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.

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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

$$H_c \;=\; -i\,c\,\alpha\cdot\nabla + c^2\beta, \tag{1}$$

where $c > 0$ is the speed of light in the above units, $\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}$, $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}$ $(k = 1,2,3)$ 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

$$(\mathrm{DF}_c)\quad \begin{cases} \overline{H}_{c,\Psi}\ \psi_k := H_c\ \psi_k - Z(\mu * \dfrac{1}{|x|})\psi_k + (\rho_\Psi * \dfrac{1}{|x|})\psi_k \\ \qquad - \displaystyle\int_{\mathbb{R}^3} \frac{R_\Psi(x,y)\,\psi_k(y)}{|x-y|}\,dy = \varepsilon_k^c\,\psi_k \quad (k = 1,...N), \\ \\ \mathrm{Gram}_{\mathrm{L}^2}\,\Psi = \mathbb{1}_{\mathrm{N}} \quad (\text{i.e } \int_{\mathbb{R}^3} \psi_{\mathrm{k}}^*\psi_{\mathrm{l}} = \delta_{\mathrm{kl}}\ ,\ 1 \le \mathrm{k},\mathrm{l} \le \mathrm{N}). \end{cases}$$

Here, $\Psi = (\psi_1,\cdots,\psi_N)$, 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, $1 \le p < 3/2$), and

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

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 $\mathrm{Gram}_{L^2}\,\Psi$ is defined by the usual formulas

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

Finally, $\varepsilon_1^c \leq ... \leq \varepsilon_N^c$ 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

$$\mathcal{E}_c(\Psi) = \sum_{k=1}^{N} \int_{\mathbb{R}^3} \psi_k^* H_c \psi_k - Z\Big(\mu * \frac{1}{|x|}\Big)\psi_k^*\psi_k$$

$$+\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\Psi(x)\rho_\Psi(y) - \mathrm{tr}\Big(R_\Psi(x,y)R_\Psi(y,x)\Big)}{|x-y|}\,dxdy$$

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$_c$), $\Big\{\Psi^{c,j}\Big\}_{j\geq 1} \subset \Big(H^{1/2}(\mathbb{R}^3)\Big)^N$, such that*

(i) $0 < \mathcal{E}_c(\Psi^{c,j}) \; < \; Nc^2$,

(ii) $\lim_{j\to+\infty} \mathcal{E}_c(\Psi^{c,j}) \; = \; Nc^2$,

(iii) $0 < c^2 - \mu_j < \varepsilon_1^{c,j} \leq ... \leq \varepsilon_N^{c,j} < c^2 - m_j$, *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 $c = 137.037...$ 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 $c = 137.037...$, 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 : $\widehat{\Lambda_c^\pm \psi}(\xi) = \hat{\Lambda}_c^\pm(\xi)\ \hat{\psi}(\xi)$, with

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

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*

$$E^c_{j,DF} := \mathcal{E}_c(\Psi^{c,j}) \leq \sup_{\substack{\Psi \in (E_c^- \oplus V)^N \\ \mathrm{Gram}_{\mathrm{L}^2}\,\Psi \leq \mathbf{1}_{\mathrm{N}}}} \mathcal{E}_c(\Psi). \tag{5}$$

In the present paper, we prove three main theorems. We first consider a sequence $c_n \to +\infty$ and a sequence $\{\Psi^n\}_n$ of solutions of (DF_{c_n}). For all n, $\Psi^n = (\psi_1^n, ..., \psi_N^n)$, 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

$$-\infty < \varliminf_{n\to+\infty} (\varepsilon_1^n - c_n^2) \leq \varlimsup_{n\to+\infty} (\varepsilon_N^n - c_n^2) < 0\,. \tag{6}$$

