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Some Connections between Dirac-Fock and Electron-Positron Hartree-Fock

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Abstract. We study the ground state solutions of the Dirac-Fock model in the case of weak electronic repulsion, using bifurcation theory. They are solutions of a min-max problem. Then we investigate a max-min problem coming from the electron-positron field theory of Bach-Barbaroux-Helffer-Siedentop. We show that given a radially symmetric nuclear charge, the ground state of Dirac-Fock solves this max-min problem for certain numbers of electrons. But we also exhibit a situation in which the max-min level does not correspond to a solution of the Dirac-Fock equations together with its associated self-consistent projector.

1 Introduction

The electrons in heavy atoms experience important relativistic effects. In computational chemistry, the Dirac-Fock (DF) model [1], or the more accurate multiconfiguration Dirac-Fock model [2], take these effects into account. These models are built on a multi-particle Hamiltonian which is in principle not physically meaningful, and whose essential spectrum is the whole real line. But they seem to function very well in practice, since approximate bound state solutions are found and numerical computations are done and yield results in quite good agreement with experimental data (see, e.g., [3]). Rigorous existence results for solutions of the DF equations can be found in [4] and [5]. An important open question is to find a satisfactory physical justification for the DF model.

It is well known that the correct theory including quantum and relativistic effects is quantum electrodynamics (QED). However, this theory leads to divergence problems, that are only solved in perturbative situations. But the QED equations in heavy atoms are nonperturbative in nature, and attacking them directly seems a formidable task. Instead, one can try to derive approximate models from QED, that would be adapted to this case. The hope is to show that the Dirac-Fock model, or a refined version of it, is one of them. Several attempts have been made in this direction (see [6, 7, 8, 9] and the references therein). Mittleman [6], in particular, derived the DF equations with "self-consistent projector" from a variational procedure applied to a QED Hamiltonian in Fock space, followed by the standard Hartree-Fock approximation. More precisely, let H^c be the free Dirac Hamiltonian, and Ω a perturbation. We denote $\Lambda^+(\Omega) = \chi_{(0,\infty)}(H^c + \Omega)$. The electronic space is the range $\mathcal{H}^+(\Omega)$ of this projector. If one computes the QED energy of Slater determinants of N wave functions in this electronic space, one obtains the DF energy functional restricted to $(\mathcal{H}^+(\Omega))^N$. Let Ψ_Ω be a minimizer of the DF energy in the projected space $(\mathcal{H}^+(\Omega))^N$ under normalization constraints. It satisfies the projected DF equations, with projector $\Lambda^+(\Omega)$. Let $E(\Omega) := \mathcal{E}(\Psi_\Omega)$. Mittleman showed (by formal arguments) that the stationarity of $E(\Omega)$ with respect to Ω implies that $\Lambda^+(\Omega)$ coincides, *on the occupied orbitals*, with the self-consistent projector associated to the mean-field Hartree-Fock Hamiltonian created by Ψ_Ω. From this he infers ([6], page 1171) : *"Hence, Ω is the Hartree-Fock potential when the Hartree-Fock approximation is made for the wave function"*.

Recently rigorous mathematical results have been obtained in a series of papers by Bach *et al.* and Barbaroux *et al.* [10, 11, 12] on a Hartree-Fock type model involving electrons and positrons. This model (that we will call EP) is related to the works of Chaix-Iracane [9] and Chaix-Iracane-Lions [13]. Note, however, that in [10, 11, 12] the vacuum polarization is neglected, contrary to the Chaix-Iracane approach. In [10], in the case of the vacuum, a max-min procedure in the spirit of Mittelman's work is introduced. In [12], in the case of N-electron atoms, it is shown that critical pairs (γ, P^+) of the electron-positron Hartree-Fock energy $\mathcal{E}_{EP}$ give solutions of the self-consistent DF equations. This result is an important step towards a rigorous justification of Mittleman's ideas. All this suggests, in the case of N-electrons atoms, to maximize the minimum $E(\Omega)$ with respect to Ω. It is natural to expect that this max-min procedure gives solutions of the DF equations, the maximizing projector being the positive projector of the self-consistent Hartree-Fock Hamiltonian. We call this belief (expressed here in rather imprecise terms) "Conjecture M".

In [14] and [15], when analyzing the nonrelativistic limit of the DF equations, Esteban and Séré derived various equivalent variational problems having as solution an "electronic" ground state for the DF equations. Among them, one can find min-max and max-min principles. But these principles are nonlinear, and do not solve Conjecture M.

In this paper we try to give a precise formulation of Conjecture M in the spirit of Mittleman's ideas and to see if it holds true or not, in the limit case of small interactions between electrons. We prove that in this perturbative regime, given a radially symmetric nuclear potential, Conjecture M may hold or not depending on the number of electrons. The type of ions which are covered by our study are those in which the number of electrons is much smaller than the number of protons in the nucleus, with, additionally, c (the speed of light) very large.

The paper is organized as follows : in Section 2 we introduce the notations and state our main results (Theorems 9 and 11). Sections 3 and 4 contain the detailed proofs.

2 Notations and main results

In the whole paper we choose a system of units in which Planck's constant, $\hbar$, and the mass of the electron are equal to 1 and $Ze^2 = 4\pi\epsilon_0$, where Z is the number of protons in the nucleus. In this system of units, the Dirac Hamiltonian can be written as

$$H^c \ = \ -ic\,\boldsymbol{\alpha}\cdot\nabla + c^2\beta, \tag{1}$$

where $c > 0$ is the speed of light , $\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}$, $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$, $\alpha_\ell = \begin{pmatrix} 0 & \sigma_\ell \\ \sigma_\ell & 0 \end{pmatrix}$ and the σ_ℓ's are the 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 the set $(-\infty, -c^2] \cup [c^2, +\infty)$.

In this paper, the charge density of the nucleus will be a smooth, radial and compactly supported nonnegative function n, with $\int n = 1$, since in our system of units $Ze^2 = 4\pi\epsilon_0$. The corresponding Coulomb potential is $V := -n * (1/|x|)$. Then $V : \mathbb{R}^3 \to (-\infty, 0)$ is a smooth negative radially symmetric potential such that

$$-\frac{1}{|x|} \le V(x) < 0 \quad (\forall x) \quad , \quad |x|\,V(x) \simeq -1 \ \text{ for } \ |x| \ \text{ large enough} .$$

Note that the smoothness condition on V is only used in step 3 of the proof of Proposition 15. Actually we believe that this condition can be removed.

It is well known that $H^c + V$ is essentially self-adjoint and for $c > 1$, the spectrum of this operator is as follows:

$$\sigma(H^c + V) = (-\infty, -c^2] \cup \{\lambda_1^c, \lambda_2^c, \dots\} \cup [c^2, +\infty),$$

with $0 < \lambda_1^c < \lambda_2^c < \cdots$ and $\lim\limits_{\ell\to+\infty} \lambda_\ell^c = c^2$.

