Mathematical remarks on the Optimized Effective Potential problem

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Abstract

We investigate mathematically a minimization problem issued from computational chemistry, and known as the Optimal Effective Potentiel (OEP) problem. We propose a weak formulation of the problem, that we show to be well-posed in a simple case, and we address various related questions.

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1 Motivation

One of the central issues of computational quantum chemistry (see e.g. [1] for an introduction) is the determination of the electronic ground state of a molecular system consisting of K nuclei and N electrons. Denoting by z_k the charge of the k-th nucleus and by $\bar{x}_k$ its position in space, this determination basically consists in finding the state Ψ minimizing

$$\inf \left\{ \langle H_N \Psi, \Psi \rangle, \quad \Psi \in L^2_a(\mathbb{R}^{3N}), \quad \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1 \right\} \tag{1}$$

where the Hamiltonian H_N is given by

$$H_N = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} \left(\sum_{k=1}^{K} \frac{z_k}{|x_i - \bar{x}_k|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} \tag{2}$$

and acts on the position x_i of each of the N electrons. In (1), the minimization runs over all antisymmetric functions of $3N$ variables (thus the subscript a). For simplicity, the functions are assumed to be real-valued and the spin variable is not accounted for in this presentation. Due to the large size of $L^2_a(\mathbb{R}^{3N})$ for physically relevant values of N, it is not possible to directly attack problem (1) and the common practice is to make use of approximations of this problem. One of the most commonly used approximations is the Hartree-Fock approximation (obtained by restricting the minimization in (1) to Ψ that are normalized determinants of N functions) and reads:

$$I^{HF} = \inf\{E^{HF}(\phi_1, \ldots, \phi_N), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \ , \ 1 \le i, j \le N \ , \ \phi_i \in H^1(\mathbb{R}^3)\} \tag{3}$$

where

$$\begin{aligned} E^{HF}(\phi_1, \ldots, \phi_N) &= \frac{1}{2}\sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 - \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\sum_{k=1}^{K} \frac{z_k}{|x_i - \bar{x}_k|} \right) |\phi_i|^2 \\ &+ \frac{1}{2} \int \int_{(\mathbb{R}^3)^2} \frac{\rho(x)\rho(y)}{|x-y|} dx dy - \frac{1}{2} \int \int_{(\mathbb{R}^3)^2} \frac{|\rho(x,y)|^2}{|x-y|} dx dy, \end{aligned} \tag{4}$$

and $\rho(x, y) = \sum_{i=1}^{N} \phi_i(x)\phi_i(y)$, $\rho(x) = \rho(x, x) = \sum_{i=1}^{N} |\phi_i(x)|^2$.

The Hartree-Fock equations are the Euler-Lagrange equations associated to this minimization problem. Up to an orthogonal transform, it can be shown that they read:

$$F_{(\phi_1, \ldots, \phi_N)} \phi_i = -\varepsilon_i \phi_i, \tag{5}$$

where the ε_i are real eigenvalues and $F_{(\phi_1, \ldots, \phi_N)}$ is the so-called Fock Hamiltonian

$$\begin{aligned} F_{(\phi_1, \ldots, \phi_N)} \phi &= -\frac{1}{2}\Delta\phi - \sum_{k=1}^{K} \frac{z_k}{|x - \bar{x}_k|} \phi + \left(\sum_{j=1}^{N} |\phi_j|^2 \star \frac{1}{|x|} \right) \phi - \left(\sum_{j=1}^{N} \phi_j \phi \star \frac{1}{|x|} \right) \phi_j \quad (6) \\ &= -\frac{1}{2}\Delta\phi - \sum_{k=1}^{K} \frac{z_k}{|x - \bar{x}_k|} \phi + \left(\rho \star \frac{1}{|x|} \right) \phi - \int_{\mathbb{R}^3} \frac{\rho(x, y)}{|x - y|} \phi(y) \, dy \end{aligned}$$

Equation (5) appears as a nonlinear eigenvalue problem involving the Fock operator $F_{(\phi_1,\dots,\phi_N)}$, which is nonlocal, because of the last term in (6). It is easily understandable that, from the computational viewpoint, constructing the Fock Hamiltonian in a given basis of discretization for the ϕ_i is a costly procedure, in particular because of the nonlocal nature of this operator. As early as in the 1960s (see [7]), the idea has therefore emerged to ask whether equations (5) could be rewritten as (or at least approximated by) a system of *local* equations

$$(-\frac{1}{2}\Delta + W)\phi_i = \lambda_i\phi_i, \ \ i = 1, \dots, N \tag{7}$$

for some eigenvalues λ_i and for some *multiplicative* potential W (independent of the index i, but of course possibly dependent of the whole family $(\phi_1, \dots, \phi_N)$), in a suitable class of regularity (say at least locally integrable functions). Consequently, the following minimization problem has been introduced

$$\begin{aligned}&\text{Minimize}\, E^{HF}(\phi_1, \dots, \phi_N), \text{ over the set of functions}\, \phi_i \,\text{that satisfy}\\ &\text{the orthonormality constraints of the standard HF problem (3) and}\\ &\text{in addition that are eigenfunctions of some operator } -\frac{1}{2}\Delta + W\end{aligned} \tag{8}$$

and labelled as the *optimized effective potential* problem (henceforth abbreviated in *OEP problem*). This is to be understood in the sense that one wishes to find the best potential W so that the energy given by some of its eigenfunctions approaches the infimum (3).

Let us point out that we formulate this problem somewhat vaguely here, for the main concern of the present work will be to give a rigorous mathematical meaning to the formal definition (8).

It turns out that the question asked above, that was primarily motivated by considerations on the computational cost, is indeed related to some theoretical questions from quantum chemistry dealing with an alternative theory allowing for a simplification of the original problem (1), namely the Density Functional Theory (see e.g. [1, 2]). Indeed, a better comprehension of the optimized effective potential problem would give some insight on the construction of accurate exchange-correlation potential for Kohn-Sham models (see [3, 4]).

As announced, we intend to give here a possible rigorous foundation to the optimized effective potential problem. As will be seen shortly, our work is a first step, for only very simple, somewhat academic, cases are addressed. We however believe it provides the main mathematical arguments and open the way to more thoroughful studies.

2 Setting of the problem and main results

Let us at once make precise that we shall not address the problem of giving a sense to (8) in the most general context, but that we shall make three simplifying assumptions.

First, we shall consider *spinless wavefunctions*, as in the above introduction. This simplification is not in fact a limitation, for all the results below can be straigthforwardly extended to the models accounting for spin which are used in computational chemistry, such as for instance the restricted Hartree-Fock (RHF) model. It is also to be remarked that for the sake of simplicity, we have chosen to mainly deal with real valued functions. When the consideration of complex valued wavefunctions slightly modify the arguments, we shall indicate it (see in particular Corollary 3.2).

A second simplification we shall make, again for the sake of simplicity, is that we shall only consider a molecular system containing *only two electrons*. The consideration of $N > 2$ electrons does not bring any new qualitative phenomenon, but requires rather tedious details that we prefer to avoid. Here and there, we shall however make some remarks in connection with the $N > 2$ case (see Remarks 2.1 and 2.2).

Contrarily to the first two ones, the third simplification we shall make is restrictive from the mathematical viewpoint. In order to establish some of our main results, we shall restrict our attention to the atomic case, which means that there is only one nucleus of charge Z, located at $\bar{x} = 0$ (and consequently that $\frac{Z}{|x|}$ replaces $\sum_{k=1}^{K} \frac{z_k}{|x - \bar{x}_k|}$ in the energy functional and in the Euler-Lagrange equation), and we shall consider *radially symmetric wavefunctions*. This assumption is restrictive both as results and arguments are concerned. Indeed, spectral theory will play a crucial role in some of our arguments, and it is a well known fact which will be again illustrated here that spectral theory in one dimension (as for radially symmetric functions) features very specific behaviours, in comparison with the situation encountered in dimensions greater than or equal to 2. Likewise, our arguments based upon tools of functional analysis will make an extensive use of the fact that we work in a one dimensional setting. For these reasons, any generalization of our results to the non radial case is unclear. In some situations (which is the case of Theorems 4.1 and 4.2 below, and also for Section 5), the same proof and result apply to the general case where functions are not assumed radially symmetric. On the other hand, for some other results, the situation is radically different, as suggested by Proposition 3.3 where we give an instance of such a difference with respect to the radial case (Theorem 3.1). In this respect,let us mention that the optimized effective potential idea has first arised in a radially symmetric setting [7], and that the consideration of this radial case is already quite relevant from the standpoint of applications in theoretical chemistry.