A (column) vector $\psi \in \mathbb{C}^4$ can be written in block form $\psi = \binom{\varphi}{\chi}$ 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 $\psi_k^n = \binom{\varphi_k^n}{\chi_k^n}$ with φ_k^n and χ_k^n in $H^1(\mathbb{R}^3, \mathbb{C}^2)$. Finally, Ψ^n splits as $\binom{\Phi^n}{\chi^n}$, where $\Phi^n := (\varphi_1^n, ..., \varphi_N^n)$ and $\chi^n := (\chi_1^n, ..., \chi_N^n)$. Our first result is that $\Psi^n = \binom{\Phi^n}{\chi^n}$ has a subsequence converging, in H^1 norm, towards $\bar\Psi = \binom{\bar\Phi}{0}$, where $\bar\Phi = (\bar\varphi_1, \cdots, \bar\varphi_N) \in \Big(H^1(\mathbb{R}^3, \mathbb{C}^2)\Big)^N$ is a solution of the Hartree-Fock equations:

$$
\text{(HF)} \qquad \begin{cases} \mathcal{H}_\Phi \varphi_k = -\dfrac{\Delta \varphi_k}{2} - Z\Big(\mu * \dfrac{1}{|x|}\Big)\varphi_k + \Big(\rho_\Phi * \dfrac{1}{|x|}\Big)\varphi_k \\ \qquad\qquad - \displaystyle\int_{\mathbb{R}^3} \frac{R_\Phi(x,y)\varphi_k(y)}{|x-y|} dy = \bar\lambda_k \varphi_k, \quad k = 1, ...N, \\ \\ \displaystyle\int_{\mathbb{R}^3} \varphi_k^* \varphi_l \, dx = \delta_{kl} \ , \quad \bar\lambda_k = \lim_{n\to+\infty} (\varepsilon_k^n - c_n^2) \ . \end{cases}
$$

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 $\Big(H^1(\mathbb{R}^3, \mathbb{C}^2)\Big)^N$ of the Hartree-Fock energy:

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

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

Theorem 3 . *Let $N < Z + 1$. Consider a sequence $c_n \to +\infty$ and a sequence $\{\Psi^n\}_n$ of solutions of (DF_{c_n}), i.e. $\Psi^n = (\psi_1^n, \cdots, \psi_N^n)$, each ψ_k^n being in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, with $\displaystyle\int_{\mathbb{R}^3} \psi_k^* \psi_l \, dx = \delta_{kl}$ 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), $\bar\Phi = (\bar\varphi_1, \cdots, \bar\varphi_N)$, with negative multipliers, $\bar\lambda_1, ..., \bar\lambda_N$, such that, after extraction of a subsequence,*

$$
\lambda_k^n := \varepsilon_k^n - (c_n)^2 \quad \underset{n\to+\infty}{\longrightarrow} \quad \bar\lambda_k \ , \quad k = 1, ..., N \ , \tag{8}
$$

$$(9) \qquad \psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix} \underset{n\to+\infty}{\longrightarrow} \begin{pmatrix} \bar\varphi_k \\ 0 \end{pmatrix} \ \text{ in } \ H^1(\mathbb{R}^3,\mathbb{C}^2)\times H^1(\mathbb{R}^3,\mathbb{C}^2),$$

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

and

$$(11) \qquad \mathcal{E}_{c_n}(\Psi^n) - Nc_n^2 \underset{n\to+\infty}{\longrightarrow} \mathcal{E}_{HF}(\bar\Phi).$$

As a particular case, we have

Corollary 4 . *If $c_n \to +\infty$ 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,*

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

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

and $\bar\Phi^j = \left(\bar\varphi_1^j,\cdots,\bar\varphi_n^j\right)$ is a solution of the Hartree-Fock equations with multipliers $\bar\lambda_1^j,\cdots,\bar\lambda_N^j$. Moreover,

$$(14) \qquad \mathcal{E}_{c_n}(\Psi^{c_n,j}) - Nc_n^2 \underset{n\to+\infty}{\longrightarrow} \mathcal{E}_{HF}(\bar\Phi^j).$$

Particular solutions of the Hartree-Fock equations are the minimizers of $\mathcal{E}_{HF}(\Phi)$ under the constraints $\mathrm{Gram}_{L^2}\,\Phi = \mathbb{1}_N$. 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 $E^c_{1,DF}$, can be considered, in some (weak) sense, as a ground state for (DF_c). Indeed, $E^c_{1,DF} - Nc^2$ 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,*

$$(15)\quad E^c_{1,DF} := \mathcal{E}_c(\Psi^{c,1}) = \min_{\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbf{1}_{\mathrm{N}}} \mathcal{E}_{HF}(\Phi) + Nc^2 + o(1)_{c\to+\infty}$$

