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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.

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,

$$eZ\mu = \sum_{i=1}^{m} eZ_i \delta_{x_i} \qquad \text{and} \qquad Z = \sum_{i=1}^{m} Z_i\,.$$

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

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

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, $\varepsilon_1^c \le ... \le \varepsilon_N^c$ 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$_c$), $\Big\{\Psi^{c,j}\Big\}_{j\ge 0} \subset \Big(H^{1/2}(\mathbb{R}^3)\Big)^N$, 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 involving a family of min-max levels $c_{\nu,p}(F_j)$ (see [6] p. 511). Note that the expression "*the* critical points" is misleading. Indeed, for each j we can define *the* min-max level $E^c_{j,DF} := \liminf_{\nu\to 0, p\to\infty} c_{\nu,p}(F_j)$, and there exists *a* critical point $\Psi^{c,j}$ such that $E^c_{j,DF} = \mathcal{E}_c(\Psi^{c,j})$; but we do not know whether this critical point is *unique*. In the present paper, we do not write the definition of the min-max levels $c_{\nu,p}(F_j)$ in its full detail (the reader is referred to [6] for a complete definition). We just state the minimal information on $E^c_{j,DF}$ 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* $j \geq 0$*, let* V *be any* $(N+j)$ *dimensional complex subspace of* E_c^+ *. Then, taking the notation of Theorem 1, we have*

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

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

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

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 $\bar\Phi = (\bar\varphi_1, \cdots, \bar\varphi_N) \in \left(H^1(\mathbb{R}^3, \mathbb{C}^2)\right)^N$ is a solution of the Hartree-Fock equations:

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

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:

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

under the constraint

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

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 $\int_{\mathbb{R}^3} \psi_k^* \psi_l \, dx = \delta_{kl}$ and $\overline{H}_{c_n, \Psi^n} \psi_k^n = \varepsilon_k^n \psi_k^n$. Assume that the multipliers ε_k^n, $k = 1, \ldots, N$, 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,*

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

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

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

and

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

As a particular case, we have

Corollary 4 *If $c_n \to +\infty$ and N, Z, μ are fixed, then for any $j \geq 0$ 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,*

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

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

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,

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

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 $N < Z+1$, but the uniqueness question remains unsolved (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 $\Psi^{c,0}$ of (DF$_c$) found in [6], whose energy level is denoted $E^c_{0,DF}$, can be considered, in some (weak) sense, as a ground state for (DF$_c$). Indeed, $E^c_{0,DF} - Nc^2$ converges to the minimum of $\mathcal{E}_{HF}$ as c goes to infinity. Moreover, for c large the multipliers $\varepsilon_k^{c,0}$ associated to $\Psi^{c,0}$ are the N smallest positive eigenvalues of the mean-field operator $\overline{H}_{c,\Psi^{c,0}}$.

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

$$E^c_{0,DF} \;=\; \min_{\mathrm{Gram}_{L^2}\Phi = \mathbb{1}_N} \mathcal{E}_{HF}(\Phi) \;+ Nc^2 + o(1)_{c\to+\infty} \;. \tag{15}$$

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

$$\mathcal{E}_{HF}(\bar\Phi^0) = \min_{\mathrm{Gram}_{L^2}\Phi = \mathbb{1}_N} \mathcal{E}_{HF}(\Phi). \tag{16}$$

Furthermore, for c large, the eigenvalues corresponding to $\Psi^{c,0}$ in (DF$_c$), $\varepsilon_1^{c,0},\dots,\varepsilon_N^{c,0}$ are the smallest positive eigenvalues of the linear operator $\overline{H}_{c,\Psi^{c,0}}$ and the $(N+1)$-th positive eigenvalue of this operator is strictly larger than $\varepsilon_N^{c,0}$.