Let us now define in detail the objects we shall manipulate throughout this article. We have already defined the Hartree-Fock minimization problem (3), and the Hartree-Fock energy functional (4) in the case of N electrons and K nuclei. For clarity, let us restate them in the restricted case of an atom ($K = 1$) with $N = 2$ electrons:

$$I^{HF} = \inf\{E^{HF}(\phi_1, \phi_2), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \ , \ 1 \leq i,j \leq 2 \ , \ \phi_i \in H^1(\mathbb{R}^3)\} \tag{9}$$

where

$$\begin{aligned} E^{HF}(\phi_1, \phi_2) &= \frac{1}{2}\int_{\mathbb{R}^3} |\nabla \phi_1|^2 + \frac{1}{2}\int_{\mathbb{R}^3} |\nabla \phi_2|^2 - \int_{\mathbb{R}^3} \frac{Z}{|x|}\phi_1^2 - \int_{\mathbb{R}^3} \frac{Z}{|x|}\phi_2^2 \\ &+ \int\int_{(\mathbb{R}^3)^2} \frac{\phi_1^2(x)\phi_2^2(y)}{|x-y|} dxdy - \int\int_{(\mathbb{R}^3)^2} \frac{\phi_1(x)\phi_1(y)\phi_2(x)\phi_2(y)}{|x-y|} dxdy. \end{aligned} \tag{10}$$

As announced, we shall mainly restrict ourselves to the case when the functions are assumed to be radially symmetric and therefore to

$$I_r^{HF} = \inf\{E^{HF}(\phi_1, \phi_2), \int_{\mathbf{R}^3} \phi_i\phi_j = \delta_{ij}\ ,\ 1 \le i,j \le 2\ ,\ \phi_i \in H_r^1(\mathbb{R}^3)\} \tag{11}$$

where $H_r^1(\mathbb{R}^3)$ denotes the set of radially symmetric functions of $H^1(\mathbb{R}^3)$. Accordingly, we shall say that (ϕ_1, ϕ_2) is a solution of the Hartree-Fock equation whenever it satisfies

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 - \frac{Z}{|x|}\phi_1 + (\phi_2^2 \star \frac{1}{|x|})\phi_1 - (\phi_1\phi_2 \star \frac{1}{|x|})\phi_2 = -\varepsilon_1\phi_1, \\ -\frac{1}{2}\Delta\phi_2 - \frac{Z}{|x|}\phi_2 + (\phi_1^2 \star \frac{1}{|x|})\phi_2 - (\phi_1\phi_2 \star \frac{1}{|x|})\phi_1 = -\varepsilon_2\phi_2, \\ \int_{\mathbf{R}^3} \phi_i\phi_j = \delta_{ij}, 1 \le i,j \le 2 \end{cases} \tag{12}$$

Most of the time, ϕ_1 and ϕ_2 will be radially symmetric.

Let us also briefly mention the complex valued case, where the Hartree-Fock minimization problem (possibly for radially symmetric functions, then indicated by the subscript r) reads

$$I_{(r)}^{HF,\mathbb{C}} = \inf\{E^{HF,\mathbb{C}}(\phi_1, \phi_2), \int_{\mathbf{R}^3} \phi_i\phi_j^* = \delta_{ij}\ ,\ 1 \le i,j \le 2\ ,\ \phi_i \in H_{(r)}^1(\mathbb{R}^3, \mathbb{C})\} \tag{13}$$

$$\begin{aligned} E^{HF,\mathbb{C}}(\phi_1, \phi_2) &= \frac{1}{2}\int_{\mathbf{R}^3} |\nabla\phi_1|^2 + \frac{1}{2}\int_{\mathbf{R}^3} |\nabla\phi_2|^2 - \int_{\mathbf{R}^3} \frac{Z}{|x|}|\phi_1|^2 - \int_{\mathbf{R}^3} \frac{Z}{|x|}|\phi_2|^2 \\ &+ \int\int_{(\mathbf{R}^3)^2} \frac{|\phi_1|^2(x)|\phi_2|^2(y)}{|x-y|}dxdy \\ &- \int\int_{(\mathbf{R}^3)^2} \frac{\phi_1(x)\phi_1^*(y)\phi_2^*(x)\phi_2(y)}{|x-y|}dxdy. \end{aligned} \tag{14}$$

while the Hartree-Fock equations read

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 - \frac{Z}{|x|}\phi_1 + (|\phi_2|^2 \star \frac{1}{|x|})\phi_1 - (\phi_1\phi_2^* \star \frac{1}{|x|})\phi_2 = -\varepsilon_1\phi_1, \\ -\frac{1}{2}\Delta\phi_2 - \frac{Z}{|x|}\phi_2 + (|\phi_1|^2 \star \frac{1}{|x|})\phi_2 - (\phi_1^*\phi_2 \star \frac{1}{|x|})\phi_1 = -\varepsilon_2\phi_2, \\ \int_{\mathbf{R}^3} \phi_i\phi_j^* = \delta_{ij}, 1 \le i,j \le 2. \end{cases} \tag{15}$$

Notation We shall make use of the notation, standard in this context,

$$D(f,g) = \int\int_{(\mathbf{R}^3)^2} \frac{f(x)g(y)}{|x-y|}dxdy, \tag{16}$$

whenever this integral makes sense.

2.1 Definition of the OEP problems

We now wish to suggest a mathematical definition for the optimized effective potential problem vaguely defined in (8). But before we get to this, we would like to introduce a variant of (8), namely

$$\begin{array}{l}\text{Minimize}\, E^{HF}(\phi_1, \ldots, \phi_N), \text{ over the set of functions}\, \phi_i \text{ that satisfy} \\ \text{the orthonormality constraints of the standard HF problem (3) and} \\ \text{in addition that are}\, \textbf{the first}\, N\, \text{eigenfunctions of some operator } -\frac{1}{2}\Delta + W. \end{array} \tag{17}$$

The reason why we introduce such a variant is the following. By a result proven in [5], any N-tuple $(\phi_1, ..., \phi_N)$ minimizing the Hartree-Fock energy is a solution of (5) that enjoys the following property: the ϕ_i are the first N eigenfunctions of the operator $F_{\phi_1,...,\phi_N}$. Therefore, both for computational reasons (because searching for the first N eigenvalues of a matrix is a specific problem) and for theoretical purposes, it is natural to introduce the variant (17). In fact, we shall concentrate most of our attention to this variant, which is indeed the physically relevant version of the OEP problem, and only consider (8) as a pedagogic and technical step.

In order to give a sense to (8) or respectively (17), a major obstacle needs to be overcome. The problem of minimizing upon W is indeed ill-posed, because a control on the minimizing sequences (W_n) is missing in any natural norm. Of course, one could introduce a penalized formulation of the problem, and we will indeed do so in Section 5 below, but we prefer to concentrate our efforts on another track. We shall introduce a "weak" formulation of the problems (see (20) and (26) below), that can be shown to lead to a well posed mathematical problem, and then check, at least formally, that this weak version indeed allows to recover the problem in a strong sense. Let us now motivate our choice for such a weak formulation.

