Nonrelativistic limit of the Dirac-Fock equations.

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Abstract. In this paper, the Hartree-Fock equations are proved to be the non relativistic limit of the Dirac-Fock equations as far as convergence of “stationary states” is concerned. This property is used to derive a meaningful definition of “ground state” energy and “ground state” solutions for the Dirac-Fock model.

AMS Subject Classification: 49 S 05, 35 J 60, 35 P 30, 35 Q 75, 81 Q 05, 81 V 70, 81 V 45, 81 V 55.

Key Words : Relativistic quantum mechanics, nonrelativistic limit, quantum chemistry, ground state, nonlinear eigenvalue problems, Dirac-Fock equations, Hartree-Fock equations, variational methods, critical points, strongly indefinite functionals, bifurcations from the essential spectrum.

1. Introduction

In this paper we prove that solutions of Dirac-Fock equations converge, in a certain sense, towards solutions of the Hartree-Fock equations when the speed of light tends to infinity.

This limiting process allows us to define a notion of ground state for the Dirac-Fock equations, valid when the speed of light is large enough.

First of all, we choose units for which $m = \hbar = 1$, where m is the mass of the electron, and $\hbar$ is Planck’s constant. We also impose $\frac{e^2}{4\pi\varepsilon_0} = 1$, with $-e$ the charge of an electron, ε_0 the permittivity of the vacuum.

The Dirac Hamiltonian can be written as

$$(1) \quad H_c = -i c \alpha \cdot \nabla + c^2 \beta,$$

where $c > 0$ is the speed of light in the above units, $\beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}$, $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}$ ($k = 1, 2, 3$) and the σ_k are the well known Pauli matrices. The operator H_c acts on 4-spinors, i.e. functions from $\mathbb{R}^3$ to $\mathbb{C}^4$, and it is self-adjoint in $L^2(\mathbb{R}^3, \mathbb{C}^4)$, with domain $H^1(\mathbb{R}^3, \mathbb{C}^4)$ and form-domain $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$. Its spectrum is $(-\infty, -c^2] \cup [c^2, +\infty)$.

Let us consider a system of N electrons coupled to a fixed nuclear charge density $eZ\mu$, where e is the charge of the proton, $Z > 0$ the total number of protons and μ is a probability measure defined on $\mathbb{R}^3$. Note that in the particular case of m point-like nuclei, each one having atomic number Z_i at a fixed location x_i , $eZ\mu = \sum_{i=1}^m eZ_i\delta_{x_i}$ and $Z = \sum_{i=1}^m Z_i$.

In our system of units, the Dirac-Fock equations for such a molecule are given by

$$(DF_c) \quad \begin{cases} \overline{H}_{c,\Psi} \psi_k := H_c \psi_k - Z(\mu * \frac{1}{|x|})\psi_k + (\rho_\Psi * \frac{1}{|x|})\psi_k \\ \quad - \int_{\mathbb{R}^3} \frac{R_\Psi(x, y) \psi_k(y)}{|x - y|} dy = \varepsilon_k^c \psi_k \quad (k = 1, \dots, N), \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \quad (\text{i.e. } \int_{\mathbb{R}^3} \psi_k^* \psi_l = \delta_{kl}, \quad 1 \leq k, l \leq N). \end{cases}$$

Here, $\Psi = (\psi_1, \dots, \psi_N)$, each ψ_k is a 4-spinor in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$ (by bootstrap, ψ_k is also in any $W^{1,p}(\mathbb{R}^3)$ space, $1 \leq p < 3/2$), and

$$(2) \quad \rho_\Psi(x) := \sum_{k=1}^N \psi_k^*(x) \psi_k(x), \quad R_\Psi(x, y) := \sum_{k=1}^N \psi_k(x) \otimes \psi_k^*(y).$$

We have denoted ψ^* the complex line vector whose components are the conjugates of those of a complex (column) vector ψ , and $\psi_1^* \psi_2$ is the inner product of two complex (column) vectors ψ_1, ψ_2 . The $n \times n$ matrix $\text{Gram}_{L^2} \Psi$ is defined by the usual formulas

$$(3) \quad (\text{Gram}_{L^2} \Psi)_{kl} := \int_{\mathbb{R}^3} \psi_k^*(x) \psi_l(x) dx.$$

Finally, $\varepsilon_1^c \leq \dots \leq \varepsilon_N^c$ are eigenvalues of $\overline{H}_{c,\Psi}$. Each one represents the energy of one of the electrons, in the mean field created by the molecule. For physical reasons, we impose $0 < \varepsilon_k^c < c^2$. Note that the scalars ε_k^c can also be seen as Lagrange multipliers. Indeed, the Dirac-Fock equations are the Euler-Lagrange equations of the Dirac-Fock energy functional

$$\begin{aligned} \mathcal{E}_c(\Psi) = & \sum_{k=1}^N \int_{\mathbb{R}^3} \psi_k^* H_c \psi_k - Z \left(\mu * \frac{1}{|x|} \right) \psi_k^* \psi_k \\ & + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Psi(x) \rho_\Psi(y) - \text{tr} \left(R_\Psi(x, y) R_\Psi(y, x) \right)}{|x - y|} dx dy \end{aligned}$$

under the constraints $\int_{\mathbb{R}^3} \psi_k^* \psi_l = \delta_{kl}$.

In [6] we proved that under some assumptions on N and Z , there exists an infinite sequence of solutions of (DF_c) . More precisely:

Theorem 1 [6]. *Let $N < Z + 1$. For any $c > \frac{\pi/2+2/\pi}{2} \max(Z, 3N - 1)$, there exists a sequence of solutions of (DF_c) , $\{\Psi^{c,j}\}_{j \geq 1} \subset \left(H^{1/2}(\mathbb{R}^3)\right)^N$, such that*

- (i) $0 < \mathcal{E}_c(\Psi^{c,j}) < Nc^2$,
- (ii) $\lim_{j \rightarrow +\infty} \mathcal{E}_c(\Psi^{c,j}) = Nc^2$,
- (iii) $0 < c^2 - \mu_j < \varepsilon_1^{c,j} \leq \dots \leq \varepsilon_N^{c,j} < c^2 - m_j$, with $\mu_j > m_j > 0$ independent of c .

The constant $\frac{\pi/2+2/\pi}{2}$ is related to a Hardy-type inequality obtained independently by Tix and Burenkov-Evans (see [15, 3, 16]), and which plays an important role in the proof of Theorem 1. With the physical value $c = 137.037\dots$ and Z an integer (the total number of protons in the molecule), our conditions become $N \leq Z$, $N \leq 41$, $Z \leq 124$. The constraint $N \leq 41$ is technical, and has no physical meaning.

Our result was recently improved by Paturel [13], who relaxed the condition on N . Paturel obtains the same multiplicity result, assuming only that $N < Z + 1$ and $\frac{\pi/2+2/\pi}{2} \max(Z, N) < c$. Taking $c = 137.037\dots$, Paturel's conditions are $N \leq Z \leq 124$: they cover all existing neutral atoms. This is an important improvement.

In [6], the critical points $\Psi^{c,j}$ are obtained by a complicated min-max argument (in [13], the argument is not simpler). Here, we do not give this min-max in its full detail. We just state the minimal information needed in the present paper. Let us denote $E := H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$. Since

$$\sigma(H_c) = (-\infty, -c^2] \cup [c^2, +\infty),$$

the Hilbert space E can be split as

$$E = E_c^+ \oplus E_c^-,$$

where $E_c^\pm := \Lambda_c^\pm E$, and $\Lambda_c^\pm := \chi_{\mathbb{R}^\pm}(H_c)$. The projectors $\Lambda_c^\pm$ have a simple expression in the Fourier domain : $\widehat{\Lambda_c^\pm \psi}(\xi) = \widehat{\Lambda}_c^\pm(\xi) \widehat{\psi}(\xi)$, with

$$(4) \quad \widehat{\Lambda}_c^\pm(\xi) := \frac{1}{2} \left(\mathbf{I}_{\mathbb{C}^4} \pm \frac{c \alpha \cdot \xi + c^2 \beta}{\sqrt{c^4 + c^2 |\xi|^2}} \right).$$

Proposition 2 [6, 13]. *For every $j \geq 1$, let V be any $(N + j - 1)$ dimensional complex subspace of E_c^+ . Then, taking the notation of Theorem 1, we have*

$$(5) \quad E_{j,DF}^c := \mathcal{E}_c(\Psi^{c,j}) \leq \sup_{\substack{\Psi \in (E_c^- \oplus V)^N \\ \text{Gram}_{L^2} \Psi \leq \mathbf{I}_N}} \mathcal{E}_c(\Psi).$$