Moreover, for any subsequence $\{\Psi^{c_n,1}\}_n$ converging in $\left(H^1(\mathbb{R}^3,\mathbb{C}^4)\right)^N$ to some $\binom{\bar\Phi^1}{0}$, $\bar\Phi^1$ is a ground state of the Hartree-Fock model, i.e.

$$(16)\qquad \mathcal{E}_{HF}(\bar\Phi^1) = \min_{\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbf{1}_{\mathrm{N}}} \mathcal{E}_{HF}(\Phi).$$

Furthermore, for c large, the eigenvalues corresponding to $\Psi^{c,1}$ in (DF_c), $\varepsilon^{c,1}_1,\dots,\varepsilon^{c,1}_N$ 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 $\varepsilon^{c,1}_N$.

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:*

$$(17)\qquad \inf\{\mathcal{E}_c(\Psi)\,;\ \mathrm{Gram}_{\mathrm{L}^2}\Psi = \mathbf{1}_{\mathrm{N}}\ ,\ \Lambda^-_\Psi\,\Psi = 0\ \}$$

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

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 $\left(H^1(\mathbb{R}^3)\right)^N$. This follows from the fact that for ν small, the operator $H_1 - \dfrac{\nu}{|x|}$ 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 $0 \le \varepsilon_k^c \le c^2$ $(k = 1, \dots, N)$, then $\Psi^c \in (H^1(\mathbb{R}^3, \mathbb{C}^4))^N$, and the following estimate holds*

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

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

Proof. The normalization constraint $\mathrm{Gram}_{L^2}\Psi^c = \mathbb{I}_{\mathrm{N}}$ implies

$$||\Psi^c||_2^2 \ =\ N\ . \tag{18}$$

Using the (DF_c) equation and the standard Hardy inequality

$$\int_{\mathbb{R}^3} \frac{u^2}{|x|^2} \ \le\ 4 \int_{\mathbb{R}^3} |\nabla u|^2\,, \tag{19}$$

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

$$(H_c\Psi^c, H_c\Psi^c) = c^4||\Psi^c||_2^2 + c^2||\nabla\Psi^c||_2^2 \tag{20}$$

$$\le c^4||\Psi^c||_2^2 + \ell(Z^2+N^2)\,||\nabla\Psi^c||_2^2 + \ell c^2 \max(N,Z)\,||\nabla\Psi^c||_2\ ,$$

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

Proof of Theorem 3. Let us split the spinors $\psi_k^n : \mathbb{R}^3 \to \mathbb{C}^4$ in blocks of upper and lower components : $\psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix}$, with $\varphi_k^n,\ \chi_k^n : \mathbb{R}^3 \to \mathbb{C}^2$. We denote $L := -i\,(\sigma\cdot\nabla)$. Then we can rewrite (DF_{c_n}) in the following way:

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

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

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

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

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

The estimate (23) together with Lemma 7 implies

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

Combining this with (22), we obtain

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

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

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

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

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

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

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

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 $\overline{\lim}_{n\to+\infty}\lambda_k^n < 0$. 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 $\bar\Phi = (\bar\varphi_1,\cdots,\bar\varphi_N)$, a solution of the Hartree-Fock equations

$$\left\{\begin{array}{l} \mathcal{H}_{\bar\Phi}\bar\varphi_k = \bar\lambda_k\ \bar\varphi_k\ , \quad k=1,...N \\[2ex] \displaystyle\int_{\mathbb{R}^3}\bar\varphi_k^*\ \bar\varphi_l \ = \ \delta_{kl}\ , \end{array}\right.$$

where $\bar\lambda_k = \lim\limits_{n'\to+\infty}\lambda_k^{n'}$.

