightarrow F$ a continuous map. We assume that*

$$\exists k \in (0, 1), \forall x \in F, \quad d(T^2(x), T(x)) \leq k d(T(x), x).$$

Then for any $x \in F$, the sequence $(T^p(x))_{p \geq 0}$ has a limit $\theta(x) \in \text{Fix}(T)$ with the estimate

$$(2.1) \quad d(\theta(x), T^p(x)) \leq \frac{k^p}{1-k} d(T(x), x).$$

The map θ obtained in this way is a continuous retraction of F onto $\text{Fix}(T)$ (i.e. for any $x \in F$: $T \circ \theta(x) = \theta(x)$ and for any $y \in \text{Fix}(T)$: $\theta(y) = y$).

Proof. This proposition is a generalisation of Banach's fixed point theorem. For the convergence of $T^n(x)$ to a fixed point, the proof is very similar: by induction one shows that $d(T^{p+1}(x), T^p(x)) \leq k^p d(T(x), x)$, so that $(T^p(x))$ is a Cauchy sequence, with the estimate

$$(2.2) \quad d(T^{p+q}(x), T^p(x)) \leq \frac{k^p}{1-k} d(T(x), x).$$

By completeness of F we conclude that $T^n(x)$ has a limit that we denote $\theta(x)$. By continuity of T , $\theta(x) \in \text{Fix}(T)$. Passing to the limit $q \rightarrow \infty$ in (2.2), we obtain the desired estimate (2.1). Moreover, if $x \in \text{Fix}(T)$ then the sequence $T^n(x)$ is constant, so $\theta(x) = x$.

Now, for any $a \in F$, by continuity of T there is a radius $r(a) > 0$ such that

$$\sup_{x \in B(a, r(a))} d(T(x), x) < \infty.$$

Then (2.1) implies that the sequence of continuous functions (T^n) converges uniformly to θ on $B(a, r(a))$, hence the continuity of θ on $F = \cup_{a \in F} B(a, r(a))$. \square

Note that T is not necessarily a contraction, so in general $\text{Fix}(T)$ is *not* reduced to a point and θ need not be constant, contrary to what happens with Banach's fixed point theorem. For instance, if $F = X$ is a Hilbert space and T the projection on a closed convex subset C of X then for any x , $T^2(x) = T(x)$. The assumptions of Proposition 2.1 are thus trivially satisfied and we just have $\theta = T$, $\text{Fix}(T) = C$.

We now want to study the differentiability of θ in a suitable framework. Usually, differentiable functions are defined on an open subset of a normed linear space, but with our application in mind we first consider a closed convex subset Γ of a Banach space X and we take an open subset \mathcal{U} of Γ (that is, $\mathcal{U} = \Gamma \cap \mathcal{O}$ for some open subset \mathcal{O} of X). We assume that T is defined on the closure of \mathcal{U} , i.e. we take $F = \bar{\mathcal{U}}$. Moreover, we assume that $\text{span}\{x - y : x, y \in \Gamma\} = X$. This last condition is not really restrictive: to enforce it, one just needs to replace X by the possibly smaller Banach space $X_\Gamma = \text{span}\{x - y : x, y \in \Gamma\}$. The standard notions of differentiability are easily adapted to this context:

If Y is a Banach space (possibly equal to X), we say that a function $\Phi : \mathcal{U} \rightarrow Y$ is differentiable on \mathcal{U} if, for each $a \in \mathcal{U}$, there is a bounded linear operator from X to Y , denoted $D\Phi(a)$, such that $\lim_{x \rightarrow a, x \in \mathcal{U}} \frac{\|\Phi(x) - \Phi(a) - D\Phi(a)(x-a)\|_Y}{\|x-a\|_X} = 0$. Note that $D\Phi(a)$ is unique, since $X = \text{span}\{x - y : x, y \in \Gamma\}$. Indeed, under this assumption, for each $a \in \mathcal{U}$ we also have $X = \text{span}\{x - a : x \in \Gamma\}$ and there is $\rho(a) > 0$ such that, for each $x \in \Gamma \setminus \{a\}$ and $t \in [0, 1]$, $a + \frac{t\rho(a)}{\|x-a\|_X}(x-a) \in \mathcal{U}$, so that $D\Phi(a)(x-a)$ is uniquely defined as a directional derivative.

We shall say that the differentiable function $\Phi : \mathcal{U} \rightarrow Y$ is in $C^{1,\text{unif}}(\mathcal{U}, Y)$ if $D\Phi$ is uniformly continuous from \mathcal{U} to $\mathcal{B}(X_\Gamma, Y)$. Lastly, we shall say that $\Phi \in C^{1,\text{lip}}(\mathcal{U}, Y)$ if $D\Phi$ is Lipschitzian on \mathcal{U} . We have the following regularity result:

Proposition 2.2. *Let Γ be a nonempty, closed and convex subset of a Banach space X such that $\text{span}\{x - y : x, y \in \Gamma\} = X$. Let \mathcal{U} be an open subset of Γ and let $F = \bar{\mathcal{U}}$. Let $T \in C^0(F, X) \cap C^{1,\text{lip}}(\mathcal{U}, X)$ be such that $T(\mathcal{U}) \subset \mathcal{U}$, $\sup_{x \in \mathcal{U}} \|T(x) - x\|_X < \infty$, $\sup_{x \in \mathcal{U}} \|DT(x)\|_{\mathcal{B}(X)} < \infty$ and*

$$\exists k \in (0, 1), \forall x \in \mathcal{U}, \quad \|T^2(x) - T(x)\|_X \leq k \|T(x) - x\|_X.$$

Then for each $x \in \mathcal{U}$, the sequence $(D(T^p)(x))_{p \geq 0}$ has a limit $\ell(x) \in \mathcal{B}(X)$ for the norm $\|\cdot\|_{\mathcal{B}(X)}$, this convergence being uniform in x . As a consequence, the function $\theta : F \rightarrow \text{Fix}(T) \subset F$ constructed thanks to Proposition 2.1 is in $C^{1,\text{unif}}(\mathcal{U}, X)$ and we have $D\theta(x) = \ell(x)$ for all $x \in \mathcal{U}$.

The end of this section is devoted to the proof of Proposition 2.2. **In the sequel, we use the same notation M for several finite constants which only depend on \mathcal{U} and T .**

We first study the behavior of $D(T^p)(x)$ for $x \in \text{Fix}(T) \cap \mathcal{U}$. In this case, $D(T^p)(x)$ coincides with the p -th power of $DT(x)$.

Lemma 2.3. *Under the assumptions of Proposition 2.2, we have an estimate of the form*

$$\forall x \in \text{Fix}(T) \cap \mathcal{U}, \quad \|DT(x)^{p+q} - DT(x)^p\|_{\mathcal{B}(X)} \leq \frac{M k^p}{1 - k}.$$

So, for any $x \in \text{Fix}(T)$, the sequence $(DT(x)^p)_{p \geq 0}$ has a limit $\ell(x)$ in $\mathcal{B}(X)$ with $\|\ell(x) - DT(x)^p\|_{\mathcal{B}(X)} \leq \frac{M k^p}{1 - k}$. Moreover we have $\|DT(x)^p\|_{\mathcal{B}(X)} \leq M$ hence $\|\ell(x)\|_{\mathcal{B}(X)} \leq M$.

Proof. Given $x \in \text{Fix}(T) \cap \mathcal{U}$ and $h \in X$, for $t \in \mathbb{R}$ nonzero and small enough,

$$\left\| \frac{T^2(x + th) - T(x + th)}{t} \right\|_X \leq k \left\| \frac{T(x + th) - x - th}{t} \right\|_X.$$

Since $x = T(x) = T^2(x)$ we infer

$$\left\| \frac{T^2(x + th) - T^2(x)}{t} - \frac{T(x + th) - T(x)}{t} \right\|_X \leq k \left\| \frac{T(x + th) - T(x)}{t} - h \right\|_X$$

and passing to the limit as t goes to zero:

$$\|DT(x)^2 h - DT(x) h\|_X \leq k \|DT(x) h - h\|_X$$

hence the lemma, since $x \rightarrow \|DT(x)\|_{\mathcal{B}(X)}$ is bounded on \mathcal{U} . □

We now consider an arbitrary point x in \mathcal{U} .

Lemma 2.4. *Under the assumptions of Proposition 2.2, we have an estimate of the form*

$$\forall p, \forall x \in \mathcal{U}, \quad \|D(T^p)(x)\|_{\mathcal{B}(X)} \leq M.$$

Proof. We denote L the Lipschitz constant of DT on \mathcal{U} :

$$\forall x, y \in \mathcal{U}, \quad \|DT(x) - DT(y)\|_{\mathcal{B}(X)} \leq L \|x - y\|_X.$$

Take $x \in \mathcal{U}$ and denote $\delta_i := DT(T^{i-1}(x)) - DT(\theta(x))$. Then

$$(2.3) \quad \|\delta_i\|_{\mathcal{B}(X)} \leq L \|T^{i-1}(x) - \theta(x)\|_X \leq \frac{M k^i}{1-k}.$$

From Lemma 2.3 we also have an estimate of the form

$$(2.4) \quad \|DT(\theta(x))^q\|_{\mathcal{B}(X)} \leq M.$$

Now

$$\begin{aligned} D(T^p)(x) &= (DT(\theta(x)) + \delta_p) \circ \cdots \circ (DT(\theta(x)) + \delta_1) \\ &= \sum_{j=0}^p \sum_{1 \leq i_1 < \cdots < i_j \leq p} DT(\theta(x))^{p-i_j} \circ \delta_{i_j} \circ \cdots \circ \delta_{i_1} \circ DT(\theta(x))^{i_1-1} \end{aligned}$$

hence, using the estimates (2.3) and (2.4) :

$$\begin{aligned} \|D(T^p)(x)\|_{\mathcal{B}(X)} &\leq \sum_{j=0}^p M^{j+1} L^j \sum_{1 \leq i_1 < \cdots < i_j \leq p} k^{i_1 + \cdots + i_j} \\ &\leq M \sum_{j=0}^p (ML)^j \frac{(\sum_{i=1}^p k^i)^j}{j!} \leq M \exp\left(\frac{MLk}{1-k}\right) \end{aligned}$$

and the lemma follows. \square

To end the proof of Proposition 2.2, we show that $(D(T^p)(x))_{p \geq 0}$ is a Cauchy sequence, uniformly in $x \in \mathcal{U}$.

Lemma 2.5. *Under the assumptions of Proposition 2.2, the following estimate holds:*

$$\forall x \in \mathcal{U}, \forall p, q \geq 0, \quad \|DT^{p+q}(x) - DT^p(x)\|_{\mathcal{B}(X)} \leq M k^{p/2}.$$

So $D^p(x)$ converges to $\ell(x) \in \mathcal{B}(X)$ and $\|\ell(x) - DT^p(x)\|_{\mathcal{B}(X)} \leq M k^{p/2}$.

Proof. Let m, n, q be nonnegative integers. As in the proof of Lemma 2.4, we denote $\delta_i := DT(T^{i-1}(x)) - DT(\theta(x))$. For $x \in \mathcal{U}$ we may write

$$D(T^{m+n+q})(x) - D(T^{m+n})(x) = (A_{m,n+q}(x) + B_{n,q}(x) - A_{m,n}(x)) \circ D(T^m)(x)$$

with

$$\begin{aligned} A_{m,r}(x) &= (DT(\theta(x)) + \delta_{m+r}) \circ \cdots \circ (DT(\theta(x)) + \delta_{m+1}) - DT(\theta(x))^r \\ &= \sum_{j=1}^r \sum_{1 \leq i_1 < \cdots < i_j \leq r} DT(\theta(x))^{r-i_j} \circ \delta_{m+i_j} \circ \cdots \circ \delta_{m+i_1} \circ DT(\theta(x))^{i_1-1} \end{aligned}$$

and $B_{n,q}(x) = DT(\theta(x))^{n+q} - DT(\theta(x))^n$.

Using the estimates (2.3) and (2.4) as in the proof of Lemma 2.4, we find

$$\begin{aligned} \|A_{m,r}(x)\|_{\mathcal{B}(X)} &\leq \sum_{j=1}^r M^{2j+1} \sum_{1 \leq i_1 < \cdots < i_j \leq r} k^{mj+i_1+\cdots+i_j} \\ &\leq M \sum_{j=1}^r (M^2 k^m)^j \frac{(\sum_{i=1}^r k^i)^j}{j!} \leq M \left[\exp\left(\frac{M^2 k^{m+1}}{1-k}\right) - 1 \right] \end{aligned}$$

which gives an estimate of the form $\|A_{m,r}(x)\|_{\mathcal{B}(X)} \leq M k^m$ for another constant M . On the other hand, from Lemma 2.3, $\|B_{n,q}(x)\|_{\mathcal{B}(X)} \leq M k^n$. From Lemma 2.4, $\|D(T^m)(x)\|_{\mathcal{B}(X)} \leq M$. Combining these estimates, we find

$$\|D(T^{m+n+q})(x) - D(T^{m+n})(x)\|_{\mathcal{B}(X)} \leq M(k^n + k^m).$$

Taking $p = n + m$ with $n = m$ or $n = m + 1$, we get the desired estimate

$$\|D(T^{p+q})(x) - D(T^p)(x)\|_{\mathcal{B}(X)} \leq M k^{p/2}.$$

This ends the proofs of Lemma 2.5 and Proposition 2.2. □

2.2 Application to Dirac-Fock.

From now on, we work in the Banach space $(X, \|\cdot\|_X)$ defined in formulas (1.2) and (1.3) of the Introduction. As closed convex subset of X , we take $\Gamma_{\leq q}$. We define $T(\gamma) := P_{V,\gamma}^+ \gamma P_{V,\gamma}^+$ with the notations of the Introduction. The map T is well-defined from $\Gamma_{\leq q}$ to itself. The goal of this section is to find conditions on α, q, V such that the assumptions of Theorem 2.2 are satisfied on a sufficiently large open subset \mathcal{U} of $\Gamma_{\leq q}$. The recall our notations $\kappa := \|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha q$ and $\lambda_0 := 1 - \alpha \max(q, Z)$.