In the present paper, we prove three main theorems. We first consider a sequence $c_n \rightarrow +\infty$ and a sequence $\{\Psi^n\}_n$ of solutions of (DF_{c_n}) . For all n , $\Psi^n = (\psi_1^n, \dots, \psi_N^n)$, each ψ_k^n is in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, with $\int_{\mathbb{R}^3} \psi_k^* \psi_l dx = \delta_{kl}$ and $\overline{H}_{c_n, \Psi^n} \psi_k^n = \varepsilon_k^n \psi_k^n$. Using the standard Hardy inequality, one can prove that the functions ψ_k^n are in $H^1(\mathbb{R}^3, \mathbb{C}^4)$ for c_n large enough. We assume that

$$(6) \quad -\infty < \varliminf_{n \rightarrow +\infty} (\varepsilon_1^n - c_n^2) \leq \overline{\lim}_{n \rightarrow +\infty} (\varepsilon_N^n - c_n^2) < 0.$$

A (column) vector $\psi \in \mathbb{C}^4$ can be written in block form $\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix}$ where $\varphi \in \mathbb{C}^2$ (respectively $\chi \in \mathbb{C}^2$) consists of the two upper (resp. lower) components of ψ . This gives the splitting $\psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix}$ with φ_k^n and χ_k^n in $H^1(\mathbb{R}^3, \mathbb{C}^2)$. Finally, Ψ^n splits as $\begin{pmatrix} \Phi^n \\ \chi^n \end{pmatrix}$, where $\Phi^n := (\varphi_1^n, \dots, \varphi_N^n)$ and $\chi^n := (\chi_1^n, \dots, \chi_N^n)$. Our first result is that $\Psi^n = \begin{pmatrix} \Phi^n \\ \chi^n \end{pmatrix}$ has a subsequence converging, in H^1 norm,

towards $\bar{\Psi} = (\bar{\Phi})$, where $\bar{\Phi} = (\bar{\varphi}_1, \dots, \bar{\varphi}_N) \in \left(H^1(\mathbb{R}^3, \mathbb{C}^2)\right)^N$ is a solution of the Hartree-Fock equations:

$$(HF) \quad \begin{cases} \mathcal{H}_\Phi \varphi_k = -\frac{\Delta \varphi_k}{2} - Z\left(\mu * \frac{1}{|x|}\right) \varphi_k + \left(\rho_\Phi * \frac{1}{|x|}\right) \varphi_k \\ \quad - \int_{\mathbb{R}^3} \frac{R_\Phi(x, y) \varphi_k(y)}{|x - y|} dy = \bar{\lambda}_k \varphi_k, \quad k = 1, \dots, N, \\ \int_{\mathbb{R}^3} \varphi_k^* \varphi_l dx = \delta_{kl}, \quad \bar{\lambda}_k = \lim_{n \rightarrow +\infty} (\varepsilon_k^n - c_n^2). \end{cases}$$

Here (as in the Dirac-Fock equations),

$$\rho_\Phi(x) = \sum_{l=1}^N \varphi_l^*(x) \varphi_l(x), \quad R_\Phi(x, y) = \sum_{l=1}^N \varphi_l(x) \otimes \varphi_l^*(y).$$

Note that the Hartree-Fock equations are the Euler-Lagrange equations corresponding to critical points in $\left(H^1(\mathbb{R}^3, \mathbb{C}^2)\right)^N$ of the Hartree-Fock energy:

$$(7) \quad \begin{aligned} \mathcal{E}_{HF}(\Phi) &:= \sum_{k=1}^N \frac{1}{2} \|\nabla \varphi_k\|_{L^2}^2 - Z \int_{\mathbb{R}^3} \left(\mu * \frac{1}{|x|}\right) |\varphi_k|^2 dx \\ &\quad + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Phi(x) \rho_\Phi(y) - \text{tr}(R_\Phi(x, y) R_\Phi(y, x))}{|x - y|} dx dy, \end{aligned}$$

under the constraint $\int_{\mathbb{R}^3} \varphi_k^* \varphi_l = \delta_{kl}$, $i, j = 1, \dots, N$.

Theorem 3 . *Let $N < Z + 1$. Consider a sequence $c_n \rightarrow +\infty$ and a sequence $\{\Psi^n\}_n$ of solutions of (DF_{c_n}) , i.e. $\Psi^n = (\psi_1^n, \dots, \psi_N^n)$, each ψ_k^n being in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, with $\int_{\mathbb{R}^3} \psi_k^* \psi_l dx = \delta_{kl}$ and $\overline{H}_{c_n, \Psi^n} \psi_k^n = \varepsilon_k^n \psi_k^n$. Assume that the multipliers ε_k^n , $k = 1, \dots, N$, satisfy (6). Then for n large enough, ψ_k^n is in $H^1(\mathbb{R}^3, \mathbb{C}^4)$, and there exists a solution of (HF), $\bar{\Phi} = (\bar{\varphi}_1, \dots, \bar{\varphi}_N)$, with negative multipliers, $\bar{\lambda}_1, \dots, \bar{\lambda}_N$, such that, after extraction of a subsequence,*

$$(8) \quad \lambda_k^n := \varepsilon_k^n - (c_n)^2 \xrightarrow{n \rightarrow +\infty} \bar{\lambda}_k, \quad k = 1, \dots, N,$$

$$(9) \quad \psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix}_{n \rightarrow +\infty} \begin{pmatrix} \bar{\varphi}_k \\ 0 \end{pmatrix} \text{ in } H^1(\mathbb{R}^3, \mathbb{C}^2) \times H^1(\mathbb{R}^3, \mathbb{C}^2),$$

$$(10) \quad \left\| \chi_k^n + \frac{i}{2c_n} (\sigma \cdot \nabla) \varphi_k^n \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = O(1/(c_n)^3),$$

and

$$(11) \quad \mathcal{E}_{c_n}(\Psi^n) - Nc_n^2 \xrightarrow{n \rightarrow +\infty} \mathcal{E}_{HF}(\bar{\Phi}).$$

As a particular case, we have

Corollary 4 . If $c_n \rightarrow +\infty$ and N, Z, μ are fixed, then for any $j \geq 1$ the sequence $\{\Psi^{c_n, j}\}_n$ of Theorem 1 satisfies the assumptions of Theorem 3 (see (iii) in Theorem 1). So it is precompact in $\left(H^1(\mathbb{R}^3, \mathbb{C}^4)\right)^N$. Up to extraction of subsequences,

$$(12) \quad \lambda_k^{c_n, j} := \varepsilon_k^{c_n, j} - c_n^2 \longrightarrow \bar{\lambda}_k^j < 0, \quad k = 1, \dots, N$$

$$(13) \quad \Psi^{c_n, j} \longrightarrow \begin{pmatrix} \bar{\Phi}^j \\ 0 \end{pmatrix} \text{ in } \left(H^1(\mathbb{R}^3, \mathbb{C}^2)\right)^N \times \left(H^1(\mathbb{R}^3, \mathbb{C}^2)\right)^N$$

and $\bar{\Phi}^j = (\bar{\varphi}_1^j, \dots, \bar{\varphi}_N^j)$ is a solution of the Hartree-Fock equations with multipliers $\bar{\lambda}_1^j, \dots, \bar{\lambda}_N^j$. Moreover,

$$(14) \quad \mathcal{E}_{c_n}(\Psi^{c_n, j}) - Nc_n^2 \xrightarrow{n \rightarrow +\infty} \mathcal{E}_{HF}(\bar{\Phi}^j).$$

Particular solutions of the Hartree-Fock equations are the minimizers of $\mathcal{E}_{HF}(\Phi)$ under the constraints $\text{Gram}_{L^2} \Phi = \mathbf{I}_N$. They are called ground states. Their existence was proved by Lieb and Simon [10] under the assumption $N < Z + 1$ (see also [11] for the existence of excited states).

It is difficult to define the notion of ground state for the Dirac-Fock model, since $\mathcal{E}_c$ has no minimum under the constraints $\int_{\mathbb{R}^3} \psi_k^* \psi_l = \delta_{kl}$. Our second main result asserts that the first solution $\Psi^{c, 1}$ of (DF_c) found in [6], whose energy level will be denoted $E_{1, DF}^c$, can be considered, in some (weak) sense, as a ground state for (DF_c) . Indeed, $E_{1, DF}^c - Nc^2$ converges to the minimum of $\mathcal{E}_{HF}$ as c goes to infinity. Moreover, for c large the multipliers $\varepsilon_k^{c, 1}$ associated to $\Psi^{c, 1}$ are the N smallest positive eigenvalues of the mean-field operator $\overline{H}_{c, \Psi^{c, 1}}$.

Theorem 5 . *Let $N < Z + 1$ and c sufficiently large. With the above notations,*

$$(15) \quad E_{1,DF}^c := \mathcal{E}_c(\Psi^{c,1}) = \min_{\text{Gram}_{L^2} \Phi = \mathbf{I}_N} \mathcal{E}_{HF}(\Phi) + Nc^2 + o(1)_{c \rightarrow +\infty}$$

Moreover, for any subsequence $\{\Psi^{c_n,1}\}_n$ converging in $(H^1(\mathbb{R}^3, \mathbb{C}^4))^N$ to some $(\bar{\Phi}_0^1)$, $\bar{\Phi}^1$ is a ground state of the Hartree-Fock model, i.e.

$$(16) \quad \mathcal{E}_{HF}(\bar{\Phi}^1) = \min_{\text{Gram}_{L^2} \Phi = \mathbf{I}_N} \mathcal{E}_{HF}(\Phi).$$

Furthermore, for c large, the eigenvalues corresponding to $\Psi^{c,1}$ in (DF_c) , $\varepsilon_1^{c,1}, \dots, \varepsilon_N^{c,1}$ are the smallest positive eigenvalues of the linear operator $\overline{H}_{c,\Psi^{c,1}}$ and the $(N+1)$ -th positive eigenvalue of this operator is strictly larger than $\varepsilon_N^{c,1}$.