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

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

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. □

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 $\binom{\bar{\Phi}^1}{0}$, and $\Big(\mathcal{E}_{c_n}(\Psi^{c_n,1}) - N(c_n)^2\Big)$ converges to $\mathcal{E}_{HF}(\bar{\Phi}^1)$. As a consequence,

$$\underline{\lim}_{c\to+\infty} \Big(\mathcal{E}_c(\Psi^{c,1}) - Nc^2\Big) \;\geq\; \inf_{\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbf{I}_{\mathrm{N}}} \mathcal{E}_{HF}(\Phi). \tag{28}$$

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

$$\overline{\lim}_{c\to+\infty} \Big(\mathcal{E}_c(\Psi^{c,1}) - Nc^2\Big) \;\leq\; \inf_{\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbf{I}_{\mathrm{N}}} \mathcal{E}_{HF}(\Phi). \tag{29}$$

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

$$V_c := \mathrm{Span}\ \{\Lambda_c^+\tbinom{\varphi_1}{0}, ..., \Lambda_c^+\tbinom{\varphi_N}{0}\}\ . \tag{30}$$

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

$$\lim_{c\to+\infty} \|\Lambda_c^-\tbinom{\varphi_k}{0}\|_{H^1} \;=\; 0\ . \tag{31}$$

So, for c sufficiently large, we have

$$\dim V_c \;=\; N\ . \tag{32}$$

Hence, by (5),

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

Let $\Psi^+ \in (E_c^+)^N$, $\Psi^- \in (E_c^-)^N$ such that $\mathrm{Gram}_{L^2}(\Psi^+ + \Psi^-) \leq \mathbf{I}_{\mathrm{N}}$. 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

$$\mathcal{E}_c(\Psi^+ + \Psi^-) \;\leq\; \mathcal{E}_c(\Psi^+) + \mathcal{E}_c^{'}(\Psi^+)\cdot\Psi^- - \frac{1}{4}\sum_{k=1}^{N}(\psi_k^-\,,\sqrt{-c^2\Delta + c^4}\;\psi_k^-)$$

$$\leq\; \mathcal{E}_c(\Psi^+) + M||\Psi^-||_{L^2} - \frac{c^2}{4}||\Psi^-||^2_{L^2}\,, \tag{34}$$

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

$$E^c_{1,DF} \;\leq\; \sup_{\Psi^+\in D(V_c)} \mathcal{E}_c(\Psi^+) + \circ(1)_{c\to+\infty}\,, \tag{35}$$

where $D(V_c) := \Big\{\Psi^+ \in (V_c)^N\;;\;\mathrm{Gram}_{\mathrm{L}^2}\Psi^+ \leq \mathbb{I}_{\mathrm{N}}\Big\}$.

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

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

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, $\sup\limits_{\Psi^+\in D(V_c)} \mathcal{E}_c(\Psi^+)$ 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

$$\mathrm{Gram}_{\mathrm{L}^2}\Psi^+_{max} = \mathbb{I}_{\mathrm{N}}\;. \tag{36}$$

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 , $\psi^+_{l,max} \;=\; \sum\limits_{1\leq k\leq N} a_{kl}\;\Lambda_c^+\binom{\varphi_k}{0}$. Then

$$A^*\;\mathrm{Gram}_{\mathrm{L}^2}\Big(\Lambda_c^+\tbinom{\Phi}{0}\Big)\,A \;=\; \mathrm{Gram}_{\mathrm{L}^2}\Psi^+_{max} = \mathbb{I}_{\mathrm{N}}\;. \tag{37}$$

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 $\mathrm{Gram}_{\mathrm{L}^2}\Phi = \mathbb{I}_{\mathrm{N}}$, we see, from (31), that $\mathrm{Gram}_{L^2}(\Lambda_c^+\binom{\Phi}{0}) = \mathbb{I}_N + \mathrm{o}(1)$. So (37) implies $A^2 = \mathbb{I}_N + \mathrm{o}(1)$, hence $A = \mathbb{I}_N + \mathrm{o}(1)$. Combining this with (31), we get

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

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

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

Finally, (35) and (38) imply

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

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 $\varepsilon_k^{c,1}$, $k = 1, \dots, N$, being the smallest eigenvalues of the operator $\overline{H}_{c,\Psi^{c,1}}$ for c large. By Corollary 4, we can translate this statement in the language of sequences. We take a sequence $c_n \to +\infty$ such that $\{\Psi^{c_n,1}\}_n$ converges in $\left(H^1(\mathbb{R}^3, \mathbb{C}^4)\right)^N$ 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

$$0 < \varepsilon_1^n \leq \ldots \leq \varepsilon_N^n < (c_n)^2 , \quad \bar\lambda_1 \leq \ldots \leq \bar\lambda_N < 0 , \quad \bar\lambda_k = \lim_{n\to+\infty}(\varepsilon_k^n - (c_n)^2) .$$

