A max-min principle for the ground state of the Dirac-Fock functional.

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Abstract. In this paper, we prove that, when the fine structure constant α is small enough, the energy of the "ground state" of the Dirac-Fock model can be obtained by a nonlinear max-min principle.

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1. The Dirac-Fock model.

In [6] we proved 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 allowed us to define a notion of ground state for the Dirac-Fock equations, valid when the fine structure constant α is small enough. In the present paper we show, as a consequence of our results in [6], that the energy of this ground state can be defined as a max-min level. We hope that this new characterization will

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help to bridge the gap between the Dirac-Fock equations and the Dirac-Fock-Bogoliubov model derived from Q.E.D. (see [4, 1, 2]).

First of all, we choose units for which $m = c = \hbar = 1$, where m is the mass of the electron, c the speed of light and $\hbar$ is Planck's constant. In these units, the free Dirac Hamiltonian can be written as

$$H_0 \;=\; -i\,\alpha\cdot\nabla+\beta, \tag{1}$$

where $\beta = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix}$, $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}$ $(k=1,2,3)$ and the σ_k are the well known Pauli matrices. The operator H_0 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 $(-\infty,-1]\cup[1,+\infty)$. Let us denote $E := H^{1/2}(\mathbb{R}^3,\mathbb{C}^4)$. Since

$$\sigma(H_0) \;=\; (-\infty,-1]\cup[1,+\infty)\ ,$$

the Hilbert space E can be split as

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

where $E^\pm := \Lambda_0^\pm E$, and $\Lambda_0^\pm := \chi_{\mathbb{R}_\pm}(H_0)$. The projectors $\Lambda_0^\pm$ have a simple expression in the Fourier domain : $\widehat{\Lambda_0^\pm\psi}(\xi) = \hat{\Lambda}_0^\pm(\xi)\ \hat{\psi}(\xi)$, with

$$\widehat{\Lambda}_0^\pm(\xi) \;:=\; \frac{1}{2}\left(\mathbf{I}_{\mathbb{C}^4} \pm \frac{\alpha\cdot\xi+\beta}{\sqrt{1+|\xi|^2}}\right)\ . \tag{2}$$

Let us consider a system of N electrons coupled to a fixed nuclear density $Z\mu$, where $Z>0$ is 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, $Z\mu = \sum_{i=1}^m Z_i\delta_{x_i}$ and $Z = \sum_{i=1}^m Z_i$.

In our system of units, the Dirac-Fock equations (first introduced in [16]) for such a molecule are given by

$$
\text{(DF)} \quad \begin{cases} \overline{H}_\Psi \, \psi_k := H_0 \, \psi_k - \alpha Z(\mu * \dfrac{1}{|x|})\psi_k + \alpha(\rho_\Psi * \dfrac{1}{|x|})\psi_k \\ \qquad -\alpha \displaystyle\int_{\mathbb{R}^3} \dfrac{R_\Psi(x,y)\,\psi_k(y)}{|x-y|}\, dy = \varepsilon_k \, \psi_k \quad (k = 1, ...N), \\ \\ \mathrm{Gram}_{\mathrm{L}^2} \Psi = \mathbb{I}_{\mathrm{N}} \quad (\mathrm{i.e} \int_{\mathbb{R}^3} \psi_{\mathrm{k}}^* \psi_{\mathrm{l}} = \delta_{\mathrm{kl}} \ , \ 1 \le \mathrm{k}, \mathrm{l} \le \mathrm{N}). \end{cases}
$$

Here, $\alpha > 0$ is a dimensionless constant called the fine structure constant. Its physical value is close to $\frac{1}{137}$, but in this paper α will be a "small" parameter. Moreover, $\Psi = (\psi_1, \cdots, \psi_N)$, 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