Considering two eigenfunctions ϕ_1 and ϕ_2 of a given operator $-\frac{1}{2}\Delta + W$

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 + W\phi_1 = \lambda_1\phi_1, \\ -\frac{1}{2}\Delta\phi_2 + W\phi_2 = \lambda_2\phi_2, \end{cases} \tag{18}$$

it is immediate to see that the following condition, henceforth designated as the *commutation condition*, is fulfilled

$$\phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = c\phi_1\phi_2 \tag{19}$$

with $c = 2(\lambda_2 - \lambda_1)$. Conversely, if two functions ϕ_1 and ϕ_2 satisfy (19), then they formally are eigenfunctions of $-\frac{1}{2}\Delta + W$ for $W = \frac{\Delta\phi_1}{2\phi_1}$ respectively for the eigenvalues 0 and $\frac{c}{2}$. Thus the idea is to introduce the following minimization problem

$$\begin{aligned} \widetilde{I^{OEP}} \;=\; & \inf\{E^{HF}(\phi_1, \phi_2), \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \;,\; 1 \leq i, j \leq 2, \\ & \phi_i \in H^1(\mathbb{R}^3), \;\; \text{such that for some}\, c \in \mathbb{R} \\ & \phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = c\phi_1\phi_2 \text{ in the sense of } \mathcal{D}'(\mathbb{R}^3)\}, \end{aligned} \tag{20}$$

in order to give a proper meaning to (8) in the case of two functions. Of course, an analogous definition can be set, in an obvious way, for $\widetilde{I_r^{OEP}}$ (radial case). Likewise, introducing the two conditions

$$\begin{cases} \phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = c\phi_1\phi_2 \\ \phi_2\Delta\phi_1^* - \phi_1^*\Delta\phi_2 = c\phi_1^*\phi_2 \end{cases} \tag{21}$$

still for c real, one may define $\widetilde{I^{OEP,\mathbb{C}}}$ (complex valued case), and $\widetilde{I_r^{OEP,\mathbb{C}}}$ (radial complex valued case). In the complex case indeed, two commutation conditions are needed to ensure that the potential W formally defined by $W = \dfrac{\Delta\phi_1}{2\phi_1}$ is real valued.

Remark 2.1 *The extension of these definitions to the case of N one-electron wavefunctions $(\phi_1, \cdots, \phi_N)$ with $(N-1)$ conditions of the type (19)*

$$\phi_k\Delta\phi_1 - \phi_1\Delta\phi_k = c_k\phi_1\phi_k \tag{22}$$

for $2 \leq k \leq N$ is left to the reader.

One purpose of the present work is to study the well-posedness of problem (20) and to show it provides a sound mathematical foundation for the vaguely stated problem (8).

In order to now account for the additional condition of being the *first* N eigenfunctions as stated in (17), we go one step further. Suppose we have at hand the first eigenfunction ϕ_1 (for a large class of W it is unique up to a sign) with eigenvalue λ_1 and one of the second eigenfunctions ϕ_2 (with eigenvalue λ_2) of some $-\frac{1}{2}\Delta + W$, the two of them forming an orthonormal system. Of course, condition (19) is indeed satisfied with some $c = 2(\lambda_2 - \lambda_1) \geq 0$, but we can also assert that

$$\forall \psi \in \mathcal{D}(\mathbb{R}^3), \quad \int_{\mathbf{R}^3} \phi_1^2 \, |\nabla\psi|^2 \geq c\left(\int_{\mathbf{R}^3} \psi^2\, \phi_1^2 - \big(\int_{\mathbf{R}^3} \psi\phi_1^2\big)^2\right), \tag{23}$$

for the same real constant c. Indeed, a simple computation shows that

$$\frac{1}{2}\int_{\mathbf{R}^3} |\nabla(\psi\phi_1)|^2 + \int_{\mathbf{R}^3} (W - \lambda_1)\,(\psi\phi_1)^2 = \frac{1}{2}\int_{\mathbf{R}^3} \phi_1^2\,|\nabla\psi|^2,$$

thus (23) amounts to

$$((-\frac{1}{2}\Delta + W)\theta, \theta) - \lambda_1 \int_{\mathbf{R}^3} \theta^2 \geq \frac{c}{2}\left(\int_{\mathbf{R}^3} \theta^2 - \big(\int_{\mathbf{R}^3} \theta\phi_1\big)^2\right) \tag{24}$$

with $c = 2(\lambda_2 - \lambda_1)$, for any function θ which writes $\theta = \psi\phi_1$. Inequality (24) obviously holds true, in fact for general θ, because ϕ_1 and ϕ_2 are respectively the first and a second eigenfunction of $-\frac{1}{2}\Delta + W$. In addition, property (24) characterizes ϕ_1 and ϕ_2, among all eigenfunctions of the operator $-\frac{1}{2}\Delta + W$. Indeed, suppose we are given two eigenfunctions ϕ_i and ϕ_j of $-\frac{1}{2}\Delta + W$ such that, according to $c \geq 0$, $\lambda_j - \lambda_i \geq 0$, and such that

$$((-\frac{1}{2}\Delta + W)\theta, \theta) - \lambda_i \int_{\mathbf{R}^3} \theta^2 \geq (\lambda_j - \lambda_i)\left(\int_{\mathbf{R}^3} \theta^2 - \big(\int_{\mathbf{R}^3} \theta\phi_i\big)^2\right). \tag{25}$$

Then, (formally) testing this condition on $\theta = \phi_1$, the first normalized eigenfunction of $-\frac{1}{2}\Delta + W$, we obtain

$$0 \geq \lambda_1 - \lambda_i \geq (\lambda_j - \lambda_i)\left(1 - \left(\int_{\mathbb{R}^3} \phi_1 \phi_i\right)^2\right).$$

Therefore, either $\left|\int_{\mathbb{R}^3} \phi_1 \phi_i\right| \geq 1$, or $\lambda_j = \lambda_i = \lambda_1$, both conditions implying that ϕ_i is the first eigenfunction ϕ_1 (up to a sign), and $\lambda_i = \lambda_1$. Next, testing condition (25) (again formally) on any eigenfunction ϕ_k of $-\frac{1}{2}\Delta + W$ different from, thus orthogonal to, ϕ_1, we obtain

$$\lambda_k - \lambda_1 \geq \lambda_j - \lambda_1,$$

which asserts that λ_j is the second eigenvalue λ_2, and that ϕ_j is a second eigenfunction.

Conversely, consider functions ϕ_1 and ϕ_2 such that (19) holds. As previously shown, they are formally eigenfunctions of some operator $-\frac{1}{2}\Delta + W$ with $W = \frac{\Delta\phi_1}{2\phi_1}$. The condition $c \geq 0$ tells that ϕ_2 is associated to an eigenvalue c, greater than (or equal to) the eigenvalue 0 associated to ϕ_1. If in addition (23) is satisfied, then it can be written in the same manner as (24) (with $\lambda_1 = 0$), and the same formal argument as above shows that ϕ_1 and ϕ_2 are the first two eigenfunctions of the operator.

Of course, all the previous arguments are not rigorous, for in many ocasions we would need to give a proper meaning to the division by ϕ_1. Nevertheless, (19), together with $c \geq 0$ and (23), appears as a convenient "weak" formulation for the property of being the first two eigenfunctions of some $-\frac{1}{2}\Delta + W$. This consequently justifies the introduction of the problem

$$\begin{aligned}\widetilde{J^{OEP}} = \inf\Big\{ & E^{HF}(\phi_1, \phi_2), \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}\ ,\ 1 \leq i, j \leq 2, \\ & \phi_i \in H^1(\mathbb{R}^3), \quad \text{such that, for some } c \geq 0 \in \mathbb{R}, \\ & \phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = c\phi_1\phi_2 \text{ in the sense of } \mathcal{D}'(\mathbb{R}^3), \\ & \text{and such that} \\ & \forall \psi \in \mathcal{D}(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \phi_1^2\, |\nabla\psi|^2 \geq c\left(\int_{\mathbb{R}^3} \psi^2\, \phi_1^2 - \left(\int_{\mathbb{R}^3} \psi\phi_1^2\right)^2\right)\Big\}\end{aligned} \tag{26}$$

as a mathematical formulation of (17). Of course, an analogous definition can be set, again in an obvious way, for $\widetilde{J_r^{OEP}}$, $\widetilde{J^{OEP,\mathbb{C}}}$, and $\widetilde{J_r^{OEP,\mathbb{C}}}$.