Finally, we are able to show that, for c large enough, the function $\Psi^{c,1}$ can be viewed as an electronic ground state for the Dirac-Fock equations in the following sense: it minimizes the Dirac-Fock energy among all electronic configurations which are orthogonal to the “Dirac sea”.

Theorem 6 . *Fix N, Z with $N < Z + 1$ and take c sufficiently large. Then $\Psi^{c,1}$ is a solution of the following minimization problem:*

$$(17) \quad \inf \{ \mathcal{E}_c(\Psi); \text{Gram}_{L^2} \Psi = \mathbf{I}_N, \Lambda_{\Psi}^{-} \Psi = 0 \}$$

where $\Lambda_{\Psi}^{-} = \chi_{(-\infty, 0)}(\overline{H}_{c,\Psi})$ is the negative spectral projector of the operator $\overline{H}_{c,\Psi}$, and $\Lambda_{\Psi}^{-} \Psi := (\Lambda_{\Psi}^{-} \psi_1, \dots, \Lambda_{\Psi}^{-} \psi_N)$.

The constraint $\Lambda_{\Psi}^{-} \Psi = 0$ has a physical meaning. Indeed, according to Dirac’s original ideas, the vacuum consists of infinitely many electrons which completely fill up the negative space of $\overline{H}_{c,\Psi}$: these electrons form the “Dirac sea”. So, by the Pauli exclusion principle, additional electronic states should be in the positive space of the mean-field Hamiltonian $\overline{H}_{c,\Psi}$. The proof of Theorem 6 will be given in Section 4. This proof uses some other interesting min-max characterizations of $\Psi^{c,1}$ (see Lemma 9).

2. The nonrelativistic limit

This section is devoted to the proof of Theorem 3. We first notice that when $N < Z + 1$, N, Z fixed, and c is sufficiently large, any solution of (DF_c) is actually in $(H^1(\mathbb{R}^3))^N$. This follows from the fact that for ν small, the operator $H_1 - \frac{\nu}{|x|}$ is essentially self-adjoint with domain $H^1(\mathbb{R}^3)$ (see [14]).

We can also obtain *a priori* estimates on H^1 norms:

Lemma 7 . *Fix $N, Z \in \mathbb{Z}^+$, take c large enough, and let Ψ^c be a solution of (DF_c) . If the multipliers ε_k^c associated to Ψ^c satisfy $0 \leq \varepsilon_k^c \leq c^2$ ($k = 1, \dots, N$), then $\Psi^c \in (H^1(\mathbb{R}^3, \mathbb{C}^4))^N$, and the following estimate holds*

$$\|\Psi^c\|_2^2 + \|\nabla \Psi^c\|_2^2 \leq K .$$

The constant K is independent of c (for c large).

Proof. The normalization constraint $\text{Gram}_{L^2} \Psi^c = \mathbf{I}_N$ implies

$$(18) \quad \|\Psi^c\|_2^2 = N .$$

Using the (DF_c) equation and the standard Hardy inequality

$$(19) \quad \int_{\mathbb{R}^3} \frac{u^2}{|x|^2} \leq 4 \int_{\mathbb{R}^3} |\nabla u|^2 ,$$

one easily proves that Ψ^c is in H^1 , and satisfies:

$$(20) \quad (H_c \Psi^c, H_c \Psi^c) = c^4 \|\Psi^c\|_2^2 + c^2 \|\nabla \Psi^c\|_2^2 \\ \leq c^4 \|\Psi^c\|_2^2 + \ell(Z^2 + N^2) \|\nabla \Psi^c\|_2^2 + \ell c^2 \max(N, Z) \|\nabla \Psi^c\|_2 ,$$

for some $\ell > 0$ independent of N, Z and c . The estimates (18) and (20) prove the lemma. $\square$

Proof of Theorem 3. Let us split the spinors $\psi_k^n : \mathbb{R}^3 \rightarrow \mathbb{C}^4$ in blocks of upper and lower components : $\psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix}$, with $\varphi_k^n, \chi_k^n : \mathbb{R}^3 \rightarrow \mathbb{C}^2$. We

denote $L := -i(\sigma \cdot \nabla)$. Then we can rewrite (DF_{c_n}) in the following way:

$$(21) \left\{ \begin{array}{l} c_n L \chi_k^n - Z \left(\mu * \frac{1}{|x|} \right) \varphi_k^n + \left(\sum_{l=1}^N (|\varphi_l^n|^2 + |\chi_l^n|^2) * \frac{1}{|x|} \right) \varphi_k^n + (c_n)^2 \varphi_k^n \\ - \sum_{l=1}^N \varphi_l^n(x) \int_{\mathbb{R}^3} \frac{(\varphi_l^n)^*(y) \varphi_k^n(y) + (\chi_l^n)^*(y) \chi_k^n(y)}{|x-y|} dy = \varepsilon_k^n \varphi_k^n \\ c_n L \varphi_k^n - Z \left(\mu * \frac{1}{|x|} \right) \chi_k^n + \left(\sum_{l=1}^N (|\varphi_l^n|^2 + |\chi_l^n|^2) * \frac{1}{|x|} \right) \chi_k^n - (c_n)^2 \chi_k^n \\ - \sum_{l=1}^N \chi_l^n(x) \int_{\mathbb{R}^3} \frac{(\varphi_l^n)^*(y) \varphi_k^n(y) + (\chi_l^n)^*(y) \chi_k^n(y)}{|x-y|} dy = \varepsilon_k^n \chi_k^n \\ \int_{\mathbb{R}^3} (\varphi_k^n)^* \varphi_l^n + (\chi_l^n)^* \chi_k^n dx = \delta_{kl} \end{array} \right.$$

Note that $\|L\chi\|_{L^2} = \|\nabla\chi\|_{L^2}$ for all $\chi \in H^1(\mathbb{R}^3, \mathbb{C}^2)$. So, dividing by c_n the first equation of (21), we get

$$(22) \quad \|\nabla \chi_k^n\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = O(1/c_n) .$$

Dividing by $2(c_n)^2$ the second equation of (21), and using the fact that $\varepsilon_k^n - (c_n)^2$ is a bounded sequence, we get

$$(23) \quad \left\| \chi_k^n - \frac{1}{2c_n} L \varphi_k^n \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = \frac{1}{(c_n)^2} O \left(\sum_{l=1}^N \|\chi_l^n\|_{H^1(\mathbb{R}^3, \mathbb{C}^2)} \right) .$$

The estimate (23) together with Lemma 7 implies

$$(24) \quad \|\chi_k^n\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = O(1/c_n) .$$

Combining this with (22), we obtain

$$(25) \quad \|\chi_k^n\|_{H^1(\mathbb{R}^3, \mathbb{C}^2)} = O(1/c_n) .$$

So $\sum_{l=1}^N \|\chi_l^n\|_{H^1(\mathbb{R}^3, \mathbb{C}^2)} = O(1/c_n)$, and (23) gives the estimate

$$(26) \quad \left\| \chi_k^n - \frac{1}{2c_n} L \varphi_k^n \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = O(1/(c_n)^3) .$$

Now, the first equation of (21), combined with (26), implies

$$\left\{ \begin{array}{l} -\frac{\Delta \varphi_k^n}{2} - Z(\mu * \frac{1}{|x|})\varphi_k^n + \left(\sum_{l=1}^N |\varphi_l^n|^2 * \frac{1}{|x|}\right)\chi_k^n \\ - \sum_{l=1}^N \varphi_l^n(x) \int_{\mathbb{R}^3} \frac{(\varphi_l^n)^*(y)\varphi_k^n(y)}{|x-y|} dy = \lambda_k^n \varphi_k^n + h_k^n, \\ \int_{\mathbb{R}^3} (\varphi_k^n)^* \varphi_l^n = \delta_{kl} + r_{kl}^n, \end{array} \right.$$

with $\lambda_k^n := \varepsilon_k^n - (c_n)^2$, and

$$\lim_{n \rightarrow +\infty} \|h_k^n\|_{H^{-1}(\mathbb{R}^3)} = 0, \quad \lim_{n \rightarrow +\infty} |r_{kl}^n| = 0 \quad \text{for all } k, l \in \{1, \dots, N\}.$$

Therefore $\Phi^n := (\varphi_1^n, \dots, \varphi_N^n)$ is a Palais-Smale sequence for the Hartree-Fock problem, and the multipliers λ_k^n satisfy $\overline{\lim}_{n \rightarrow +\infty} \lambda_k^n < 0$. At this point, we just invoke an argument used in [11] to obtain the convergence in H^1 norm of some subsequence $\{\Phi^{n'}\}$ towards $\bar{\Phi} = (\bar{\varphi}_1, \dots, \bar{\varphi}_N)$, a solution of the Hartree-Fock equations

$$\left\{ \begin{array}{l} \mathcal{H}_{\bar{\Phi}} \bar{\varphi}_k = \bar{\lambda}_k \bar{\varphi}_k, \quad k = 1, \dots, N \\ \int_{\mathbb{R}^3} \bar{\varphi}_k^* \bar{\varphi}_l = \delta_{kl}, \end{array} \right.$$

where $\bar{\lambda}_k = \lim_{n' \rightarrow +\infty} \lambda_k^{n'}$.