We start with a lemma gathering estimates that we will use in the sequel:

Lemma 2.6. *Let $\gamma \in X$.*

- *The following Hardy-type estimates hold:*

$$(2.5) \quad \max \left(\left\| \rho_\gamma * \frac{1}{|\cdot|} \right\|_\infty, \|W_\gamma\|_{\mathcal{B}(\mathcal{H})}, \left\| \frac{\gamma(x,y)}{|x-y|} \right\|_{\mathcal{B}(\mathcal{H})} \right) \leq \frac{\pi}{2} \|(-\Delta)^{\frac{1}{4}} \gamma (-\Delta)^{\frac{1}{4}}\|_{\sigma_1(\mathcal{H})},$$

$$(2.6) \quad \|W_\gamma (-\Delta)^{-\frac{1}{2}}\|_{\mathcal{B}(\mathcal{H})} \leq 2 \|\gamma\|_{\sigma_1(\mathcal{H})},$$

$$(2.7) \quad \|V(-\Delta)^{-\frac{1}{2}}\|_{\mathcal{B}(\mathcal{H})} \leq 2\alpha Z.$$

- *If $\kappa < 1$ and $\|\gamma\|_{\sigma_1(\mathcal{H})} \leq q$ then:*

$$(2.8) \quad \|\mathcal{D}_{V,\gamma}^s |\mathcal{D}|^{-s}\|_{\mathcal{B}(\mathcal{H})} \leq (1 + \kappa)^s, \quad \forall 0 < s \leq 1,$$

$$(2.9) \quad \|\mathcal{D}^s |\mathcal{D}_{V,\gamma}|^{-s}\|_{\mathcal{B}(\mathcal{H})} \leq (1 - \kappa)^{-s}, \quad \forall 0 < s \leq 1,$$

$$(2.10) \quad \|\mathcal{D}^{-\frac{1}{2}} P_{V,\gamma}^+ |\mathcal{D}|^{\frac{1}{2}}\|_{\mathcal{B}(\mathcal{H})} \leq \left(\frac{1 + \kappa}{1 - \kappa} \right)^{\frac{1}{2}}.$$

- *If $\alpha \max(q, Z) < \frac{2}{\pi/2 + 2/\pi}$ and $\gamma \in \Gamma_{\leq q}$ then:*

$$(2.11) \quad \inf |\sigma(\mathcal{D}_{V,\gamma})| \geq \lambda_0 > 0.$$

Proof. If $\gamma \in X$ then $(-\Delta)^{\frac{1}{4}} \gamma (-\Delta)^{\frac{1}{4}} \in \sigma_1(\mathcal{H})$ and $\|(-\Delta)^{\frac{1}{4}} \gamma (-\Delta)^{\frac{1}{4}}\|_{\sigma_1(\mathcal{H})} \leq \|\gamma\|_X$, since $\|(-\Delta)^{\frac{1}{4}} (1 - \Delta)^{-1/4}\|_{\mathcal{B}(\mathcal{H})} \leq 1$.

We may thus write $(-\Delta)^{\frac{1}{4}} \gamma (-\Delta)^{\frac{1}{4}} = \sum_{n=0}^{\infty} d_n |\varphi_n\rangle \langle \varphi_n|$ where (φ_n) is orthonormal in \mathcal{H} , $d_n \in \mathbb{R}$ and $\sum_{n=0}^{\infty} |d_n| = \|(-\Delta)^{\frac{1}{4}} \gamma (-\Delta)^{\frac{1}{4}}\|_{\sigma_1(\mathcal{H})}$.

For each n , we define $\tilde{\varphi}_n = (-\Delta)^{-\frac{1}{4}} \varphi_n$. Then $W_\gamma = \sum_{n=0}^{\infty} \gamma_n W_{|\tilde{\varphi}_n\rangle\langle\tilde{\varphi}_n|}$. For each n , the operator of multiplication by $|\tilde{\varphi}_n|^2 * \frac{1}{|\cdot|}$, the exchange operator of kernel $\frac{\tilde{\varphi}_n(x) \otimes \tilde{\varphi}_n^*(y)}{|x-y|}$ and their difference $W_{|\tilde{\varphi}_n\rangle\langle\tilde{\varphi}_n|}$ are symmetric and positive on \mathcal{H} , so, by the Cauchy-Schwartz inequality, in order to prove (2.5) we just need to show that for any $\psi \in \mathcal{H}$, $(\psi, (|\tilde{\varphi}_n|^2 * \frac{1}{|\cdot|})\psi)_{\mathcal{H}} \leq \frac{\pi}{2} \|\psi\|_{\mathcal{H}}^2$. This is done thanks to the Kato-Herbst inequality $\int_{\mathbb{R}^3} \frac{|f|^2}{|x|} \leq \frac{\pi}{2} \int_{\mathbb{R}^3} |(-\Delta)^{\frac{1}{4}} f|^2$ [27]:

$$(\psi, (|\tilde{\varphi}_n|^2 * \frac{1}{|\cdot|})\psi)_{\mathcal{H}} = \int \frac{|\psi|^2(x) |\tilde{\varphi}_n|^2(y)}{|x-y|} dx dy \leq \frac{\pi}{2} \int |\psi|^2(x) \|\varphi_n\|_{\mathcal{H}}^2 dx = \frac{\pi}{2} \|\psi\|_{\mathcal{H}}^2.$$

Now, in order to prove (2.6) we write $\gamma = \sum_{n=0}^{\infty} \gamma_n |f_n\rangle\langle f_n|$ where (f_n) is orthonormal in \mathcal{H} , $\gamma_n \in \mathbb{R}$ and $\sum_{n=0}^{\infty} |\gamma_n| = \|\gamma\|_{\sigma_1(\mathcal{H})}$. Taking ψ in $\dot{H}^1(\mathbb{R}^3, \mathbb{C}^4)$, χ in \mathcal{H} , we have

$$|(\chi, W_\gamma \psi)_{\mathcal{H}}| \leq \sum_{n=0}^{\infty} |\gamma_n| |(\chi, W_{|f_n\rangle\langle f_n|} \psi)_{\mathcal{H}}|.$$

Denoting $\psi = (\psi^\alpha)_{1 \leq \alpha \leq 4}$ and using the same notation for the other spinors, we have

$$\begin{aligned} & |(\chi, W_{|f_n\rangle\langle f_n|} \psi)_{\mathcal{H}}| \\ &= \frac{1}{2} \left| \iint \sum_{\alpha, \beta} \frac{\det \begin{pmatrix} \bar{f}_n^\alpha(x) & \bar{\chi}^\alpha(x) \\ \bar{f}_n^\beta(y) & \bar{\chi}^\beta(y) \end{pmatrix} \det \begin{pmatrix} f_n^\alpha(x) & \psi^\alpha(x) \\ f_n^\beta(y) & \psi^\beta(y) \end{pmatrix}}{|x-y|} dx dy \right| \\ &\leq \frac{1}{2} \left(\iint \sum_{\alpha, \beta} \left| \det \begin{pmatrix} f_n^\alpha(x) & \chi^\alpha(x) \\ f_n^\beta(y) & \chi^\beta(y) \end{pmatrix} \right|^2 dx dy \right)^{\frac{1}{2}} \left(\iint \sum_{\alpha, \beta} \frac{\left| \det \begin{pmatrix} f_n^\alpha(x) & \psi^\alpha(x) \\ f_n^\beta(y) & \psi^\beta(y) \end{pmatrix} \right|^2}{|x-y|^2} dx dy \right)^{\frac{1}{2}} \\ &= \left(\iint |f_n(x)|^2 |\chi(y)|^2 - |f_n^*(x) \chi(y)|^2 \right)^{\frac{1}{2}} \left(\iint \sum_{\alpha, \beta} \frac{|f_n(x)|^2 |\psi(y)|^2 - |f_n^*(x) \psi(y)|^2}{|x-y|^2} \right)^{\frac{1}{2}} \\ &\leq 2 \|\chi\|_{\mathcal{H}} \|(-\Delta)^{1/2} \psi\|_{\mathcal{H}} \end{aligned}$$

by Hardy's inequality. Estimate (2.6) follows.

To prove estimate (2.7) one just needs to write

$$\|V\psi\|_{\mathcal{H}} = \alpha \left\| \int_{\mathbb{R}^3} \frac{\psi}{|\cdot - y|} d\mathbf{n}(y) \right\|_{\mathcal{H}} \leq \alpha \int_{\mathbb{R}^3} \left\| \frac{\psi}{|\cdot - y|} \right\|_{\mathcal{H}} d\mathbf{n}(y) \leq 2\alpha Z \|(-\Delta)^{1/2} \psi\|_{\mathcal{H}}.$$

Now, by the triangular inequality and (2.6), we have

$$(2.12) \quad \|\mathcal{D}_{V, \gamma} \psi\|_{\mathcal{H}} \leq (1 + \|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha \|\gamma\|_{\sigma_1(\mathcal{H})}) \|\mathcal{D}\psi\|_{\mathcal{H}}.$$

If $\|\gamma\|_{\sigma_1(\mathcal{H})} \leq q$, recalling the notation $\kappa := \|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha q$, we may thus write $\mathcal{D}_{V, \gamma}^2 \leq (1 + \kappa)^2 \mathcal{D}^2$, hence, by interpolation, $|\mathcal{D}_{V, \gamma}|^{2s} \leq (1 + \kappa)^{2s} |\mathcal{D}|^{2s}$ for all $0 < s \leq 1$: this estimate is the same as (2.8). Assuming that $\kappa < 1$, one proves (2.9) in a similar way. Since $P_{V, \gamma}^+$ commutes with $|\mathcal{D}_{V, \gamma}|^{1/2}$, estimate (2.10) directly follows from (2.8), (2.9) for $s = 1/2$.

To prove (2.11) we use Tix' inequality [40][41] as in Lemma 3.1 of [15]: if we have $\max(q, Z) < \frac{2}{\pi/2+2/\pi}$, $\gamma \in \Gamma_{\leq q}$ and $\psi \in \text{Dom}(\mathcal{D}_{V,\gamma})$ then

$$\begin{aligned} \|\psi\|_{\mathcal{H}} \|\mathcal{D}_{V,\gamma}\psi\|_{\mathcal{H}} &\geq (\Lambda^+\psi - \Lambda^-\psi, \mathcal{D}_{V,\gamma}\Lambda^+\psi + \mathcal{D}_{V,\gamma}\Lambda^-\psi)_{\mathcal{H}} \\ &= (\Lambda^+\psi, \mathcal{D}_{V,\gamma}\Lambda^+\psi)_{\mathcal{H}} - (\Lambda^-\psi, \mathcal{D}_{V,\gamma}\Lambda^-\psi)_{\mathcal{H}} \\ &\geq (1 - \alpha \max(q, Z)) \|\psi\|_{\mathcal{H}}^2. \end{aligned}$$

The lemma is thus proved. \square

We now study the dependence of $P_{V,\gamma}^+$ on γ .

Lemma 2.7. *With the notations of Theorem 1.2, assume that $\kappa < 1$, $\alpha \max(q, Z) < \frac{2}{\pi/2+2/\pi}$ and let*

$$a := \frac{\pi\alpha}{4}(1 - \kappa)^{-1/2}\lambda_0^{-1/2}.$$

Then the map

$$Q: \gamma \rightarrow (P_{V,\gamma}^+ - P_{V,0}^+)$$

is in $C^{1,\text{lip}}(\Gamma_{\leq q}, Y)$ with $Y := \mathcal{B}(\mathcal{H}, \mathcal{F})$ (recalling that $\mathcal{F} = H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$ is the form-domain of \mathcal{D}) and we have the estimates

$$(2.13) \quad \forall \gamma, \gamma' \in \Gamma_{\leq q} : \|Q(\gamma') - Q(\gamma)\|_Y \leq a \|\gamma' - \gamma\|_X$$

$$(2.14) \quad \forall \gamma, \gamma' \in \Gamma_{\leq q} : \|DQ(\gamma') - DQ(\gamma)\|_{\mathcal{B}(X,Y)} \leq K\alpha \|\gamma' - \gamma\|_X$$

where K is a positive constant which remains bounded when κ stays away from 1.

Proof. The proof consists in calculations similar to those of [20], Lemma 1 or [26], Lemma 1. One writes, for $\gamma, \gamma' \in \Gamma_{\leq q}$ and $\chi, \psi \in \mathcal{H}$:

$$\begin{aligned} &(\chi, |\mathcal{D}|^{1/2}(Q(\gamma') - Q(\gamma))\psi)_{\mathcal{H}} \\ &= \frac{\alpha}{2\pi} \int_{\mathbb{R}} (\chi, |\mathcal{D}|^{1/2}(\mathcal{D}_{V,\gamma} + iz)^{-1} W_{\gamma'-\gamma}(\mathcal{D}_{V,\gamma'} + iz)^{-1} \psi)_{\mathcal{H}} dz \end{aligned}$$

hence, noting $\tilde{\chi} := |\mathcal{D}_{V,\gamma}|^{-1/2} |\mathcal{D}|^{1/2} \chi$,

$$\begin{aligned} &|(\chi, |\mathcal{D}|^{1/2}(Q(\gamma') - Q(\gamma))\psi)_{\mathcal{H}}| \\ &\leq \frac{\alpha \|W_{\gamma'-\gamma}\|_{\mathcal{B}(\mathcal{H})}}{2\pi} \left(\int_{\mathbb{R}} (\tilde{\chi}, |\mathcal{D}_{V,\gamma}|(\mathcal{D}_{V,\gamma}^2 + z^2)^{-1} \tilde{\chi})_{\mathcal{H}} dz \right)^{\frac{1}{2}} \left(\int_{\mathbb{R}} (\psi, (\mathcal{D}_{V,\gamma'}^2 + z^2)^{-1} \psi)_{\mathcal{H}} dz \right)^{\frac{1}{2}} \\ &= \frac{\alpha \|W_{\gamma'-\gamma}\|_{\mathcal{B}(\mathcal{H})}}{2} \|\tilde{\chi}\|_{\mathcal{H}} \| |\mathcal{D}_{V,\gamma}|^{-1/2} \psi \|_{\mathcal{H}}. \end{aligned}$$

From (2.9) we have

$$\|\tilde{\chi}\|_{\mathcal{H}} \leq (1 - \kappa)^{-1/2} \|\chi\|_{\mathcal{H}}$$

and from (2.11) we have

$$\| |\mathcal{D}_{V,\gamma}|^{-1/2} \psi \|_{\mathcal{H}} \leq \lambda_0^{-1/2} \|\psi\|_{\mathcal{H}}.$$

As a consequence,

$$\|Q(\gamma') - Q(\gamma)\|_Y \leq \frac{\alpha}{2} (1 - \kappa)^{-1/2} \lambda_0^{-1/2} \|W_{\gamma'-\gamma}\|_{\mathcal{B}(\mathcal{H})}.$$

Finally, from (2.5) we have

$$\|W_{\gamma'-\gamma}\|_{\mathcal{B}(\mathcal{H})} \leq \frac{\pi}{2} \|\gamma' - \gamma\|_X.$$

Estimate (2.13) of Lemma 2.7 is thus proved.