Let us denote $e_1^n \leq \ldots \leq e_i^n \leq \cdots$ the sequence of eigenvalues of $\overline{H}_n$, in the interval $(0, c_n^2)$, counted with multiplicity. Similarly, we shall denote $\bar\nu_1 \leq \ldots \leq \bar\nu_i \leq \cdots$ 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

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

converges in norm towards the operator $L(z)\ :\ \binom{\varphi}{\chi}\to\binom{\bar{R}(z)\varphi}{0}$, where $\bar{R}(z):=\Big(z\,I-\mathcal{H}_\infty\Big)^{-1}$ is the resolvent of $\mathcal{H}_\infty$. So, by the standard spectral theory, $\lim\limits_{n\to+\infty}(e_i^n-(c_n)^2)=\bar{\nu}_i$ 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 $H^{\frac12}(\mathbb{R}^3,\mathbb{C}^4)$ is a bounded operator on $H^{\frac12}(\mathbb{R}^3,\mathbb{C}^4)$.*
Given $\varepsilon>0$, P^+ is ε-close to Λ_c^+ if and only if, for all $\psi\in H^{\frac12}(\mathbb{R}^3,\mathbb{C}^4)$,

$$\left\|\Big(-c^2\Delta+c^4\Big)^{\frac14}\Big(P^+-\Lambda_c^+\Big)\psi\right\|_{L^2(\mathbb{R}^3,\mathbb{C}^4)}\leq\varepsilon\,\left\|\Big(-c^2\Delta+c^4\Big)^{\frac14}\psi\right\|_{L^2(\mathbb{R}^3,\mathbb{C}^4)}.$$

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 $P^-=\mathbb{1}_{L^2}-\mathrm{P}^+$, and define*

$$E(P^+):=\inf_{\substack{\Phi^+\in(P^+H^{\frac12})^N\\ \mathrm{Gram}_{L^2}\Phi^+=\mathbb{1}_N}}\ \sup_{\substack{\Psi\in(P^-H^{\frac12}\oplus\mathrm{Span}(\Phi^+))^N\\ \mathrm{Gram}_{L^2}\Psi=\mathbb{1}_N}}\mathcal{E}_c(\Psi)\ .$$

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 $c > \dfrac{\pi/2 + 2/\pi}{2}$, 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

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

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

The interest of this rescaled energy $\widetilde{\mathcal{E}}_c$ is that for c large and $\mathrm{Gram}_{L^2}\Psi \leq \mathbb{1}_N$, we have

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

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

$$
(42) \quad \begin{cases}
\left\|\Big(-\Delta+1\Big)^{\frac14}\Big(\widetilde{P}^+ - \widetilde{\Lambda}^+\Big)\psi\right\|_{L^2(\mathbb{R}^3,\mathbb{C}^4)} \\
\qquad\qquad \leq \varepsilon \left\|\Big(-\Delta+1\Big)^{\frac14}\psi\right\|_{L^2(\mathbb{R}^3,\mathbb{C}^4)}, \quad \forall \psi \in H^{\frac12}(\mathbb{R}^3, \mathbb{C}^4).
\end{cases}
$$

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

$$(\Phi \bullet A) := (\sum_{k=1}^{N} a_{k1}\varphi_k, \ldots, \sum_{k=1}^{N} a_{kN}\varphi_k) \ . \tag{43}$$

Given $\Phi^+ = (\varphi_1^+, \ldots, \varphi_N^+) \in \left(\widetilde{P}^+ H^{1/2}\right)^N$ such that $\mathrm{Gram}_{\mathrm{L}^2} \Phi^+ = \mathbb{1}_{\mathrm{N}}$, and $\Phi^- \in \left(\widetilde{P}^- H^{1/2}\right)^N$, we define

$$\begin{aligned} g_{_{\Phi^+}}(\Phi^-) \ &:= \ (\Phi^+ + \Phi^-) \bullet \left[\mathrm{Gram}_{\mathrm{L}^2} \ (\Phi^+ + \Phi^-)\right]^{-\frac{1}{2}} \\ &= \ (\Phi^+ + \Phi^-) \bullet \left[\mathbb{1}_{\mathrm{N}} + \mathrm{Gram}_{\mathrm{L}^2} \ \Phi^-\right]^{-\frac{1}{2}} \ . \end{aligned} \tag{44}$$

