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DIRAC-FOCK MODELS FOR ATOMS AND MOLECULES AND RELATED TOPICS

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1. Introduction

Relativistic effects are important in the electrons' dynamics and bound state energies in heavy atoms and molecules. When the nuclei involved are heavily charged, the velocities of the electrons of the inner layers are quite large, and so nonrelativistic modelling will lead to important errors. The usual strategies to address this issue are : either use nonrelativistic models together with relativistic corrections, or use relativistic models based on the Dirac operator.

The free Dirac operator is the simplest first order (in time and space) constant coefficient operator which is invariant under the action of the Lorentz group, *i.e.* its is compatible with Relativity Theory. The free Dirac operator can be written as:

$$i\partial_t + H_c,$$

where

$$H_c = -i c \hbar \alpha \cdot \nabla + mc^2 \beta, \quad \text{with } \alpha_1, \alpha_2, \alpha_3, \beta \in \mathcal{M}_{4 \times 4}(\mathbb{C})$$

$$\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}, \quad \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}$$

and the matrices σ_k are the Pauli matrices:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Two of the main properties of H_c are that its square is a shifted Schrödinger operator:

$$H_c^2 = -c^2 \hbar^2 \Delta + m^2 c^4, \tag{1}$$

and that its spectrum is unbounded below and above:

$$\sigma(H_c) = (-\infty, -mc^2] \cup [mc^2, +\infty), \tag{2}$$

and therefore has a gap, $(-mc^2, mc^2)$.

Looking for bound states for an electron in an external potential V of the form

$$\tilde{\psi}(t, x) = e^{-i\lambda t} \psi(x)$$

is equivalent to looking for eigenvalues λ of the operator $H_c + V$ associated with the eigenfunctions ψ . In the case of N electrons, by analogy with the nonrelativistic case, the Hamiltonian should be written as : $H_{c,x_1} + \dots + H_{c,x_N} + V$. But as Brown and Ravenhall remarked in [5], for potentials V not too singular, the spectrum of this Hamiltonian is the whole real line. So, no isolated eigenvalues can correspond to bound state energies. But by analogy to the nonrelativistic case, one could still try to find eigenfunctions of $H_{c,x_1} + \dots + H_{c,x_N} + V$ as Slater determinants, that is, in the form:

$$\psi := \frac{1}{\sqrt{N!}} \det(\psi_i(x_j)), \quad i, j = 1, \dots, N, \quad (3)$$

the functions ψ_j being mutually orthogonal and of norm 1 in the space $L^2(\mathbb{R}^3, \mathbb{C})$ (the constant $\frac{1}{\sqrt{(N!)}}$ appearing in the above expression just for the sake of normalization). The reason to consider Slater determinants is the Pauli principle which states that one cannot find two electrons in the same state. Hence, the eigenfunctions should be antisymmetric and the simplest antisymmetric function is the determinant.

The Dirac-Fock equations can be found in the above manner. In that sense, they are the relativistic counterpart of the nonrelativistic Hartree-Fock equations which are derived in the same way from the Hamiltonian $-\Delta_{x_1} - \dots - \Delta_{x_N} + V$. Despite their non very physical derivation, the Dirac-Fock model is widely used in computational atomic physics and quantum chemistry to study atoms and molecules involving heavy nuclei. These equations were first introduced by Swirls in [29]. One can find many articles in the Physics litterature about the Dirac-Fock equations (or more complicated models, like the multi-configuration Dirac-Fock model in the case of atoms and molecules with open shells) : see for instance [6, 7, 9, 10, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 27, 28].

An interesting question is why these equations have bound state solutions (see below) and give very satisfactory numerical results. Why are these equations so well fitted to describe the stable electronic configuration in atoms and molecules if the model is not physically "well posed"? In Section 3 we will discuss a possible link between the Dirac-Fock equations and models of Quantum field theory which could maybe explain these phenomena.