Note that taking $\gamma' = 0$ in (2.13) we find that $Q(\gamma) \in Y$, since $Q(0) = 0$. So up to now we have proved that Q is a Lipschitz map from $\Gamma_{\leq q}$ to Y with Lipschitz constant a .

Noting $\dot{\gamma} := \gamma' - \gamma$ and pushing the expansion one step further, one gets

$$Q(\gamma') - Q(\gamma) = \mathcal{L}_\gamma(\dot{\gamma}) + R_\gamma(\dot{\gamma})$$

where

$$\begin{aligned} \mathcal{L}_\gamma(\dot{\gamma}) &:= \frac{\alpha}{2\pi} \int_{\mathbb{R}} (\mathcal{D}_{V,\gamma} + iz)^{-1} W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma} + iz)^{-1} dz, \\ R_\gamma(\dot{\gamma}) &:= -\frac{\alpha}{2\pi} \int_{\mathbb{R}} (\mathcal{D}_{V,\gamma} + iz)^{-1} W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma} + iz)^{-1} W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma+\dot{\gamma}} + iz)^{-1} dz. \end{aligned}$$

Then, using estimates similar to the ones above, one finds that \mathcal{L}_γ is in $\mathcal{B}(X, Y)$ with $\|\mathcal{L}_\gamma\|_{\mathcal{B}(X, Y)} \leq a$ and

$$\begin{aligned} \|R_\gamma(\dot{\gamma})\|_Y &\leq \frac{\alpha}{2} (1 - \kappa)^{-1/2} \lambda_0^{-1/2} \sup_{z \in \mathbb{R}} \|W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma} + iz)^{-1} W_{\dot{\gamma}}\|_{\mathcal{B}(\mathcal{H})} \\ &\leq \frac{\pi^2 \alpha}{8} (1 - \kappa)^{-1/2} \lambda_0^{-3/2} \|\dot{\gamma}\|_X^2. \end{aligned}$$

As a consequence, Q is differentiable at γ and $DQ(\gamma) = \mathcal{L}_\gamma$.

Finally, for $h \in X$ one writes

$$(\mathcal{L}_{\gamma'} - \mathcal{L}_\gamma)h = A_\gamma(\dot{\gamma}, h) + B_\gamma(\dot{\gamma}, h)$$

with

$$A_\gamma(\dot{\gamma}, h) := -\frac{\alpha}{2\pi} \int_{\mathbb{R}} (\mathcal{D}_{V,\gamma+\dot{\gamma}} + iz)^{-1} W_h (\mathcal{D}_{V,\gamma+\dot{\gamma}} + iz)^{-1} W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma} + iz)^{-1} dz$$

and

$$B_\gamma(\dot{\gamma}, h) := -\frac{\alpha}{2\pi} \int_{\mathbb{R}} (\mathcal{D}_{V,\gamma+\dot{\gamma}} + iz)^{-1} W_{\dot{\gamma}} (\mathcal{D}_{V,\gamma} + iz)^{-1} W_h (\mathcal{D}_{V,\gamma} + iz)^{-1} dz.$$

Proceeding as above with each of these expressions, one gets

$$\|(\mathcal{L}_{\gamma'} - \mathcal{L}_\gamma)h\|_Y \leq \frac{\pi^2 \alpha}{4} (1 - \kappa)^{-1/2} \lambda_0^{-3/2} \|\dot{\gamma}\|_X \|h\|_X.$$

Estimate (2.14) follows, with $K := \frac{\pi^2}{4} (1 - \kappa)^{-1/2} \lambda_0^{-3/2}$. So $Q \in C^{1, \text{lip}}(\Gamma_{\leq q}, Y)$ and the lemma is proved. \square

We are now able to study the map T . Our first result is:

Proposition 2.8. *Assume that $\kappa < 1$, $\alpha \max(q, Z) < \frac{2}{\pi/2+2/\pi}$ and let a be as in Lemma 2.7.*

Then the map $T : \gamma \rightarrow P_{V,\gamma}^+ \gamma P_{V,\gamma}^+$ is well-defined from $\Gamma_{\leq q}$ to itself, and for any $\gamma \in \Gamma_{\leq q}$:

$$\begin{aligned} &\|T^2(\gamma) - T(\gamma)\|_X \\ (2.15) \quad &\leq 2a \left(\|T(\gamma)\|_{\mathcal{D}}^{1/2} \|\sigma_1(\mathcal{H})\| + \frac{aq}{2} \|T(\gamma) - \gamma\|_X \right) \|T(\gamma) - \gamma\|_X. \end{aligned}$$

Moreover T is differentiable on $\Gamma_{\leq q} \subset X$ and there are two positive constants C_κ, L_κ such that

$$(2.16) \quad \forall \gamma \in \Gamma_{\leq q}, \quad \|DT(\gamma)\|_{\mathcal{B}(X)} \leq C_\kappa \left(1 + \alpha \|\gamma\|_{\sigma_1(\mathcal{H})} |\mathcal{D}|^{1/2}\right),$$

$$(2.17) \quad \forall \gamma, \gamma' \in \Gamma_{\leq q}, \quad \|DT(\gamma') - DT(\gamma)\|_{\mathcal{B}(X)} \leq L_\kappa \left(1 + \alpha \|\gamma\|_{\sigma_1(\mathcal{H})} |\mathcal{D}|^{1/2}\right) \|\gamma' - \gamma\|_X.$$

Proof. If $\gamma \in \Gamma_{\leq q}$ then $T(\gamma) \in X$, $0 \leq T(\gamma) \leq id_{\mathcal{H}}$ and $\text{tr}_{\mathcal{H}} T(\gamma) \leq \text{tr}_{\mathcal{H}} \gamma \leq q$, so $T(\gamma) \in \Gamma_{\leq q}$. We have

$$\begin{aligned} T^2(\gamma) - T(\gamma) &= P_{V, T(\gamma)}^+ T(\gamma) P_{V, T(\gamma)}^+ - P_{V, \gamma}^+ T(\gamma) P_{V, \gamma}^+ \\ &= (Q(T(\gamma)) - Q(\gamma)) T(\gamma) + T(\gamma) (Q(T(\gamma)) - Q(\gamma)) \\ &\quad + (Q(T(\gamma)) - Q(\gamma)) T(\gamma) (Q(T(\gamma)) - Q(\gamma)) \end{aligned}$$

hence

$$\begin{aligned} \|T^2(\gamma) - T(\gamma)\|_X &\leq 2 \left\| |\mathcal{D}|^{1/2} (Q(T(\gamma)) - Q(\gamma)) T(\gamma) |\mathcal{D}|^{1/2} \right\|_{\sigma_1(\mathcal{H})} \\ &\quad + \left\| |\mathcal{D}|^{1/2} (Q(T(\gamma)) - Q(\gamma)) T(\gamma) (Q(T(\gamma)) - Q(\gamma)) |\mathcal{D}|^{1/2} \right\|_{\sigma_1(\mathcal{H})} \\ &\leq 2 \|Q(T(\gamma)) - Q(\gamma)\|_Y \|T(\gamma)\|_{\sigma_1(\mathcal{H})} |\mathcal{D}|^{1/2} \\ &\quad + \|Q(T(\gamma)) - Q(\gamma)\|_Y^2 \|T(\gamma)\|_{\sigma_1(\mathcal{H})}. \end{aligned}$$

But we have seen that $\|Q(T(\gamma)) - Q(\gamma)\|_Y \leq a \|T(\gamma) - \gamma\|_X$ and $\|T(\gamma)\|_{\sigma_1(\mathcal{H})} \leq q$, so estimate (2.15) holds.

Now, from Lemma 2.7, T is in $C^1(\Gamma_{\leq q}, X)$ with the following formula:

$$DT(\gamma)h = (DQ(\gamma)h)\gamma P_{V, \gamma}^+ + (\text{adjoint}) + P_{V, \gamma}^+ h P_{V, \gamma}^+.$$

Using the inequality (2.10) of Lemma 2.6, we may write

$$\begin{aligned} \|(DQ(\gamma)h)\gamma P_{V, \gamma}^+\|_X &\leq \|DQ(\gamma)h\|_Y \|\gamma\|_{\sigma_1(\mathcal{H})} \left\| |D|^{-1/2} P_{V, \gamma}^+ |D|^{1/2} \right\|_{\mathcal{B}(\mathcal{H})} \\ &\leq a \|h\|_X \|\gamma\|_{\sigma_1(\mathcal{H})} |\mathcal{D}|^{1/2} \left(\frac{1 + \kappa}{1 - \kappa} \right)^{1/2}, \end{aligned}$$

$$\begin{aligned} \|P_{V, \gamma}^+ h P_{V, \gamma}^+\|_X &\leq \left\| |D|^{-1/2} P_{V, \gamma}^+ |D|^{1/2} \right\|_{\mathcal{B}(\mathcal{H})}^2 \|h\|_X \\ &\leq \left(\frac{1 + \kappa}{1 - \kappa} \right) \|h\|_X. \end{aligned}$$

Estimate (2.16) follows from these bounds. The proof of estimate (2.17) is more tedious but goes along the same lines, so we omit the details: one just needs to estimate each term of the sum

$$\begin{aligned} (DT(\gamma') - DT(\gamma))h &= \{((DQ(\gamma') - DQ(\gamma))h)\gamma' P_{V, \gamma'}^+ + (DQ(\gamma)h)(\gamma' - \gamma) P_{V, \gamma}^+ \\ &\quad + (DQ(\gamma)h)\gamma P_{V, \gamma}^+ (Q(\gamma') - Q(\gamma))\} + \{\text{adjoint}\} \\ &\quad + (Q(\gamma') - Q(\gamma))h P_{V, \gamma'}^+ + P_{V, \gamma}^+ h (Q(\gamma') - Q(\gamma)). \end{aligned}$$

□

We now define an open subset \mathcal{U} of $\Gamma_{\leq q}$ such that T maps \mathcal{U} into \mathcal{U} .

Proposition 2.9. *Assume that $\kappa < 1$, $\alpha \max(q, Z) < \frac{2}{\pi/2+2/\pi}$ and take a as in Lemma 2.7. Given $R < \frac{1}{2a}$, let $A := \max\left(\frac{2+aq}{2}, \frac{1}{2-4aR}\right)$ and*

$$\mathcal{U} := \{\gamma \in \Gamma_{\leq q} ; \|\gamma |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + A\|T(\gamma) - \gamma\|_X < R\}.$$

Then \mathcal{U} satisfies the assumptions of Proposition 2.2 with $k := 2aR$.

Proof. First of all, if $\gamma \in \mathcal{U}$, then

$$\begin{aligned} \|T(\gamma) |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} &\leq \|\gamma |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + \|(T(\gamma) - \gamma) |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} \\ &\leq \|\gamma |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + \|T(\gamma) - \gamma\|_X, \end{aligned}$$

hence, using the inequalities $\|T(\gamma)\|_{\sigma_1(\mathcal{H})} \leq \|\gamma\|_{\sigma_1(\mathcal{H})}$ and $A \geq \frac{2+aq}{2}$,

$$\begin{aligned} \|T(\gamma) |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + \frac{aq}{2} \|T(\gamma) - \gamma\|_X \\ \leq \|\gamma |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + \frac{2+aq}{2} \|T(\gamma) - \gamma\|_X < R. \end{aligned}$$

Then (2.15) implies that

$$\|T^2(\gamma) - T(\gamma)\|_X \leq k\|T(\gamma) - \gamma\|_X$$

with $k = 2aR < 1$. Moreover (2.16) implies that $\sup_{\gamma \in \mathcal{U}} \|DT(\gamma)\|_X < \infty$ and (2.17) implies that DT is Lipschitzian on \mathcal{U} .

Finally, remembering that $k = 2aR$ and using the inequality $A \geq \frac{1}{2-4aR}$, we get

$$\begin{aligned} \|T(\gamma) |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + A\|T^2(\gamma) - T(\gamma)\|_X \\ \leq \|\gamma |\mathcal{D}|^{1/2}\|_{\sigma_1(\mathcal{H})} + (1 + Ak)\|T(\gamma) - \gamma\|_X < R, \end{aligned}$$

so $T(\gamma) \in \mathcal{U}$. □

We are now ready to state the main result of this Section:

Theorem 2.10. *Assume that $\kappa < 1$, $\alpha \max(q, Z) < \frac{2}{\pi/2+2/\pi}$. Let a be as in Lemma 2.7 and $R < \frac{1}{2a}$. Let \mathcal{U} and k be as in Proposition 2.9. Then the sequence of iterated maps $(T^p)_{p \geq 0}$ converges uniformly on $\bar{\mathcal{U}}$ to a limit θ with $\theta(\bar{\mathcal{U}}) \subset \Gamma_{\leq q}^+ \cap \bar{\mathcal{U}}$ and $\text{Fix}(\theta) = \Gamma_{\leq q}^+ \cap \mathcal{U}$. We have the estimate*

$$\forall \gamma \in \bar{\mathcal{U}}, \|\theta(\gamma) - T^p(\gamma)\|_X \leq \frac{k^p}{1-k} \|T(\gamma) - \gamma\|_X.$$

Moreover $\theta \in C^{1, \text{unif}}(\mathcal{U}, X)$ and $D(T^p)$ converges uniformly to $D\theta$ on \mathcal{U} .

In this way we obtain a continuous retraction θ of $\bar{\mathcal{U}}$ onto $\Gamma_{\leq q}^+ \cap \bar{\mathcal{U}}$ whose restriction to \mathcal{U} is of class $C^{1, \text{unif}}$. More precisely, $\text{id}_{\mathcal{U}} - \theta$ and its differential are bounded and uniformly continuous on \mathcal{U} .

For any $\gamma \in \text{Fix}(T) \cap \mathcal{U}$ and any $h \in X$, the operator $S = D\theta(\gamma)h$ satisfies

$$P_{V, \gamma}^+ S P_{V, \gamma}^+ = P_{V, \gamma}^+ h P_{V, \gamma}^+ \quad \text{and} \quad P_{\gamma}^- S P_{\gamma}^- = 0.$$

In other words, the splitting $\mathcal{H} = P_{V, \gamma}^+ \mathcal{H} \oplus P_{V, \gamma}^- \mathcal{H}$ gives a block decomposition of $D\theta(\gamma)h$ of the form

$$(2.18) \quad D\theta(\gamma)h = \begin{pmatrix} P_{V, \gamma}^+ h P_{V, \gamma}^+ & b_{\gamma}(h)^* \\ b_{\gamma}(h) & 0 \end{pmatrix}$$

Proof. The existence and regularity properties of the retraction θ follow from Proposition 2.2 and Proposition 2.9. To end the proof, it suffices to show (2.18).