Finally define the spectral subspaces $\mathcal{M}_i^c = \mathrm{Ker}(H^c + V - \lambda_i^c\,\mathbb{1})$ and let N_i^c denote $\mathcal{M}_i^c$'s dimension.

Since the potential is radial, it is well known that the eigenvalues λ_i^c are degenerate (see, *e.g.*, [16]). For completeness, let us explain this in some detail. To any $A \in SU(2)$ is associated a unique rotation $R_A \in SO(3)$ such that $\forall x \in \mathbb{R}^3$, $(R_A x)\cdot\sigma = A(x\cdot\sigma)A^{-1}$, where $\sigma = (\sigma_1, \sigma_2, \sigma_3)$. This map is a morphism of Lie groups. It is onto, and its kernel is $\{I, -I\}$. It leads to a natural unitary representation $\bullet$ of $SU(2)$ in the Hilbert spaces of 2-spinors $L^2(S^2, \mathbb{C}^2)$ and $L^2(\mathbb{R}^3, \mathbb{C}^2)$, given by

$$(A\bullet\phi)(x) := A\,\phi(R_A^{-1}x)\ . \tag{2}$$

Then, on the space of 4-spinors $L^2(\mathbb{R}^3, \mathbb{C}^4) = L^2(\mathbb{R}^3, \mathbb{C}^2) \oplus L^2(\mathbb{R}^3, \mathbb{C}^2)$, one can define the following unitary representation (denoted again by $\bullet$)

$$\left(A\bullet\begin{pmatrix}\phi\\ \chi\end{pmatrix}\right)(x) := \begin{pmatrix}(A\bullet\phi)(x)\\ (A\bullet\chi)(x)\end{pmatrix} = \begin{pmatrix}A\phi(R_A^{-1}x)\\ A\chi(R_A^{-1}x)\end{pmatrix}\ . \tag{3}$$

The radial symmetry of V implies that $H^c + V$ commutes with $\bullet$. The eigenspaces $\mathcal{M}_i^c$ are thus $SU(2)$ invariant. Now, let $\hat{J} = (\hat{J}_1, \hat{J}_2, \hat{J}_3)$ be the total angular momentum operator associated to the representation $\bullet$. The eigenvalues of $\hat{J}^2 = \hat{J}_1^2 + \hat{J}_2^2 + \hat{J}_3^2$ are the numbers $(j^2 - 1/4)$, where j takes all positive integer values. If ϕ is an eigenvector of $\hat{J}^2$ with eigenvalue $(j^2 - 1/4)$, then the $SU(2)$ orbit of ϕ generates an $SU(2)$ invariant complex subspace of dimension $2j \geq 2$. This implies the following fact, which will be used repeatedly in the present paper:

Lemma 1. *If $\phi \in L^2(\mathbb{R}^3, \mathbb{C}^2)$ is not the zero function, then there is $A \in SU(2)$ such that ϕ and $A \bullet \phi$ are two linearly independent functions.*

Proof of the Lemma. Assume, by contradiction, that $\mathbb{C}\,\phi$ is $SU(2)$ invariant. Then ϕ is an eigenvector of J_ℓ for $\ell = 1, 2, 3$, hence it is eigenvector of $\hat{J}^2$. But we have seen that in such a case, the $SU(2)$ orbit of ϕ must contain at least two independent vectors: this is absurd. □

As a consequence of the Lemma, the spaces $\mathcal{M}_i^c$ have complex dimension at least 2. The degeneracy is higher in general: for each $j \geq 1$, $H^c + V$ has infinitely many eigenvalues of multiplicity at least $2j$. Note that in the case of the Coulomb potential, the eigenvalues are even more degenerate (see, *e.g.*, [16]).

Now, on the Grassmannian manifold

$$G_N(H^{1/2}) := \{W \text{ subspace of } \; H^{1/2}(\mathbb{R}^3, \mathbb{C}^4); \dim_{\mathbb{C}}(W) = N\}$$

we define the Dirac-Fock energy $\mathcal{E}_\kappa^c$ as follows

$$\begin{aligned} \mathcal{E}_\kappa^c(W) := \mathcal{E}_\kappa^c(\Psi) := & \sum_{i=1}^{N} \int_{\mathbb{R}^3} ((H^c + V)\psi_i, \psi_i) dx \\ & + \frac{\kappa}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Psi(x)\rho_\Psi(y) - |R_\Psi(x,y)|^2}{|x-y|} dx dy \ , \end{aligned} \tag{4}$$

where $\kappa > 0$ is a small constant, equal to $e^2/4\pi\epsilon_0$ in our system of units, $\{\psi_1, \dots \psi_N\}$ is any orthonormal basis of W, Ψ denotes the N-uple $(\psi_1, \dots, \psi_N)$, ρ_Ψ is a scalar and R_Ψ is a 4×4 complex matrix, given by

$$\rho_\Psi(x) \;=\; \sum_{\ell=1}^{N} \Big(\psi_\ell(x), \psi_\ell(x)\Big) \, , \quad R_\Psi(x,y) \;=\; \sum_{\ell=1}^{N} \psi_\ell(x) \otimes \psi_\ell^*(y) \, . \tag{5}$$

Saying that the basis $\{\psi_1, \dots, \psi_N\}$ is orthonormal is equivalent to saying that

$$\mathrm{Gram}_{L^2} \Psi = \mathbb{1}_N \ . \tag{6}$$

We will use interchangeably the notations $\mathcal{E}_\kappa^c(W)$ or $\mathcal{E}_\kappa^c(\Psi)$. The energy can be considered as a function of W only, because if $u \in U(N)$ is a unitary matrix,

$$\mathcal{E}_\kappa^c(u\Psi) = \mathcal{E}_\kappa^c(\Psi) \tag{7}$$

with the notation $(u\Psi)_k = \sum_l u_{kl} \psi_l$.

Note that since V is radial, the DF functional is also invariant under the representation $\bullet$ defined above. Its set of critical points will thus be a union of $SU(2)$ orbits.

Finally let us introduce a set of projectors as follows:

Definition 2. *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 said to be ε-close to $\Lambda_c^+ := \chi_{(0,+\infty)}(H^c)$ if and only if, for all $\psi \in H^{\frac{1}{2}}(\mathbb{R}^3,\mathbb{C}^4)$,*

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

In [14] the following result is proved:

Theorem 3 ([14]). *Take V, N fixed. For c large and ϵ_0, κ small enough, for all P ε_0-close to Λ_+^c,*

$$c(P) := \inf_{W^+ \in G_N(PH^{1/2})} \sup_{\substack{W \in G_N(H^{1/2}) \\ P(W) = W^+}} \mathcal{E}_\kappa^c(W)$$

is independent of P and we denote it by E_κ^c. Moreover, E_κ^c is achieved by a solution W_κ =span$\{\psi_1,\ldots,\psi_N\}$ of the Dirac-Fock equations:

$$\begin{cases} H^c_{\kappa,W_\kappa}\psi_i = \epsilon_i^c\,\psi_i^c,\ 0 < \epsilon_i^c < 1, \\ \mathrm{Gram}_{L^2}\Psi = 1_{\mathbb{N}} \end{cases} \tag{DF}$$

with

$$H^c_{\kappa,W}\,\varphi := (H^c + V + \kappa\,\rho_\Psi * \frac{1}{|x|})\varphi - \kappa \int_{\mathbb{R}^3} \frac{R_\Psi(x,y)\varphi(y)}{|x-y|}dy . \tag{MF}$$

Remark. It is easy to verify that $\varepsilon_0 > 0$ given, for c large and κ small enough, $\chi_{(0,\infty)}(H^c_{\kappa,W_\kappa})$ is ε_0-close to Λ_c^+.