A function $\Psi \in \Sigma := \{\Psi = (\psi_1, \dots, \psi_N); (\psi_\ell, \psi_k)_{L^2} = \delta_{k\ell}\}$ is said to satisfy the Dirac-Fock equations if for $k = 1, \dots, N$,

$$\bar{H}_{c,\Psi} \psi_k = \lambda_k \psi_k, \quad \lambda_k \in (-mc^2, mc^2), \quad (4)$$

where the mean-field operator $\bar{H}_{c,\Psi}$ is defined by

$$\bar{H}_{c,\Psi} \psi_k = (H_c + V) \psi_k + (\rho * \frac{1}{|x|}) \psi_k - \int_{\mathbb{R}^3} \frac{R(x, y) \psi_k(y)}{|x - y|} dx dy, \quad (5)$$

ρ being the (scalar) electronic density and the 4×4 complex matrix R , the exchange matrix which comes from the antisymmetry of the Slater determinant :

$$\rho(x) = \sum_{\ell=1}^N \left(\psi_\ell(x), \psi_\ell(x) \right)_{\mathbb{C}^4}, \quad R(x, y) = \sum_{\ell=1}^N \psi_\ell(x) \otimes \psi_\ell^*(y).$$

Formally, the solutions of DF equations are the stationary points of the “energy functional”

$$\mathcal{E}_c(\Psi) = \sum_{k=1}^N \left((H_c + V)\psi_k, \psi_k \right)_{L^2} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y) - |R(x,y)|^2}{|x-y|} dx dy,$$

in the set

$$\Sigma := \{ \Psi = (\psi_1, \dots, \psi_N); (\psi_\ell, \psi_k)_{L^2} = \delta_{k\ell} \}.$$

Remark. The infimum of $\mathcal{E}_c$ over the set S is equal to $-\infty$. So, the solutions of DF will have to be some kind of saddle points for $\mathcal{E}_c$.

2. The Dirac-Fock equations and their nonrelativistic limit

In an atomic or molecular model, the external potential can be approximately described by

$$V = -Z\mu * \frac{1}{|x|},$$

where the measure $Z\mu$ represents the nuclear charge distribution, and in the particular case of a molecule with K point nuclei with charge Z_i and situated at the points $\bar{x}_i, i = 1, \dots, K$, the measure $Z\mu$ takes the form $Z\mu = \sum_i Z_i \delta_{\bar{x}_i}$. So, Z is the total nuclear charge.

As already said in the Introduction, finding solutions of (4) is then reduced to finding critical points of the functional $\mathcal{E}_c$ on the set Σ . Once again, the unboundedness (from above and below) of the spectrum of the free Dirac operator makes the functional $\mathcal{E}_c$ totally indefinite. This together with the *a priori* lack of compactness of the problem ($\mathbb{R}^3$ is unbounded) and the fact that we have to work on a manifold Σ and not in the whole functional space, makes the variational problem difficult. A minimization procedure is once again out of the question and another method has to be found. In [11] the authors defined a penalized variational problem which could be solved by first maximizing on some part of the spinor functions ψ_i and then defining a more standard min-max argument for a reduced functional.

The theorem proved in [11] states the following :

Theorem 2.1. ([11]) *With the above notations, assume that N and Z are two positive integers satisfying $\max(Z, 3N - 1) < \frac{2c^2}{\pi/2 + 2/\pi}$ and $N < Z + 1$. Then, there exists an infinite sequence $(\Psi^{c,j})_{j \geq 1}$ of critical points of the DF functional $\mathcal{E}_c$ on Σ . The function vectors $(\psi_1^{c,j}, \dots, \psi_N^{c,j})$ belong to Σ and they are strong solutions, in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4) \cap \bigcap_{1 \leq q < 3/2} W^{1,q}(\mathbb{R}^3, \mathbb{C}^4)$, of the Dirac-Fock equations, that is, for all $j \geq 1$,*

$$\bar{H}_{\Phi^{c,j}} \psi_k^{c,j} = \epsilon_k^{c,j} \psi_k^{c,j}, \quad 1 \leq k \leq N, \quad (6)$$

$$0 < \epsilon_1^{c,j} \leq \dots \leq \epsilon_N^{c,j} < mc^2. \quad (7)$$

Moreover,

$$0 < \mathcal{E}_c(\Phi^{c,j}) < Nmc^2, \quad (8)$$

$$\lim_{j \rightarrow \infty} \mathcal{E}_c(\Phi^{c,j}) = Nmc^2. \quad (9)$$

Remark 2.1. Since μ is arbitrary, the assumptions of the above theorem contain the case of point-like nuclei as well as more realistic nuclear potentials of the form $-\sum_i \rho_i(x) * \frac{1}{|x|}$,

where $\rho_i \in L^\infty \cap L^1$, $\rho_i \geq 0$, $\sum_i \int_{\mathbb{R}^3} \rho_i = Z$.