We recall that for any $\gamma \in \Gamma_{\leq q}$ and $h \in X$,

$$DT(\gamma)h = (DQ(\gamma)h)\gamma P_{V,\gamma}^+ + (\text{adjoint}) + P_{V,\gamma}^+ h P_{V,\gamma}^+.$$

Multiplying this formula from both sides by $P_{V,\gamma}^-$, we get

$$P_{V,\gamma}^-(DT(\gamma)h)P_{V,\gamma}^- = 0.$$

On the other hand, we have $P_{V,\gamma}^+ P_{V,\gamma}^- = 0$. Differentiating this identity, we find

$$(DQ(\gamma)h)P_{V,\gamma}^- - P_{V,\gamma}^+(DQ(\gamma)h) = 0.$$

Multiplying this formula from the right by $P_{V,\gamma}^+$ we get

$$P_{V,\gamma}^+(DQ(\gamma)h)P_{V,\gamma}^+ = 0.$$

But for $\gamma \in \text{Fix}(T) \cap \mathcal{U}$ the formula for $DT(\gamma)$ can be rewritten in the form

$$DT(\gamma)h = (DQ(\gamma)h)P_{V,\gamma}^+ \gamma P_{V,\gamma}^+ + (\text{adjoint}) + P_{V,\gamma}^+ h P_{V,\gamma}^+.$$

Multiplying this formula from both sides by $P_{V,\gamma}^+$, we get

$$P_{V,\gamma}^+(DT(\gamma)h)P_{V,\gamma}^+ = P_{V,\gamma}^+ h P_{V,\gamma}^+.$$

Moreover, since $T(\gamma) = \gamma$, for any integer $p \geq 1$ we have

$$D(T^p)(\gamma)h = DT(\gamma)(D(T^{p-1})(\gamma)h).$$

So we immediately get

$$P_{V,\gamma}^-(D(T^p)(\gamma)h)P_{V,\gamma}^- = 0$$

and we easily prove that

$$P_{V,\gamma}^+(D(T^p)(\gamma)h)P_{V,\gamma}^+ = P_{V,\gamma}^+ h P_{V,\gamma}^+$$

by induction on p .

Passing to the limit $p \rightarrow +\infty$ we conclude that

$$P_{V,\gamma}^-(D\theta(\gamma)h)P_{V,\gamma}^- = 0 \quad \text{and} \quad P_{V,\gamma}^+(D\theta(\gamma)h)P_{V,\gamma}^+ = P_{V,\gamma}^+ h P_{V,\gamma}^+.$$

This proves (2.18). □

The question we address now is whether a minimizing sequence for $\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma)$ in $\Gamma_{\leq q}^+$ lies in the set \mathcal{U} . For this purpose we need the following result.

Proposition 2.11. *Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$. Let $\gamma \in \Gamma_{\leq q}^+$ be such that*

$$\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma) \leq 0.$$

Then

$$\|\gamma\|_X \leq \left(1 - \kappa - \frac{\pi}{4}\alpha q\right)^{-1} q.$$

Proof. Let $\gamma \in \Gamma_{\leq q}^+$ such that $\mathcal{E}_{DF}(\gamma) - \text{tr}_{\mathcal{H}}(\gamma) \leq 0$. As $D_\gamma \gamma = |D_\gamma| \gamma$ and from Lemma 2.6, we have

$$\begin{aligned} \mathcal{E}_{DF}(\gamma) - \text{tr}_{\mathcal{H}}(\gamma) &= \text{tr}[(D_\gamma - 1 - \frac{\alpha}{2} W_\gamma) \gamma] \\ &= \text{tr}[(|D_\gamma| - 1 - \frac{\alpha}{2} W_\gamma) \gamma] \\ &\geq (1 - \kappa - \frac{\pi}{4} \alpha q) \|\gamma\|_X - \|\gamma\|_{\sigma_1(\mathcal{H})}, \end{aligned}$$

hence,

$$\|\gamma\|_X \leq (1 - \kappa - \frac{\pi}{4} \alpha q)^{-1} [\mathcal{E}_{DF}(\gamma) - \text{tr}_{\mathcal{H}}(\gamma) + q] \leq (1 - \kappa - \frac{\pi}{4} \alpha q)^{-1} q.$$

□

By construction of \mathcal{U} , Proposition 2.11 has the following consequence:

Corollary 2.12. *Assume that $\kappa < 1 - \frac{\pi}{4} \alpha q$, $\alpha \max(q, Z) < \frac{2}{\pi/2 + 2/\pi}$ and that condition (1.4) of Theorem 1.2 is satisfied. Let a be as in Lemma 2.7.*

Then there are $R < \frac{1}{2a}$ and $\rho > 0$ such that, if $\gamma \in \Gamma_{\leq q}^+$ satisfies $\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma) \leq 0$, then $B_X(\gamma, \rho) \cap \Gamma_{\leq q} \subset \mathcal{U}$.

Proof. Proposition 2.11 implies that $\|\gamma\|_X \leq (1 - \kappa - \frac{\pi}{4} \alpha q)^{-1} q$. So, by Cauchy-Schwartz,

$$\|\gamma |D|^{1/2}\|_{\sigma_1(\mathcal{H})} \leq \|\gamma\|_X^{1/2} \|\gamma\|_{\sigma_1(\mathcal{H})}^{1/2} \leq (1 - \kappa - \frac{\pi}{4} \alpha q)^{-1/2} q.$$

Now, condition (1.4) tells us that $(1 - \kappa - \frac{\pi}{4} \alpha q)^{-1/2} q < \frac{1}{2a}$. Moreover, since $\gamma \in \Gamma_{\leq q}^+$ one has $\|T(\gamma) - \gamma\|_X = 0$. So, taking ρ and $\frac{1}{2a} - R$ positive and small enough, using (2.16) one finds that for any $\gamma' \in B_X(\gamma, \rho) \cap \Gamma_{\leq q}$,

$$\|\gamma' |D|^{1/2}\|_{\sigma_1(\mathcal{H})} + A \|T(\gamma') - \gamma'\|_X < R,$$

where A is the same as in Proposition 2.9. This inequality means that $\gamma' \in \mathcal{U}$. □

Remark 2.13. *The self-adjoint operator $D + V$ has infinitely many eigenvalues in the interval $(0, 1)$ (see e.g. [15]). Taking Π a projector of rank 1 such that $\Pi \leq \mathbb{1}_{[0, \mu]}(D + V)$ for some $0 < \mu < 1$, for $\varepsilon > 0$ small enough we have $\varepsilon \Pi \in \mathcal{U}$, $\theta(\varepsilon \Pi) \in \Gamma_{\leq q}^+$ and $\mathcal{E}_{DF}(\theta(\varepsilon \Pi)) - \text{tr}(\theta(\varepsilon \Pi)) < 0$, so the infimum of $\gamma \rightarrow (\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma))$ on $\Gamma_{\leq q}^+$ is negative. Then Corollary 2.12 implies that for any minimizing sequence (γ_n) , after some rank, $B_X(\gamma_n, \rho) \cap \Gamma_{\leq q} \subset \mathcal{U}$.*

Finally we give another estimate related to the mean-field operator, which will be useful in the sequel.

Proposition 2.14. *Assume that $\kappa < 1$. Let $\tilde{\gamma} \in \Gamma_{\leq q}$ and let $\gamma \in \sigma_1(\mathcal{H})$ be such that $0 \leq \gamma \leq \mathbb{1}_{[0, \nu]}(D_{V, \tilde{\gamma}})$ for some $\nu > 0$. Then $\mathcal{D} \gamma \mathcal{D} \in \sigma_1(\mathcal{H})$ and the following estimate holds:*

$$\|\mathcal{D} \gamma \mathcal{D}\|_{\sigma_1(\mathcal{H})} \leq (1 - \kappa)^{-2} \nu^2 \text{tr}_{\mathcal{H}} \gamma.$$

Proof. By assumption $\gamma = \mathbb{1}_{[0, \nu]}(D_{V, \tilde{\gamma}}) \gamma \mathbb{1}_{[0, \nu]}(D_{V, \tilde{\gamma}})$ and $\text{tr}_{\mathcal{H}} \gamma = \|\gamma\|_{\sigma_1(\mathcal{H})}$, so

$$\|\mathcal{D}_{V, \tilde{\gamma}} \gamma \mathcal{D}_{V, \tilde{\gamma}}\|_{\sigma_1(\mathcal{H})} \leq \|\mathcal{D}_{V, \tilde{\gamma}} \mathbb{1}_{[0, \nu]}(D_{V, \tilde{\gamma}})\|_{\mathcal{B}(\mathcal{H})}^2 \|\gamma\|_{\sigma_1(\mathcal{H})} \leq \nu^2 \text{tr}_{\mathcal{H}} \gamma.$$

Then, using (2.9) for $s = 1$, one gets

$$\|\mathcal{D} \gamma \mathcal{D}\|_{\sigma_1(\mathcal{H})} \leq \|\mathcal{D} \mathcal{D}_{V, \tilde{\gamma}}^{-1}\|_{\mathcal{B}(\mathcal{H})}^2 \|\mathcal{D}_{V, \tilde{\gamma}} \gamma \mathcal{D}_{V, \tilde{\gamma}}\|_{\sigma_1(\mathcal{H})} \leq (1 - \kappa)^{-2} \nu^2 \text{tr}_{\mathcal{H}} \gamma.$$

□

3 Existence of a ground state.

In order to prove Theorem 1.2 we have to study the convergence of minimizing sequences for $\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma)$. The first lemma of this section gives a crucial property of these sequences: their terms are approximate ground states of their mean-field Hamiltonian.

Lemma 3.1. *Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$ and that condition (1.4) is satisfied. Let (γ_n) be a minimizing sequence for $\mathcal{E}_{DF}(\gamma) - \text{tr}(\gamma)$ in $\Gamma_{\leq q}^+$. Then*

$$\text{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma_n) - \inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_n}^+ \gamma} \text{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma) \rightarrow 0.$$

Proof. Otherwise, there would be $\varepsilon_0 > 0$ such that, after extraction,

$$\text{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma_n) \geq \inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_n}^+ \gamma} ((\mathcal{D}_{V,\gamma_n} - 1)\gamma) + \varepsilon_0.$$

But we have seen (as a consequence of Lemma 2.12) that for n large enough, $\Gamma_{\leq q} \cap B_X(\gamma_n, \rho) \subset \mathcal{U}$ with $\rho > 0$ independent of n . Now, for each $d > 0$ and each n there exists an operator g_n of rank q such that $g_n \leq \mathbb{1}_{[0,1+d]}(\mathcal{D}_{V,\gamma_n})$ and

$$\text{tr}((\mathcal{D}_{V,\gamma_n} - 1)g_n) \leq \inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_n}^+ \gamma} \text{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma) + \frac{\varepsilon_0}{2}.$$

Taking for instance $d = 1$, from Lemma 2.14 with $\nu = 2$ we have a bound on $\|g_n\|_X$. So there is $\sigma > 0$ such that for any n large enough and any $s \in [0, \sigma]$, $(1-s)\gamma_n + s g_n \in \Gamma_{\leq q} \cap B_X(\gamma_n, \rho) \subset \mathcal{U}$. Then, from Theorem 2.10, the function $f_n : s \in [0, \sigma] \rightarrow (\mathcal{E}_{DF} - \text{tr})(\theta[(1-s)\gamma_n + s g_n])$ is of class C^1 and the sequence of derivatives (f'_n) is equicontinuous on $[0, \sigma]$. From Formula (2.18),

$$f'_n(0) = \text{tr}((\mathcal{D}_{V,\gamma_n} - 1)(g_n - \gamma_n)) \leq -\frac{\varepsilon_0}{2}$$

so there is $0 < s_0 < \sigma$ independent of n , such that $\forall s \in [0, s_0]$, $f'_n(s) \leq -\frac{\varepsilon_0}{4}$. Hence

$$(\mathcal{E}_{DF} - \text{tr})(\theta[(1-s_0)\gamma_n + s_0 g_n]) = f_n(s_0) \leq f_n(0) - \frac{\varepsilon_0 s_0}{4} = (\mathcal{E}_{DF} - \text{tr})(\gamma_n) - \frac{\varepsilon_0 s_0}{4}.$$

But $\theta[(1-s_0)\gamma_n + s_0 g_n] \in \Gamma_{\leq q}^+$ and $(\mathcal{E}_{DF} - \text{tr})(\gamma_n) \rightarrow E_q$. This is a contradiction. So Lemma 3.1 is proved. \square

As we will see, minimizing sequences enjoy better compactness properties in the case of positive ions. So our first task will be to prove the following proposition, which contains the case $q < Z$ of Theorem 1.2:

Proposition 3.2. *Consider the Dirac-Fock problem with $q < Z$. Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$ and that condition (1.4) is satisfied. Then there exists $\gamma_* \in \Gamma_q^+$ such that*

$$\mathcal{E}_{DF}(\gamma_*) - \text{tr}(\gamma_*) = E_q.$$

Any such ground state may be written $\gamma_ = \mathbb{1}_{(0,\mu)}(\mathcal{D}_{V,\gamma_*}) + \delta$ with $0 \leq \delta \leq \mathbb{1}_{\{\mu\}}(\mathcal{D}_{V,\gamma_*})$ for some $\mu \in (0, 1)$.*

Moreover, for $h > 0$ and small, one has $E_{q+h} < E_q$.