Corollary 4 ([14]). *Take V, N fixed. Choose c large and κ small enough. If we define the projector*

$$P^+_{\kappa,W} = \chi_{(0,\infty)}(H^c_{\kappa,W})$$

with $H^c_{\kappa,W}$ given by formula (MF), then

$$E_\kappa^c = \min_{\substack{W \in G_n(H^{1/2}) \\ P^+_{\kappa,W}W = W}} \mathcal{E}_\kappa^c(W) = \min_{\substack{W \in G_N(H^{1/2}) \\ W \text{ solution of (DF)}}} \mathcal{E}_\kappa^c(W) . \tag{8}$$

Another variational problem was introduced in the works of Bach *et al.* and Barbaroux *et al.* ([10, 11, 12]): define

$$\widetilde{\mathcal{P}}_\kappa = \{P^+_{\kappa,\widetilde{W}} = \chi_{[0,\infty)}(H^c_{\kappa,\widetilde{W}})\ ;\ \widetilde{W} \in G_N(H^{1/2})\}, \tag{9}$$

and

$$\begin{aligned} S^N_{\kappa,\widetilde{W}} \;:=\; & \{\gamma \in S_1(L^2)\,,\ \gamma = \gamma^*\,,\ H^c_{\kappa,\widetilde{W}}\gamma \in S_1\,, \\ & P^+_{\kappa,\widetilde{W}}\gamma P^-_{\kappa,\widetilde{W}} = 0\,,\ -P^-_{\kappa,\widetilde{W}} \le \gamma \le P^+_{\kappa,\widetilde{W}}\,,\ \mathrm{tr}\,\gamma = N\}, \end{aligned}$$

with the notation $P^-_{\kappa,\widetilde{W}} := \mathbf{1} - \mathrm{P}^+_{\kappa,\widetilde{\mathrm{W}}}$, and S_1 being the Banach space of trace-class operators on $L^2(\mathbb{R}^3, \mathbb{C}^4)$. For all $\gamma \in S^N_{\kappa,\widetilde{W}}$, let

$$\mathcal{F}^c_\kappa(\gamma) = \mathrm{tr}\,((H^c + V)\gamma) + \frac{\kappa}{2}\int \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\mathrm{d}x\,\mathrm{d}y - \frac{\kappa}{2}\int \frac{|\gamma(x,y)|^2}{|x-y|}\mathrm{d}x\,\mathrm{d}y.$$

Here, $\rho_\gamma(x) := \sum_{s=1}^4 \gamma_{s,s}(x,\,x) = \sum_n w_n|\psi_n(x)|^2$, with w_n the eigenvalues of γ and ψ_n the eigenspinors of γ, and $\gamma(x,y) = \sum_n w_n\psi_n(x) \otimes \overline{\psi_n}(y)$, i.e., $\gamma(x,y)$ is the kernel of γ.

In [12] it has been proved that for every $P^+_{\kappa,\widetilde{W}} \in \widetilde{\mathcal{P}}_\kappa$, the infimum of $\mathcal{F}^c_\kappa$ on the set $S^N_{\kappa,\widetilde{W}}$ is actually equal to the infimum defined in the smaller class of Slater determinants. More precisely, with the above notations,

Theorem 5 ([12]). *For κ small enough and for all $P^+_{\kappa,\widetilde{W}} \in \widetilde{\mathcal{P}}_\kappa$, one has*

$$\inf_{\gamma \in S^N_{\kappa,\widetilde{W}}} \mathcal{F}^c_\kappa(\gamma) = \inf_{W \in G_N(P^+_{\kappa,\widetilde{W}} H^{1/2})} \mathcal{E}^c_\kappa(W) \tag{10}$$

Moreover, the infimum is achieved by a solution of the projected Dirac-Fock equations, namely

$$\gamma_{\min} = \sum_{i=1}^N \langle \psi_i\,,.\rangle\psi_i$$

with $P^+_{\kappa,\widetilde{W}}\psi_i = \psi_i$ $(i = 1,\dots,N)$, and for $W_{\min} := span(\psi_1,\dots,\psi_N)$,

$$\begin{cases} P^+_{\kappa,\widetilde{W}} H^c_{\kappa,W_{\min}} P^+_{\kappa,\widetilde{W}}\psi_i = \epsilon_i\psi_i,\ 0 < \epsilon_i < 1, \\ \mathrm{Gram}_{L^2}\Psi = 1_{\mathbb{N}} \end{cases} \tag{11}$$

Let us now define the following sup-inf:

$$e^c_\kappa := \sup_{P^+_{\kappa,\widetilde{W}} \in \widetilde{\mathcal{P}}_\kappa} \ \inf_{W \in G_N(P^+_{\kappa,\widetilde{W}} H^{1/2})} \mathcal{E}^c_\kappa(W)\,. \tag{12}$$

Then, Theorem 5 has the following consequence:

Corollary 6. *If κ is small enough,*

$$e^c_\kappa = \sup_{P^+_{\kappa,\widetilde{W}} \in \widetilde{\mathcal{P}}_\kappa} \ \inf_{\gamma \in S^N_{\kappa,\widetilde{W}}} \mathcal{F}^c_\kappa(\gamma).$$

From the above definitions, Theorem 3, Corollary 4 and the remark made after Theorem 3, we clearly see that for all κ small and c large,

$$E_\kappa^c \geq e_\kappa^c. \tag{13}$$

One can hope more:

Conjecture M: *The energy levels E_κ^c and e_κ^c coincide, and there is a solution W_κ^c of the DF equations such that*

$$\mathcal{E}_\kappa^c(W_\kappa^c) = e_\kappa^c = \inf_{V \in G_N(P^+_{\kappa, W_\kappa^c} H^{1/2})} \mathcal{E}_\kappa^c(V)\,.$$

In other words, the max-min level e_κ^c is attained by a pair $(W, P^+_{\kappa,\widetilde{W}})$ such that $\widetilde{W} = W$.

This paper is devoted to discussing this conjecture, which, if it were true, would allow us to interpret the Dirac-Fock model as a variational approximation of QED.

In order to study the different cases that can appear when studying the problems E_κ^c and e_κ^c for κ small, we begin by discussing the case $\kappa = 0$.