Finally, let us prove that $\mathcal{E}_{c_{n'}}(\Psi^{n'}) - N(c_{n'})^2$ converges to $\mathcal{E}_{HF}(\bar{\Phi})$. From Lemma 7 and the estimate (26), one easily gets

$$(27) \quad \mathcal{E}_{c_n}(\Psi^n) - Nc_n^2 = \mathcal{E}_{HF}(\Phi^n) + O(1/(c_n)^2).$$

Since $\Phi^{n'}$ converges in H^1 norm to $\bar{\Phi}$, the energy level $\mathcal{E}_{HF}(\Phi^{n'})$ converges to $\mathcal{E}_{HF}(\bar{\Phi})$. So (27) implies the desired convergence. This ends the proof of Theorem 3. $\square$

3. Ground state for Dirac-Fock equations in the nonrelativistic limit.

The aim of this section is to prove Theorem 5. The estimate given in Proposition 2 on the energy $\mathcal{E}_c(\Psi^{c,i})$ and the expression of $\hat{\Lambda}_c^\pm$ given in (4), will be crucial.

Proof of Theorem 5. By Corollary 4, for any sequence c_n going to infinity, $\Psi^{c_n,1}$ is precompact in H^1 norm. If it converges, its limit is of the form $(\bar{\Phi}_0^1)$, and $\left(\mathcal{E}_{c_n}(\Psi^{c_n,1}) - N(c_n)^2\right)$ converges to $\mathcal{E}_{HF}(\bar{\Phi}^1)$. As a consequence,

$$(28) \quad \underline{\lim}_{c \rightarrow +\infty} \left(\mathcal{E}_c(\Psi^{c,1}) - Nc^2 \right) \geq \inf_{\text{Gram}_{L^2} \Phi = \mathbf{I}_N} \mathcal{E}_{HF}(\Phi).$$

In order to prove (15) and (16) of Theorem 5, we just have to show that

$$(29) \quad \overline{\lim}_{c \rightarrow +\infty} \left(\mathcal{E}_c(\Psi^{c,1}) - Nc^2 \right) \leq \inf_{\text{Gram}_{L^2} \Phi = \mathbf{I}_N} \mathcal{E}_{HF}(\Phi).$$

Take $\Phi = (\varphi_1, \dots, \varphi_N) \in \left(H^1(\mathbb{R}^3, \mathbb{C}^2) \right)^N$, with $\text{Gram}_{L^2} \Phi = \mathbf{I}_N$. Let V_c be the complex subspace of E_c^+ defined by

$$(30) \quad V_c := \text{Span} \{ \Lambda_c^+(\varphi_1), \dots, \Lambda_c^+(\varphi_N) \}.$$

From formula (4) and Lebesgue's convergence theorem, one easily gets, for $k = 1, \dots, N$,

$$(31) \quad \lim_{c \rightarrow +\infty} \|\Lambda_c^-(\varphi_k)\|_{H^1} = 0.$$

So, for c sufficiently large, we have

$$(32) \quad \dim V_c = N.$$

Hence, by (5),

$$(33) \quad E_{1,DF}^c := \mathcal{E}_c(\Psi^{c,1}) \leq \sup_{\substack{\Psi \in (E^- \oplus V_c)^N \\ \text{Gram}_{L^2} \Psi \leq \mathbf{I}_N}} \mathcal{E}_c(\Psi).$$

Let $\Psi^+ \in (E_c^+)^N$, $\Psi^- \in (E_c^-)^N$ such that $\text{Gram}_{L^2}(\Psi^+ + \Psi^-) \leq \mathbf{I}_N$. By the concavity property of $\mathcal{E}_c$ in the E_c^- direction (see [6], Lemma 2.2), if c

is large enough, we have

$$\begin{aligned}
\mathcal{E}_c(\Psi^+ + \Psi^-) &\leq \mathcal{E}_c(\Psi^+) + \mathcal{E}'_c(\Psi^+) \cdot \Psi^- - \frac{1}{4} \sum_{k=1}^N (\psi_k^-, \sqrt{-c^2 \Delta + c^4} \psi_k^-) \\
(34) \quad &\leq \mathcal{E}_c(\Psi^+) + M \|\Psi^-\|_{L^2} - \frac{c^2}{4} \|\Psi^-\|_{L^2}^2,
\end{aligned}$$

for some constant $M > 0$ independent of c . Hence, for c large,

$$(35) \quad E_{1,DF}^c \leq \sup_{\Psi^+ \in D(V_c)} \mathcal{E}_c(\Psi^+) + o(1)_{c \rightarrow +\infty},$$

where $D(V_c) := \left\{ \Psi^+ \in (V_c)^N ; \text{Gram}_{L^2} \Psi^+ \leq \mathbf{I}_N \right\}$.

If c is large enough, it follows from Hardy's inequality (19) that the map $\Psi^+ \rightarrow \mathcal{E}_c(\Psi^+)$ is strictly convex on the convex set

$$\mathcal{A}^+ := \{ \Psi^+ \in (E_c^+)^N ; \text{Gram}_{L^2} \Psi^+ \leq \mathbf{I}_N \}.$$

Indeed, its second derivative at any point Ψ^+ of $\mathcal{A}^+$ is of the form

$$\mathcal{E}_c''(\Psi^+)[d\Psi^+]^2 = 2 \sum_{k=1}^N (d\psi_k, \sqrt{c^4 - c^2 \Delta} d\psi_k)_{L^2} + Q(d\Psi^+)$$

with Q a quadratic form on $(H^{1/2}(\mathbb{R}^3, \mathbb{C}^4))^N$ bounded independently of c and $\Psi^+ \in \mathcal{A}^+$.

As a consequence, $\sup_{\Psi^+ \in D(V_c)} \mathcal{E}_c(\Psi^+)$ is achieved by an extremal point Ψ_{max}^+ of the convex set $D(V_c) = \mathcal{A}^+ \cap (V_c)^N$. Being extremal in $D(V_c)$, the point Ψ_{max}^+ satisfies

$$(36) \quad \text{Gram}_{L^2} \Psi_{max}^+ = \mathbf{I}_N.$$

Since $\psi_{k,max}^+ \in V_c$, there is a matrix $A = (a_{kl})_{1 \leq k, l \leq N}$ such that, for all l , $\psi_{l,max}^+ = \sum_{1 \leq k \leq N} a_{kl} \Lambda_c^+ \begin{pmatrix} \varphi_k \\ 0 \end{pmatrix}$. Then

$$(37) \quad A^* \text{Gram}_{L^2} \left(\Lambda_c^+ \begin{pmatrix} \Phi \\ 0 \end{pmatrix} \right) A = \text{Gram}_{L^2} \Psi_{max}^+ = \mathbf{I}_N.$$

Using the $U(N)$ invariance of $D(V_c)$ and $\mathcal{E}_c$, and the polar decomposition of square matrices, one can assume, without restricting the generality, that $A = A^*$ and A is positive definite. Recalling that $\text{Gram}_{L^2} \Phi = \mathbf{I}_N$, we see,

from (31), that $\text{Gram}_{L^2}(\Lambda_c^+(\Phi)) = \mathbf{I}_N + o(1)$. So (37) implies $A^2 = \mathbf{I}_N + o(1)$, hence $A = \mathbf{I}_N + o(1)$. Combining this with (31), we get

$$\|\psi_{k,max}^+ - \binom{\varphi_k}{0}\|_{H^1} = o(1)_{c \rightarrow +\infty}.$$

Now, since $\psi_{k,max}^+ \in E_c^+$, $H_c \psi_{k,max}^+ = \sqrt{c^4 - c^2 \Delta} \psi_{k,max}^+$. But

$$\sqrt{c^4 - c^2 \Delta} \leq c^2 - \frac{\Delta}{2}.$$

This inequality is easily obtained in the Fourier domain: it follows from $\sqrt{1+x} \leq 1 + \frac{x}{2}$ ($\forall x \geq 0$). So we get

$$\sum_{k=1}^N (H_c \psi_{k,max}^+, \psi_{k,max}^+)_{L^2} \leq Nc^2 + \frac{1}{2} \sum_{k=1}^N \|\nabla \psi_{k,max}^+\|_{L^2}^2.$$

Combining this with (31), we find

$$(38) \quad \mathcal{E}_c(\Psi_{max}^+) \leq Nc^2 + \mathcal{E}_{HF}(\Phi) + o(1)_{c \rightarrow +\infty}.$$

Finally, (35) and (38) imply

$$(39) \quad \begin{aligned} E_{1,DF}^c &\leq \mathcal{E}_c(\Psi_{max}^+) + o(1)_{c \rightarrow +\infty} \\ &\leq Nc^2 + \mathcal{E}_{HF}(\Phi) + o(1)_{c \rightarrow +\infty}. \end{aligned}$$

Since Φ is arbitrary, (39) implies (29). The formulas (15), (16) of Theorem 5 are thus proved.