It follows directly from the definition of E_q that the function $q \rightarrow E_q$ is nonincreasing, so the last statement of Proposition 3.2 directly implies the strict binding inequalities for positive ions and neutral atoms:

Corollary 3.3. *Consider the Dirac-Fock problem with $q \leq Z$. Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$ and that condition (1.4) is satisfied. Then the map $r \rightarrow E_r$ is strictly decreasing on $[0, q]$, so the strict binding inequalities (1.6) hold.*

In our proof of Proposition 3.2, a crucial tool is a uniform estimate on the spectrum of the operators $\mathcal{D}_{V,\gamma}$. If $\lceil q \rceil$ denotes the smallest integer larger or equal to q , this estimate is given in the following lemma:

Lemma 3.4. *Assume that $\alpha Z < \frac{2}{\pi/2+2/\pi}$ and that $q < Z$. Then:*

- *There is a constant $e \in (0, 1)$ such that for any $\gamma \in \Gamma_{\leq q}$, the mean-field operator $\mathcal{D}_{V,\gamma}$ has at least $\lceil q \rceil$ eigenvalues (counted with multiplicity) in the interval $[0, 1 - e]$.*
- *There is a nonnegative integer N such that for any $\gamma \in \Gamma_{\leq q}$, the mean-field operator $\mathcal{D}_{V,\gamma}$ has at most $\lceil q \rceil + N$ eigenvalues (counted with multiplicity) in $[0, 1 - \frac{e}{2}]$.*

Proof. For the first statement of the lemma, the arguments are similar to the proof of Lemma 4.6 in [15], with some necessary adaptations. One takes a subspace S of $C_c^\infty((0, \infty); \mathbb{R})$ of dimension $\lceil q \rceil$. Given $t > 1$ we call G_t the $\lceil q \rceil$ -dimensional subspace of $C_c^\infty(\mathbb{R}^3; \mathbb{C}^4)$ consisting of all functions ψ of the form

$$(3.1) \quad \psi(x) = \begin{pmatrix} f(|x|/t) \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad f \in S.$$

One easily finds two constants $0 < c_* < c^* < \infty$ such that, for any $t > 1$ and $\psi \in G_t$,

$$(3.2) \quad (\Lambda^+ \psi, \sqrt{1 - \Delta} \Lambda^+ \psi)_{L^2} \leq \left(1 + \frac{c^*}{t^2}\right) \|\psi\|_{L^2}^2,$$

$$(3.3) \quad \|\nabla \psi\|_{L^2}^2 \leq \frac{c^*}{t^2} \|\psi\|_{L^2}^2,$$

$$(3.4) \quad \left(\psi, \frac{1}{|\cdot|} \psi\right)_{L^2} \geq \frac{c_*}{t} \|\psi\|_{L^2}^2,$$

$$(3.5) \quad \|\Lambda^- \psi\|_{L^2} \leq \frac{c^*}{t} \|\psi\|_{L^2},$$

$$(3.6) \quad \|\nabla(\Lambda^- \psi)\|_{L^2} \leq \frac{c^*}{t^2} \|\psi\|_{L^2},$$

$$(3.7) \quad (\psi, V\psi)_{L^2} \leq -\alpha Z \left(\psi, \frac{1}{|\cdot|} \psi\right)_{L^2} + o\left(\frac{1}{t}\right)_{t \rightarrow \infty} \|\psi\|_{L^2}^2.$$

Now, we recall that for $\gamma \in \Gamma_{\leq q}$ one has $W_\gamma \leq \rho_\gamma * \frac{1}{|\cdot|}$. Moreover, since ψ in G_t is radial, one has $\left(\psi, \rho_\gamma * \frac{1}{|\cdot|} \psi\right)_{L^2} \leq \left(\psi, \frac{q}{|\cdot|} \psi\right)_{L^2}$, so that, for some $c'_* > 0$:

$$(3.8) \quad \left(\psi, (V + \alpha W_\gamma) \psi\right)_{L^2} \leq -\alpha(Z - q) \frac{c'_*}{t} \|\psi\|_{L^2}^2.$$

On the other hand, $\|(V + \alpha W_\gamma) \Lambda^- \psi\|_{L^2} \leq 2\alpha(Z + q) \|\nabla(\Lambda^- \psi)\|_{L^2}$, so there is a positive constant c''_* such that

$$(3.9) \quad \left(\Lambda^+ \psi, (V + \alpha W_\gamma) \Lambda^+ \psi\right)_{L^2} \leq -\frac{c''_*}{t} \|\Lambda^+ \psi\|_{L^2}^2.$$

Now, combining (3.3) and (3.9) one finds $\underline{t} > 1$ and $\underline{e} > 0$ such that for any $\gamma \in \Gamma_{\leq q}$, $e \in (0, 1)$, $t \geq \underline{t}$ and any ψ^+ in the $\lceil q \rceil$ -dimensional complex vector space $G_t^+ := \Lambda^+ G_t$:

$$\begin{aligned} \mathcal{Q}_{1-e}(\psi^+) &:= (\psi^+, \sqrt{1-\Delta} \psi^+) \\ &\quad + \left(\psi^+, (V + \alpha W_\gamma - 1 + e) \psi^+ \right) \\ &\quad + \left(\psi^+, (V + \alpha W_\gamma) \Lambda^- (\sqrt{1-\Delta} - V - \alpha W_\gamma + 1 - e)^{-1} \Lambda^- (V + \alpha W_\gamma) \psi^+ \right) \\ &< \left(e - \frac{\underline{e}}{\underline{t}} \right) \|\psi^+\|_{L^2}^2. \end{aligned}$$

Now we fix $t = \underline{t}$ and $e = \frac{\underline{e}}{2\underline{t}}$. Then the above inequality tells us that the quadratic form \mathcal{Q}_{1-e} is negative on $G_{\underline{t}}^+$. Applying the abstract min-max theorem of [12] to the self-adjoint operator $\mathcal{D}_{V,\gamma}$ and the splitting of \mathcal{H} associated with the free projectors $\Lambda^\pm = P_{0,0}^\pm$, we thus conclude that there are at least $\lceil q \rceil$ eigenvalues of $\mathcal{D}_{V,\gamma}$ (counted with multiplicity) in the interval $(0, 1 - e)$. Indeed, for $\psi^+ \in \Lambda^+ C_c^\infty(\mathbb{R}^3, \mathbb{C}^4)$ one has

$$\mathcal{Q}_{1-e}(\psi^+) = \sup_{\psi^- \in \Lambda^- C_c^\infty(\mathbb{R}^3, \mathbb{C}^4)} \left\{ \left(\psi^+ + \psi^-, \mathcal{D}_{V,\gamma}(\psi^+ + \psi^-) \right) - (1-e) \|\psi^+ + \psi^-\|_{L^2}^2 \right\}.$$

So, if $\lambda_{k,\gamma}$ denotes the k -th positive eigenvalue of $\mathcal{D}_{V,\gamma}$ counted with multiplicity, from [12] we find that

$$1 - e \geq \inf_{\substack{\mathcal{V} \text{ subspace of } \Lambda^+ C_c^\infty \\ \dim \mathcal{V} = \lceil q \rceil}} \sup_{\psi \in (\mathcal{V} \oplus \Lambda^- C_c^\infty) \setminus \{0\}} \frac{(\psi, \mathcal{D}_{V,\gamma} \psi)}{\|\psi\|_{L^2}^2} = \lambda_{\lceil q \rceil, \gamma}.$$

The first statement of the lemma is thus proved.

The second statement is easier. We notice that $\mathcal{D}_{V,\gamma} \geq \mathcal{D}_{V,0}$, so, invoking once again the min-max principle of [12], we see that $\lambda_{k,\gamma} \geq \lambda_{k,0}$. Moreover the essential spectrum of $\mathcal{D}_{V,0}$ is $\mathbb{R} \setminus (-1, 1)$, so $\lim_{k \rightarrow \infty} \lambda_{k,0} = 1$. Taking $N \geq 0$ such that $\lambda_{\lceil q \rceil + N + 1, 0} > 1 - e/2$, we conclude that for any $\gamma \in \Gamma_{\leq q}$ there are at most $\lceil q \rceil + N$ eigenvalues of $\mathcal{D}_{V,\gamma}$ in the interval $[0, 1 - e/2]$ and the lemma is proved. \square

Thanks to Lemma 3.4, we can obtain more information on minimizing sequences:

Lemma 3.5. *Consider the Dirac-Fock problem with $q < Z$. Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$ and that condition (1.4) is satisfied. Let (γ_n) be a minimizing sequence for $(\mathcal{E}_{DF} - \text{tr}_{\mathcal{H}})$ in $\Gamma_{\leq q}^+$. For each n define $p_n := \mathbb{1}_{[0, 1 - \frac{e}{2}]}(\mathcal{D}_{V,\gamma_n})$ where e is given in Lemma 3.4. Then*

$$\text{tr}(\gamma_n) \rightarrow q \quad \text{and} \quad \|\gamma_n - p_n \gamma_n p_n\|_X \rightarrow 0.$$

Proof. Let $\mu_n \in (0, 1 - e]$ be such that there are less than $\lceil q \rceil$ eigenvalues of \mathcal{D}_{V,γ_n} (counted with their multiplicity) in the interval $[0, \mu_n)$ and at least $\lceil q \rceil$ in the interval $[0, \mu_n]$. Then

$$\inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_n}^+ \gamma} \text{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma) = \text{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n) \mathbb{1}_{[0, \mu_n)}(\mathcal{D}_{V,\gamma_n})) + (\mu_n - 1)q.$$

We denote $p'_n := \mathbb{1}_{(1 - \frac{e}{2}, \infty)}(\mathcal{D}_{V,\gamma_n})$. Since $\gamma_n = T(\gamma_n)$ we may write

$$\text{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)\gamma_n) = \text{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)p_n \gamma_n p_n) + \text{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \gamma_n p'_n),$$

hence

$$\begin{aligned} & \operatorname{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma_n) - \inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_n}^+ \gamma} \operatorname{tr}((\mathcal{D}_{V,\gamma_n} - 1)\gamma) \\ &= \operatorname{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \gamma_n p'_n) \\ &+ \operatorname{tr}[(\mathcal{D}_{V,\gamma_n} - \mu_n)(p_n \gamma_n p_n - \mathbb{1}_{[0,\mu_n]}(\mathcal{D}_{V,\gamma_n}))] + (1 - \mu_n)(q - \operatorname{tr}(\gamma_n)) . \end{aligned}$$

But the terms $\operatorname{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \gamma_n p'_n)$, $\operatorname{tr}[(\mathcal{D}_{V,\gamma_n} - \mu_n)(p_n \gamma_n p_n - \mathbb{1}_{[0,\mu_n]}(\mathcal{D}_{V,\gamma_n}))]$ and $(1 - \mu_n)(q - \operatorname{tr}(\gamma_n))$ are nonnegative.

So Lemma 3.1 implies that $\operatorname{tr}(\gamma_n) \rightarrow q$ and $\operatorname{tr}((\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \gamma_n p'_n) \rightarrow 0$.

But $p'_n(\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \geq \frac{\varepsilon}{2}p'_n$ and $p'_n(\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \geq p'_n(|\mathcal{D}_{V,\gamma_n}| - 1 + e)p'_n$ so that, taking a convex combination of these two estimates:

$$p'_n(\mathcal{D}_{V,\gamma_n} - \mu_n)p'_n \geq \frac{e}{2-e} p'_n |\mathcal{D}_{V,\gamma_n}| p'_n .$$

Hence $\|p'_n \gamma_n p'_n\|_X = \operatorname{tr}(p'_n |\mathcal{D}_{V,\gamma_n}| p'_n) \leq (1 - \kappa)^{-1} \operatorname{tr}(p'_n |\mathcal{D}_{V,\gamma_n}| p'_n) \rightarrow 0$.

It remains to study the limit of $u_n := p'_n \gamma_n p_n$ as n goes to infinity. Since $(\gamma_n)^2 \leq \gamma_n$, we have

$$\begin{aligned} & (p'_n \gamma_n p'_n)^2 + u_n u_n^* = p'_n (\gamma_n)^2 p'_n \leq p'_n \gamma_n p'_n \\ & \text{hence } \operatorname{tr}(|\mathcal{D}_{V,\gamma_n}|^{1/2} u_n u_n^* |\mathcal{D}_{V,\gamma_n}|^{1/2}) \rightarrow 0 . \end{aligned}$$

Now, take $A \in \mathcal{B}(\mathcal{H})$. By the Cauchy-Schwartz inequality,

$$\begin{aligned} & \operatorname{tr}(A |\mathcal{D}_{V,\gamma_n}|^{1/2} u_n^* |\mathcal{D}_{V,\gamma_n}|^{1/2}) \\ & \leq [\operatorname{tr}(|\mathcal{D}_{V,\gamma_n}|^{1/2} p_n A^* A p_n |\mathcal{D}_{V,\gamma_n}|^{1/2})]^{1/2} [\operatorname{tr}(|\mathcal{D}_{V,\gamma_n}|^{1/2} u_n u_n^* |\mathcal{D}_{V,\gamma_n}|^{1/2})]^{1/2} . \end{aligned}$$

But p_n has rank at most $\lceil q \rceil + N$ and $\|p_n |\mathcal{D}_{V,\gamma_n}|^{1/2}\|_{\mathcal{B}(\mathcal{H})} \leq 1$. As a consequence,

$$\operatorname{tr}(|\mathcal{D}_{V,\gamma_n}|^{1/2} p_n A^* A p_n |\mathcal{D}_{V,\gamma_n}|^{1/2}) \leq (\lceil q \rceil + N) \|A\|_{\mathcal{B}(\mathcal{H})}^2 .$$

Since A is arbitrary, this shows that $\| |\mathcal{D}_{V,\gamma_n}|^{1/2} u_n |\mathcal{D}_{V,\gamma_n}|^{1/2} \|_{\sigma_1(\mathcal{H})} \rightarrow 0$, hence $\|u_n\|_X \rightarrow 0$.

Finally, $\|\gamma_n - p_n \gamma_n p_n\|_X \leq \|p'_n \gamma_n p'_n\|_X + 2\|u_n\|_X \rightarrow 0$. \square

Now we have

Corollary 3.6. *With the same assumptions and notations as in Lemma 3.5, there exists $\gamma_* \in \Gamma_{\leq q}$ such that, after extraction of a subsequence, $\|\gamma_n - \gamma_*\|_X \rightarrow 0$ as n goes to infinity.*

Proof. The projector p_n has rank at most $\lceil q \rceil + N$ so, after extraction, we may assume that its rank equals a constant d . Then for each n there is an orthonormal family $(\varphi_n^1, \dots, \varphi_n^d)$ of eigenfunctions of \mathcal{D}_{V,γ_n} with eigenvalues $\lambda_n^1, \dots, \lambda_n^d \in [0, 1 - \frac{\varepsilon_n}{2}]$ such that $p_n = \sum_{i=1}^d |\varphi_n^i\rangle\langle\varphi_n^i|$. There is also a hermitian matrix $G_n = (G_n^{ij})_{1 \leq i,j \leq d}$ with $0 \leq G_n \leq \mathbf{1}_d$ and $p_n \gamma_n p_n = \sum_{1 \leq i,j \leq d} G_n^{ij} |\varphi_n^i\rangle\langle\varphi_n^j|$.