Finally, we are able to show that, for c large enough, the function $\Psi^{c,0}$ 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 $\Psi^{c,0}$ is a solution of the following minimization problem:*

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

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 $\Psi^{c,0}$ (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 $H_1 - \dfrac{\nu}{|x|}$ 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 $0 \le \varepsilon_k^c \le c^2 \quad (k = 1, \ldots, N)$, 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 $\mathrm{Gram}_{L^2} \Psi^c = \mathbb{1}_N$ 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:

$$\psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix}, \qquad \text{with} \qquad \varphi_k^n, \ \chi_k^n : \mathbb{R}^3 \to \mathbb{C}^2 .$$

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

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

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

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

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

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

Therefore $\Phi^n := (\varphi_1^n, \ldots, \varphi_N^n)$ 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

$$\begin{cases} \mathcal{H}_{\bar\Phi} \bar\varphi_k = \bar\lambda_k \ \bar\varphi_k \ , \quad k = 1, \ldots N \\ \displaystyle\int_{\mathbb{R}^3} \bar\varphi_k^* \ \bar\varphi_l \ = \ \delta_{kl} \ , \end{cases}$$

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

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

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

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 $\mathcal{E}_c(\Psi^{c,j})$ 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, $\Psi^{c_n,0}$ is precompact in H^1 norm. If it converges, its limit is of the form $\binom{\bar\Phi^0}{0}$, and

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

$$\varliminf_{c\to+\infty}\Big(\mathcal{E}_c(\Psi^{c,0}) - Nc^2\Big) \;\geq\; \inf_{\mathrm{Gram}_{L^2}\Phi=\mathbb{1}_N} \mathcal{E}_{HF}(\Phi). \tag{28}$$

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

$$\varlimsup_{c\to+\infty}\Big(\mathcal{E}_c(\Psi^{c,0}) - Nc^2\Big) \;\leq\; \inf_{\mathrm{Gram}_{L^2}\Phi=\mathbb{1}_N} \mathcal{E}_{HF}(\Phi). \tag{29}$$

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

$$V_c := \mathrm{Span}\,\{\Lambda_c^+\big(\begin{smallmatrix}\varphi_1\\0\end{smallmatrix}\big), ..., \Lambda_c^+\big(\begin{smallmatrix}\varphi_N\\0\end{smallmatrix}\big)\}\ . \tag{30}$$

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

$$\lim_{c\to+\infty} \|\Lambda_c^-\big(\begin{smallmatrix}\varphi_k\\0\end{smallmatrix}\big)\|_{H^1} \;=\; 0\ . \tag{31}$$

So, for c sufficiently large, we have

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

Hence, by (5),

$$E_{0,DF}^c = \mathcal{E}_c(\Psi^{c,0}) \;\leq\; \sup_{\substack{\Psi\in(E^-\oplus V_c)^N\\ \mathrm{Gram}_{L^2}\Psi\leq\mathbb{1}_N}} \mathcal{E}_c(\Psi)\ . \tag{33}$$

Let $\Psi^+ \in \left(E_c^+\right)^N$, $\Psi^- \in \left(E_c^-\right)^N$ such that $\mathrm{Gram}_{L^2}(\Psi^+ + \Psi^-) \leq \mathbb{1}_N$. 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

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

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

$$E_{0,DF}^c \;\leq\; \sup_{\Psi^+\in D(V_c)} \mathcal{E}_c(\Psi^+) + \circ(1)_{c\to+\infty}\ , \tag{35}$$

where $D(V_c) := \Big\{\Psi^+ \in (V_c)^N\ ;\ \mathrm{Gram}_{L^2}\Psi^+ \leq \mathbb{1}_N\Big\}$.

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

$$\mathcal{A}^+ := \{\Psi^+ \in (E_c^+)^N\,;\ \mathrm{Gram}_{L^2}\,\Psi^+ \leq \mathbb{1}_N\}\,.$$

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

$$\mathrm{Gram}_{L^2}\,\Psi^+_{max} = \mathbb{1}_N\ . \tag{36}$$

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

$$A^*\ \mathrm{Gram}_{L^2}\left(\Lambda_c^+\tbinom{\Phi}{0}\right) A\ =\ \mathrm{Gram}_{L^2}\,\Psi^+_{max} = \mathbb{1}_N\ . \tag{37}$$

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

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

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

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

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

$$\begin{aligned} E^c_{0,DF} &\leq \mathcal{E}_c(\Psi^+_{max}) + \circ(1)_{c\to+\infty} \\ &\leq Nc^2 + \mathcal{E}_{HF}(\Phi) + \circ(1)_{c\to+\infty} . \end{aligned} \tag{39}$$