We now check the last assertion about the $\varepsilon_k^{c_n,1}$, $k = 1, \dots, N$, being the smallest eigenvalues of the operator $\overline{H}_{c,\Psi^{c_n,1}}$ for c large. By Corollary 4, we can translate this statement in the language of sequences. We take a sequence $c_n \rightarrow +\infty$ such that $\{\Psi^{c_n,1}\}_n$ converges in $(H^1(\mathbb{R}^3, \mathbb{C}^4))^N$ to some $\binom{\bar{\Phi}^1}{0}$, for n large enough. Let $\overline{H}_n := \overline{H}_{c_n,\Psi^{c_n,1}}$ and $\mathcal{H}_\infty := \mathcal{H}_{\bar{\Phi}^1}$. We have $\overline{H}_n \psi_k^{c_n,1} = \varepsilon_k^n \psi_k^{c_n,1}$ and $\mathcal{H}_\infty \bar{\varphi}_k^1 = \bar{\lambda}_k \bar{\varphi}_k^1$, with

$$0 < \varepsilon_1^n \leq \dots \leq \varepsilon_N^n < (c_n)^2, \quad \bar{\lambda}_1 \leq \dots \leq \bar{\lambda}_N < 0, \quad \bar{\lambda}_k = \lim_{n \rightarrow +\infty} (\varepsilon_k^n - (c_n)^2).$$

Let us denote $e_1^n \leq \dots \leq e_i^n \leq \dots$ the sequence of eigenvalues of $\overline{H}_n$, in the interval $(0, c_n^2)$, counted with multiplicity. Similarly, we shall denote $\bar{\nu}_1 \leq \dots \leq \bar{\nu}_i \leq \dots$ the sequence of eigenvalues of $\mathcal{H}_\infty$ in the interval

$(-\infty, 0)$, counted with multiplicity. Let $z \in \mathbb{C} \setminus \sigma(\mathcal{H}_\infty)$. Then for n large enough, $z + (c_n)^2 \in \mathbb{C} \setminus \sigma(\overline{H}_n)$, and the resolvent

$$R_n(z + (c_n)^2) := \left((z + (c_n)^2)I - \overline{H}_n \right)^{-1}$$

converges in norm towards the operator $L(z) : \begin{pmatrix} \varphi \\ \chi \end{pmatrix} \rightarrow \begin{pmatrix} \bar{R}(z)\varphi \\ 0 \end{pmatrix}$, where $\bar{R}(z) := \left(zI - \mathcal{H}_\infty \right)^{-1}$ is the resolvent of $\mathcal{H}_\infty$. So, by the standard spectral theory, $\lim_{n \rightarrow +\infty} (e_i^n - (c_n)^2) = \bar{\nu}_i$ for all $i \geq 1$.

We know that $\bar{\Phi}^1$ is a ground state of the Hartree-Fock model. So a result proved in [1] tells us that $\bar{\nu}_k = \bar{\lambda}_k$ for all $1 \leq k \leq N$, and $\bar{\nu}_{N+1} > \bar{\lambda}_N$. But $(\varepsilon_N^n - (c_n)^2)$ converges to $\bar{\lambda}_N$, and $(e_{N+1}^n - (c_n)^2)$ converges to $\bar{\nu}_{N+1}$, as n goes to infinity. So, for n large enough, $e_{N+1}^n > \varepsilon_N^n$, hence $\varepsilon_k^n = e_k^n$ for all $1 \leq k \leq N$. This ends the proof of Theorem 5. $\square$

4. Proof of Theorem 6

In this section, both Φ and Ψ will denote N -uples of 4-spinors (functions from $\mathbb{R}^3$ into $\mathbb{C}^4$). As already noted above, in [6] the solution $\Psi^{c,1}$ was obtained by a complicated min-max argument. For c large, we will show that this argument can be simplified.

First of all, we introduce the notion of projector “ ε -close to Λ_c^+ ”, where $\Lambda_c^+ = \frac{1}{2}|H_c|^{-1}(H_c + |H_c|)$ is the positive free-energy projector.

Definition 8 : Let P^+ be an orthogonal projector in $L^2(\mathbb{R}^3, \mathbb{C}^4)$, whose restriction to $H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^4)$ is a bounded operator on $H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^4)$.

Given $\varepsilon > 0$, P^+ is ε -close to Λ_c^+ if and only if, for all $\psi \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^4)$,

$$\left\| \left(-c^2\Delta + c^4 \right)^{\frac{1}{4}} \left(P^+ - \Lambda_c^+ \right) \psi \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^4)} \leq \varepsilon \left\| \left(-c^2\Delta + c^4 \right)^{\frac{1}{4}} \psi \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^4)}.$$

An obvious example of projector ε -close to Λ_c^+ is Λ_c^+ itself. More interesting examples will be given below. Let us now give a min-max principle associated to P^+ :

Lemma 9 . Fix N, Z with $N < Z + 1$. Take $c > 0$ large enough, and P^+ a projector ε -close to Λ_c^+ , for $\varepsilon > 0$ small enough. Let $P^- = \mathbf{1}_{L^2} - P^+$, and define

$$E(P^+) := \inf_{\substack{\Phi^+ \in (P^+ H^{\frac{1}{2}})^N \\ \text{Gram}_{L^2} \Phi^+ = \mathbf{1}_N}} \sup_{\substack{\Psi \in (P^- H^{\frac{1}{2}} \oplus \text{Span}(\Phi^+))^N \\ \text{Gram}_{L^2} \Psi = \mathbf{1}_N}} \mathcal{E}_c(\Psi).$$

Then $E(P^+)$ does not depend on P^+ and $\mathcal{E}_c(\Psi^{c,1}) \leq E(P^+)$.

Remark. In the case $N = 1$, $\mathcal{E}_c$ is the quadratic form $(\psi, H\psi)_{L^2}$ associated to the operator $H = H_c - Z\mu * \frac{1}{|x|}$. Then $E(\Lambda_c^+)$ coincides with the min-max level $\lambda_1(V)$ defined in [4], for $V = -Z\mu * \frac{1}{|x|}$. By Theorem 3.1 of [4], if $c > \frac{\pi/2 + 2/\pi}{2}$, then $\lambda_1(V)$ is the first positive eigenvalue of H .

Proof of Lemma 9.

The idea behind this lemma is inspired by [2]. Note that, under our assumptions, $E(P^+) < Nc^2(1 + K\varepsilon)$ for some $K > 0$ independent of c and ε . This follows from arguments similar to those used in the proof of Lemma 5.3 of [6]. In [6] the free energy projectors $\Lambda_c^\pm$ were used. With these projectors, it was seen that $E(\Lambda_c^+) < Nc^2$ (thanks to a careful choice of Φ^+). When P^+ is ε -close to Λ_c^+ , we then get $E(P^+) < Nc^2(1 + K\varepsilon)$.

To continue the proof of the lemma we perform a change of physical units. In mathematical language, this change corresponds to a dilation in space by the factor c , and to dividing the energies by c^2 . Let $(d_c\varphi)(x) = c^{3/2}\varphi(cx)$ and

$$\begin{aligned} \tilde{\mathcal{E}}_c(\Phi) &:= \frac{1}{c^2} \mathcal{E}_c(d_c\Phi) \\ (40) \quad &= \sum_{k=1}^N \int_{\mathbb{R}^3} \left(\varphi_k, (-i\alpha \cdot \nabla + \beta)\varphi_k \right) - \frac{Z}{c} \left(\tilde{\mu} * \frac{1}{|x|} \right) |\varphi_k|^2 \\ &\quad + \frac{1}{2c} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Phi(x)\rho_\Phi(y) - \|R_\Phi(x, y)\|^2}{|x - y|} d^3x d^3y \end{aligned}$$

where $\tilde{\mu}(E) = \mu(c^{-1}E)$ for any Borel subset E of $\mathbb{R}^3$.