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

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

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

Finally, $\varepsilon_1 \le ... \le \varepsilon_N$ are eigenvalues of $\overline{H}_\Psi$. Each one represents the energy of one of the electrons, in the mean field created by the molecule. For physical reasons, we impose $0 < \varepsilon_k < 1$. Note that the scalars ε_k can also be seen as Lagrange multipliers. Indeed, the Dirac-Fock equations are the Euler-Lagrange equations of the Dirac-Fock energy functional

$$
\mathcal{E}(\Psi) = \sum_{k=1}^{N} \int_{\mathbb{R}^3} \psi_k^* H_0 \psi_k - \alpha Z\Big(\mu * \frac{1}{|x|}\Big)\psi_k^*\psi_k
$$
$$
+ \frac{\alpha}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Psi(x)\rho_\Psi(y) - \mathrm{tr}\Big(R_\Psi(x,y) R_\Psi(y,x)\Big)}{|x-y|}\, dxdy
$$

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

The definition of a ground state is not easy : the DF functional is not bounded from below. This fact is at the origin of serious difficulties in the numerical implementation, as well as the interpretation, of the DF equations (see [4] and the references therein). One way to deal with this problem, is to restrict the energy functional to the space $(\Lambda^+E)^N$, Λ^+ being the projector on the space of positive states of a perturbed Dirac operator $H_0+\Omega$ [3, 14, 12, 15]. The associated Euler-Lagrange equations are the "projected" Dirac-Fock equations

$$\Lambda^+ \overline{H}_\Psi \Lambda^+ \psi_k \;=\; \epsilon_k \psi_k \;. \tag{4}$$

The difficulty here is in the choice of the projector. Note that, in the case $\epsilon_k > 0$, the "unprojected" (DF) equations can be written

$$\Lambda_\Psi^+ \overline{H}_\Psi \Lambda_\Psi^+ \psi_k \;=\; \epsilon_k \psi_k \;. \tag{5}$$

Here, Λ_Ψ^+ is the "self-consistent" projector on the positive spectral space of $\overline{H}_\Psi$. Numerical computations with various choices of projectors, and comparisons with experimental data, show that this self-consistent projector is the best choice (see e.g. [7, 11]). In fact, when Λ^+ in (4) is not equal to Λ_Ψ^+, the eigenvalues ε_k and the total energy $\mathcal{E}(\Psi)$ are underestimated (see [9] for an theoretical explanation based on perturbation theory). In [12] Mittleman derived the DF equations with "self-consistent projector" (5), from a variational procedure applied to a QED Hamiltonian in Fock space, followed by the standard Hartree-Fock approximation. More precisely, let $\Lambda^+ = \chi_{(0,\infty)}(H_0 + \Omega)$, let Ψ_Ω be a minimizer of the DF energy in the projected space $(\Lambda^+E)^N$ under normalization constraints, and let $E(\Omega) := \mathcal{E}(\Psi_\Omega)$. Mittleman showed that the stationarity of $E(\Omega)$ with respect to Ω implies that Λ^+ is the self-consistent projector associated to Ψ_Ω. His arguments are formal. One of our motivations in the present work, is to present a rigorous max-min method related to Mittelman's ideas.

In [5] and [13], under some assumptions on α, N and Z, an infinite sequence $(\Psi^j)_{j\geq 0}$ of solutions of (DF) was found. The assumptions in [13] cover all existing atoms. In [6], we were able to prove that, for α small enough, the first solution Ψ^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 1 *[6]. Fix N, Z with $N < Z+1$ and take α sufficiently small. Then there exists a solution Ψ^0 of the (DF) equations, such that*

$$\mathcal{E}(\Psi^0) = \min\{\mathcal{E}(\Psi)\,;\; \mathrm{Gram}_{L^2}\Psi = \mathbf{I}_N\,,\; \Lambda_\Psi^- \Psi = 0\;\} \tag{6}$$

where $\Lambda^-_\Psi = \chi_{(-\infty,0)}(\overline{H}_\Psi)$ *is the negative spectral projector of the mean-field operator* $\overline{H}_\Psi$*, 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 $\overline{H}_\Psi$: 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 $\overline{H}_\Psi$.