After extraction, we may assume that for each i, j the sequence of coefficients $(G_n^{ij})_{n \geq 0}$ has a limit G_*^{ij} . Moreover, arguing as in [Esteban-S. '99, Proof of Lemma 2.1 (b) p. 514-515], one shows that, after extraction, for each i the sequence $(\varphi_n^i)_{n \geq 0}$ has a limit φ_*^i for the strong topology of $H^{1/2}(\mathbb{R}^3, \mathbf{C}^4)$. The Corollary is proved, taking $\gamma_* := \sum_{1 \leq i,j \leq d} G_*^{ij} |\varphi_*^i\rangle\langle\varphi_*^j|$. \square

As a consequence of Corollary 3.6, $\mathcal{E}_{DF}(\gamma_n)$ converges to $\mathcal{E}_{DF}(\gamma_*)$ and from Lemma 2.7 (continuity of Q), $P_{\gamma_n}^+ - P_{\gamma_*}^+$ converges to zero for the norm of $\mathcal{B}(\mathcal{H}, \mathcal{F})$. So $P_{\gamma_*}^+ \gamma_* = \gamma_*$ and γ_* is a minimizer of $\mathcal{E}_{DF} - \text{tr}$ on $\Gamma_{\leq q}^+$. For any such minimizer, applying Lemma 3.1 we get

$$\text{tr}((\mathcal{D}_{V, \gamma_*} - 1)\gamma_*) = \inf_{\gamma \in \Gamma_{\leq q}, \gamma = P_{\gamma_*}^+ \gamma} \text{tr}((\mathcal{D}_{V, \gamma_*} - 1)\gamma).$$

This immediately implies that $\gamma_* = \mathbb{1}_{(0, \mu)}(\mathcal{D}_{V, \gamma_*}) + \delta$ with $0 \leq \delta \leq \mathbb{1}_{\{\mu\}}(\mathcal{D}_{V, \gamma_*})$ where $\mu = \lambda_{[q], \gamma_*}$ is the $[q]$ -th positive eigenvalue of $\mathcal{D}_{V, \gamma_*}$. Moreover $\text{tr}(\gamma_*) = q$ since $\mu \leq 1 - e < 1$. Now, let ψ be a normalized eigenvector of $\mathcal{D}_{V, \gamma_*}$ with eigenvalue $\lambda \in (1 - e, 1)$. Then $\gamma_* \psi = 0$ and for $h \in (0, 1)$ the density operator $\gamma(h) := \gamma_* + h|\psi\rangle\langle\psi|$ belongs to Γ_{q+h} and satisfies $\gamma(h) = P_{V, \gamma_*}^+ \gamma(h) P_{V, \gamma_*}^+$. So, using (2.18) we find that for h positive and small,

$$E_{q+h} \leq (\mathcal{E}_{DF} - \text{tr}_{\mathcal{H}}) \circ \theta(\gamma(h)) = E_q + (\lambda - 1)h + o(h) < E_q.$$

This ends the proof of Proposition 3.2.

It remains to study the ground state problem for neutral molecules. We already proved the strict binding inequalities (1.6) for $q = Z$ (see Corollary 3.3). So this last case of Theorem 1.2 will be obtained as a consequence of the following more general statement in which we do *not* assume that $q \leq Z$:

Proposition 3.7. *Assume that $\kappa < 1 - \frac{\pi}{4}\alpha q$ and that conditions (1.4) and (1.6) are satisfied. Then there exists an admissible mixed Dirac-Fock density operator $\gamma_* \in \Gamma_q^+$ such that*

$$\mathcal{E}_{DF}(\gamma_*) - \text{tr}(\gamma_*) = E_q.$$

For any such minimizer, there is an energy level $\mu \in (0, 1]$ such that

$$(3.10) \quad \gamma_* = \mathbb{1}_{(0, \mu)}(\mathcal{D}_{V, \gamma_*}) + \delta \quad \text{with} \quad 0 \leq \delta \leq \mathbb{1}_{\{\mu\}}(\mathcal{D}_{V, \gamma_*}).$$

In order to prove Proposition 3.7, we perturb the nuclear charge distribution. We first introduce a function $G \in C_c^\infty(\mathbb{R}_+)$ with $G(r) \geq 0$ for all $r \geq 0$, $G(r) = 0$ when $0 \leq r \leq 1$ or $r \geq 4$, $G(r) = 1$ for $2 \leq r \leq 3$ and $4\pi \int_0^\infty G(r)r^2 dr = 1$. Then, to any positive integer ℓ we associate the function $g_\ell(x) := \ell^{-3}G(|x|/\ell)$ and the perturbed charge distribution $\mathbf{n}_\ell := \mathbf{n} + (q - Z + \ell^{-1})g_\ell$. The measure \mathbf{n}_ℓ is positive and one has $Z_\ell := \mathbf{n}_\ell(\mathbb{R}^3) = q + \ell^{-1} > q$. The corresponding perturbed Coulomb potential is $V_\ell = -\alpha \mathbf{n}_\ell * \frac{1}{|\cdot|}$. Note that $V_\ell - V$ is radial and satisfies $-\frac{q-Z+\ell^{-1}}{|x|} \leq (V_\ell - V)(x) \leq 0$ for $|x| \geq \ell$ and $-\frac{q-Z+\ell^{-1}}{\ell} \leq (V_\ell - V)(x) \leq 0$ for $|x| \leq \ell$, so $\|V_\ell - V\|_\infty \leq \frac{q-Z+\ell^{-1}}{\ell}$, hence $\lim_{\ell \rightarrow \infty} \|V_\ell - V\|_\infty = 0$.

From what we have just seen, if $Z = \int_{\mathbb{R}^3} \mathbf{n}$ and $\kappa = \|V\mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha q$ satisfy (1.4) then for ℓ large enough, Z_ℓ and $\kappa_\ell := \|V_\ell \mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} + 2\alpha q$ will also satisfy (1.4) with, in addition, $q < Z_\ell$. So we may apply Proposition 3.2 to the Dirac-Fock problem with nuclear charge density \mathbf{n}_ℓ and atomic number q . This gives us the existence of a ground state γ_*^ℓ of the corresponding Dirac-Fock energy \mathcal{E}_{DF}^ℓ with charge number q .

We now study the behavior of the minimizers γ_*^ℓ when $\ell \rightarrow +\infty$. First of all, since $\|V_\ell - V\|_\infty \rightarrow 0$, $\mathcal{E}_{DF}^\ell \rightarrow \mathcal{E}_{DF}$ uniformly on $\Gamma_{\leq q}$, so the DF ground state energy associated to the potential V_ℓ converges to the DF ground state energy E_q associated to V . In other words,

$$\lim (\mathcal{E}_{DF}^\ell(\gamma_*^\ell) - \text{tr} \gamma_*^\ell) = E_q.$$

Moreover we have the following local compactness result:

Lemma 3.8. *Under the above assumptions and notations, after extraction of a subsequence still denoted (γ_*^ℓ) , there exist $\gamma_* \in \Gamma_{\leq q}$ and a sequence of positive numbers R_ℓ with $\lim R_\ell = +\infty$, such that for any smooth, compactly supported function $\eta \in C_c^\infty(\mathbb{R}^3, \mathbb{R})$, the integral operator with kernel $\eta(R_\ell^{-1}x)(\gamma_*^\ell - \gamma_*)(x, y)\eta(R_\ell^{-1}y)$ converges to zero for the topology of X as ℓ goes to infinity.*

Proof. Since $0 \leq \gamma_*^\ell \leq \mathbf{1}_{(0,1)}(\mathcal{D}_{V_\ell, \gamma_*^\ell})$, the operator $T^\ell = (1 - \Delta)^{\frac{1}{2}} \gamma_*^\ell (1 - \Delta)^{\frac{1}{2}}$ is bounded in $\sigma_1(\mathcal{H})$ independently of ℓ , so after extraction it has a weak-* limit $T = (1 - \Delta)^{1/2} \gamma_* (1 - \Delta)^{1/2}$ as $\ell \rightarrow \infty$. Consider a function $\eta_0 \in C_c^\infty(\mathbb{R}^3, \mathbb{R})$ such that $\eta_0 \equiv 1$ on $B(0, 1)$. For any $\rho > 0$, the operator $K_\rho = (1 - \Delta)^{1/4} \eta_0(\rho^{-1} \cdot) (1 - \Delta)^{-1/2}$ is compact. This implies that $\lim_{\ell \rightarrow \infty} \|K_\rho(T^\ell - T)K_\rho^*\|_{\sigma_1(\mathcal{H})} = 0$ (see e.g. [28] Lemma 9 for a similar argument). Then, we may choose a sequence of positive numbers ρ_ℓ such that $\lim_{\ell \rightarrow \infty} \rho_\ell = +\infty$ and $\lim_{\ell \rightarrow \infty} \|K_{\rho_\ell}(T^\ell - T)K_{\rho_\ell}^*\|_{\sigma_1(\mathcal{H})} = 0$: for this, we just need the growth of ρ_ℓ to be sufficiently slow. Now, define $R_\ell := \rho_\ell^{1/2}$. For any $\eta \in C_c^\infty(\mathbb{R}^3, \mathbb{R})$, there is ℓ_0 such that for all $\ell \geq \ell_0$ and $x \in \mathbb{R}^3$, $\eta(R_\ell^{-1}x)\eta_0(\rho_\ell^{-1}x) = \eta(R_\ell^{-1}x)$. Moreover the operator $L_{R_\ell} := (1 - \Delta)^{1/4} \eta(R_\ell^{-1} \cdot) (1 - \Delta)^{-1/4}$ is bounded independently of ℓ . So $\lim_{\ell \rightarrow \infty} \|L_{R_\ell} K_{\rho_\ell}(T^\ell - T)K_{\rho_\ell}^* L_{R_\ell}^*\|_{\sigma_1(\mathcal{H})} = 0$. But for $\ell \geq \ell_0$ one has $L_{R_\ell} K_{\rho_\ell}(T^\ell - T)K_{\rho_\ell}^* L_{R_\ell}^* = (1 - \Delta)^{1/4} \eta(R_\ell^{-1} \cdot) (\gamma_*^\ell - \gamma_*) \eta(R_\ell^{-1} \cdot) (1 - \Delta)^{1/4}$, so the lemma is proved. \square

We now introduce two radial cut-off functions $\chi_\epsilon \in C^\infty(\mathbb{R}^3, \mathbb{R}_+)$ ($\epsilon = 0, 1$) such that $\chi_0(x) = 0$ for $|x| \geq 2$, $\chi_1(x) = 0$ for $|x| \leq 1$ and $\chi_0^2 + \chi_1^2 = 1$. We define the dilated cut-off functions $\chi_{\epsilon, \ell}(x) = \chi_\epsilon(R_\ell^{-1}x)$ and the associated localized density operators

$$\gamma_\epsilon^\ell(x, y) := \chi_{\epsilon, \ell}(x) \gamma_*^\ell(x, y) \chi_{\epsilon, \ell}(y), \quad \epsilon \in \{0, 1\}.$$

We have the following result:

Lemma 3.9. *Assume that $\gamma_*^\ell \in X$ converges to γ_* in the local sense of Lemma 3.8 as $\ell \rightarrow \infty$. Then $\gamma_0^\ell, \gamma_1^\ell$ belong to $\Gamma_{\leq q}$ and one has*

$$(3.11) \quad \text{tr}_{\mathcal{H}} \gamma_*^\ell = \text{tr}_{\mathcal{H}} \gamma_0^\ell + \text{tr}_{\mathcal{H}} \gamma_1^\ell, \quad \lim \{\mathcal{E}_{DF}^\ell(\gamma_*^\ell) - \mathcal{E}_{DF}^\ell(\gamma_0^\ell) - \mathcal{E}_{DF}^\ell(\gamma_1^\ell)\} = 0,$$

$$(3.12) \quad \lim_{\ell \rightarrow \infty} \left\| \mathcal{D}_{V_\ell, \gamma_\epsilon^\ell} \chi_{\epsilon, \ell} - \chi_{\epsilon, \ell} \mathcal{D}_{V_\ell, \gamma_*^\ell} \right\|_{B(\mathcal{H})} = 0, \quad \epsilon = 0, 1.$$

Proof. The statement (3.11) is in the spirit of the concentration-compactness theory of P.L. Lions [31] (dichotomy case). Its proof presents some similarities with the proof of Lemma 4 in [23] but it is less technical, as the present functional framework is simpler.

Obviously, one has

$$\text{tr}_{\mathcal{H}} (\gamma_*^\ell) = \text{tr}_{\mathcal{H}} (\gamma_*^\ell \chi_{0, \ell}^2) + \text{tr}_{\mathcal{H}} (\gamma_*^\ell \chi_{1, \ell}^2) = \text{tr}_{\mathcal{H}} (\gamma_0^\ell) + \text{tr}_{\mathcal{H}} (\gamma_1^\ell).$$

Let $\zeta(x) = \chi_0(\frac{2}{5}x) \chi_1(4x)$. Then $\zeta \in C_c^\infty(\mathbb{R}^3, \mathbb{R})$, $0 \leq \zeta \leq 1$, $\zeta(x) = 1$ for $\frac{1}{2} \leq |x| \leq \frac{5}{2}$ and $\zeta(x) = 0$ for $|x| \leq \frac{1}{4}$ or $|x| \geq 5$. We introduce the dilated function $\zeta_\ell(x) = \zeta(R_\ell^{-1}x)$ and the associated integral operator

$$\gamma_2^\ell(x, y) = \zeta_\ell(x) \gamma_*^\ell(x, y) \zeta_\ell(y).$$

From Lemma 3.8,

$$\lim_{\ell \rightarrow \infty} \left\| \gamma_2^\ell - \zeta_\ell(x) \gamma_* (x, y) \zeta_\ell(y) \right\|_X = 0.$$

Moreover, we may write $\gamma_* = \sum_{n \geq 1} c_n |\psi_n\rangle \langle \psi_n|$ with $(\psi_n, \psi_{n'})_{H^{1/2}} = \delta_{n, n'}$, $c_n \geq 0$ and $\sum_{n \geq 1} c_n \|\psi_n\|_{H^{1/2}}^2 = \|\gamma_*\|_X < \infty$. Then for each n , $\lim_{\ell \rightarrow \infty} \|\zeta_\ell \psi_n\|_{H^{1/2}} = 0$,

since ζ vanishes on $B(0, 1/4)$. In addition, there is $C > 0$ such that, for all $\ell \geq 1$ and $\psi \in H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, $\|\zeta_\ell \psi\|_{H^{1/2}} \leq C \|\psi\|_{H^{1/2}}$. So, when $\ell \rightarrow \infty$, Lebesgue's dominated convergence theorem tells us that

$$\|\zeta_\ell(x) \gamma_*(x, y) \zeta_\ell(y)\|_X = \sum_{n \geq 1} c_n \|\zeta_\ell \psi_n\|_{H^{1/2}}^2 \rightarrow 0,$$

hence $\lim_{\ell \rightarrow \infty} \|\gamma_2^\ell\|_X = 0$. So, using inequality (2.5), we find that the norms $\left\| \rho_{\gamma_2^\ell} * \frac{1}{|\cdot|} \right\|_{L^\infty(\mathbb{R}^3)}$, $\left\| W_{\gamma_2^\ell} \right\|_{\mathcal{B}(\mathcal{H})}$ and $\left\| \frac{\gamma_2^\ell(x, y)}{|x - y|} \right\|_{\mathcal{B}(\mathcal{H})}$ converge to 0 as $\ell \rightarrow \infty$.