We obtain a smooth map $g_{_{\Phi^+}}$, from $\left(\widetilde{P}^- \ H^{\frac{1}{2}}\right)^N$ to

$$\Sigma_{_{\Phi^+}} := \left\{\Psi \in \left(\widetilde{P}^- H^{\frac{1}{2}} \oplus \mathrm{Span}\,(\varphi_1^+, \ldots, \varphi_N^+)\right)^N / \ \mathrm{Gram}_{\mathrm{L}^2}\Psi \ = \ \mathbb{1}_{\mathrm{N}}\right\} \ .$$

In fact, the values of $g_{_{\Phi^+}}$ lie in the following subset of $\Sigma_{_{\Phi^+}}$:

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

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

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

As a consequence,

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

One easily computes

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

Hence

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

and finally

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

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

$$\Sigma'_{\Phi^+} = \bigcup_{\substack{\Phi^- \in (\widetilde{P}^- H^{\frac12})^N \\ U \in \mathcal{U}(N)}} g_{\Phi^+}(\Phi^-) \bullet U\,.$$

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

$$\sup_{\substack{\Psi \in (\widetilde{P}^- H^{\frac12} \oplus \mathrm{Span}(\Phi^+))^N \\ \mathrm{Gram}_{L^2}\Psi = \mathbb{1}_N}} \widetilde{\mathcal{E}}_c(\Psi) = \sup_{\Phi^- \in (\widetilde{P}^- H^{\frac12})^N} \widetilde{\mathcal{E}}_c\Big(g_{\Phi^+}(\Phi^-)\Big)\,. \tag{45}$$

We now prove Lemma 9 in three steps.

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

$$\mathcal{S}^+_\delta = \left\{\Phi^+ \in \left(\widetilde{P}^+ H^{1/2}\right)^N / \,\mathrm{Gram}_{L^2}\,\Phi^+ = \mathbb{1}_N\,,\ \widetilde{\mathcal{E}}_c(\Phi^+) \le \mathrm{N} + \delta\right\}$$

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

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

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

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

$$\widetilde{\mathcal{E}}_c\Big(g_{\Phi^+}(0)\Big) = \widetilde{\mathcal{E}}_c(\Phi^+) \ge N - \frac{\delta}{2}\,.$$

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

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

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

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

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 $\Phi_i^+ \in \left(\widetilde{P}_i^+ H^{1/2}\right)^N$, with $\mathrm{Gram}_{\mathrm{L}^2}\Phi_i^+ = \mathbb{1}_{\mathrm{N}}$ and $\widetilde{\mathcal{E}}_c(\Phi_i^+) \le N+\delta$, let

$$J^i(\Phi_i^+) := \max_{\substack{\Phi^-\in(\widetilde{P}_i^- H^{1/2})^N \\ \mathrm{Gram}_{\mathrm{L}^2}\Phi^- = \mathbb{1}_{\mathrm{N}}}} \widetilde{\mathcal{E}}_c\Big(g^i_{\Phi_i^+}(\Phi^-)\Big) \tag{46}$$
$$= \widetilde{\mathcal{E}}_c \circ g^i_{\Phi_i^+}\left(k^i(\Phi_i^+)\right) \, .$$

Here, $g^i_{\Phi^+}$ and k^i are the maps associated to P_i^+ in Step 1.
By Ekeland's variational principle [5], there is a minimizing sequence $\left(\Phi_{1,n}^+\right)_{n\ge 0}$ for J^1, such that $(J^1)'\left(\Phi_{1,n}^+\right) \underset{n\longrightarrow+\infty}{\longrightarrow} 0$ in $\left(H^{-1/2}\right)^N$. Let $\Psi_n := g^1_{\Phi_{1,n}^+}\left(k^1(\Phi_{1,n}^+)\right)$. Then Ψ_n is a Palais-Smale sequence for $\widetilde{\mathcal{E}}_c$ in the manifold