Remark 2.2. In our units, the above conditions become

$$Z \leq 124, \quad N \leq 41, \quad N \leq Z.$$

The proof of the above theorem is done by defining a sequence of variational problems corresponding to increasing 'topological complexity' or Morse index. By the application of our 'first variational argument' we find solutions $\Psi^{c,1}$, that will play an important role (see below), since for c large they will be actually 'electronic ground states'.

Soon after this result was published, E. Paturel used an alternative method to prove the same result but without the unnatural condition

$$\max(Z, 3N - 1) < \frac{2c^2}{\pi/2 + 2/\pi}, \quad (10)$$

(see [27]). Note that the assumption $N < Z + 1$ is already present in all the existing results for the nonrelativistic Hartree-Fock equations. Also, the conditions Z and N less than $2c^2/(2\pi + \pi/2)$ are not that unnatural, since already in the linear case such a condition is necessary to use Hardy-like inequalities ensuring the existence of a gap of the spectrum of $H_c + V$ around 0 (see for instance [30, 31] and [8]). But condition (10) was clearly related to the particular method of proof in [11]. Paturel's theorem gets rid of (10) and proves the same as Theorem 2.1, but under the sole assumptions

$$Z < \frac{2c^2}{\pi/2 + 2/\pi}, \quad N < \frac{2c^2}{\pi/2 + 2/\pi}, \quad N < Z + 1.$$

Natural questions which arise from the above results are the following:

- Is there a notion of ground-state in this model?
- Is there a link between these solutions and the solutions of the usual Hartree-Fock solutions?
- Can we find the solutions in a simple way? By a "simple" variational argument?

To answer the above questions, it is useful to investigate the nonrelativistic limit of the Dirac-Fock equations. Of course, their formal limite are the well-known Hartree-Fock equations, which are identical to the Dirac-Fock ones, but replacing the Dirac operator H_c with the Schrödinger operator $-\frac{\Delta}{2}$. In [12], this was proved rigorously, and as we see below, this result has been of importance to better understand the variational structure of the Dirac-Fock problem and in particular to obtain a good definition of an electronic ground-state energy, which is *a priori* not clear because of the unboundedness of the Dirac-Fock energy.

The following is proved in [12].

Theorem 2.2. *Let $N < Z + 1$. Consider a sequence of numbers $c_n \rightarrow +\infty$ and a sequence $\{\Psi^n\}_n$ of solutions of (4), i.e. $\Psi^n = (\psi_1^n, \dots, \psi_N^n)$, each ψ_k^n being in $H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$, with $\int_{\mathbb{R}^3} \psi_k^{n*} \psi_l^n dx = \delta_{kl}$ and $\bar{H}_{c_n, \Psi^n} \psi_k^n = \varepsilon_k^n \psi_k^n$. Assume also that the multipliers ε_k^n ($k = 1, \dots, N$) satisfy*

$$0 < c^2 - \mu_j < \varepsilon_1^{c,j} \leq \dots \leq \varepsilon_N^{c,j} < c^2 - m_j, \quad \text{with } \mu_j > m_j > 0 \text{ independent of } n.$$

Then for n large enough, ψ_k^n is in $H^1(\mathbb{R}^3, \mathbb{C}^4)$ and there exists a solution of the Hartree-Fock equations, $\bar{\Phi} = (\bar{\varphi}_1, \dots, \bar{\varphi}_N)$, with negative multipliers, $\bar{\lambda}_1, \dots, \bar{\lambda}_N$, such that, after extraction of a subsequence,

$$\lambda_k^n := \varepsilon_k^n - (c_n)^2 \xrightarrow{n \rightarrow +\infty} \bar{\lambda}_k, \quad k = 1, \dots, N, \quad (11)$$

$$\psi_k^n = \begin{pmatrix} \varphi_k^n \\ \chi_k^n \end{pmatrix} \xrightarrow{n \rightarrow +\infty} \begin{pmatrix} \bar{\varphi}_k \\ 0 \end{pmatrix} \quad \text{in } H^1(\mathbb{R}^3, \mathbb{C}^2) \times H^1(\mathbb{R}^3, \mathbb{C}^2), \quad (12)$$

$$\left\| \chi_k^n + \frac{i}{2c_n} (\sigma \cdot \nabla) \varphi_k^n \right\|_{L^2(\mathbb{R}^3, \mathbb{C}^2)} = O(1/(c_n)^3), \quad (13)$$

and

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

Actually the above theorem can be made more precise : the sequence of the solutions $\Psi^{c,1}$ given by Theorem 2.1 are shown to converge towards ground state solutions of the Hartree-Fock problem when c goes to $+\infty$. This gives a “particular” status to that solution of the Dirac-Fock equations. It does not minimize the Dirac-Fock energy among all functions in the set Σ , since $\inf_{\Sigma} \mathcal{E}_c = -\infty$, but when taking the nonrelativistic limit, they approach those solutions of the Hartree-Fock equations which minimize the corresponding Hartree-Fock energy. Actually, there is more to it. In [12] the following theorem was proved :