2. A new "max-min" principle.

First of all, note that the Dirac-Fock energy only depends on the N-dimensional space spanned by Ψ. So, in the sequel, we consider that $\mathcal{E}$ is defined on the Grassmannian manifold

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

Similarly, since the mean-field operator $\overline{H}_\Psi$ only depends on $V = Span(\Psi)$, we shall denote it $\overline{H}_V$. The associated positive and negative energy projectors will be denoted Λ^+_V and Λ^-_V.

Recalling that $E := H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, $E^\pm := \Lambda^\pm_0(E)$, let

$$G^+ := \{V \in G \ ; \ V \subset E^+\} .$$

Then the set

$$\mathcal{U} := \{V \in G \ ; \ dim_{\mathbb{C}}(\Lambda^+_0(V)) = N\}$$

is an open neighborhood of G^+ in G. Moreover, it has the structure of a fiber bundle over G^+, with canonical projection $\tau \ : \ V \in \mathcal{U} \to \Lambda^+_0(V) \in G^+$. Note that $\mathcal{U}$ is isomorphic to the vector bundle

$$\bigcup_{V^+ \in G^+} \{V^+\} \times \mathcal{L}_{\mathbb{C}}(V^+, E^-) .$$

This is due to the fact that any $V \in \mathcal{U}$ is the graph of a unique linear map $L_V \ : \ \Lambda^+_0(V) \to E^-$. Now, let

$$\Gamma := \{s \in C^\infty(G^+, \mathcal{U}) \ ; \ \tau \circ s = Id_{G^+} \} .$$

In terms of differential geometry, Γ is the set of smooth sections of $\mathcal{U}$ over G^+. Note that the canonical injection $s_0 \ : \ G^+ \to \mathcal{U}$ belongs to Γ.

More generally, let F be a Hilbert subspace of E such that the restriction λ_F of Λ_0^+ to F is an isomorphism between F and E^+. Then the map

$$s_F \ : \ V^+ \in G^+ \to \lambda_F^{-1}(V^+) \in \mathcal{U}$$

belongs to Γ. The next lemma gives another important example of a smooth section over G^+.

Lemma 2 . *Fix N, Z with $N < Z+1$. Take $\alpha > 0$ small enough. Consider the set*

$$\tilde{S} := \{V \in G \ : \ \Lambda_V^-(V) = 0\}\,.$$

Then $\tilde{S} \subset \mathcal{U}$, and the map $V \in \tilde{S} \to \Lambda_0^+(V) \in G^+$ has a unique inverse $\tilde{s} \ : \ G^+ \to \tilde{S}$. The map $\tilde{s}$ belongs to Γ.

Proof of Lemma 2. Denoting $K_V := \frac{1}{\alpha}(\overline{H}_V - H_0)$, we find, as in the proof of Lemma 1 of [8],

$$\Lambda_0^+ - \Lambda_V^- = \frac{\alpha}{\pi}\int_0^{+\infty} dz\,\left[H_0^2 + z^2\right]^{-1}\left(H_0 K_V \overline{H}_V - z^2 K_V\right)\left[\left(\overline{H}_V\right)^2 + z^2\right]^{-1}.$$

Since K_V is independent of α we find, by estimates similar to those in [8] (proof of Lemma 3), that the map

$$V \in G \to \frac{1}{\alpha}(\Lambda_0^+ - \Lambda_V^-) \in \mathcal{L}(E)$$

is bounded in C^1, independently of α. As a consequence,

$$V \in G \to \Lambda_V^- \in \mathcal{L}(E)$$

is C^1-close to the constant map $V \to \Lambda_0^-$, for α small. Then Lemma 2 directly follows from the implicit functions theorem. Note that when α goes to 0, $\tilde{s}$ converges in C^1 to the canonical injection s_0.