The interest of this rescaled energy $\tilde{\mathcal{E}}_c$ is that for c large and $\text{Gram}_{L^2} \Psi \leq \mathbf{I}_N$, we have

$$(41) \quad \tilde{\mathcal{E}}_c(\Psi) = \sum_{k=1}^N \int_{\mathbb{R}^3} \left(\psi_k, (-i\alpha \nabla + \beta)\psi_k \right) + O\left(\frac{1}{c} \|\Psi\|_{(H^{1/2})^N}^2\right).$$

Let us denote $\tilde{P}^\pm := d_{c^{-1}} \circ P^\pm \circ d_c$, $\tilde{\Lambda}^\pm := d_{c^{-1}} \circ \Lambda_c^\pm \circ d_c = \chi_{\mathbb{R}^\pm}(-i\alpha \cdot \nabla + \beta)$. Note that $\tilde{\Lambda}^\pm$ does not depend on c . Now, P^+ is ε -close to Λ_c^+ if and only if

$$(42) \quad \left\{ \begin{aligned} &\left\| (-\Delta + 1)^{\frac{1}{4}} (\tilde{P}^+ - \tilde{\Lambda}^+) \psi \right\|_{L^2(\mathbb{R}^3, \mathbb{T}^4)} \\ &\leq \varepsilon \left\| (-\Delta + 1)^{\frac{1}{4}} \psi \right\|_{L^2(\mathbb{R}^3, \mathbb{T}^4)}, \quad \forall \psi \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{T}^4). \end{aligned} \right.$$

We denote $\Phi \bullet A$ the right action of an $N \times N$ matrix $A = (a_{kl})_{1 \leq k, l \leq N}$ on an N -uple $\Phi = (\varphi_1, \dots, \varphi_N) \in (L^2(\mathbb{R}^3, \mathbb{C}^4))^N$. More precisely,

$$(43) \quad (\Phi \bullet A) := \left(\sum_{k=1}^N a_{k1} \varphi_k, \dots, \sum_{k=1}^N a_{kN} \varphi_k \right).$$

Given $\Phi^+ = (\varphi_1^+, \dots, \varphi_N^+) \in (\tilde{P}^+ H^{1/2})^N$ such that $\text{Gram}_{L^2} \Phi^+ = \mathbf{I}_N$, and $\Phi^- \in (\tilde{P}^- H^{1/2})^N$, we define

$$(44) \quad \begin{aligned} g_{\Phi^+}(\Phi^-) &:= (\Phi^+ + \Phi^-) \bullet \left[\text{Gram}_{L^2}(\Phi^+ + \Phi^-) \right]^{-\frac{1}{2}} \\ &= (\Phi^+ + \Phi^-) \bullet \left[\mathbf{I}_N + \text{Gram}_{L^2} \Phi^- \right]^{-\frac{1}{2}}. \end{aligned}$$

We obtain a smooth map g_{Φ^+} , from $(\tilde{P}^- H^{\frac{1}{2}})^N$ to

$$\Sigma_{\Phi^+} := \left\{ \Psi \in \left(\tilde{P}^- H^{\frac{1}{2}} \oplus \text{Span}(\varphi_1^+, \dots, \varphi_N^+) \right)^N / \text{Gram}_{L^2} \Psi = \mathbf{I}_N \right\}.$$

In fact, the values of g_{Φ^+} lie in the following subset of Σ_{Φ^+} :

$$\Sigma'_{\Phi^+} := \left\{ \Psi \in \Sigma_{\Phi^+} / \text{Gram}_{L^2}(\tilde{P}^+ \Psi) > 0 \right\}.$$

Now, take an arbitrary $\Psi \in \Sigma'_{\Phi^+}$. Then there is an invertible $N \times N$ matrix B such that $\tilde{P}^+ \Psi = \Phi^+ \bullet B$. So we may write

$$\Psi \bullet B^{-1} = \Phi^+ + \tilde{P}^- \Psi \bullet B^{-1}.$$

As a consequence,

$$g_{\Phi^+}(\tilde{P}^- \Psi \bullet B^{-1}) = (\Psi \bullet B^{-1}) \bullet \left[\text{Gram}_{L^2}(\Psi \bullet B^{-1}) \right]^{-\frac{1}{2}}.$$

One easily computes

$$\text{Gram}_{L^2}(\Psi \bullet B^{-1}) = (B^*)^{-1} \left(\text{Gram}_{L^2} \Psi \right) B^{-1} = (B B^*)^{-1}.$$

Hence

$$g_{\Phi^+}(\tilde{P}^- \Psi \bullet B^{-1}) = (\Psi \bullet B^{-1}) \bullet (B B^*)^{1/2} = \Psi \bullet (B^{-1} (B B^*)^{1/2}),$$

and finally

$$\Psi = g_{\Phi^+}(\tilde{P}^- \Psi \bullet B^{-1}) \bullet U,$$

where $U := (B B^*)^{-1/2} B \in \mathcal{U}(N)$ is the unitary matrix appearing in the polar decomposition of B . So we have proved that

$$\Sigma'_{\Phi^+} = \bigcup_{\substack{\Phi^- \in (\tilde{P}^- H^{\frac{1}{2}})^N \\ U \in \mathcal{U}(N)}} g_{\Phi^+}(\Phi^-) \bullet U .$$

Now, $\mathcal{E}_c$ is invariant under the $\mathcal{U}(N)$ action “ $\bullet$ ”, and Σ'_{Φ^+} is dense in Σ_{Φ^+} for the norm of $(H^{1/2}(\mathbb{R}^3, \mathbb{C}^4))^N$. Hence

$$(45) \quad \sup_{\substack{\Psi \in (\tilde{P}^- H^{\frac{1}{2}} \oplus \text{Span}(\Phi^+))^N \\ \text{Gram}_{L_2} \Psi = \mathbf{I}_N}} \tilde{\mathcal{E}}_c(\Psi) = \sup_{\Phi^- \in (\tilde{P}^- H^{\frac{1}{2}})^N} \tilde{\mathcal{E}}_c(g_{\Phi^+}(\Phi^-)) .$$

We now prove Lemma 9 in three steps.

Step 1. Let $\Phi^+ \in (\tilde{P}^+ H^{1/2})^N$ be such that $\text{Gram}_{L_2} \Phi^+ = \mathbf{I}_N$ and such that $\tilde{\mathcal{E}}_c(\Phi^+) \leq N + \delta$, for some $\delta > 0$ small. For ε small and c large, there is a unique $\Phi^- \in (\tilde{P}^- H^{1/2})^N$ maximizing $\tilde{\mathcal{E}}_c \circ g_{\Phi^+}$ and lying in a small neighborhood of 0. If we denote $k(\Phi^+)$ this maximizer, the map k is smooth from

$$\mathcal{S}_\delta^+ = \left\{ \Phi^+ \in (\tilde{P}^+ H^{1/2})^N / \text{Gram}_{L_2} \Phi^+ = \mathbf{I}_N, \tilde{\mathcal{E}}_c(\Phi^+) \leq N + \delta \right\}$$

to $(\tilde{P}^- H^{1/2})^N$, and equivariant for the $\mathcal{U}(N)$ action.

Proof of Step 1. Take $r > 0$. For ε, δ small and c large, if $\Phi^+ \in \mathcal{S}_\delta^+$, $\Phi^- \in (\tilde{P}^- H^{1/2})^N$, and $\|\Phi^-\|_{H^{1/2}}$ is not smaller than r , then

$$\tilde{\mathcal{E}}_c(g_{\Phi^+}(\Phi^-)) < N - \delta ,$$

by (41). On the other hand, for c large enough, using (41) once again, one has

$$\tilde{\mathcal{E}}_c(g_{\Phi^+}(0)) = \tilde{\mathcal{E}}_c(\Phi^+) \geq N - \frac{\delta}{2} .$$

So, if we define $\mathcal{V}_r := \left\{ \Phi^- \in (\tilde{P}^- H^{1/2})^N / \|\Phi^-\|_{H^{1/2}} \leq r \right\}$, no maximizer of $\tilde{\mathcal{E}}_c \circ g_{\Phi^+}$ can be outside $\mathcal{V}_r$. Moreover, choosing r small, and then taking c large and ε small, the map

$$\Phi^- \in \mathcal{V}_r \longmapsto \tilde{\mathcal{E}}_c \circ g_{\Phi^+}(\Phi^-)$$

is strictly concave. Indeed, its second derivative at $\Phi^- \in \mathcal{V}_r$ is very close in norm to the negative form

$$\Psi^- \in (\tilde{P}^- H^{1/2})^N \longmapsto -2 \sum_{i=1}^N \|\psi_i^-\|_{H^{1/2}}^2 - 2 \sum_{1 \leq i, j \leq N} (\varphi_j^+, \varphi_i^+)_{H^{1/2}} (\psi_i^-, \psi_j^-)_{L^2}.$$

Step 1 immediately follows from these facts. $\square$

Step 2. *The min-max level $E(P^+)$ does not depend on P^+ .*

Proof of Step 2. Take two projectors P_1^+, P_2^+ , both ε -close to Λ_c^+ . For $i = 1, 2$, and $\Phi_i^+ \in (\tilde{P}_i^+ H^{1/2})^N$, with $\text{Gram}_{L^2} \Phi_i^+ = \mathbf{I}_N$ and $\tilde{\mathcal{E}}_c(\Phi_i^+) \leq N + \delta$, let

$$\begin{aligned} J^i(\Phi_i^+) &:= \max_{\substack{\Phi^- \in (\tilde{P}_i^- H^{1/2})^N \\ \text{Gram}_{L^2} \Phi^- = \mathbf{I}_N}} \tilde{\mathcal{E}}_c(g_{\Phi_i^+}^i(\Phi^-)) \\ (46) \quad &= \tilde{\mathcal{E}}_c \circ g_{\Phi_i^+}^i(k^i(\Phi_i^+)). \end{aligned}$$

Here, $g_{\Phi_i^+}^i$ and k^i are the maps associated to P_i^+ in Step 1.