Now, we write

$$\mathcal{E}_{DF}^\ell(\gamma_*^\ell) - \mathcal{E}_{DF}^\ell(\gamma_0^\ell) - \mathcal{E}_{DF}^\ell(\gamma_1^\ell) = A_\ell + B_\ell$$

where

$$A_\ell = \frac{i}{R_\ell} \sum_{\epsilon=0}^1 \text{tr}_{\mathcal{H}} \{ (\alpha \cdot \nabla \chi_\epsilon) (R_\ell^{-1} x) \gamma_*^\ell(x, y) \chi_{\epsilon, \ell}(y) \} = \mathcal{O}\left(\frac{1}{R_\ell}\right)$$

and

$$B_\ell = \alpha \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{(\chi_{0, \ell})^2(x) (\chi_{1, \ell})^2(y)}{|x - y|} \left(\rho_{\gamma_*^\ell}(x) \rho_{\gamma_*^\ell}(y) - |\gamma_*^\ell(x, y)|^2 \right) d^3x d^3y.$$

We have

$$\begin{aligned} \frac{\chi_{0, \ell}(x) \chi_{1, \ell}(y)}{|x - y|} &= \frac{\chi_{0, \ell}(x) \chi_{1, \ell}(y)}{|x - y|} \left(\mathbb{1}_{\{|x - y| \leq \frac{R_\ell}{2}\}} + \mathbb{1}_{\{|x - y| > \frac{R_\ell}{2}\}} \right) \\ &\leq \frac{1}{|x - y|} \mathbb{1}_{\{\frac{R_\ell}{2} \leq |x| \leq \frac{5R_\ell}{2}\}} \mathbb{1}_{\{\frac{R_\ell}{2} \leq |y| \leq \frac{5R_\ell}{2}\}} + \frac{2}{R_\ell}, \end{aligned}$$

hence

$$(3.13) \quad \frac{\chi_{0, \ell}(x) \chi_{1, \ell}(y)}{|x - y|} \leq \frac{(\zeta_\ell)^2(x) (\zeta_\ell)^2(y)}{|x - y|} + \frac{2}{R_\ell}.$$

In addition, we have the inequalities $0 \leq \rho_{\gamma_*^\ell}(x) \rho_{\gamma_*^\ell}(y) - |\gamma_*^\ell(x, y)|^2 \leq \rho_{\gamma_*^\ell}(x) \rho_{\gamma_*^\ell}(y)$ and the identity $(\zeta_\ell)^2(x) (\zeta_\ell)^2(y) \rho_{\gamma_*^\ell}(x) \rho_{\gamma_*^\ell}(y) = \rho_{\gamma_2^\ell}(x) \rho_{\gamma_2^\ell}(y)$. As a consequence, we get the estimate

$$0 \leq B_\ell \leq \alpha \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_{\gamma_2^\ell}(x) \rho_{\gamma_2^\ell}(y)}{|x - y|} + \mathcal{O}\left(\frac{1}{R_\ell}\right) \leq \alpha q \left\| \rho_{\gamma_2^\ell} * \frac{1}{|\cdot|} \right\|_{L^\infty(\mathbb{R}^3)} + \mathcal{O}\left(\frac{1}{R_\ell}\right),$$

so (3.11) is proved.

In order to prove (3.12) one writes

$$(3.14) \quad \mathcal{D}_{V_\ell, \gamma_0^\ell} \chi_{0, \ell} - \chi_{0, \ell} \mathcal{D}_{V_\ell, \gamma_*^\ell} = [\mathcal{D}_{V_\ell, \gamma_*^\ell}, \chi_{0, \ell}] - \alpha W_{\gamma_*^\ell - \gamma_0^\ell} \chi_{0, \ell}.$$

One has

$$[\mathcal{D}_{V_\ell, \gamma_*^\ell}, \chi_{0, \ell}] = \frac{-i}{R_\ell} (\alpha \cdot \nabla \chi_0) (R_\ell^{-1} x) + \alpha \frac{\chi_{0, \ell}(y) - \chi_{0, \ell}(x)}{|x - y|} \gamma_*^\ell(x, y),$$

so

$$(3.15) \quad \left\| [\mathcal{D}_{V_\ell, \gamma_*^\ell}, \chi_{0, \ell}] \right\|_{\mathcal{B}(\mathcal{H})} = \mathcal{O}\left(\frac{1}{R_\ell}\right).$$

Now, for any test function $\psi \in C_c^\infty(\mathbb{R}^3, \mathbb{C}^4)$,

$$\begin{aligned} (W_{\gamma_*^\ell - \gamma_0^\ell} \chi_{0,\ell} \psi)(x) &= \int_{\mathbb{R}^3} \frac{\chi_{0,\ell}(x) (\chi_{1,\ell})^2(y) \rho_{\gamma_*^\ell}(y) \psi(y)}{|x-y|} d^3y \\ &\quad - \int_{\mathbb{R}^3} \frac{(1 - \chi_{0,\ell}(x) \chi_{0,\ell}(y)) \chi_{0,\ell}(y) \gamma_*^\ell(x, y) \psi(y)}{|x-y|} d^3y. \end{aligned}$$

Using (3.13) once again, one gets

$$\left\| \int_{\mathbb{R}^3} \frac{\chi_{0,\ell}(x) (\chi_{1,\ell})^2(y) \rho_{\gamma_*^\ell}(y) \psi(y)}{|x-y|} d^3y \right\|_{L^2(d^3x)} \leq \left(\left\| \rho_{\gamma_*^\ell} * \frac{1}{|\cdot|} \right\|_{L^\infty(\mathbb{R}^3)} + \frac{2q}{R_\ell} \right) \|\psi\|_{\mathcal{H}}.$$

Moreover, arguing as in the proof of (3.13), one easily gets

$$(3.16) \quad \frac{(1 - \chi_{0,\ell}(x) \chi_{0,\ell}(y)) \chi_{0,\ell}(y)}{|x-y|} \leq \frac{\zeta_\ell(x) \zeta_\ell(y)}{|x-y|} + \frac{2}{R_\ell},$$

hence

$$\begin{aligned} \left\| \int_{\mathbb{R}^3} \frac{(1 - \chi_{0,\ell}(x) \chi_{0,\ell}(y)) \chi_{0,\ell}(y) \gamma_*^\ell(x, y) \psi(y)}{|x-y|} d^3y \right\|_{L^2(d^3x)} \\ \leq \left(\left\| \frac{\gamma_*^\ell(x, y)}{|x-y|} \right\|_{\mathcal{B}(\mathcal{H})} + \frac{2}{R_\ell} \right) \|\psi\|_{\mathcal{H}}. \end{aligned}$$

The above estimates imply that $\lim_{\ell \rightarrow \infty} \|W_{\gamma_*^\ell - \gamma_0^\ell} \chi_{0,\ell}\|_{\mathcal{B}(\mathcal{H})} = 0$. Combining this with (3.14) and (3.15) one gets (3.12) for $\epsilon = 0$. The case $\epsilon = 1$ is proved in the same way. \square

Before proving Proposition 3.7 we need a last lemma:

Lemma 3.10. *Assume that $\gamma_*^\ell \in X$ converges to γ_* in the local sense of Lemma 3.8 as $\ell \rightarrow \infty$. Then:*

$$(3.17) \quad P_{V, \gamma_*}^- \gamma_* = 0,$$

$$(3.18) \quad \liminf_{\ell \rightarrow \infty} (\mathcal{E}_{DF}^\ell - \text{tr}_{\mathcal{H}})(\gamma_1^\ell) \geq 0.$$

Proof. Let $\xi(\ell) = \|V_\ell - V\|_{L^\infty(\mathbb{R}^3)} + \max_{\epsilon=0,1} \left\| \mathcal{D}_{V_\ell, \gamma_\epsilon^\ell} \chi_{\epsilon,\ell} - \chi_{\epsilon,\ell} \mathcal{D}_{V_\ell, \gamma_*^\ell} \right\|_{\mathcal{B}(\mathcal{H})}$.

From the definition of V_ℓ and from (3.12), we know that $\lim_{\ell \rightarrow \infty} \xi(\ell) = 0$. From the Euler-Lagrange equation satisfied by γ_*^ℓ , there is a (finite or infinite) set I_ℓ of integers and an orthonormal sequence $(\psi_n^\ell)_{n \in I_\ell}$ of common eigenvectors of γ_*^ℓ and $\mathcal{D}_{V, \gamma_*^\ell}$. The vectors ψ_n^ℓ satisfy

$$\begin{aligned} \mathcal{D}_{V, \gamma_*^\ell} \psi_n^\ell &= \lambda_n^\ell \psi_n^\ell, \quad \gamma_*^\ell = \sum_{n \in I_\ell} g_n^\ell |\psi_n^\ell\rangle \langle \psi_n^\ell|, \quad (\psi_n^\ell, \psi_{n'}^\ell)_{\mathcal{H}} = \delta_{n,n'}, \\ 0 < g_n^\ell &\leq 1, \quad \sum_{n \in I_\ell} g_n^\ell = \text{tr}_{\mathcal{H}}(\gamma_*^\ell) = q, \quad 0 < \lambda_n^\ell \leq 1. \end{aligned}$$

Then $\gamma_\epsilon^\ell = \sum_{n \in I_\ell} g_n^\ell |\psi_{\epsilon,n}^\ell\rangle \langle \psi_{\epsilon,n}^\ell|$ with $\psi_{\epsilon,n}^\ell(x) = \chi_{\epsilon,\ell}(x) \psi_n^\ell(x)$, $\epsilon = 0, 1$. Moreover,

$$\text{tr}_{\mathcal{H}}(\gamma_\epsilon^\ell) = \|\gamma_\epsilon^\ell\|_{\sigma_1(\mathcal{H})} = \sum_{n \in I_\ell} g_n^\ell \|\psi_{\epsilon,n}^\ell\|_{\mathcal{H}}^2, \quad \|\gamma_\epsilon^\ell\|_X = \sum_{n \in I_\ell} g_n^\ell \|\psi_{\epsilon,n}^\ell\|_{H^{1/2}}^2.$$

For $n \in I_\ell$ we have $\left\| \left(D_{V, \gamma_0^\ell} - \lambda_n^\ell \right) \psi_{0,n}^\ell \right\|_{\mathcal{H}} \leq \xi(\ell)$, hence $\left\| P_{V, \gamma_0^\ell}^- \psi_{0,n}^\ell \right\|_{\mathcal{H}} \leq \lambda_0^{-1} \xi(\ell)$. As a consequence,

$$\left\| P_{V, \gamma_0^\ell}^- \gamma_0^\ell \right\|_{\sigma_1(\mathcal{H})} \leq \sum_{n \in I_\ell} g_n^\ell \left\| P_{V, \gamma_0^\ell}^- \psi_{0,n}^\ell \right\|_{\mathcal{H}} \|\psi_{0,n}^\ell\|_{\mathcal{H}} \leq q \lambda_0^{-1} \xi(\ell) = o(1)_{\ell \rightarrow \infty}.$$

Then, remembering that $\lim_{\ell \rightarrow \infty} \|\gamma_0^\ell - \gamma_*\|_X = 0$ and using (2.13), we get (3.17).

In order to prove (3.18), we write

$$\begin{aligned} \text{tr} \left(\mathcal{D}_{V, \gamma_1^\ell} \gamma_1^\ell (\Lambda^+ - \Lambda^-) \right) &= \text{tr} \left(\mathcal{D}_{0, \gamma_1^\ell} \Lambda^+ \gamma_1^\ell \Lambda^+ \right) - \text{tr} \left(\mathcal{D}_{0, \gamma_1^\ell} \Lambda^- \gamma_1^\ell \Lambda^- \right) \\ &\quad + \text{tr} \left((V_\ell \chi_{1,\ell}) \gamma_*^\ell \chi_{1,\ell} (\Lambda^+ - \Lambda^-) \right). \end{aligned}$$

We have

$$\text{tr} \left(\mathcal{D}_{0, \gamma_1^\ell} \Lambda^+ \gamma_1^\ell \Lambda^+ \right) \geq \text{tr} \left(\mathcal{D} \Lambda^+ \gamma_1^\ell \Lambda^+ \right) = \|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X.$$

Moreover, using Tix' inequality [41] one gets

$$- \text{tr} \left(\mathcal{D}_{0, \gamma_1^\ell} \Lambda^- \gamma_1^\ell \Lambda^- \right) \geq \left(1 - \alpha \left(\frac{\pi}{4} + \frac{1}{\pi} \right) q \right) \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X.$$

In addition, one has

$$\begin{aligned} \|V \chi_{1,\ell} \mathcal{D}^{-1}\|_{\mathcal{B}(\mathcal{H})} &= \left\| \left((\mathbf{n}_\ell \mathbf{1}_{|\cdot| \leq R_\ell/2}) * |\cdot|^{-1} + (\mathbf{n}_\ell \mathbf{1}_{|\cdot| > R_\ell/2}) * |\cdot|^{-1} \right) \chi_{1,\ell} \mathcal{D}^{-1} \right\|_{\mathcal{B}(\mathcal{H})} \\ &\leq \frac{2(Z + \ell^{-1})}{R_\ell} + 2\mathbf{n}_\ell(\mathbb{R}^3 \setminus B(0, R_\ell/2)) = o(1)_{\ell \rightarrow \infty} \end{aligned}$$

and the Euler-Lagrange equation satisfied by γ_*^ℓ implies that $\|\mathcal{D} \gamma_*^\ell \mathcal{D}\|_{\sigma_1(\mathcal{H})} = \mathcal{O}(1)$, so

$$\lim_{\ell \rightarrow \infty} \text{tr} \left((V_\ell \chi_{1,\ell}) \gamma_*^\ell \chi_{1,\ell} (\Lambda^+ - \Lambda^-) \right) = 0.$$