□

We now define the max-min level

$$e^0 := \sup_{s\in\Gamma}\ \inf_{V\in s(G^+)} \mathcal{E}(V)\ .$$

Our main result is the following:

Theorem 3 . *Let $N < Z + 1$. Take $\alpha > 0$ small enough. Then*

$$e^0 = \inf_{V \in \tilde{S}} \mathcal{E}(V) = \mathcal{E}(\Psi^0)$$

with Ψ^0 defined in Theorem 1, and $\tilde{S}$ defined in Lemma 2.

Proof of Theorem 3. Lemma 2 implies that

$$\inf_{V \in \tilde{S}} \mathcal{E}(V) = \inf_{V \in \tilde{s}(G^+)} \mathcal{E}(V) \leq e^0 \, .$$

Now, if we denote $V^0 := Span(\Psi^0)$ and $V^{0,+} := \tau(V^0) = \Lambda_0^+(V^0)$, it follows directly from [6] (proof of Lemma 9, Step 1), that

$$\mathcal{E}(V^0) = \sup_{\substack{W \in G \\ \Lambda_0^+(W) = V^{0,+}}} \mathcal{E}(W). \tag{7}$$

As a consequence, for any $s \in \Gamma$,

$$\mathcal{E}(V^0) \geq \mathcal{E}(s(V^{0,+})) \, ,$$

since $\Lambda_0^+(s(V^{0,+})) = \tau \circ s(V^{0,+}) = V^{0,+}$. We thus have

$$\mathcal{E}(V^0) \geq \sup_{s \in \Gamma} \mathcal{E}(s(V^{0,+})) \geq e^0 \, .$$

But if we replace, in Theorem 1, the variable Ψ by the more intrinsic variable $V = Span(\Psi)$, we get

$$\inf_{V \in \tilde{S}} \mathcal{E}(V) = \mathcal{E}(V^0) \, .$$

So Theorem 3 is proved. □

Remark : One could try the following simpler "max-min" principle. Let $\mathcal{F}$ be the family of all Hilbert subspaces F of E such that the restriction λ_F of Λ_0^+ to F is an isomorphism between F and E^+. This family contains, in particular, the positive spectral subspaces associated to the perturbed Dirac operators $H_0 + \Omega$, for Ω "not too large". Let

$$c'^0 := \sup_{F \in \mathcal{F}} \inf_{\substack{V \in G \\ V \subset F}} \mathcal{E}(V) \, . \tag{8}$$

We have already seen that the formula $s(V^+) := \lambda_F^{-1}(V^+)$, $V^+ \in G^+$, defines a section $s_F \in \Gamma$, for all $F \in \mathcal{F}$. As a consequence, $c'^0 \leq c^0$.

For $N = 1$, the mean-field Hamiltonian $\overline{H}_V$ is simply the Dirac operator with fixed potential $-\alpha Z \mu * \frac{1}{|x|}$, so it does not depend on V. Let $\tilde{F}$ be its positive spectral subspace. Then the definition of $\tilde{S}$ (see Lemma 2) reduces to $\tilde{S} = \{V \in G \; ; \; V \subset \tilde{F}\}$. So Theorem 3 reduces to

$$c^0 = \inf_{\substack{V \in G \\ V \subset \tilde{F}}} \mathcal{E}(V) \; .$$

When α is small enough, $\tilde{F}$ belongs to the class $\mathcal{F}$, and the above formula implies that $c^0 \leq c'^0$. So, in the case $N = 1$, $c'^0 = c^0$, and this energy level is the first positive eigenvalue λ_1 of $H_0 - \alpha Z \mu * \frac{1}{|x|}$. A formula similar to $c'^0 = \lambda_1$ has already been obtained in an unpublished work by Barbaroux and Siedentop (personal communication), in the more general context of the Dirac-Fock-Bogoliubov model, but with the same restriction $N = 1$. In the case $N \geq 2$, it would be interesting to show that $c'^0 = c^0$. Unfortunately, we do not know how to prove this, even when α is very small.

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