By Ekeland's variational principle [5], there is a minimizing sequence $(\Phi_{1,n}^+)_{n \geq 0}$ for J^1 , such that $(J^1)'(\Phi_{1,n}^+) \xrightarrow{n \rightarrow +\infty} 0$ in $(H^{-1/2})^N$. Let $\Psi_n := g_{\Phi_{1,n}^+}^1(k^1(\Phi_{1,n}^+))$. Then Ψ_n is a Palais-Smale sequence for $\tilde{\mathcal{E}}_c$ in the manifold

$$\Sigma := \left\{ \Psi \in (H^{1/2})^N / \text{Gram}_{L^2} \Psi = \mathbf{I}_N \right\},$$

with $\tilde{\mathcal{E}}_c(\Psi_n) \geq N - \frac{\delta}{2}$, where $\delta > 0$ is the constant of the first step. So $\text{Gram}_{L^2}(\tilde{P}_2^+ \Psi_n) > 0$. We denote

$$(47) \quad \begin{cases} \Phi_{2,n}^+ := \tilde{P}_2^+ \Psi_n \bullet [\text{Gram}_{L^2}(\tilde{P}_2^+ \Psi_n)]^{-\frac{1}{2}}, \\ \Phi_{2,n}^- := \tilde{P}_2^- \Psi_n \bullet [\text{Gram}_{L^2}(\tilde{P}_2^+ \Psi_n)]^{-\frac{1}{2}}. \end{cases}$$

One easily checks that $\Psi_n = g_{\Phi_{2,n}^+}^2(\Phi_{2,n}^-)$. Since $\tilde{\mathcal{E}}_c(\Psi_n) \geq N - \frac{\delta}{2}$, we have $\|\Phi_{2,n}^-\|_{H^{1/2}} \leq r$, where $r > 0$ is the same as in the proof of step 1. Since Ψ_n is a Palais-Smale sequence for $\tilde{\mathcal{E}}_c$, the derivative of $\tilde{\mathcal{E}}_c \circ g_{\Phi_{2,n}^+}^2$ at the point

$\Phi_{2,n}^-$ converges to 0 as n goes to infinity. So, by the concavity properties of $\tilde{\mathcal{E}}_c \circ g_{\Phi_{2,n}^+}^2$ in the domain

$$\mathcal{V}_{2,r} := \left\{ \Phi^- \in \left(\tilde{P}_2^- H^{1/2} \right)^N / \|\Phi^-\|_{H^{1/2}} \leq r \right\}$$

(see the proof of step 1), we get

$$\|\Phi_{2,n}^- - k^2(\Phi_{2,n}^+)\|_{H^{1/2}} \xrightarrow{n \rightarrow +\infty} 0 \quad \text{and} \quad \tilde{\mathcal{E}}_c(\Psi_n) - J^2(\Phi_{2,n}^+) \xrightarrow{n \rightarrow +\infty} 0.$$

As a consequence,

$$E(P_1^+) = \inf_{\substack{\Phi_1^+ \in (\tilde{P}_1^+ H^{1/2})^N \\ \text{Gram}_{L^2} \Phi_1^+ = \mathbf{I}_N}} J^1(\Phi_1^+) \geq \inf_{\substack{\Phi_2^+ \in (\tilde{P}_2^+ H^{1/2})^N \\ \text{Gram}_{L^2} \Phi_2^+ = \mathbf{I}_N}} J^2(\Phi_2^+) = E(P_2^+).$$

Since 1, 2 play symmetric roles in the above arguments, we conclude that $E(P^+)$ does not depend on P^+ , for c large enough and ε small enough. $\square$

Step 3. $\mathcal{E}_c(\Psi^{c,1}) \leq E(\Lambda_c^+)$, where $\Psi^{c,1}$ is the first solution of (D-F) found in [E-S].

Proof of Step 3.

For c large enough, if $\Psi^- \in \Lambda_c^- H^{1/2}$ satisfies $\text{Gram}_{L^2} \Psi^- \leq \mathbf{I}_N$, it follows from Hardy's inequality that the map $\Psi^+ \rightarrow \mathcal{E}_c(\Psi^+ + \Psi^-)$ is strictly convex on

$$W(\Psi^-) := \{ \Psi^+ \in (\Lambda_c^+ H^{1/2})^N ; \text{Gram}_{L^2}(\Psi^+ + \Psi^-) \leq \mathbf{I}_N \}.$$

As a consequence, for an arbitrary N -dimensional subspace V of $\Lambda_c^+ H^{1/2}$, $S_V(\Psi^-) := \sup_{\Psi^+ \in W(\Psi^-) \cap V^N} \mathcal{E}_c(\Psi^+ + \Psi^-)$ is achieved by an extremal point Ψ_{max}^+ of the convex set $W(\Psi^-) \cap V^N$. Being extremal, Ψ_{max}^+ must satisfy the constraints $\text{Gram}_{L^2}(\Psi_{max}^+ + \Psi^-) = \mathbf{I}_N$.

So we have

$$\sup_{\substack{\Psi \in (\Lambda_c^- H^{1/2} \oplus V)^N \\ \text{Gram}_{L^2} \Psi \leq \mathbf{I}_N}} \mathcal{E}_c(\Psi) = \sup_{\substack{\Psi^- \in (\Lambda_c^- H^{1/2})^N \\ \text{Gram}_{L^2} \Psi^- \leq \mathbf{I}_N}} S_V(\Psi^-) = \sup_{\substack{\Psi \in (\Lambda_c^- H^{1/2} \oplus V)^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N}} \mathcal{E}_c(\Psi).$$

By proposition 2,

$$\mathcal{E}_c(\Psi^{c,1}) \leq \sup_{\substack{\Psi \in (\Lambda_c^- H^{1/2} \oplus V)^N \\ \text{Gram}_{L^2} \Psi \leq \mathbf{I}_N}} \mathcal{E}_c(\Psi) .$$

Finally we get, for c large,

$$\mathcal{E}_c(\Psi^{c,1}) \leq \inf_{\substack{\Phi^+ \in (\Lambda_c^+ H^{1/2})^N \\ \text{Gram}_{L^2} \Phi^+ = \mathbf{I}_N}} \sup_{\substack{\Psi \in (\Lambda_c^- H^{1/2} \oplus \text{Span}(\Phi^+))^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N}} \mathcal{E}_c(\Psi) = E(\Lambda_c^+) .$$

(The correspondence between Φ^+ and V is $V = \text{Span}(\Phi^+)$). This ends the proof of Step 3 and of Lemma 9. $\square$

Thanks to Lemma 9, we are able to write the following inequalities for c large, and P^+ ε -close to Λ_c^+ , ε small :

$$\begin{aligned} E(P^+) = E(\Lambda_c^+) &\geq \mathcal{E}_c(\Psi^{c,1}) \\ &\geq \inf_{\substack{\Psi \text{ solution of } (DF_c) \\ \Lambda_\Psi^- \Psi = 0}} \mathcal{E}_c(\Psi) \\ (48) \quad &\geq \inf_{\substack{\Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_\Psi^- \Psi = 0}} \mathcal{E}_c(\Psi) \end{aligned}$$

As announced before, we now give some important examples of projectors ε -close to Λ_c^+ :

Lemma 10 . *Fix N, Z , and take c large enough. Then, for any $\Phi \in (H^{1/2})^N$, with $\text{Gram}_{L^2} \Phi \leq \mathbf{I}_N$, the projector $\Lambda_\Phi^+ = \chi_{(0,+\infty)}(\overline{H}_{c,\Phi})$ is ε -close to Λ_c^+ .*

Proof of Lemma 10. We adapt a method of Griesemer, Lewis, Siedentop [7] to the Hamiltonian $\overline{H}_{c,\Phi}$. Once again, it is more convenient to work in a system of units such that $\overline{H}_{c,\Phi}$ becomes

$$\begin{aligned} \tilde{H}_{c,\tilde{\Phi}} : \psi \mapsto d_{c-1} \circ \overline{H}_{c,\Phi} \circ d_c(\psi) &= \left(-i\alpha \cdot \nabla + \beta \right) \psi - \frac{Z}{c} \left(\tilde{\mu} * \frac{1}{|x|} \right) \psi \\ &\quad + \frac{1}{c} \left(\rho_{\tilde{\Phi}} * \frac{1}{|x|} \right) \psi - \frac{1}{c} \int_{\mathbb{R}^3} R_{\tilde{\Phi}}(x, y) \frac{\psi(y)}{|x-y|} dy \end{aligned}$$

with $\tilde{\mu}(E) = \mu(c^{-1}E)$, $\tilde{\Phi}(x) = c^{-3/2}\Phi(c^{-1}x)$.