Proposition 7. *Conjecture M is true in the case $\kappa = 0$.*

Proof. The case $\kappa = 0$ is obvious. Indeed, all projectors $P^+_{0,\widetilde{W}}$ coincide with the projector $\chi_{[0,\infty)}(H^c + V)$. The level E_0^c, seen as the minimum of Corollary 2, is achieved by any N-dimensional space $W_{\min}$ spanned by N orthogonal eigenvectors of $H^c + V$ whose eigenvalues are the N first positive eigenvalues of $H^c + V$, counted with multiplicity. Then E_0^c is the sum of these N first positive eigenvalues. Clearly, $(W_{\min}, \chi_{[0,\infty)}(H^c + V))$ realizes e_0^c. □

The interesting case is, of course, $\kappa > 0$, when electronic interaction is taken into account. For $\kappa > 0$ and small two very different situations occur, depending on the number N of electrons.

The **first situation** (perturbation from the linear closed shell atom) corresponds to

$$N = \sum_{i=1}^{I} N_i^c, \quad I \in \mathbb{Z}^+ \tag{14}$$

is treated in detail in Section 3.

We recall that N_i^c is the dimension of the eigenspace $\mathcal{M}_i^c = \mathrm{Ker}(H^c + V - \lambda_i^c \mathbb{1})$ already defined. Under assumption (14), for $\kappa = 0$, there is a unique solution, W_0^c, to the variational problems defining E_0^c and e_0^c,

$$W_0^c = \bigoplus_{i=1}^{I} \mathcal{M}_i^c.$$

The "shells" of energy λ_i^c , $1 \le i \le I$, are "closed": each one is occupied by the maximal number of electrons allowed by the Pauli exclusion principle. The subspace W_0^c is invariant under the representation $\bullet$ of $SU(2)$.

We are interested in solutions W_κ^c of the Dirac-Fock equations lying in a neighborhood $\Omega \subset G_N(H^{1/2})$ of W_0^c, for κ small. Using the implicit function theorem, we are going to show that for each κ small, W_κ^c exists, is unique, and is a smooth function of κ.

Information about the properties enjoyed by W_κ^c is given by

Proposition 8. *Fix c large enough. Under assumption* (14), *for κ small enough,*

$$E_\kappa^c = \mathcal{E}_\kappa^c(W_\kappa^c) = \inf_{W \in G_N(P^+_{\kappa, W_\kappa^c} H^{1/2})} \mathcal{E}_\kappa^c(W), \tag{15}$$

and W_κ^c is the unique solution of this minimization problem.

This proposition will be proved in Section 3. Our first main result follows from it:

Theorem 9. *Under assumption* (14), *for $c > 0$ fixed and κ small enough, $E_\kappa^c = e_\kappa^c$ and both variational problems are achieved by the same solution W_κ^c of the self-consistent Dirac-Fock equations. For e_κ^c, the optimal projector in $\widetilde{\mathcal{P}}_\kappa$ is P^+_{κ, W_κ^c}.*

Proof. The above proposition implies that for κ small,

$$e_\kappa^c \ge \inf_{W \in G_N(P^+_{\kappa, W_\kappa^c} H^{1/2})} \mathcal{E}_\kappa^c(W) = \mathcal{E}_\kappa^c(W_\kappa^c) = E_\kappa^c. \tag{16}$$

Therefore, $e_\kappa^c = E_\kappa^c$. Moreover, by Proposition 8, e_κ^c is achieved by a couple (W_κ^c, P) such that $P = P^+_{\kappa, W_\kappa^c}$, W_κ^c being a solution of the Dirac-Fock equations. This ends the proof. □

The **second situation** (perturbation from the linear open shell case) occurs when

$$N = \sum_{i=1}^{I} N_i^c + k, \ I \in \mathbb{Z}^+, \ 0 < k < N_{I+1}^c \,. \tag{17}$$

It is treated in detail in Section 4.

When (17) holds and when $\kappa = 0$, there exists a manifold of solutions, S_0, whose elements are the spaces

$$\bigoplus_{i=1}^{I} \mathcal{M}_i^c \oplus W_{I+1,k}^c,$$

for all $W_{I+1,k}^c \in G_k(M_{I+1}^c)$. These spaces are all the solutions of the variational problems defining E_0^c and e_0^c. The $(I+1)$th "shell" of energy λ_{I+1}^c is "open": it is occupied by k electrons, while the Pauli exclusion principle would allow $N_{I+1}^c - k$ more. *Note that we use the expression "open shell" in the linear case* $\kappa = 0$ *only:* indeed, adapting an idea of Bach *et al.* [17], one can easily see that for κ *positive* and small, the solutions to (DF) at the minimal level E_κ^c have no unfilled shells.

For $\kappa > 0$ and small we look for solutions of the DF equations near S_0 (see Section 4). We could simply quote the existence results of [15], and show the convergence of solutions of (DF) at level E_κ^c, towards points of S_0, as κ goes to 0. But we prefer to give another existence proof, using tools from bifurcation theory. This approach gives a more precise picture of the set of solutions to (DF) near the level E_κ^c (Theorem 12).

In particular, we obtain in this way all the solutions of (DF) with smallest energy E_κ^c (Proposition 13).

We now choose one of these minimizers, and we call it W_κ^c. We have $P^-_{\kappa,W_\kappa^c}(W_\kappa^c) = 0$. Since V is radial, W_κ^c belongs to an $SU(2)$ orbit of minimizers. We are interested in cases where this orbit is not reduced to a point. Then the mean-field operator H^c_{κ,W_κ^c} should not commute with the action $\bullet$ of $SU(2)$, and one expects the following property to hold:

(P): *Given c large enough, if* κ *is small, then for any solution* W_κ^c *of (DF) at level* E_κ^c*, there is a matrix* $A \in SU(2)$ *such that*

$$P^-_{\kappa,W_\kappa^c}(A \bullet W_\kappa^c) \neq 0\,. \tag{18}$$

The next proposition shows that whenever **(P)** holds, Conjecture M does not. This result will imply that Conjecture M is indeed wrong.

Proposition 10. *If* **(P)** *is satisfied, then for c large enough and* κ *small, given any solution* W_κ^c *of the nonlinear Dirac-Fock equations such that* $\mathcal{E}_\kappa^c(W_\kappa^c) = E_\kappa$*, we have*

$$E_\kappa^c = \mathcal{E}_\kappa^c(W_\kappa^c) > \inf_{\substack{W \in G_N(H^{1/2}) \\ P^-_{\kappa,W_\kappa^c} W = 0}} \mathcal{E}_\kappa^c(W). \tag{19}$$

This proposition will be proved in Section 4. Moreover, we verify (see Proposition 15) that (P) holds when $I \geq 1$ and $k = 1$, *i.e.*, when in the linear case there is a single electron in the highest nonempty shell.

Our second main result follows directly from Propositions 10 and 15.