Remark 2.2 *Likewise, the definition of problem (26) can be extended to the case of N wavefunctions using the $(N-1)$ conditions (22) together with the $(N-1)$ inequalities*

$$\forall \psi \in \mathcal{D}(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \phi_k^2\, |\nabla\psi|^2 \geq \sum_{j=1}^{k} c_j \left(\int_{\mathbb{R}^3} \psi\phi_k\phi_j\right)^2 + c_{k+1}\left(\int_{\mathbb{R}^3} \psi^2\, \phi_k^2 - \sum_{j=1}^{k}\left(\int_{\mathbb{R}^3} \psi\phi_k\phi_j\right)^2\right)$$

for $1 \leq k \leq N-1$, with $c_1 = 0$.

Remark 2.3 *It might be useful to remark, and we shall indeed make use of this observation in some of our arguments, that condition (23) indeed enforces ϕ_1 to satisfy $\phi_1 \equiv 0$ or $\int_{\mathbb{R}^3} \phi_1^2 = 1$ as soon as $c > 0$. This can indeed easily be proven, letting ψ go to the constant function 1 over $\mathbb{R}^3$.*

We shall study to what extent problem (26) provides a rigorous setting for problem (17).

2.2 Main results

We briefly overview here the main results obtained in the present work. We only give formal statements, postponing the precise statements until the next sections.

First, we investigate the question: can a critical point for the Hartree-Fock energy be a solution to the OEP problem?

The answer is as follows (Theorem 3.1): in the radial setting, a solution of the Hartree-Fock equations cannot satisfy a condition of the type $\phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = c\phi_1\phi_2$. The results holds for both real and complex valued functions. Nevertheless, the situation is radically different when allowing for non radially symmetric functions, as shown in Proposition 3.3.

Secondly, we show that the $\widetilde{\text{OEP}}$ problems as defined above are well-posed, i.e. that the infimum is attained. This is the purpose of Theorems 4.1 and 4.2, and their corollaries. There, the wavefunctions are not restricted to be radially symmetric, and may be either real valued or complex valued. For the sake of consistency, we also indicate, in Section 5, that penalized forms of the original OEP problems can be considered and show them to be well posed.

We finally explain in Section 6 to what extent a minimizer of the problem (26) is solution to the original OEP problems as vaguely defined in (17). Here, we need to restrict ourselves to radially symmetric functions (cf. Proposition 6.4).

The remainder of this article is devoted to the detailed proofs of the above statements.

3 Exploring the link between the HF and the OEP problem

First we shall prove:

Theorem 3.1 (Radial case) *A* radial *solution $(\phi_1, \phi_2) \in \left(H^1_r(\mathbb{R}^3)\right)^2$ to the Hartree-Fock equations (12) cannot satisfy the commutation condition (19). A fortiori, it cannot be a solution to (7). As a corollary, no radial minimizer of the Hartree-Fock problem is a solution to a system of type (7).*

Corollary 3.2 *The conclusions of Theorem 3.1 hold true* mutatis mutandis *in the case of complex valued functions.*

In Theorem 3.1 and its corollary, it is crucial that the functions are radial as shown in the following:

Proposition 3.3 (Non radial case) *There exists a pair (ϕ_1, ϕ_2) of (non radially symmetric) functions solution to both the Hartree-Fock equations (12) and a system of type (7).*

We begin by proving Theorem 3.1, next show how it can be extended to cover the complex-valued case as claimed in Corollary 3.2 above, and then turn to the existence of the counterexample announced of Proposition 3.3.

Proof of Theorem 3.1. For brevity, we rewrite equations (12) in the form:

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 + V_2\phi_1 - V\phi_2 = 0 \\ -\frac{1}{2}\Delta\phi_2 + V_1\phi_2 - V\phi_1 = 0 \end{cases} \tag{27}$$

where we have denoted by

$$\begin{aligned} V_1 &= -\frac{Z}{|x|} + \phi_1^2 \star \frac{1}{|x|} + \varepsilon_2, \\ V_2 &= -\frac{Z}{|x|} + \phi_2^2 \star \frac{1}{|x|} + \varepsilon_1, \\ V &= (\phi_1\phi_2) \star \frac{1}{|x|}. \end{aligned}$$

Let us argue by contradiction and assume (ϕ_1, ϕ_2) is an orthonormal system, solution to the above equations (27), that in addition satisfies the commutation condition (19). By a standard elliptic regularity result, we know that ϕ_1 and ϕ_2 are H^2, continuous on $\mathbb{R}^3$, and that they both are C^∞ outside the origin. In particular, equations (27) holds almost everywhere in $\mathbb{R}^3$ and continuously outside the origin. The same applies to (19).

Step 1 We begin by showing there exists some open set Ω in $\mathbb{R}^3$ such that, for any $x \in \Omega$

$$\begin{cases} \left(\phi_1\phi_2 \star \frac{1}{|x|}\right)(x) \neq 0 \\ \phi_1(x)\phi_2(x) \neq 0 \end{cases} \tag{28}$$

For this purpose, we argue by contradiction, and assume (in view of the continuity) that we have

$$(\phi_1\phi_2 \star \frac{1}{|x|})\phi_1\phi_2 \equiv 0 \,\text{on}\, \mathbb{R}^3. \tag{29}$$

If in addition $\phi_1\phi_2 \not\equiv 0$ on $\mathbb{R}^3$, we may find some open set $\omega \neq \emptyset$ such that $\phi_1\phi_2$ has no zero on ω, and thus (29) yields $\phi_1\phi_2\star\frac{1}{|x|} = 0$ on ω. But this implies $\Delta(\phi_1\phi_2\star\frac{1}{|x|}) = 4\pi\phi_1\phi_2 = 0$ on ω and we reach a contradiction. Therefore (29) indeed implies:

$$\phi_1\phi_2 \equiv 0 \,\text{on}\, \mathbb{R}^3. \tag{30}$$

Consequently $V = \phi_1\phi_2 \star \frac{1}{|x|} = 0$ and (27) reads

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 + V_2\phi_1 = 0 \\ -\frac{1}{2}\Delta\phi_2 + V_1\phi_2 = 0 \end{cases}$$

In addition, since $\phi_1 \not\equiv 0$ because $\int_{\mathbb{R}^3} \phi_1^2 = 1$, we know using (30) that $\phi_2 = 0$ on some (non empty) open set. Since ϕ_2 satisfies $-\frac{1}{2}\Delta\phi_2 + V_1\phi_2 = 0$ and vanishes on an open set, we obtain by unique continuation [6] that $\phi_2 \equiv 0$ on $\mathbb{R}^3$. We then reach a contradiction because $\int_{\mathbb{R}^3} \phi_2^2 = 1$, and this concludes this first step.

Step 2

We now show we necessarily have $c = 0$ in equation (19) i.e:

$$\phi_1\Delta\phi_2 - \phi_2\Delta\phi_1 = 0. \tag{31}$$

Indeed, combining the two equations of (27) by multiplying the first one by ϕ_2 and the second one by ϕ_1, next adding the two, we obtain:

$$(-\frac{c}{2} + V_2 - V_1)\phi_1\phi_2 - V(\phi_2^2 - \phi_1^2) = 0.$$

As we have $\frac{1}{4\pi}\Delta(V_2 - V_1) = \phi_1^2 - \phi_2^2$ and $-\frac{1}{4\pi}\Delta V = \phi_1\phi_2$, we rewrite this equation as:

$$g\Delta f - f\Delta g = 0 \tag{32}$$

where $f = V$ and $g = -\frac{c}{2} + V_2 - V_1$. So,

$$\operatorname{div}(g\nabla f - f\nabla g) = 0$$

and therefore

$$g\frac{df}{dr} - f\frac{dg}{dr} = \frac{a}{r^2},$$

for some real constant a (note that we explicitely use the fact that we work with radially symmetric functions). As f, $\frac{df}{dr}$, g, $\frac{dg}{dr}$ are bounded (this is a consequence of Cauchy-Schwarz and Hardy inequalities) $\frac{a}{r^2}$ must also be bounded when $r \longrightarrow 0$, which implies $a = 0$. It follows that $g\frac{df}{dr} - f\frac{dg}{dr} = 0$. On an open set Ω where f has no zero, as defined by Step 1, it implies that $\frac{d}{dr}(\frac{g}{f}) = 0$, so $g = bf$ on Ω for some constant b, and therefore $\Delta g = b\Delta f$ which yields $(\frac{\phi_2}{\phi_1})^2 - 1 = b\frac{\phi_2}{\phi_1}$ since ϕ_1 has no zero either on Ω, by Step 1. So on some open subset Ω', connex component of Ω, we have $\phi_2 = \alpha\phi_1$ for some constant α. Inserting this in (19), we obtain $c = 0$ and Step 2 is completed.