Theorem 2.3. ([12]) *Fix N, Z with $N < Z + 1$ and take c sufficiently large. Then $\Psi^{c,1}$ is a solution of the following minimization problem:*

$$\inf \{ \mathcal{E}_c(\Psi); \text{Gram}_{L^2} \Psi = \mathbb{I}_N, \Lambda_{\Psi}^{-} \Psi = 0 \} \quad (15)$$

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

Actually, in [12] we call *electronic configurations* those functions Ψ in Σ which satisfy $\Lambda_{\Psi}^{-} \Psi = 0$ (note that all solutions of the Dirac-Fock equations with positive eigenvalues ε_k are electronic configurations by definitio). Thus, the above result shows that the Dirac-Fock energy is bounded from below in the set of all electronic configurations, and $\Psi^{c,1}$ is a minimizer for it in that set.

The above theorems answer some of the questions made above. Another question that we asked was that of finding a non very complicated variational argument to find the solutions exhibited in Theorem 2.1, since the proofs in that theorem are very involved technically and very difficult to implement in actual computations. In order to do this, in [12] we introduced the notion of projector “ ε -close to Λ_c^+ ”, where $\Lambda_c^+ = \frac{1}{2}|H_c|^{-1}(H_c + |H_c|)$ is the positive free-energy spectral projector.

Definition 2.1. : 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 Λ_c^+ if and only if, for all $\psi \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^4)$,

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

An obvious example of projector ε -close to Λ_c^+ is Λ_c^+ itself. Other interesting examples are the mean-field operators $\bar{H}_{c,\Psi}$ for c large enough. Let us now give a min-max principle associated to P^+ :

Theorem 2.4. 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 $P^- = \mathbb{I}_{L^2} - P^+$, and define

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

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

This result shows that when we want to find the electronic ground-state of the Dirac-Fock problem by a “simple min-max”, we have a large choice of projectors in the limit $c \rightarrow +\infty$. Other characterizations of the ground-state energy for c large can be found in [13].

3. The Dirac-Fock equations and a Hartree-Fock model in Fock's space

Atomic and molecular models based on Q.E.D. seem to be better motivated than the Dirac-Fock equations. In a Q.E.D. formulation one should be able to write an energy functional which is bounded below in a well chosen subset of the Fock space. In such a model one cannot fix the number of particles (electrons) but only the charge, since one has to admit the possible presence of electron-positron pairs, which do not change the charge, but change the number of particles. In all models based on Q.E.D. there are some choices to be made, for instance, a notion of electron, that is, a positive energy space (and its corresponding projector). Also, the kind of configurations that are allowed in the model has to be made precise, in order to see if multiconfiguration is allowed or not.

In [1, 2] such a model has been proposed and the case of no electrons completely treated (the empty set). In [4] the same kind of model has been used to treat the case of positive charges ($N \geq 0$). More concretely, in these models one chooses $P^+ \in \mathcal{P}$, “a positive projector” (choice of electronic space), and

$$S^{N,P^+} = \{ \gamma \in S_1(L^2), \gamma = \gamma^*, -(1 - P^+) \leq \gamma \leq P^+, P^+ \gamma (1 - P^+) = 0, \text{tr } \gamma \leq N \},$$

where $S_1(L^2)$ is the trace class operators Hilbert space.

Let us now define

$$\mathcal{F}_\alpha^c(\gamma) = \text{tr}((H_c + V - mc^2)\gamma) + \frac{1}{2} \int \frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y}) - |\gamma(x, y)|^2}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y},$$

$$I(c, N, P^+) = \min_{\gamma \in S^{N, P^+}} \mathcal{F}_c(\gamma). \quad (16)$$