Theorem 11. *Take*

$$N = \sum_{i=1}^{I} N_i^c + 1, \quad I \geq 1\,.$$

For c *large and* $\kappa > 0$ *small, there is no solution* W_* *of the nonlinear Dirac-Fock equations with positive Lagrange multipliers, such that the couple*

$$(W_*, P^+_{\kappa,W_*})$$

realizes the max-min e_κ^c*. So Conjecture M is wrong.*

Remark. Note that the fact that Conjecture M is wrong in the case $N = \sum_{i=1}^{I} N_i^c + 1$, $I \geq 1$, is related to nonuniqueness of the minimizer for the problem

$$\inf_{\substack{W \in G_N(H^{1/2}) \\ P^-_{\kappa, W^c_\kappa} W = 0}} \mathcal{E}^c_\kappa(W) \,.$$

When such a situation happens, it is well known that one has to be very careful when considering *max-min* (resp. *min-max*) problems, since even when solvable, they do not always deliver critical points of the considered functional. A very simple example for this fact is provided by the function $f : \mathbb{R}^2 \to \mathbb{R}$ defined by $f(x, y) := (1 - x^2)^2 + xy$. It is easy to verify that

$$\sup_{y \in R} \inf_{x \in R} f(x, y) = 0 \,,$$

that the unique maximizer is $y = 0$ and that there are exactly two minimizers of $x \mapsto f(x, 0)$, $x_\pm = \pm 1$. But neither $(-1, 0)$ nor $(1, 0)$ are critical points of f.

3 Perturbation from the linear closed shells case

Let us recall that we are in the case

$$N = \sum_{i=1}^{I} N_i^c, \quad I \in \mathbb{Z}^+ \,,$$

N_i^c being the dimension of the eigenspace $\mathcal{M}_i^c = \mathrm{Ker}(H^c + V - \lambda_i^c \,\mathbb{1})$. We want to apply the implicit function theorem in a neighborhood of W_0^c, for κ small. For this purpose, we need a local chart near W_0^c. Take an orthonormal basis $(\psi_1, \ldots, \psi_N)$ of W_0^c, whose elements are eigenvectors of $H^c + V$, the associated eigenvalues being $\mu_1 \leq \cdots \leq \mu_N$ (*i.e.*, $\lambda_1^c, \ldots, \lambda_I^c$ counted with multiplicity). Let $\mathcal{Z}$ be the orthogonal space of W_0^c for the L^2 scalar product, in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$. Then $\mathcal{Z}$ is a Hilbert space for the $H^{1/2}$ scalar product. The map

$$C \,:\, \chi = (\chi_1, \ldots, \chi_N) \to \mathrm{span}(\psi_1 + \chi_1, \ldots, \psi_N + \chi_N) \,,$$

defined on a small neighborhood $\mathcal{O}$ of 0 in $\mathcal{Z}^N$, is the desired local chart. Denote G_χ the $N \times N$ matrix of scalar products $(\chi_l, \chi_\ell)_{L^2}$. Then

$$\mathcal{E}^c_\kappa \circ C(\chi) = \mathcal{E}^c_\kappa\big((I + G_\chi)^{-1/2}(\psi + \chi)\big) \,.$$

The differential of this functional defines a smooth map $F_\kappa \,:\, \mathcal{O} \subset \mathcal{Z}^N \to (\mathcal{Z}')^N$, where $\mathcal{Z}' \subset H^{-1/2}$ is the topological dual of $\mathcal{Z}$ for the $H^{1/2}$ topology, identified with the orthogonal space of W_0^c for the duality product in $H^{-1/2} \times H^{1/2}$. Note that F_κ depends smoothly on the parameter κ. A subspace $C(\chi)$ is solution of

(DF) if and only if $F_\kappa(\chi) = 0$. To apply the implicit function theorem, we just have to check that the operator $L := D_\chi F_0(0)$ is an isomorphism from $\mathcal{Z}^N$ to its dual $(\mathcal{Z}')^N$. This operator is simply the Hessian of the DF energy expressed in our local coordinates:

$$L\chi = \big((H_c + V - \mu_1)\chi_1, \ldots, (H_c + V - \mu_N)\chi_N\big) \ . \tag{20}$$

Under assumption (14), the scalars μ_k, $k = 1, \ldots, N$, are not eigenvalues of the restriction of $H^c + V$ to the L^2-orthogonal subspace of W_0^c. This implies that L is an isomorphism. As a consequence, there exists a neighborhood of $W_0^c \times \{0\}$ in $G_N(H^{1/2}) \times \mathbb{R}$, $\Omega \times (-\kappa_0, \kappa_0)$ and a smooth function $h^c : (-\kappa_0, \kappa_0) \to \Omega$ such that for $\kappa \in (-\kappa_0, \kappa_0)$, $W_\kappa^c := h^c(\kappa)$ is the unique solution of the Dirac-Fock equations in Ω. Moreover, for all $\kappa \in (-\kappa_0, \kappa_0)$, the following holds:

$$u(W_\kappa^c) = W_\kappa^c \ , \ \forall u \in SU(2) \ . \tag{21}$$

Indeed, the subset A of parameters κ such that (21) holds is obviously nonempty (it contains 0) and closed in $(-\kappa_0, \kappa_0)$. Now, for κ in a small neighborhood of A, the $SU(2)$ orbit of W_κ^c stays in Ω. But this orbit consists of solutions of the Dirac-Fock equations, so, by uniqueness in Ω, it is reduced to a point. This shows that A is also open. A is thus the whole interval of parameters $(-\kappa_0, \kappa_0)$.

Now we are in the position to prove Proposition 8.

Proof of Proposition 8. Remember that for $\kappa = 0$, P^+_{0,W_0^c} coincides with $\chi_{(0,\infty)}(H^c + V)$. Now, W_0^c is clearly the unique minimizer of $\mathcal{E}_0^c$ on the Grassmannian submanifold $G_0^+ := G_N(P^+_{0,W_0^c} H^{1/2})$. More precisely, in topological terms, for any neighborhood $\mathcal{V}$ of W_0^c in $G_N(H^{1/2})$, there is a constant $\delta = \delta(\mathcal{V}) > 0$ such that

$$\mathcal{E}_0^c(W) \geq \mathcal{E}_0^c(W_0^c) + \delta \ , \ \forall W \in G_0^+ \cap (G_N(H^{1/2}) \setminus \mathcal{V}) \ . \tag{22}$$