Step 3

Let us now consider $x \in \mathbb{R}^3$. We claim we have:

- If $\phi_1(x) \neq 0$, there exists some real α_1 and an open set Ω' containing x such that: $\phi_2 = \alpha_1\phi_1$ on Ω'. If in addition $\alpha_1 \neq 0$, then $V_2 - V_1 = (\alpha_1 - \frac{1}{\alpha_1})V$ on Ω'.

- If $\phi_2(x) \neq 0$, there exists some real α_2 and an open set Ω' containing x such that: $\phi_1 = \alpha_2 \phi_2$ on Ω'. If in addition $\alpha_2 \neq 0$, then $V_1 - V_2 = (\alpha_2 - \frac{1}{\alpha_2})V$ on Ω'.

We for instance treat the case $\phi_1(x) \neq 0$. By continuity, there exists an open set Ω' containing x where ϕ_1 has no zero. Integrating (31) and arguing as in Step 2, we first deduce the existence of some real constant a such that $\phi_2 \frac{d\phi_1}{dr} - \phi_1 \frac{d\phi_2}{dr} = \frac{a}{r^2}$ on the whole space, and secondly obtain $a = 0$. This yields $\phi_2 = \alpha_1 \phi_1$ on the connex component of Ω' containing x. If in addition $\alpha_1 \neq 0$, system (27) reads

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 + V_2\phi_1 - V\alpha_1\phi_1 = 0, \\ -\frac{1}{2}\Delta\phi_2 + V_1\phi_2 - V\frac{\phi_2}{\alpha_1} = 0, \end{cases} \tag{33}$$

on this connex component, and combining these two equations we obtain:

$$\frac{1}{2}(\phi_1\Delta\phi_2 - \phi_2\Delta\phi_1) + (V_2 - V_1 - (\alpha_1 - \frac{1}{\alpha_1})V)\phi_1\phi_2 = 0$$

thus, using (31) and the fact that $\phi_1\phi_2$ has no zero on Ω',

$$V_2 - V_1 - (\alpha_1 - \frac{1}{\alpha_1})V = 0.$$

The case $\phi_2(x) \neq 0$ is treated in the same manner. Of course when $\phi_1(x)\phi_2(x) \neq 0$ we have $\alpha_1\alpha_2 \neq 0$ and $\alpha_2 = \frac{1}{\alpha_1}$.

Step 4 Let us introduce the function R defined by:

$$R(x) = \begin{cases} 0 & \text{when} \quad \phi_1(x) = \phi_2(x) = 0 \\ V(x)\frac{\phi_2(x)}{\phi_1(x)} & \text{when} \quad \phi_1(x) \neq 0 \\ V(x)\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x) & \text{when} \quad \phi_2(x) \neq 0 \end{cases}$$

In order to prove that R is well defined, the only fact we have to show is that when $\phi_1(x) \neq 0$ and $\phi_2(x) \neq 0$, the two definitions of $R(x)$ yield the same value. It is a simple consequence of Step 3, since for such x: $V(x)\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x) = V(x)\frac{\phi_2(x)}{\phi_1(x)}$.
Let us now prove that $R \in L^\infty(\mathbb{R}^3)$. First if $\phi_2(x) = 0$ then $R(x) = 0$. Secondly, if $\phi_1(x) = 0$ and $\phi_2(x) \neq 0$, using $R(x) = V\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x)$ we have $R(x) = V_2(x) - V_1(x)$. Thirdly, if $\phi_1(x)\phi_2(x) \neq 0$, we can make use of both expressions $R(x) = V\frac{\phi_2(x)}{\phi_1(x)}$ and $R(x) = V\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x)$. Therefore, if $\left|\frac{\phi_2(x)}{\phi_1(x)}\right| \leq 1$, we use $R(x) = V(x)\frac{\phi_2(x)}{\phi_1(x)}$ and obtain $|R(x)| = \left|V\frac{\phi_2(x)}{\phi_1(x)}\right| \leq |V|$. Alternatively, if if $\left|\frac{\phi_1(x)}{\phi_2(x)}\right| \leq 1$, we use $R(x) =$

$V(x)\dfrac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x)$, and obtain

$$|R(x)| = |V(x)\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x)| \leq |V(x)| + |V_2(x) - V_1(x)|.$$

In either case we have $|R(x)| \leq |V(x)| + |V_2(x) - V_1(x)|$, and since V and $V_2 - V_1$ are in $L^\infty(\mathbb{R}^3)$ we conclude that $R \in L^\infty(\mathbb{R}^3)$.

Step 5

Let us now check that both functions ϕ_1 and ϕ_2 are solutions to

$$(-\frac{1}{2}\Delta + V_2 - R)\phi = 0. \tag{34}$$

For this purpose, in view of the regularity of the ϕ_i, we only have to check that this equation holds pointwise for all $x \neq 0$.

To begin with, we remark that if for $x \neq 0$ we have $\phi_i(x) = 0$ (for $i = 1$ or $i = 2$) then $\Delta\phi_i(x) = 0$. Indeed, if $\phi_1(x) = \phi_2(x) = 0$, $\Delta\phi_1(x) = \Delta\phi_2(x) = 0$ using (27). If $\phi_1(x) \neq 0$ and $\phi_2(x) = 0$, using (31) we get $\phi_1(x)\Delta\phi_2(x) = 0$ so $\Delta\phi_2(x) = 0$. And if $\phi_1(x) = 0$ and $\phi_2(x) \neq 0$, using (31) again we get $\phi_2(x)\Delta\phi_1(x) = 0$ so $\Delta\phi_1(x) = 0$.

We are now in position to check (34) holds for all $x \neq 0$:

(a) If $\phi_1(x) = \phi_2(x) = 0$, then $\Delta\phi_1(x) = \Delta\phi_1(x) = 0$ thus (34) holds.

(b) If $\phi_1(x) \neq 0$ and $\phi_2(x) = 0$, then (34) is satified by ϕ_2 at x, and, since the first equation of (27) gives $-\frac{1}{2}\Delta\phi_1(x) + V_2(x)\phi_1(x) = 0$ and $R(x) = V(x)\dfrac{\phi_2(x)}{\phi_1(x)} = 0$, we have $-\frac{1}{2}\Delta\phi_1(x) + (V_2(x) - R(x))\phi_1(x) = 0$.

(c) If $\phi_1(x) = 0$ and $\phi_2(x) \neq 0$, then

$$-\frac{1}{2}\Delta\phi_1(x) + (V_1(x) - R(x))\phi_1(x) = 0$$

and as the second equation of (27) gives $-\frac{1}{2}\Delta\phi_2(x) + V_1(x)\phi_2(x) = 0$,

$$\begin{aligned} -\frac{1}{2}\Delta\phi_2(x) + (V_2(x) - R(x))\phi_1(x) &= -V_1(x)\phi_2(x) + (V_2(x) - R(x))\phi_2(x) \\ &= -V_1(x)\phi_2(x) + V_2(x)\phi_2(x) \\ &\quad -(V(x)\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x))\phi_2(x) \\ &= -V(x)\phi_1(x) = 0 \end{aligned}$$

by using $R(x) = V(x)\dfrac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x)$.