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 $\varepsilon_k^{c,0}, k = 1, \dots, N$, being the smallest eigenvalues of the operator $\overline{H}_{c,\Psi^{c,0}}$ 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 $\{\Psi^{c_n,0}\}_n$ converges in $\left(H^1(\mathbb{R}^3, \mathbb{C}^4)\right)^N$ to some $\binom{\bar\Phi^0}{0}$, for n large enough. Let $\overline{H}_n := \overline{H}_{c_n,\Psi^{c_n,0}}$ and $\mathcal{H}_\infty := \mathcal{H}_{\bar\Phi^0}$. We have $\overline{H}_n\, \psi_k^{c_n,0} = \varepsilon_k^n \psi_k^{c_n,0}$ and $\mathcal{H}_\infty\, \bar\varphi_k^0 = \bar\lambda_k \bar\varphi_k^0$, with

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

Let us denote $e_1^n \leq \cdots \leq e_i^n \leq \cdots$ the sequence of eigenvalues of $\overline{H}_n$, in the interval $(0, c_n^2)$, counted with multiplicity. Similarly, we shall denote $\bar\nu_1 \leq \cdots \leq \bar\nu_i \leq \cdots$ 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, $\lim_{n\to+\infty} (e_i^n - (c_n)^2) = \bar\nu_i$ for all $i \geq 1$.

We know that $\bar\Phi^0$ 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. □

4 Proof of Theorem 6.

In this section, both Φ and Ψ will denote N-uples of 4-spinors (i.e. N-uples of functions from $\mathbb{R}^3$ into $\mathbb{C}^4$). As explained in the Introduction of the present paper, "the" solution $\Psi^{c,0}$ was obtained in [6] by a complicated min-max argument. Note that we are not able to prove that this min-max argument leads to a unique critical point (this is not surprising: even in the simpler case of nonrelativistic Hartree-Fock, no uniqueness result is known for "the" ground state). However, the min-max level $E^c_{0,DF} = \mathcal{E}_c(\Psi^{c,0})$ is well defined and unique. For c large, we will show that the definition of $E^c_{0,DF}$ can be simplified.

First of all, we introduce the notion of projector "ε-close to Λ_c^+", where $\Lambda_c^+ = \frac{1}{2}\big|H_c\big|^{-1}\big(H_c + \big|H_c\big|\big)$ 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 $\psi \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^4)$,

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

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

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

Then $E(P^+)$ does not depend on P^+ and $\mathcal{E}_c(\Psi^{c,0}) \leq E(P^+)$.

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

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

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 $\mathrm{Gram}_{L^2}\Psi \le 1\!\!1_N$, we have

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

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

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

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 $\Phi=(\varphi_1,\dots,\varphi_N)\in(L^2(\mathbb{R}^3,\mathbb{C}^4))^N$. More precisely,

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

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

$$\begin{aligned} g_{\Phi^+}(\Phi^-) \;&:=\; (\Phi^++\Phi^-)\bullet\Big[\mathrm{Gram}_{L^2}\,(\Phi^++\Phi^-)\Big]^{-\frac12} \\ &=\; (\Phi^++\Phi^-)\bullet\Big[1\!\!1_N+\mathrm{Gram}_{L^2}\,\Phi^-\Big]^{-\frac12} . \end{aligned} \tag{44}$$

We obtain a smooth map g_{Φ^+}, from $\Big(\widetilde{P}^-\,H^{\frac12}\Big)^N$ to

$$\Sigma_{\Phi^+} := \Big\{\Psi\in\Big(\widetilde{P}^-H^{\frac12}\oplus\mathrm{Span}\,(\varphi_1^+,\dots,\varphi_N^+)\Big)^N /\ \mathrm{Gram}_{L^2}\Psi \;=\; 1\!\!1_N\Big\} .$$

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

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

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,

$$g_{\Phi^+}(\widetilde{P}^-\Psi\bullet B^{-1}) \;=\; (\Psi\bullet B^{-1})\bullet\Big[\mathrm{Gram}_{L^2}\,(\Psi\bullet B^{-1})\Big]^{-\frac12} .$$

One easily computes

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

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

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

We now prove Lemma 9 in three steps.