Moreover, looking at formula (20), one easily sees that the Hessian of $\mathcal{E}_0^c$ on G_0^+ is positive definite at W_0^c. We now take $\kappa > 0$ small, and we consider again the chart C constructed above. We define the submanifold $G_\kappa^+ := G_N(P^+_{\kappa,W_\kappa^c} H^{1/2})$. Then the restriction C_κ^+ of C to $(P^+_{\kappa,W_\kappa^c}\mathcal{Z})^N$ is a local chart of G_κ^+ near W_κ^c. For κ small enough, there is a neighborhood $\mathcal{U}$ of 0 in $\mathcal{Z}^N$ such that the second derivative of $\mathcal{E}_\kappa^c \circ C_\kappa^+$ is positive definite on $\mathcal{U}_\kappa^+ := \mathcal{U} \cap (P^+_{\kappa,W_\kappa^c}\mathcal{Z})^N$. The functional $\mathcal{E}_\kappa^c \circ C_\kappa^+$ is thus strictly convex on $\mathcal{U}_\kappa^+$. Now, for κ small, there is a unique $\chi_\kappa \in \mathcal{U}_\kappa^+$ such that $C_\kappa^+(\chi_\kappa) = W_\kappa^c$. Then the derivative of $\mathcal{E}_\kappa^c \circ C_\kappa^+$ vanishes at χ_κ. As a consequence $W_\kappa^c = C_\kappa^+(\chi_\kappa)$ is the unique minimizer of $\mathcal{E}_\kappa^c$ on $\mathcal{V}_\kappa^+ := C_\kappa^+(\mathcal{U}_\kappa^+)$. Now, we choose, as neighborhood of W_0^c in $G_N(H^{1/2})$, the set $\mathcal{V} := C(\mathcal{U})$, and we consider the constant $\delta > 0$ such that (22) is satisfied. Taking $\kappa > 0$ even smaller, we can impose

$$\min_{\mathcal{V}_\kappa^+} \mathcal{E}_\kappa^c + \delta/2 \leq \inf_{G_\kappa^+ \setminus \mathcal{V}_\kappa^+} \mathcal{E}_\kappa^c.$$

Hence, W_κ^c is the unique solution to the minimization problem (15). □

4 Bifurcation from the linear open shell case

Recall that here we are in the case

$$N = \sum_{i=1}^{I} N_i^c + k,\ I \in \mathbb{Z}^+,\ 0 < k < N_{I+1}^c\,.$$

For $\kappa = 0$, there exists a manifold of solutions, S_0, whose elements are the spaces

$$\bigoplus_{i=1}^{I} \mathcal{M}_i^c \oplus W_{I+1,k}^c,$$

for all $W_{I+1,k}^c \in G_\ell(M_{I+1}^c)$. These spaces are all the solutions of the variational problems defining E_0^c and e_0^c.

For $\kappa > 0$ and small we want to find solutions of the DF equations near S_0, by using tools from bifurcation theory.

If λ_{I+1} has only multiplicity 2, then (17) implies $k = 1$ and by Lemma 1 of §2, S_0 is an $SU(2)$ orbit. Then, as in Section 3, one can find, in a neighborhood of S_0, a unique $SU(2)$ orbit S_κ of solutions of (DF). But there are also more degenerate cases in which λ_{I+1} has a higher multiplicity, and S_0 contains a continuum of $SU(2)$ orbits. In such situations, $\kappa = 0$ is a bifurcation point, and one expects, according to bifurcation theory, that the manifold of solutions S_0 will break up for $\kappa \neq 0$, and that there will only remain a finite number of $SU(2)$ orbits of solutions. To find these orbits, one usually starts with a Lyapunov-Schmidt reduction: one builds a suitable manifold S_κ which is diffeomorphic to S_0 (see, *e.g.*, [18]). When S_0 contains several $SU(2)$ orbits, the points of S_κ are not necessarily solutions of (DF), but S_κ contains all the solutions sufficiently close to S_0. Moreover, all critical points of the restriction of $\mathcal{E}_\kappa^c$ to S_κ are solutions of (DF). The submanifold S_κ is constructed thanks to the implicit function theorem. More precisely, we consider the projector $\Pi\ :\ L^2 \to \bigoplus_{i=1}^{I+1} \mathcal{M}_i^c$. To each point $z \in S_0$ we associate the submanifold $F_z := \{w \in G_N(H^{1/2})\ :\ \Pi w = z\}$. For w a point of F_z, let $\Delta_w := T_w F_z \subset T_w G_N(H^{1/2})$. Then the following holds:

Theorem 12. *Under the above assumptions, there exist a neighborhood Ω of S_0 in $G_N(H^{1/2})$, a small constant $\kappa_0 > 0$, and a smooth function $h\ :\ S_0 \times (-\kappa_0, \kappa_0) \to \Omega$ such that*

(a) $h(z,0) = z \quad \forall z \in S_0$

(b) *Denoting $S_\kappa := h(S_0, \kappa)$, S_κ is also the set of all points w in Ω such that*

$$\langle (\mathcal{E}_\kappa^c)'(w), \xi \rangle = 0, \quad \forall \xi \in \Delta_w \tag{23}$$

(c) $h(z,\kappa) \in F_z\ , \quad \forall (z,\kappa) \in S_0 \times (-\kappa_0, \kappa_0)$.

Proof. We first fix a point z in S_0. Let $\mathcal{N}$ be the orthogonal space of $\bigoplus_{i=1}^{I+1} \mathcal{M}_i^c$ in $H^{1/2}$ for the L^2 scalar product. As in Section 3, we can define a local chart

$C_z\ :\ \mathcal{O} \subset (\mathcal{N})^N \to F_z$ near z, by the formula $C(\chi) = \mathrm{span}(\psi + \chi)$, where $\psi = (\psi_1, \ldots, \psi_N)$ is an orthonormal basis of z consisting of eigenvectors of $H^c + V$, with eigenvalues $\mu_1 \leq \cdots \leq \mu_N$ (*i.e.*, $\lambda_1^c, \ldots, \lambda_I^c$ counted with multiplicity). The Hessian of $\mathcal{E}_0^c \circ C_z$ at $\chi = 0$ is given once again by formula (20). It is an isomorphism between $(\mathcal{N})^N$ and its dual. So, arguing as in Section 3, we find, by the implicit function theorem, a small constant $\kappa_z > 0$, a neighborhood ω_z of z in F_z and a function $\tilde{h}_z\ :\ (-\kappa_z, \kappa_z) \to \widetilde{\Omega}_z$ such that:

(i) $\tilde{h}_z(0) = z$

(ii) $\tilde{h}_z(\kappa)$ is the unique point w in $\widetilde{\Omega}_z$ such that

$$\langle (\mathcal{E}_\kappa^c)'(w), \xi \rangle = 0, \quad \forall \xi \in \Delta_w \tag{24}$$

Since S_0 is compact and $\mathcal{E}_\kappa^c(w)$ a smooth function of (w, κ), it is possible to choose κ_z , $\widetilde{\Omega}_z$ such that $\kappa_0 := \inf_{z \in S_0} \kappa_z > 0$, with $\Omega := \bigcup_{z \in S_0} \widetilde{\Omega}_z$ a neighborhood of S_0, and $h(z, \kappa) := \tilde{h}_z(\kappa)$ a smooth function on $S_0 \times (-\kappa_0, \kappa_0)$ with values in Ω. This function satisfies (a,b,c). $\square$

From (b) any critical point of $\mathcal{E}_\kappa^c$ in Ω must lie on S_κ. From (c) it follows that S_κ is a submanifold diffeomorphic to S_0, and transverse to each fiber F_z in $G_N(H^{1/2})$. If $z \in S_0$ is a critical point of $\mathcal{E}_\kappa^c \circ h(\cdot, \kappa)$, then, taking $w = h(z, \kappa)$, the derivative of $\mathcal{E}_\kappa^c$ at w vanishes on $T_w S_\kappa$. From (b), it also vanishes on the subspace Δ_w which is transverse to $T_w S_\kappa$ in $T_z G_N(H^{1/2})$, hence $(\mathcal{E}_\kappa^c)'(w) = 0$. This shows that the set of critical points of $\mathcal{E}_\kappa^c$ in Ω coincides with the set of critical points of the restriction of $\mathcal{E}_\kappa^c$ to S_κ. Arguing as in the proof of Proposition 8, one gets more:

Proposition 13. *For $\kappa > 0$ small, the solutions of (DF) of smallest energy E_κ^c are exactly the minimizers of $\mathcal{E}_\kappa^c$ on S_κ.*

We are now ready to prove Proposition 10.