Gathering these informations, we get the lower estimate

$$\text{tr} \left(\mathcal{D}_{V, \gamma_1^\ell} \gamma_1^\ell (\Lambda^+ - \Lambda^-) \right) \geq \|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X + \left(1 - \alpha \left(\frac{\pi}{4} + \frac{1}{\pi} \right) q \right) \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X + o(1)_{\ell \rightarrow \infty}.$$

On the other hand, we may write $\text{tr} \left(\mathcal{D}_{V, \gamma_1^\ell} \gamma_1^\ell (\Lambda^+ - \Lambda^-) \right) = C_\ell + D_\ell + E_\ell$ with

$$\begin{aligned} C_\ell &= \text{tr}_{\mathcal{H}} \left((\mathcal{D}_{V_\ell, \gamma_1^\ell} \chi_{1,\ell} - \chi_{1,\ell} \mathcal{D}_{V_\ell, \gamma_*^\ell}) \gamma_*^\ell \chi_{1,\ell} (\Lambda^+ - \Lambda^-) \right) \\ D_\ell &= \text{tr}_{\mathcal{H}} \left(\Lambda^+ \chi_{1,\ell} \mathcal{D}_{V, \gamma_*^\ell} \gamma_*^\ell \chi_{1,\ell} \Lambda^+ \right), \\ E_\ell &= - \text{tr}_{\mathcal{H}} \left(\Lambda^- \chi_{1,\ell} \mathcal{D}_{V, \gamma_*^\ell} \gamma_*^\ell \chi_{1,\ell} \Lambda^- \right). \end{aligned}$$

From (3.12), $\lim_{\ell \rightarrow \infty} C_\ell = 0$. Moreover the Euler-Lagrange equation satisfied by γ_*^ℓ implies that $\mathcal{D}_{V, \gamma_*^\ell} \gamma_*^\ell$ is a self-adjoint operator satisfying $0 \leq \mathcal{D}_{V, \gamma_*^\ell} \gamma_*^\ell \leq \gamma_*^\ell$. As a consequence, $D_\ell \leq \text{tr}_{\mathcal{H}} (\Lambda^+ \gamma_1^\ell \Lambda^+)$ and $E_\ell \leq 0$, so

$$\text{tr} \left(\mathcal{D}_{V, \gamma_1^\ell} \gamma_1^\ell (\Lambda^+ - \Lambda^-) \right) \leq \text{tr}_{\mathcal{H}} (\Lambda^+ \gamma_1^\ell \Lambda^+) + o(1)_{\ell \rightarrow \infty}.$$

Combining our lower and upper estimates on $\text{tr} \left(\mathcal{D}_{V, \gamma_1^\ell} \gamma_1^\ell (\Lambda^+ - \Lambda^-) \right)$ we conclude that

$$\left(1 - \alpha \left(\frac{\pi}{4} + \frac{1}{\pi} \right) q \right) \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X + \|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X - \text{tr}_{\mathcal{H}} (\Lambda^+ \gamma_1^\ell \Lambda^+) \leq o(1)_{\ell \rightarrow \infty}.$$

But $(1 - \alpha(\frac{\pi}{4} + \frac{1}{\pi})q) \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X$ and $(\|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X - \text{tr}_{\mathcal{H}}(\Lambda^+ \gamma_1^\ell \Lambda^+))$ are both nonnegative, so

$$\lim_{\ell \rightarrow \infty} \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X = \lim_{\ell \rightarrow \infty} (\|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X - \text{tr}_{\mathcal{H}}(\Lambda^+ \gamma_1^\ell \Lambda^+)) = 0.$$

As a consequence,

$$\begin{aligned} (\mathcal{E}_{DF}^\ell - \text{tr}_{\mathcal{H}})(\gamma_1^\ell) &\geq \text{tr}(\mathcal{D}_{V_\ell} \gamma_1^\ell) - \text{tr}_{\mathcal{H}}(\gamma_1^\ell) \\ &= \|\Lambda^+ \gamma_1^\ell \Lambda^+\|_X - \text{tr}_{\mathcal{H}}(\Lambda^+ \gamma_1^\ell \Lambda^+) \\ &\quad - \|\Lambda^- \gamma_1^\ell \Lambda^-\|_X - \text{tr}_{\mathcal{H}}(\Lambda^- \gamma_1^\ell \Lambda^-) + \text{tr}((V_\ell \chi_{1,\ell}) \gamma_*^\ell \chi_{1,\ell}) \\ &= o(1)_{\ell \rightarrow \infty} \end{aligned}$$

and (3.18) is proved. \square

Using lemmas 3.8, 3.9 and 3.10 we are now going to prove Proposition 3.7.

Remembering that $\lim_{\ell \rightarrow \infty} (\mathcal{E}_{DF}^\ell(\gamma_*^\ell) - \text{tr} \gamma_*^\ell) = E_q$, we deduce from (3.11) and (3.18) the inequality $\limsup_{\ell \rightarrow \infty} (\mathcal{E}_{DF}^\ell(\gamma_0^\ell) - \text{tr} \gamma_0^\ell) \leq E_q$. But from Lemma 3.8, we find that $\lim_{\ell \rightarrow \infty} \|\gamma_0^\ell - \gamma_*\|_X = 0$, so

$$\mathcal{E}_{DF}(\gamma_*) - \text{tr}_{\mathcal{H}} \gamma_* = \lim_{\ell \rightarrow \infty} (\mathcal{E}_{DF}^\ell(\gamma_0^\ell) - \text{tr}_{\mathcal{H}} \gamma_0^\ell) \leq E_q.$$

On the other hand, $r := \text{tr}_{\mathcal{H}} \gamma_* = \lim_{\ell \rightarrow \infty} \text{tr}_{\mathcal{H}} \gamma_0^\ell \leq q$, and (3.17) tells us that γ_* is in $\Gamma_{\leq r}^+$, hence $\mathcal{E}_{DF}(\gamma_*) - \text{tr}_{\mathcal{H}} \gamma_* \geq E_r \geq E_q$.

We conclude that γ_* is a minimizer of $(\mathcal{E}_{DF} - \text{tr}_{\mathcal{H}})$ both on $\Gamma_{\leq r}^+$ and $\Gamma_{\leq q}^+$. Then the strict binding inequality (1.6) implies that $r = q$. Finally, applying Lemma 3.1 to the constant sequence $\gamma_n = \gamma_*$ we find that

$$\text{tr}((\mathcal{D}_{V, \gamma_*} - 1)\gamma_*) = \min_{g \in \Gamma_{\leq q}, P_{\gamma_*}^+ g = g} \text{tr}((\mathcal{D}_{V, \gamma_*} - 1)g).$$

So γ_* is of the form $p + \delta$ with $p = \mathbb{1}_{(0, \mu)}(\mathcal{D}_{V, \gamma_*})$ and $0 \leq \delta \leq \mathbb{1}_{\{\mu\}}(\mathcal{D}_{V, \gamma_*})$ for some $0 < \mu \leq 1$.

Proposition 3.7 is thus true. This ends the proof of Theorem 1.2.

References

- [1] V. Bach. Error bound for the Hartree-Fock energy of atoms and molecules. *Commun. Math. Phys.* **147** (1992), p. 527–548.
- [2] V. Bach, J.-M. Barbaroux, B. Helffer and H. Siedentop. On the stability of the relativistic electron-positron field. *Commun. Math. Phys.* **201** (1999), p. 445–460.
- [3] V. Bach, E.H. Lieb, M. Loss and J.P. Solovej. There are no unfilled shells in unrestricted Hartree-Fock theory. *Phys. Rev. Lett.* **72** (1994), p. 2981–2983.
- [4] J.-M. Barbaroux, M.-J. Esteban and E. Séré. Some connections between Dirac-Fock and electron-positron Hartree-Fock. *Ann. Henri Poincaré* **6** (2005), p. 85–102.
- [5] J.-M. Barbaroux, W. Farkas, B. Helffer and H. Siedentop. On the Hartree-Fock equations of the electron-positron field. *Commun. Math. Phys.* **255** (2005), no. 1, p. 131–159.

- [6] J.-M. Barbaroux, B. Helffer and H. Siedentop. Remarks on the Mittleman max-min variational method for the electron-positron field. *J. Phys. A: Math. Gen.* **39** (2006), p. 85–98.
- [7] E. Cancès, C. Le Bris. Can we outperform the DIIS approach for electronic structure calculations? *Int. J. Quantum Chem.* **79** (2000), no. 2, p. 82–90.
- [8] I. Catto, L. Meng, E. Paturel and E. Séré. Solutions of a Dirac-Fock model for crystals, Preprint arXiv.2212.01142.
- [9] P. Chaix, D. Iracane. From quantum electrodynamics to mean field theory: I. The Bogoliubov-Dirac-Fock formalism. *J. Phys. B.* **22** (1989), p. 3791–3814.
- [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** (1989), p. 3815–3828.
- [11] V. Coti Zelati, M. Nolasco. Ground state for the relativistic one electron atom in a self-generated electromagnetic field. *SIAM J. Math. Anal.* **51** (2019), no. 3, p. 2206–2230.
- [12] J. Dolbeault, M.J. Esteban and E. Séré. On the eigenvalues of operators with gaps. Application to Dirac operators. *J. Funct. Anal.* **174** (2000), no. 1, p. 208–226. Corrigendum in *J. Funct. Anal.* **284** (2023), no. 1, 109651.
- [13] M.J. Esteban, M. Lewin and E. Séré. Variational methods in relativistic quantum mechanics. *Bull. Amer. Math. Soc. (N.S.)* **45** (2008), p. 535–593.
- [14] M.J. Esteban, M. Lewin and E. Séré. Dirac-Coulomb operators with general charge distribution. I. Distinguished extension and min-max formulas, *Annales Henri Lebesgue* **4** (2021), p. 1421–1456.
- [15] M.J. Esteban, E. Séré. Solutions of the Dirac-Fock Equations for Atoms and Molecules. *Commun. Math. Phys.* **203** (1999), p. 499–530.
- [16] M.J. Esteban, E. Séré. Nonrelativistic limit of the Dirac-Fock equations. *Ann. Henri Poincaré* **2** (2001), no. 5, p. 941–961.
- [17] M.J. Esteban, E. Séré. A max-min principle for the ground state of the Dirac-Fock functional. *Contemp. Math.* **307** (2002), p. 135–141.
- [18] S. Fournais, M. Lewin and A. Triay. The Scott correction in Dirac-Fock theory. *Commun. Math. Phys.* **378** (2020), no. 1, p. 569–600.
- [19] P. Gravejat, M. Lewin and E. Séré. Ground state and charge renormalization in a nonlinear model of relativistic atoms. *Commun. Math. Phys.* **286** (2009), p. 179–215.
- [20] M. Griesemer, R.T. Lewis and H. Siedentop. A minimax principle for eigenvalues in spectral gaps: Dirac operators with Coulomb potentials. *Doc. Math.* **4** (1999), p. 275–283.
- [21] C. Hainzl, M. Lewin and E. Séré. Existence of a stable polarized vacuum in the Bogoliubov-Dirac-Fock approximation. *Commun. Math. Phys.* **257**(3) (2005), p. 515–562.
- [22] C. Hainzl, M. Lewin and E. Séré. Self-consistent solution for the polarized vacuum in a no-photon QED model. *J. Phys. A: Math. and Gen.* **38** (2005), p. 4483–4499.

- [23] C. Hainzl, M. Lewin and E. Séré. Existence of Atoms and Molecules in the Mean-Field Approximation of No-Photon Quantum Electrodynamics. *Arch. Rational Mech. Anal.* **192** (2009), no. 3, p. 453-499.
- [24] C. Hainzl, M. Lewin and J.P. Solovej. The mean-field approximation in Quantum Electrodynamics. The no-photon case. *Comm. Pure Appl. Math.* **60** (2007), no. 4, p. 546-596.
- [25] C. Hainzl, M. Lewin, E. Séré and J.P. Solovej. A Minimization Method for Relativistic Electrons in a Mean-Field Approximation of Quantum Electrodynamics. *Phys. Rev. A* **76** (2007), 052104.
- [26] M. Huber, H. Siedentop. Solutions of the Dirac-Fock equations and the energy of the electron-positron field. *Arch. Rational Mech. Anal.* **184** (2007), no. 1, p. 1-22.
- [27] T. Kato. *Perturbation theory for linear operators*, Springer-Verlag, 1966.
- [28] M. Lewin. Geometric methods for nonlinear many-body quantum systems. *J. Funct. Anal.*, **260** (2011), no. 12, p. 3535-3595.
- [29] E. H. Lieb. Variational Principle for Many-Fermion Systems. *Phys. Rev. Lett.* **46** (1981), no. 7, p. 457-459 and **47** (1981), no. 1, p. 69(E).
- [30] E. H. Lieb, B. Simon. The Hartree-Fock theory for Coulomb systems. *Commun. Math. Phys.* **53** (1977), p. 185-194.
- [31] P.-L. Lions. The concentration-compactness method in the Calculus of Variations. The locally compact case. Part. I: *Anal. non-linéaire, Ann. IHP* **1** (1984), p. 109-145. Part. II: *Anal. non-linéaire, Ann. IHP* **1** (1984), p. 223-283.
- [32] P.-L. Lions. Solutions of Hartree-Fock equations for Coulomb systems. *Commun. Math. Phys.* **109** (1987): 33-97.
- [33] M.H. Mittleman. Theory of relativistic effects on atoms: Configuration-space Hamiltonian. *Phys. Rev. A* **24**(3) (1981), p. 1167-1175.
- [34] E. Paturel. Solutions of the Dirac-Fock equations without projector. *Ann. Henri Poincaré* **1** (2000), p. 1123-1157.
- [35] M. Reiher, A. Wolf. *Relativistic quantum chemistry; the fundamental theory of molecular science, Second edition*. Wiley, 2014.
- [36] J.P. Solovej. The ionization conjecture in Hartree-Fock theory. *Annals of Math.* **158** (2003), no. 2, p. 509-576.
- [37] B. Swirles. The relativistic self-consistent field. *Proc. Roy. Soc. A* **152** (1935), p. 625-649.
- [38] J. D. Talman. Minimax principle for the Dirac equation. *Phys. Rev. Lett.* **57** (1986), p. 1091-1094.
- [39] B. Thaller. *The Dirac Equation*. Springer Verlag, 1992.
- [40] C. Tix. Lower bound for the ground state energy of the no-pair Hamiltonian. *Phys. Lett. B* **405** (1997), p. 293-296.
- [41] C. Tix. Strict positivity of a relativistic Hamiltonian due to Brown and Ravenhall. *Bull. London Math. Soc.* **30** (1998), no. 3, p. 283-290.