$$\Sigma := \left\{\Psi \in \left(H^{1/2}\right)^N / \,\mathrm{Gram}_{\mathrm{L}^2}\Psi = \mathbb{1}_{\mathrm{N}}\right\} \, ,$$

with $\widetilde{\mathcal{E}}_c\Big(\Psi_n\Big) \ge N - \dfrac{\delta}{2}$, where $\delta > 0$ is the constant of the first step. So $\mathrm{Gram}_{\mathrm{L}^2}\left(\widetilde{P}_2^+\Psi_n\right) > 0$. We denote

$$\left\{\begin{array}{l} \Phi_{2,n}^+ := \widetilde{P}_2^+ \ \Psi_n \bullet \left[\mathrm{Gram}_{\mathrm{L}^2}\left(\widetilde{P}_2^+ \ \Psi_n\right)\right]^{-\frac{1}{2}} \, , \\ \Phi_{2,n}^- := \widetilde{P}_2^- \ \Psi_n \bullet \left[\mathrm{Gram}_{\mathrm{L}^2}\left(\widetilde{P}_2^+ \ \Psi_n\right)\right]^{-\frac{1}{2}} \, . \end{array}\right. \tag{47}$$

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

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

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

(see the proof of step 1), we get

$$\|\Phi^-_{2,n} - k^2(\Phi^+_{2,n})\|_{H^{1/2}} \underset{n\to+\infty}{\longrightarrow} 0 \quad \text{and} \quad \widetilde{\mathcal{E}}_c\Big(\Psi_n\Big) - J^2\Big(\Phi^+_{2,n}\Big) \underset{n\to+\infty}{\longrightarrow} 0 \ .$$

As a consequence,

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

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. □

Step 3. $\mathcal{E}_c\Big(\Psi^{c,1}\Big) \leq E\Big(\Lambda_c^+\Big)$, *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 $\mathrm{Gram}_{L^2} \Psi^- \leq \mathbb{1}_N$, it follows from Hardy's inequality that the map $\Psi^+ \to \mathcal{E}_c(\Psi^+ + \Psi^-)$ is strictly convex on

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

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 contraints $\mathrm{Gram}_{L^2}(\Psi^+_{max} + \Psi^-) = \mathbb{1}_N$.

So we have

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

By proposition 2,

$$\mathcal{E}_c\Big(\Psi^{c,1}\Big) \;\leq\; \sup_{\substack{\Psi\in(\Lambda_c^- H^{1/2}\oplus V)^N \\ \mathrm{Gram}_{\mathrm{L}^2}\Psi\leq \mathbb{1}_{\mathrm{N}}}} \mathcal{E}_c\Big(\Psi\Big)\ .$$

Finally we get, for c large,

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

(The correspondence between Φ^+ and V is $V = \mathrm{Span}(\Phi^+)$). 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 :

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

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 $\Phi \in \Big(H^{1/2}\Big)^N$, with $\mathrm{Gram}_{\mathrm{L}^2}\Phi \leq \mathbb{1}_{\mathrm{N}}$, the projector $\Lambda_\Phi^+ = \chi_{(0,+\infty)}\Big(\overline{H}_{c,\Phi}\Big)$ 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

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

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

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

$$\Big(\widetilde{\Lambda}^+_{\tilde\Phi}-\widetilde{\Lambda}^+\Big)\psi=\frac{1}{\pi c}\int_0^{+\infty}dz\,\Big[H_1^2+z^2\Big]^{-1}\Big(H_1K_{\tilde\Phi}\widetilde{H}_{c,\tilde\Phi}-z^2K_{\tilde\Phi}\Big)\Big[\Big(\widetilde{H}_{c,\tilde\Phi}\Big)^2+z^2\Big]^{-1}\psi\,,$$