Proof of Proposition 10. Since κ is small, for any matrix $A \in SU(2)$ the map $P^+_{\kappa, A \bullet W_\kappa^c}$ induces a diffeomorphism between the submanifolds $G_N(P^+_{\kappa, W_\kappa^c} H^{1/2})$ and $G_N(P^+_{\kappa,\, A \bullet W_\kappa^c} H^{1/2})$.

Now, we fix $A \in SU(2)$ such that (18) holds. Then there exists a unique point $W^+ \in G_N(H^{1/2})$ such that

$$P^-_{\kappa, W_\kappa^c} W^+ = 0, \quad P^+_{\kappa,\, A \bullet W_\kappa^c} W^+ = A \bullet W_\kappa^c \tag{25}$$

By (18), we have

$$W^+ \neq A \bullet W_\kappa^c.$$

On the other hand, in [14] it was proved that

$$\mathcal{E}_\kappa^c(A \bullet W_\kappa^c) = \sup_{\substack{W \in G_N(H^{1/2}) \\ P^+_{\kappa, A \bullet W_\kappa^c} W = A \bullet W_\kappa^c}} \mathcal{E}_\kappa^c(W) \tag{26}$$

and $A \bullet W^c_\kappa$ is the unique solution of this maximization problem. Therefore,

$$\mathcal{E}^c_\kappa(A \bullet W^c_\kappa) > \mathcal{E}^c_\kappa(W^+) \, .$$

But

$$\mathcal{E}^c_\kappa(W^+) \geq \inf_{W \in G_N(P^+_{\kappa, W^c_\kappa} H^{1/2})} \mathcal{E}^c_\kappa(W) \, ,$$

hence, by invariance of $\mathcal{E}^c_\kappa$ under the action of $SU(2)$,

$$E^c_\kappa = \mathcal{E}^c_\kappa(A \bullet W^c_\kappa) > \inf_{W \in G_N(P^+_{\kappa, W^c_\kappa} H^{1/2})} \mathcal{E}^c_\kappa(W) \, ,$$

and the proposition is proved. □

Since there are no solutions of (DF) under level E^c_κ, and $e^c_\kappa \leq E^c_\kappa$, Proposition 10 has the following consequence:

Corollary 14. *If* **(P)** *is satisfied, then for c large enough and κ small, there is no solution W_* of the nonlinear Dirac-Fock equations with positive Lagrange multipliers, such that the couple*

$$(W_*, P^+_{\kappa, W_*})$$

realizes the max-min e^c_κ. So Conjecture M is wrong when **(P)** *holds.*

We now exhibit a case where **(P)** holds.

Proposition 15. *Assume that* $N = \sum_{i=1}^{I} N^c_i + 1, \ I \geq 1$. *Then* **(P)** *is satisfied.*

Proof. Step 0. Fix c large enough and take a sequence of positive parameters $(\kappa_\ell)_{\ell \geq 0}$ converging to 0. Let $(W^c_\ell)_{\ell \geq 0}$ be a sequence in $G_N(H^{1/2})$, with W^c_ℓ a minimizer of $\mathcal{E}^c_{\kappa_\ell}$ on S_{κ_ℓ}. Let $\psi^c_\ell \in W^c_\ell$ be an eigenvector of the mean-field Hamiltonian $H^c_{\kappa_\ell, W^c_\ell}$, normalized in L^2 and corresponding to the highest occupied level. Extracting a subsequence if necessary, we may assume that $\psi^c_\ell \to \psi^c \in \mathcal{M}^c_{I+1} = \mathrm{Ker}(H^c + V - \lambda^c_{I+1})$. Moreover, from Theorem 12 we have

$$W^c_\ell \to W^c_0 = \bigoplus_{i=1}^{I} \mathcal{M}^c_i \oplus \mathbb{C}\, \psi^c \, .$$

Step 1. Fix $c \geq 1$. Since $P^-_{\kappa_\ell, W^c_\ell} \psi^c_\ell = 0$, we can write, by a classical result due to Kato,

$$\begin{aligned} P^-_{\kappa_\ell, A \bullet W^c_\ell} \psi^c_\ell &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Big[(H^c_{\kappa_\ell, W^c_\ell} - i\eta)^{-1} - (H^c_{\kappa_\ell, A \bullet W^c_\ell} - i\eta)^{-1} \Big] \, \psi^c_\ell \, d\eta \qquad (27) \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} (H^c_{\kappa_\ell, W^c_\ell} - i\eta)^{-1} (H^c_{\kappa_\ell, A \bullet W^c_\ell} - H^c_{\kappa_\ell, W^c_\ell}) (H^c_{\kappa_\ell, A \bullet W^c_\ell} - i\eta)^{-1} \psi^c_\ell \, d\eta \\ &= \frac{\kappa_\ell}{2\pi} \int_{-\infty}^{+\infty} (H^c + V - i\eta)^{-1} (\Omega_{A \bullet W^c_0} - \Omega_{W^c_0}) (H^c + V - i\eta)^{-1} \psi^c \, d\eta + o(\kappa_\ell) \, , \end{aligned}$$

where by Ω_W we denote the nonlinear part of $H^c_{\kappa,W}$:

$$H^c_{\kappa,W} = H^c + V + \kappa\,\Omega_W\,.$$

But note that since the space $\bigoplus_{i=1}^I \mathcal{M}^c_i$ is invariant under the action of $SU(2)$,

$$\Omega_{A\bullet W^c_0} - \Omega_{W^c_0} = \Omega_{A\bullet\psi^c} - \Omega_{\psi^c}\,.$$

So, we just have to prove that for c sufficiently large and for all $\psi^c \in M^c_{I+1}$, there exists $A \in SU(2)$ such that

$$\int_{-\infty}^{+\infty} (H^c + V - i\eta)^{-1}(\Omega_{A\bullet\psi^c} - \Omega_{\psi^c})(H^c + V - i\eta)^{-1}\psi^c\, d\eta \neq 0\,. \tag{28}$$