Step 1. *Let $\Phi^+ \in (\widetilde{P}^+H^{1/2})^N$ be such that $\mathrm{Gram}_{\mathrm{L}^2}\Phi^+ = \mathbb{1}_{\mathrm{N}}$ 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 $\Phi^- \in \Big(\widetilde{P}^-\ H^{1/2}\Big)^N$ 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*

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

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

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

Step 1 immediately follows from these facts. □

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 $\mathrm{Gram}_{L^2}\Phi_i^+ = 1\!\!1_N$ and $\widetilde{\mathcal{E}}_c(\Phi_i^+) \leq N + \delta$, let

$$\begin{aligned} J^i(\Phi_i^+) := & \max_{\substack{\Phi^- \in (\tilde{P}_i^- H^{1/2})^N \\ \mathrm{Gram}_{L^2}\Phi^- = 1\!\!1_N}} \widetilde{\mathcal{E}}_c\Big(g^i_{\Phi_i^+}(\Phi^-)\Big) \\ & = \widetilde{\mathcal{E}}_c \circ g^i_{\Phi_i^+}\Big(k^i(\Phi_i^+)\Big) \; . \end{aligned} \tag{46}$$

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 $\left(\Phi_{1,n}^+\right)_{n\geq 0}$ 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

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

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

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

One easily checks that $\Psi_n = g^2_{\Phi_{2,n}^+}(\Phi_{2,n}^-)$. Since $\widetilde{\mathcal{E}}_c\Big(\Psi_n\Big) \geq N - \dfrac{\delta}{2}$, 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 $\widetilde{\mathcal{E}}_c$, 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

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

(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,

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

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. $\mathcal{E}_c\Big(\Psi^{c,0}\Big) \le E\Big(\Lambda_c^+\Big)$*, where* $\Psi^{c,0}$ *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 $\mathrm{Gram}_{\mathrm{L}^2} \Psi^- \le \mathbb{1}_{\mathrm{N}}$, it follows from Hardy's inequality that the map $\Psi^+ \to \mathcal{E}_c(\Psi^+ + \Psi^-)$ is strictly convex on

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

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

So we have

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

By proposition 2,

$$\mathcal{E}_c\Big(\Psi^{c,0}\Big) \ \le \sup_{\substack{\Psi \in (\Lambda_c^- H^{1/2} \oplus V)^N \\ \mathrm{Gram}_{\mathrm{L}^2} \Psi \le \mathbb{1}_{\mathrm{N}}}} \mathcal{E}_c\Big(\Psi\Big) \ .$$

Finally we get, for c large,

$$\mathcal{E}_c(\Psi^{c,0}) \leq \inf_{\substack{\Phi^+\in(\Lambda_c^+ H^{1/2})^N \\ \mathrm{Gram}_{L^2}\Phi^+=1\!\!1_N}} \ \sup_{\substack{\Psi\in(\Lambda_c^- H^{1/2}\oplus \mathrm{Span}(\Phi^+))^N \\ \mathrm{Gram}_{L^2}\Psi=1\!\!1_N}} \mathcal{E}_c(\Psi) = E(\Lambda_c^+) \ .$$

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

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

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

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 $\Phi \in \left(H^{1/2}\right)^N$, with* $\mathrm{Gram}_{L^2}\Phi \leq 1\!\!1_N$, *the projector $\Lambda_\Phi^+ = \chi_{(0,+\infty)}\left(\overline{H}_{c,\Phi}\right)$ 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],

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

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

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

for c large enough (M is a constant independent of c). As a consequence, if c is large enough and bigger than $\dfrac{M}{\varepsilon}$, then Λ^+_Φ is ε-close to Λ^+_c. This ends the proof of Lemma 10. □

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 $\Phi \in \Big(H^{1/2}\Big)^N$, $\mathrm{Gram}_{\mathrm{L}^2}\Phi = \mathbb{1}_{\mathrm{N}}$, $\Lambda^-_\Phi\Phi = 0$ and $\mathcal{E}_c(\Phi) \leq Nc^2$, then*

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

Proof of Lemma 11. If $\Lambda^-_\Phi\Phi = 0$ and $\mathrm{Gram}_{\mathrm{L}^2}\Phi = \mathbb{1}_{\mathrm{N}}$, 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 $g_\Phi(\Psi^-) = \Big(\Phi + \Psi^-\Big) \bullet \Big[\mathbb{1}_{\mathrm{N}} + \mathrm{Gram}_{\mathrm{L}^2}\Psi^-\Big]^{-1/2}$. 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. □

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

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

hence

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

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 $\mathcal{E}_c(\Psi) \le Nc^2$, then, from Lemma 11 and from the definition of $E(\Lambda^+_\Psi)$, we have $E(\Lambda^+_c) = E(\Lambda^+_\Psi) \le \mathcal{E}_c(\Psi)$. So

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

and therefore,

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

and Theorem 6 is proved. □

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