(d) If $\phi_1(x)\phi_2(x)(x) \neq 0$ so using the equation (27) we obtain:

$$\begin{aligned} -\frac{1}{2}\Delta\phi_1(x) + (V_2(x) - R(x))\phi_1(x) &= -\frac{1}{2}\Delta\phi_1(x) + V_2(x)\phi_1(x) - V\frac{\phi_2(x)}{\phi_1(x)}\phi_1(x) \\ &= -\frac{1}{2}\Delta\phi_1(x) + V_2(x)\phi_1(x) - V(x)\phi_2(x) \\ &= 0, \end{aligned}$$

and

$$\begin{aligned}
-\frac{1}{2}\Delta\phi_2(x) + (V_2(x) - R(x))\phi_2(x) &= -\frac{1}{2}\Delta\phi_2(x) + V_2(x)\phi_2(x) \\
&\quad -(V(x)\frac{\phi_1(x)}{\phi_2(x)} + V_2(x) - V_1(x))\phi_2(x) \\
&= -\frac{1}{2}\Delta\phi_2(x) + V_1(x)\phi_2(x) - V(x)\phi_1(x) \\
&= 0.
\end{aligned}$$

Step 6. We now can conclude the proof. Since ϕ_1 is continuous and normalized (for the L^2 norm), there exists an open set Ω on which ϕ_1 has no zero. Using Step 3, there exists α_1 such that $\phi_2 = \alpha_1\phi_1$ on a subset Ω' of Ω. Next, by Step 5, ϕ_1 and ϕ_2 are solutions to $(-\frac{1}{2}\Delta + V_2 - R)\phi = 0$, so $\alpha_1\phi_1$ and ϕ_2 are solutions to this equation. Therefore, the functions $\alpha_1\phi_1$ and ϕ_2 are solutions to this equation almost everywhere in $\mathbb{R}^3$, and coincide on Ω'. Hence, $\phi_2 = \alpha_1\phi_1$ everywhere by unique continuation. We reach a contradiction because $\int_{\mathbb{R}^3}\phi_1\phi_2 = 0$ and $\int_{\mathbb{R}^3}\phi_2^2 = 1$. ◊

We now turn to the proof in the case of complex valued functions, which requires some slight modifications of the above arguments.

Proof of Corollary 3.2

In the case of two complex valued functions, the HF equations (27) read:

$$\begin{cases} -\frac{1}{2}\Delta\phi_1 + V_2\phi_1 - V\phi_2 = 0 \\ -\frac{1}{2}\Delta\phi_2^* + V_1\phi_2^* - V\phi_1^* = 0 \end{cases} \tag{35}$$

where, $V_1 = -\frac{Z}{|x|} + |\phi_1|^2 \star \frac{1}{|x|} + \varepsilon_2$, $V_2 = -\frac{Z}{|x|} + |\phi_2|^2 \star \frac{1}{|x|} + \varepsilon_1$ and $V = (\phi_1\phi_2^*) \star \frac{1}{|x|}$.
In Step 1, equation (28) becomes:

$$\begin{cases} \left(\phi_1\phi_2^* \star \frac{1}{|x|}\right)(x) \neq 0 \\ \phi_1(x)\phi_2^*(x) \neq 0 \end{cases} \tag{36}$$

and the proof follows the same pattern. As for Steps 3 to 6, there are only minor changes needed and we leave them to the reader. The only modification that is not straightforward lies in Step 2. The purpose of this step is to show the analogous equation to (31), namely

$$\phi_2^*\Delta\phi_1 - \phi_1\Delta\phi_2^* = 0. \tag{37}$$

Using the same arguments, we obtain

$$\phi_1\phi_2^*(V_2 - V_1 - \frac{c}{2}) + V(|\phi_1|^2 - |\phi_2|^2) = 0 \tag{38}$$

and thus $|\frac{\phi_2}{\phi_1}|^2 - 1 = b\left(\frac{\phi_2}{\phi_1}\right)^*$ on an open set Ω as defined by Step 1, for some $b \in \mathbb{C}$. Defining $z(x) = \left(\frac{\phi_2}{\phi_1}\right)^*(x)$, this condition reads $|z|^2 - 1 = bz$. Contrary to the real valued case where the conclusion was easily reached, we here have to make a different argument, depending on $b \neq 0$ or $b = 0$. The case $b \neq 0$ is the easy one. Indeed, if $b \neq 0$, it is a simple calculation to show that this implies, for some complex number $\alpha \neq 0$, $\phi_2 = \alpha\phi_1$ on a open subset $\Omega' \subset \Omega$, thus $\phi_2^*\Delta\phi_1 - \phi_1\Delta\phi_2^* = \alpha(\phi_1^*\Delta\phi_1 - \phi_1\Delta\phi_1^*)$, and therefore

$$\phi_1^*\Delta\phi_1 - \phi_1\Delta\phi_1^* = c|\phi_1|^2.$$

It follows that $c = 0$ because the left hand side is imaginary while the right hand side is real.

The case $b = 0$ requires more efforts. We then have $|\phi_2|^2 = |\phi_1|^2$ on Ω. Thus, there exists real valued functions f_1, f_2 and ψ such that $\phi_1(r) = e^{if_1(r)}\psi(r)$ and $\phi_2(r) = e^{if_2(r)}\psi(r)$ on Ω. Rewriting the commutation condition

$$\phi_2\Delta\phi_1^* - \phi_1^*\Delta\phi_2 = c\phi_1^*\phi_2$$

in terms of f_1, f_2 and ψ, we obtain:

$$\psi^2(f_1'' - f_2'') + 2i(f_1' + f_2')(\psi'\psi + \frac{\psi^2}{r}) = c\psi^2.$$

Since $c \in \mathbb{R}$, we have

$$(f_1' + f_2')(\psi'\psi + \frac{\psi^2}{r}) = 0 \,\text{on}\, \Omega. \tag{39}$$

If there exists an open subset $\Omega' \subset \Omega$ where $\psi'\phi + \frac{\psi^2}{r}$ is not identically zero, then on such an open set $f_1' + f_2' = 0$, then $\phi_2^* = \alpha\phi_1$ and (37) follows. So, in order to conclude, what we have to rule out is the following situation: on any open set such that (36) holds, we have $\phi_1(r) = e^{if_1(r)}\psi(r)$, $\phi_2(r) = e^{if_2(r)}\psi(r)$, $\psi(r) = \frac{\alpha}{r}$ for some constant α. If there is no such open set, the proof is completed, so we suppose there is at least one such Ω_1, say an interval $]\lambda, \mu[$, where $\phi_1(r) = e^{if_1(r)}\psi(r)$, $\phi_2(r) = e^{if_2(r)}\psi(r)$, $\psi(r) = \frac{\alpha}{r}$ for some constant α. We now make a connexity argument. Let us introduce $d \in \overline{\mathbb{R}}$ defined by

$$\begin{aligned} d = \sup\{ \quad & y \text{ such that } \forall x \in]\lambda, y[, \\ & \phi_1(r) = e^{if_1(r)}\psi(r),\ \phi_2(r) = e^{if_2(r)}\psi(r),\ \psi(r) = \frac{\alpha}{r}\}. \end{aligned}$$

We will show that both cases d finite and $d = +\infty$ lead to a contradiction. Suppose d is finite. By continuity of ψ, $\psi(d) = \frac{\alpha}{d}$ so $\phi_1\phi_2^*(d) \neq 0$. In addition, $\left(\phi_1\phi_2^* \star \frac{1}{|x|}\right)(d) = 0$: otherwise there exists, $\eta > 0$ such that on $]d - \eta, d + \eta[$, (36) holds, thus we have $\psi' + \frac{\psi}{r} = 0$ identically and this contradicts the definition of d. In addition, d necessarily is an accumulation point of $\{\phi_1\phi_2^* \star \frac{1}{|x|}(r) = 0\}$. Otherwise, there exists $\eta > 0$ such that on $]d, d + \eta[$, (36) holds, and again we may deduce $\psi' + \frac{\psi}{r} = 0$, which contradicts the definition of d. Therefore, $\Delta(\phi_1\phi_2^* \star \frac{1}{|x|})(d) = 0$, i.e. $(\phi_1\phi_2^*)(d) = 0$ which is false. If we now assume $d = +\infty$, this implies $\psi = \dfrac{\alpha}{r}$ at infinity, which contradicts $\phi_1 \in L^2(\mathbb{R}^3)$. This concludes the proof of Step 2, and thus that of the Corollary. ♢