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

$$\Big(\chi\,,\,(-\Delta+1)^{1/4}(\widetilde{\Lambda}^+_{\tilde\Phi}-\widetilde{\Lambda}^+)\psi\Big)_{L^2}\;\le\;\frac{M}{c}\|\chi\|_{L^2}\|(-\Delta+1)^{1/4}\psi\|_{L^2}$$

for c large enough (M is a constant independent of c). As a consequence, if c is large enough and bigger than $\dfrac{M}{\varepsilon}$, then Λ^+_Φ 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 $\Phi\in\Big(H^{1/2}\Big)^N$, $\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbb{I}_{\mathrm{N}}$, $\Lambda^-_\Phi\Phi=0$ and $\mathcal{E}_c(\Phi)\le Nc^2$, then*

$$\mathcal{E}_c(\Phi)\;=\;\max\Big\{\mathcal{E}_c(\Psi)\,;\;\Psi\in\Big[\Lambda^-_\Phi H^{1/2}\oplus\mathrm{Span}(\Phi)\Big]^N,\;\mathrm{Gram}_{\mathrm{L}^2}\Psi\;=\;\mathbb{I}_{\mathrm{N}}\Big\}\;.$$

Proof of Lemma 11. If $\Lambda^-_\Phi\Phi=0$ and $\mathrm{Gram}_{\mathrm{L}^2}\Phi=\mathbb{I}_{\mathrm{N}}$, then 0 is a critical point of the map

$$\Psi^-\in\Big(\Lambda^-_\Phi H^{1/2}\Big)^N\longmapsto\mathcal{E}_c\Big(g_\Phi(\Psi^-)\Big),$$

with $g_\Phi(\Psi^-)=\Big(\Phi+\Psi^-\Big)\bullet\Big[\mathbb{I}_{\mathrm{N}}+\mathrm{Gram}_{\mathrm{L}^2}\Psi^-\Big]^{-1/2}$. Take $\varepsilon>0$ small. By Lemma 10, Λ^+_Φ 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 $\Lambda^-_\Phi(H^{1/2})$ and this critical point is the unique maximizer of $\mathcal{E}_c\circ g_\Phi$ in $\Lambda^-_\Phi(H^{1/2})$. 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,

$$Nc^2\;>\;E\Big(\Lambda^+_c\Big)\;\ge\;\mathcal{E}_c(\Psi^{c,1})\;\ge\;\inf_{\left\{\begin{array}{l}\Psi\in(H^{1/2})^N\\ \mathrm{Gram}_{\mathrm{L}^2}\Psi=\mathbb{I}_{\mathrm{N}}\\ \Lambda^-_\Psi\;\Psi=0\end{array}\right.}\mathcal{E}_c(\Psi)\quad,$$

hence

$$\inf_{\begin{cases}\Psi\in(H^{1/2})^N\\ \mathrm{Gram}_{\mathrm{L}^2}\Psi=\mathbb{1}_{\mathrm{N}}\\ \Lambda^-_{\Psi}\ \Psi=0\end{cases}} \mathcal{E}_c(\Psi) \;=\; \inf_{\begin{cases}\Psi\in(H^{1/2})^N\\ \mathrm{Gram}_{\mathrm{L}^2}\Psi=\mathbb{1}_{\mathrm{N}}\\ \Lambda^-_{\Psi}\ \Psi=0\\ \mathcal{E}_c(\Psi)\leq Nc^2\end{cases}} \mathcal{E}_c(\Psi)\ .$$

Take $\varepsilon > 0$. By Lemma 10, for any $\Psi \in (H^{1/2})^N$ with $\mathrm{Gram}_{\mathrm{L}^2}\Psi = \mathbb{1}_{\mathrm{N}}$, 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

$$E\Big(\Lambda^+_c\Big) \leq \inf_{\begin{cases}\Psi\in(H^{1/2})^N\\ \mathrm{Gram}_{\mathrm{L}^2}\Psi=\mathbb{1}_{\mathrm{N}}\\ \Lambda^-_{\Psi}\ \Psi=0\end{cases}} \mathcal{E}_c(\Psi)\,,$$

and therefore,

$$E\Big(\Lambda^+_c\Big) \;=\; \mathcal{E}_c(\Psi^{c,1}) \;=\; \inf_{\begin{cases}\Psi\in(H^{1/2})^N\\ \mathrm{Gram}_{\mathrm{L}^2}\Psi=\mathbb{1}_{\mathrm{N}}\\ \Lambda^-_{\Psi}\ \Psi=0\end{cases}} \mathcal{E}_c(\Psi)$$

and Theorem 6 is proved. □

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