Denoting $H_1 := -i\alpha \cdot \nabla + \beta$, $\tilde{\Lambda}_{\tilde{\Phi}}^+ := \chi_{(0,\infty)}(\tilde{H}_{c,\tilde{\Phi}})$, $\tilde{\Lambda}^+ := \chi_{(0,\infty)}(H_1)$, $K_{\tilde{\Phi}} := c(\tilde{H}_{c,\tilde{\Phi}} - H_1)$, we find, as in the proof of Lemma 1 of [7],

$$(\tilde{\Lambda}_{\tilde{\Phi}}^+ - \tilde{\Lambda}^+)\psi = \frac{1}{\pi c} \int_0^{+\infty} dz [H_1^2 + z^2]^{-1} (H_1 K_{\tilde{\Phi}} \tilde{H}_{c,\tilde{\Phi}} - z^2 K_{\tilde{\Phi}}) [(\tilde{H}_{c,\tilde{\Phi}})^2 + z^2]^{-1} \psi,$$

and for any $\chi \in L^2(\mathbb{R}^3, \mathbb{C}^4)$, following [7] (proof of Lemma 3), we get

$$\left(\chi, (-\Delta + 1)^{1/4} (\tilde{\Lambda}_{\tilde{\Phi}}^+ - \tilde{\Lambda}^+) \psi \right)_{L^2} \leq \frac{M}{c} \|\chi\|_{L^2} \|(-\Delta + 1)^{1/4} \psi\|_{L^2}$$

for c large enough (M is a constant independent of c). As a consequence, if c is large enough and bigger than $\frac{M}{\varepsilon}$, then $\Lambda_{\tilde{\Phi}}^+$ is ε -close to Λ_c^+ . This ends the proof of Lemma 10. $\square$

Now, to end the proof of Theorem 6, we just need the following result :

Lemma 11 . *Fix N, Z and take $c > 0$ large enough. If $\Phi \in (H^{1/2})^N$, $\text{Gram}_{L^2} \Phi = \mathbf{I}_N$, $\Lambda_{\Phi}^- \Phi = 0$ and $\mathcal{E}_c(\Phi) \leq Nc^2$, then*

$$\mathcal{E}_c(\Phi) = \max \left\{ \mathcal{E}_c(\Psi) ; \Psi \in \left[\Lambda_{\Phi}^- H^{1/2} \oplus \text{Span}(\Phi) \right]^N, \text{Gram}_{L^2} \Psi = \mathbf{I}_N \right\}.$$

Proof of Lemma 11. If $\Lambda_{\Phi}^- \Phi = 0$ and $\text{Gram}_{L^2} \Phi = \mathbf{I}_N$, then 0 is a critical point of the map

$$\Psi^- \in \left(\Lambda_{\Phi}^- H^{1/2} \right)^N \longmapsto \mathcal{E}_c(g_{\Phi}(\Psi^-)),$$

with $g_{\Phi}(\Psi^-) = (\Phi + \Psi^-) \bullet \left[\mathbf{I}_N + \text{Gram}_{L^2} \Psi^- \right]^{-1/2}$. Take $\varepsilon > 0$ small. By Lemma 10, $\Lambda_{\tilde{\Phi}}^+$ is ε -close to Λ_c^+ for c large enough. From the proof of Lemma 9 (Step 1), there is a unique critical point of $\mathcal{E}_c \circ g_{\Phi}$ in a small neighborhood $\mathcal{V}_r$ of 0 in $\Lambda_{\tilde{\Phi}}^-(H^{1/2})$ and this critical point is the unique maximizer of $\mathcal{E}_c \circ g_{\Phi}$ in $\Lambda_{\tilde{\Phi}}^-(H^{1/2})$. So, 0 is this maximizer. This proves Lemma 11. $\square$

Let us explain why Theorem 6 is now proved. We know that, for c large enough,

$$Nc^2 > E(\Lambda_c^+) \geq \mathcal{E}_c(\Psi^{c,1}) \geq \begin{cases} \inf_{\substack{\Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_{\Psi}^- \Psi = 0}} \mathcal{E}_c(\Psi) \end{cases},$$

hence

$$\inf_{\left\{ \begin{array}{l} \Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_{\Psi}^- \Psi = 0 \end{array} \right.} \mathcal{E}_c(\Psi) = \inf_{\left\{ \begin{array}{l} \Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_{\Psi}^- \Psi = 0 \\ \mathcal{E}_c(\Psi) \leq Nc^2 \end{array} \right.} \mathcal{E}_c(\Psi) .$$

Take $\varepsilon > 0$. By Lemma 10, for any $\Psi \in (H^{1/2})^N$ with $\text{Gram}_{L^2} \Psi = \mathbf{I}_N$, the projector Λ_{Ψ}^+ is ε -close to Λ_c^+ , if c is large. Hence $E(\Lambda_{\Psi}^+) = E(\Lambda_c^+)$ (by Lemma 9), if we have chosen ε small enough. But if Ψ also satisfies $\Lambda_{\Psi}^- \Psi = 0$ and $\mathcal{E}_c(\Psi) \leq Nc^2$, then, from Lemma 11 and from the definition of $E(\Lambda_{\Psi}^+)$, we have $E(\Lambda_c^+) = E(\Lambda_{\Psi}^+) \leq \mathcal{E}_c(\Psi)$. So

$$E(\Lambda_c^+) \leq \inf_{\left\{ \begin{array}{l} \Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_{\Psi}^- \Psi = 0 \end{array} \right.} \mathcal{E}_c(\Psi) ,$$

and therefore,

$$E(\Lambda_c^+) = \mathcal{E}_c(\Psi^{c,1}) = \inf_{\left\{ \begin{array}{l} \Psi \in (H^{1/2})^N \\ \text{Gram}_{L^2} \Psi = \mathbf{I}_N \\ \Lambda_{\Psi}^- \Psi = 0 \end{array} \right.} \mathcal{E}_c(\Psi)$$

and Theorem 6 is proved. $\square$

Acknowledgements. The authors are grateful to Boris Buffoni for explaining them the work [2], and suggesting that it might be useful in the study of the Dirac-Fock functional. The proof of Lemma 9 is inspired by this paper.

References

- [1] V. Bach, E.H. Lieb, M. Loss, J.P. Solovej. There are no unfilled shells in unrestricted Hartree-Fock theory. Phys. Rev. Lett. **72**(19) (1994), p. 2981-2983.
- [2] B. Buffoni, L. Jeanjean. Minimax characterization of solutions for a semi-linear elliptic equation with lack of compactness. Ann. Inst. H. Poincaré **10**(4) (1993), p. 377-404.

- [3] V.I. Burenkov, W.D. Evans. On the evaluation of the norm of an integral operator associated with the stability of one-electron atoms. Proc. Roy. Soc. Edinburgh, sect. A **128** (5) (1998), p. 993-1005.
- [4] J. Dolbeault, M.J. Esteban, E. Séré. Variational characterization for eigenvalues of Dirac operators. Cal. Var. and PDE **10** (4) (2000), p. 321-347.
- [5] I. Ekeland. On the variational principle. J. Math. Anal. **47** (1974), p. 324-353.
- [6] M.J. Esteban, E. Séré. Solutions for the Dirac-Fock equations for atoms and molecules. Comm. Math. Phys. **203** (1999), p. 499-530.
- [7] M. Griesemer, R.T. Lewis, H. Siedentop. A minimax principle for eigenvalues in spectral gaps : Dirac operators with Coulomb potentials. Doc. Math. **4** (1999), p. 275-283.
- [8] I.W. Herbst. Spectral theory of the operator $(p^2 + m^2)^{1/2} - ze^2/r$. Comm. Math. Phys. **53** (1977), p. 285-294.
- [9] Y.-K. Kim. Relativistic self-consistent field theory for closed-shell atoms. Phys. Rev. **154** (1967), p. 17-39.
- [10] E. H. Lieb, B. Simon. The Hartree-Fock theory for Coulomb systems. Comm. Math. Phys., **53** (1977), p. 185-194.
- [11] P.-L. Lions. Solutions of Hartree-Fock equations for Coulomb systems. Comm. Math. Phys. **109** (1987), p. 33-97.
- [12] A. Messiah. *Mécanique quantique*. Dunod, 1965.
- [13] E. Paturel. Solutions of the Dirac equations without projector. To appear in A.H.P.
- [14] B. Thaller. *The Dirac equation*. Springer-Verlag, 1992.
- [15] C. Tix. Strict positivity of a relativistic Hamiltonian due to Brown and Ravenhall. Bull. London Math. Soc. **30**(3) (1998), p. 283-290.
- [16] C. Tix. Lower bound for the ground state energy of the no-pair Hamiltonian. Phys. Lett. B **405** (1997), p. 293-296.