Proof of Proposition 3.3

We present here an example of some (ϕ_1, ϕ_2) both solution of the Hartree-Fock equations (12) and of the Optimized Effective Potential equation (7) as announced in Proposition 3.3. We search for (ϕ_1, ϕ_2) in the form

$$(\phi_1, \phi_2) = (f(r,\theta)\cos(\varphi), f(r,\theta)\sin(\varphi)) \tag{40}$$

where (r, θ, φ) denote the spherical coordinates and f is a real valued function. The Hartree-Fock equations (12) also read

$$\left\{ \begin{array}{l} -\dfrac{1}{2}\Delta\phi_i - \dfrac{Z}{|x|}\phi_i + \left(\rho \star \dfrac{1}{|x|}\right)\phi_i - \displaystyle\int_{\mathbf{R}^3} \dfrac{\rho(x,y)}{|x-y|}\,\phi_i(y)\,dx\,dy = -\epsilon_i\phi_i \\ \displaystyle\int_{\mathbf{R}^3} \phi_i\phi_j = \delta_{ij} \end{array} \right. \tag{41}$$

with $\rho(x,y) = \displaystyle\sum_{i=1}^{2} \phi_i(x)\phi_i(y)$ and $\rho(x) = \rho(x,x)$.

If (ϕ_1, ϕ_2) is of the form (40) with f satisfying the normalization condition $\displaystyle\int_{\mathbf{R}^3} f^2 = 2$, then $\phi_1 = f(r,\theta)\cos(\varphi)$ and $\phi_2 = f(r,\theta)\sin(\varphi)$ automatically satisfy the orthonormality conditions

$$\int_{\mathbf{R}^3} \phi_i\phi_j = \delta_{ij}.$$

Besides, $\rho(x,y) = f(r_x,\theta_x)\,f(r_y,\theta_y)\,\cos(\varphi_x - \varphi_y)$, $\rho(x) = f(r_x,\theta_x)^2$, and therefore

$$\int_{\mathbf{R}^3} \frac{\rho(x,y)}{|x-y|}\,\phi_1(y)\,dx\,dy$$

$$= \int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} \frac{f(r_x,\theta_x)\,f(r_y,\theta_y)\,\cos(\varphi_x-\varphi_y)\,f(r_y,\theta_y)\cos(\varphi_y)\,\sin(\theta_y)\,dr_y\,d\theta_y\,d\varphi_y}{\left(r_x^2+r_y^2-2r_xr_y\left(\cos(\theta_x)\cos(\theta_y)+\sin(\theta_x)\sin(\theta_y)\cos(\varphi_x-\varphi_y)\right)\right)^{1/2}}$$

$$= \int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} \frac{f(r_x,\theta_x)\,f(r_y,\theta_y)\,\cos(\varphi)\,f(r_y,\theta_y)\cos(\varphi_x-\varphi)\,\sin(\theta_y)\,dr_y\,d\theta_y\,d\varphi}{\left(r_x^2+r_y^2-2r_xr_y\left(\cos(\theta_x)\cos(\theta_y)+\sin(\theta_x)\sin(\theta_y)\cos(\varphi)\right)\right)^{1/2}}$$

$$= \int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} \frac{f(r_x,\theta_x)\,f(r_y,\theta_y)\,\cos(\varphi)\,f(r_y,\theta_y)\left(\cos(\varphi_x)\cos(\varphi)+\sin(\varphi_x)\sin(\varphi)\right)\,\sin(\theta_y)\,dr_y\,d\theta_y\,d\varphi}{\left(r_x^2+r_y^2-2r_xr_y\left(\cos(\theta_x)\cos(\theta_y)+\sin(\theta_x)\sin(\theta_y)\cos(\varphi)\right)\right)^{1/2}}.$$

Therefore

$$\int_{\mathbf{R}^3} \frac{\rho(x,y)}{|x-y|}\,\phi_1(y)\,dx\,dy = W_0(x)\,\phi_1(x),$$

with

$$W_0(x) = \int_0^{+\infty} \int_0^{\pi} \int_0^{2\pi} \frac{f(r_y, \theta_y)^2 \, \cos(\varphi)^2}{\left(r_x^2 + r_y^2 - 2 r_x r_y \left(\cos(\theta_x)\cos(\theta_y) + \sin(\theta_x)\sin(\theta_y)\cos(\varphi)\right)\right)^{1/2}} \sin(\theta_y) \, dr_y \, d\theta_y \, d\varphi;$$

similarly

$$\int_{\mathbf{R}^3} \frac{\rho(x,y)}{|x-y|} \, \phi_2(y) \, dx \, dy = W_0(x) \, \phi_2(x)$$

(with the same W_0). For (ϕ_1, ϕ_2) of the form (40), one therefore has

$$-\frac{1}{2}\Delta\phi_i - \frac{Z}{|x|}\phi_i + \left(\rho \star \frac{1}{|x|}\right)\phi_i - \int_{\mathbf{R}^3} \frac{\rho(x,y)}{|x-y|} \, \phi_i(y) \, dx \, dy = -\Delta\phi_i + W\phi_i$$

where W is a local potential. It remains to exhibit a solution (ϕ_1, ϕ_2) to equations (41) of the form (40). A simple calculation shows that the goal is reached if one can find $f(r, \theta)$ such that

$$\int_{\mathbf{R}^3} |\nabla f|^2 + \int_{\mathbf{R}^3} \frac{f^2}{r^2 \sin^2\theta} < +\infty \tag{42}$$

solution to

$$\begin{cases} -\dfrac{1}{2}\Delta f + \dfrac{1}{2\, r^2 \, \sin^2\theta} f - \dfrac{Z}{r} f + \left(\displaystyle\int_{\mathbf{R}^3} G(x,y) \, f(y)^2 \, dy\right) f = -\epsilon f \\ \displaystyle\int_{\mathbf{R}^3} f^2 = 2 \end{cases} \tag{43}$$

where $G(x,y)$ is the integral kernel

$$G(x,y) = \frac{\sin(\varphi_x - \varphi_y)^2}{|x-y|}.$$

We are going to prove that such a function f can be obtained by solving the variational problem

$$\inf \left\{ E(u), \quad u \in H^1(\mathbb{R}^3), \; \int_{\mathbf{R}^3} u^2 \leq 2 \right\} \tag{44}$$

where

$$E(u) = \frac{1}{2}\int_{\mathbf{R}^3} |\nabla u|^2 - \int_{\mathbf{R}^3} \frac{Z}{r} u^2 + \int_{\mathbf{R}^3} \frac{u^2}{2r^2 \sin^2\theta} + \frac{1}{2} \int\int_{(\mathbf{R}^3)^2} G(x,y) \, u^2(x) \, u^2(y) \, dx \, dy.$$

The proof next falls in four steps.

Step 1. We first prove that the infimum of (44) is attained. Let us consider a minimizing sequence (u^n); (u^n) being bounded in $H^1(\mathbb{R}^3)$, we can assume that it converges toward $u \in H^1(\mathbb{R}^3)$, weakly in H^1, strongly in L^p_{loc} for $1 \leq p < 6$ and almost everywhere. It is then easy to pass to the limit both in the constraint and in the energy to prove that u is a minimizer of (44). As $E(|u|) = E(u)$ for any $u \in H^1(\mathbb{R}^3)$, we can assume in addition that $u \geq 0$.