Since

$$(H^c + V - i\eta)^{-1}\psi^c = \frac{\psi^c}{\lambda^c_{I+1} - i\eta} \quad \text{and} \quad \Omega_{\psi^c}\,\psi^c = 0\,,$$

what we need to prove is that for all nonzero $\psi^c \in M^c_{I+1}$, there exists $A \in SU(2)$ such that $\mathcal{L}^c(\Omega_{A\bullet\psi^c}\,\psi^c) \neq 0$, with

$$\mathcal{L}^c := \int_{-\infty}^{+\infty} (H^c + V - i\eta)^{-1}\frac{d\eta}{\lambda^c_{I+1} - i\eta}\,.$$

Step 2. We give an asymptotic expression for $\mathcal{L}^c$ when $c \to +\infty$:

$$\mathcal{L}^c = \frac{1}{c^2}\int_{-\infty}^{+\infty}\left(\frac{1}{c^2}(H^c + V) - i\frac{\eta}{c^2}\right)^{-1}\frac{d(\eta/c^2)}{\frac{\lambda^c_{I+1}}{c^2} - i\frac{\eta}{c^2}} = \frac{1}{c^2}\left(L_c + O\Big(\frac{1}{c^2}\Big)\right)\,, \tag{29}$$

where L_c, in the Fourier domain, is the operator of multiplication by the matrix

$$\hat{L}_c(p) = \int_{-\infty}^{+\infty} (-iu + \beta + (\boldsymbol{\alpha}\cdot p)/c)^{-1}(-iu + 1)^{-1}\, du\,. \tag{30}$$

Here, we have used the standard fact that

$$\frac{\lambda^c_{I+1}}{c^2} = 1 + O\Big(\frac{1}{c^2}\Big)\,.$$

We have

$$(-iu + \beta + (\boldsymbol{\alpha}\cdot p)/c)^{-1} = \frac{1}{-iu + \omega^c(p)}\hat{\Lambda}^c_+(p) + \frac{1}{-iu - \omega^c(p)}\hat{\Lambda}^c_-(p)$$

with

$$\omega^c(p) := \sqrt{1 + |p|^2/c^2}\,, \quad \hat{\Lambda}^c_\pm(p) = \frac{\omega^c(p) \pm (\beta + (\boldsymbol{\alpha}\cdot p)/c)}{2\omega^c(p)}\,.$$

Hence, by the residues theorem,

$$\frac{2}{\pi}\hat{L}_c(p) = \beta - 1 + \frac{(\boldsymbol{\alpha}\cdot p)}{c} + O\Big(\frac{|p|^2}{c^2}\Big)\,.$$

Step 3. It is well known (see [16]) that ψ^c can be written as

$$\psi^c = \begin{pmatrix} \phi \\ \frac{-i(\sigma\cdot\nabla)\phi}{2c} \end{pmatrix} + O\Big(\frac{1}{c^2}\Big)\,,$$

$\phi \in L^2(\mathbb{R}^3, \mathbb{C}^2)$ being an eigenstate of $(\frac{-\Delta}{2} + V)$, with eigenvalue $\mu = \lim_{c\to+\infty}$ $(\lambda^c_{I+1} - c^2)$. Since we have assumed that V is smooth, this asymptotic result holds for the topology of the Schwartz space $\mathcal{S}(\mathbb{R}^3)$. So,

$$\frac{2c^2}{\pi}\mathcal{L}^c(\Omega_{A\bullet\psi^c}\,\psi^c) = \frac{i}{c}\begin{pmatrix} 0 \\ f(A,\phi) \end{pmatrix} + O\Big(\frac{1}{c^2}\Big)\,,$$

where

$$f(A,\phi) := \Big(|A\bullet\phi|^2 * \frac{x\cdot\sigma}{|x|^3}\Big)\phi - \Big(\langle A\bullet\phi, \phi\rangle_{\mathbb{C}^2} * \frac{x\cdot\sigma}{|x|^3}\Big)(A\bullet\phi)\,. \tag{31}$$

What remains to prove is:

Step 4. For any eigenvector ϕ of the Schrödinger operator $-\frac{\Delta}{2} + V$, there exists an $A \in SU(2)$ such that $f(A,\phi) \not\equiv 0$.

Proof of Step 4. We consider the integral

$$I_{A,\phi}(r) := \int_{S^2} \langle (x\cdot\sigma)\phi, f(A,\phi)\rangle_{\mathbb{C}^2}(r\,\omega)d\omega\,.$$

Since ϕ has exponential fall-off at infinity, the electrostatic field $|A\bullet\phi|^2 * \frac{x}{|x|^3}$ takes the asymptotic form $\Big(\int_{\mathbb{R}^3}|A\bullet\phi|^2\Big)\frac{x}{|x|^3} + O\Big(\frac{1}{|x|^3}\Big)$ when $|x|$ is large. The same phenomenon holds for the convolution product $< A\bullet\phi, \phi >_{\mathbb{C}^2} * \frac{x}{|x|^3}$. As a consequence, for r large,

$$\begin{aligned} r\,I_{A,\phi}(r) \;=\; & \Big(\int_{\mathbb{R}^3}|A\bullet\phi|^2\Big)\Big(\int_{S^2}|\phi|^2(r\,\omega)\,d\omega\Big) \\ & -\Big(\int_{\mathbb{R}^3}\langle A\bullet\phi,\phi\rangle_{\mathbb{C}^2}\Big)\Big(\int_{S^2}\langle\phi, A\bullet\phi\rangle_{\mathbb{C}^2}(r\,\omega)\,d\omega\Big) \\ & +O\Big(\frac{1}{r}\Big)\Big(\int_{S^2}|\phi|^2(r\,\omega)\,d\omega\Big)\,. \end{aligned}$$

Since $\bullet$ is unitary, the Cauchy-Schwarz inequality gives

$$\int_{S^2}|\phi|^2(r\,\omega)\,d\omega = \int_{S^2}|A\bullet\phi|^2(r\,\omega)\,d\omega \geq \Big|\int_{S^2}\langle A\bullet\phi,\phi\rangle_{\mathbb{C}^2}(r\,\omega)\,d\omega\Big|\,.$$

By Lemma 1 of Section 1, we can choose A such that ϕ and $A\bullet\phi$ are not colinear. Then

$$\int_{\mathbb{R}^3}|A\bullet\phi|^2 \;=\; \int_{\mathbb{R}^3}|\phi|^2 \quad > \quad \Big|\int_{\mathbb{R}^3}\langle A\bullet\phi,\phi\rangle_{\mathbb{C}^2}\Big|\,.$$

So there is a constant $\delta > 0$ such that, for r large enough,

$$|r\, I_{A,\phi}(r)| \geq \delta \Big(\int_{\mathbb{R}^3} |\phi|^2 \Big) \Big(\int_{S^2} |\phi|^2 (r\, \omega)\, d\omega \Big) \,. \tag{32}$$

Being an eigenvector of the Schrödinger operator $-\frac{\Delta}{2} + V$, the function ϕ cannot have compact support. So the lower estimate (32) implies that the function $I_{A,\phi}(r)$ is not identically 0, hence $f(A,\phi) \not\equiv 0$. Step 4 is thus proved, and **(P)** is satisfied. $\square$

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