In a recent result, Barbaroux, Farkas, Helffer and Siedentop have proved that when one chooses the class of projectors

$$\mathcal{P} := \{P_\Psi^+, P_\Psi^+ = \chi_{[0, \infty)}(\bar{H}_{c, \Psi}), \Psi \in \Sigma\},$$

the minimization problem (16) has a solution. Moreover, under some (reasonable) conditions, the minimizer of $\mathcal{F}_c$ in S^{N, P^+} is no-pair (purely electronic), that is, there exists

functions $\bar{\psi}_1, \dots, \bar{\psi}_N$ such that : $\gamma_{min} = \sum_{k=1}^N \langle \bar{\psi}_k, \cdot \rangle \bar{\psi}_k$ and

$$P^+(\bar{H}_{c, \Psi}) P^+ \bar{\psi}_k = \lambda_k \bar{\psi}_k, \quad \lambda_k \in (0, mc^2), \quad (17)$$

that is, the $\bar{\psi}_k$'s are solutions to the projected Dirac-Fock equations (projected in the image of the chosen projector P^+ , of course).

Now, in [26], Mittleman proved (somehow formally, but the main ingredients of a proof are present in the paper) that any stationary solution (stationary in P^+ and γ) of a related QED functional would be a solution of the self-consistent Dirac-Fock equations. Hence, when we take the energy $\mathcal{F}_c$ to depend both on P^+ and γ , any stationary point of this new functional, $(\bar{\Psi}, \bar{P}^+)$, should be a solution of (17) with $\bar{P}^+ = \chi_{(0, +\infty)}(\bar{H}_{c, \bar{\Psi}})$.

A natural idea would be to find stationary points in P^+ and γ by considering the max-min problem:

$$\sup_{P^+ \in \mathcal{P}} \inf_{\gamma \in S^{N, P^+}} \mathcal{F}_c(\gamma). \quad (18)$$

This problem was shown to have a unique solution in the case $N = 0$ in [1, 2]. In the case $N > 0$, Barbaroux, Farkas, Helffer and Siedentop prove that indeed Mittleman's result holds in their context. It is then natural to ask whether the max-min problem defined above has a solution or not, and in the affirmative case, whether the solution of that variational problem is a stationary point of the energy functional or not.

In a recent joint work with Barbaroux ([3]), we prove that the answer to the above question is yes in some particular cases (for instance when the "neighboring" linear case corresponds to a closed shell atom), but it is *no* in the general case; indeed, we exhibit a case where even if the max-min defined above were attained by some $(\bar{\Psi}, \bar{P}^+)$, $(\bar{\Psi}, \bar{P}^+)$ would not be a solution of the self-consistent Dirac-Fock equations, that is $\bar{P}^+ \neq \chi_{(0, +\infty)}(\bar{H}_{c, \bar{\Psi}})$.

More precisely, it is well known that the Dirac operator is invariant under the action of the Lorentz group. This means that for every spatial rotation R , there is a unique matrix $U(R) \in SU_2$ such that the Dirac Hamiltonian is invariant under the transformation

$$\psi(\cdot) \mapsto A(R) \bullet \psi := \begin{pmatrix} U(R) & 0 \\ 0 & U(R) \end{pmatrix} \psi(R \cdot),$$

and viceversa.

Then, we prove in [3] the following

Proposition 3.1. *Assume that $\mu_{c,k}$ (resp. $N_{c,k}$) denotes the k -th eigenvalue of the operator $H_c + V$, not counted with multiplicity (resp. its multiplicity). If $N = \sum_{k=1}^I N_{c,k}$ for some positive integer I , then for c large enough, the max-min defined in (18) is achieved by a solution of the (self-consistent) Dirac-Fock equations, that is, if we denote by $(\bar{\Psi}, \bar{P}^+)$ a solution of (18), then $\bar{P}^+ = \chi_{(0,+\infty)}(\bar{H}_{c,\bar{\Psi}})$ for c large enough.*

Remark. The main reason why the above proposition holds true is that under the assumptions of the proposition, when c is large enough, for every spatial rotation R , for every $\Psi \in \Sigma$, Ψ solution of the Dirac-Fock equations, $\bar{H}_{c,\Psi} = \bar{H}_{c,A(R)\bullet\Psi}$.

In fact we conjecture that when there is no positive integer I such that $N = \sum_{k=1}^I N_{c,k}$ (open shell case), the above proposition is not true. Actually, in a special case where V is a “small” Coulomb potential, c is large enough and $N = 1 + \sum_{k=1}^I N_{c,k}$, I being any positive integer, we have proved that Proposition 3.1 does not hold.

The above results show that there is a clear link between the Dirac-Fock equations and some variational problem issued from Q.E.D. since in some cases both methods have the same solutions. But this is not the case for every electronic number.

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