Step 2. Let $\chi \in \mathcal{D}(\mathbb{R}^3)$ supported in the Ball $B_{1/2} = \left\{x \in \mathbb{R}^3,\ |x| < 1/2\right\}$ and such that $\int_{\mathbf{R}^3} \chi^2 = 1$. For $\sigma > 0$ and $\tau > 0$, we denote by

$$\chi_{\sigma,\tau}(x) = \tau^{1/2}\,\sigma^{3/2}\,\chi(\sigma x - e_1)$$

where e_1 is the first unit vector of the cartesian coordinates. As $\sin^2 \geq 3/4$ in $\mathrm{Supp}(\chi_{\sigma,\tau})$ and as $0 < G(x,y) \leq \frac{1}{|x-y|}$,

$$E(\chi_{\sigma,\tau}) \leq \frac{\tau\sigma^2}{2}\int_{\mathbf{R}^3} |\nabla\chi|^2 + \frac{1}{3}\tau\sigma^2 \int_{\mathbf{R}^3} \frac{\chi^2}{|x+e_1|^2} - \tau\sigma \int_{\mathbf{R}^3} \frac{Z}{|x+e_1|}\chi^2 + \tau^2\,\sigma\, D(\chi^2,\chi^2).$$

For τ and σ small enough, $\chi_{\sigma,\tau}$ satisfies the constraint $\int_{\mathbf{R}^3} \chi_{\sigma,\tau}^2 \leq 2$ and $E(\chi_{\sigma,\tau}) < 0$. Therefore, $u \neq 0$ and consequently u satisfies the Euler-Lagrange equation

$$-\frac{1}{2}\Delta u + \frac{u}{2r^2\sin^2\theta} - \frac{Z}{r}u + \left(\int_{\mathbf{R}^3} G(x,y)\,u(y)^2\,dy\right) u = -\epsilon u. \tag{45}$$

Step 3. Assume $\int_{\mathbf{R}^3} u^2 < 2$. Then $\epsilon = 0$ in (45) and u is a positive eigenvector of the self-adjoint operator on $L^2(\mathbb{R}^3)$ formally defined by

$$A = -\frac{1}{2}\Delta + \frac{1}{2r^2\sin^2\theta} - \frac{Z}{r} + \left(\int_{\mathbf{R}^3} G(x,y)\,u(y)^2\,dy\right)$$

associated with the eigenvalue 0. As $\sigma_{ess}(A) = [0,+\infty[$, u is the ground state of A. But on the other hand, $(A\chi_{\sigma,1},\chi_{\sigma 1}) < 0$ when σ is small enough. Indeed

$$\begin{aligned}(A\chi_{\sigma,1},\chi_{\sigma,1}) \ \leq\ & \frac{\sigma^2}{2}\int_{\mathbf{R}^3}|\nabla\chi|^2 + \frac{1}{3}\sigma^2\int_{\mathbf{R}^3}\frac{\chi^2}{|x+e_1|^2} \\ & -\sigma\left[Z\int_{\mathbf{R}^3}\frac{\chi^2(x)}{|x+e_1|}\,dx - \int\int_{(\mathbf{R}^3)^2}\frac{u(y)^2\,\chi(x)^2}{|x+e_1-\sigma y|}\,dx\,dy\right],\end{aligned}$$

and

$$Z\int_{\mathbf{R}^3}\frac{\chi^2(x)}{|x+e_1|}\,dx - \int\int_{(\mathbf{R}^3)^2}\frac{u(y)^2\,\chi(x)^2}{|x+e_1-\sigma y|}\,dx\,dy \underset{\sigma\to 0}{\longrightarrow} \left(Z - \int_{\mathbf{R}^3} u^2\right)\int_{\mathbf{R}^3}\frac{\chi^2(x)}{|x+e_1|}\,dx > 0$$

since $\int_{\mathbf{R}^3} u^2 < 2 \leq Z$ by assumption. We thus reach a contradiction. Therefore $\int_{\mathbf{R}^3} u^2 = 2$.

Step 4. The function $\rho = u^2$ is solution to

$$\inf\left\{\widetilde{E}(\rho),\quad \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbf{R}^3}\rho \leq 2\right\} \tag{46}$$

with $\widetilde{E}(\rho) = E(\sqrt{\rho})$. As $\widetilde{E}$ is strictly convex on the convex set

$$C = \left\{\rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbf{R}^3}\rho \leq 2\right\},$$

the solution ρ to (46) is unique. In addition, it follows from the definition of the integral kernel $G(x,y)$ that $\widetilde{E}(\mathcal{R}_{\varphi_0}\rho) = \widetilde{E}(\rho)$ for any $\varphi_0 \in \mathbb{R}$, where $\mathcal{R}_{\varphi_0}$ is the rotation operator defined in spherical coordinates by $(\mathcal{R}_{\varphi_0}\rho)(r,\theta,\varphi) = \rho(r,\theta,\varphi-\varphi_0)$. Consequently, the solution $\rho(r,\theta,\varphi)$ to (46) in actually independent on the variable φ ($\rho(r,\theta,\varphi) = \rho(r,\theta)$) and therefore, so is $u = \sqrt{\rho}$ since $u > 0$ in $\mathbb{R}^3 \setminus (\mathbb{R}e_3)$ (by Harnack inequality applied to (45)). The function $f(r,\theta) = u(r,\theta)$ therefore satisfies the requirements (42)-(43). $\diamondsuit$

4 The OEP problems are well posed

We now study the energy of the minimization problems introduced above. In the case of real valued functions we have:

Theorem 4.1 (Radial or non radial case) *For $Z \geq 2$ (neutral atom or positive ion), there exists a minimizer (ϕ_1, ϕ_2) of the minimization problem $\widetilde{I^{OEP}}$ defined by (20). The same conclusion holds for the minimization problem $\widetilde{I_r^{OEP}}$ (defined analogously and restricted to radially symmetric functions).*

Theorem 4.2 (Radial or non radial case) *For $Z \geq 2$ (neutral atom or positive ion), there exists a minimizer (ϕ_1, ϕ_2) of the minimization problem $\widetilde{J^{OEP}}$ defined by (26). The same conclusion holds for the minimization problem $\widetilde{J_r^{OEP}}$ (defined analogously and restricted to radially symmetric functions).*

Corollary 4.3 *The conclusions of Theorems 4.1 and 4.2 hold true for complex valued functions, ie for the minimization problems $\widetilde{I^{OEP,C}}$, $\widetilde{I_r^{OEP,C}}$, $\widetilde{J^{OEP,C}}$, $\widetilde{J_r^{OEP,C}}$.*

As we know that there exists a minimizer of radial Hartree-Fock problem (11), we obtain using Theorem 3.1 that

Theorem 4.4 (Radial case) *For $Z \geq 2$ (neutral atom or positive ion), $I_r^{HF} < I_r^{OEP} \leq J_r^{OEP}$.*

Corollary 4.5 *The conclusion of Theorem 4.4 holds true in the complex valued case.*

This section is articulated as follows. We first prove Theorem 4.1 for general functions (not necessarily radially symmetric), the proof of the radial case being the same. Next, we prove Theorem 4.2, again in the general case. The proof of Theorem 4.4 is straightforward and we skip it. We also skip the proofs of Corollary 4.3 and Corollary 4.5, that follow the same lines as those of Theorem 4.1 and Theorem 4.2 respectively.

Proof of Theorem 4.1

Step 1

We begin by proving an *a priori* estimate for the energy:

$$\widetilde{I^{OEP}} < I = \inf\left\{\int_{\mathbb{R}^3}\left(\frac{1}{2}|\nabla\psi|^2 - \frac{Z}{|x|}\psi^2\right),\ \int_{\mathbb{R}^3}\psi^2 = 1\right\} < 0. \tag{47}$$

For this purpose, we consider for any $Z' > 0$, $\psi_1^{Z'}$ and $\psi_2^{Z'}$ the first two normalized radial eigenfunctions of the operator $-\frac{1}{2}\Delta - \frac{Z'}{|x|}$ on $L^2(\mathbb{R}^3)$ which are respectively defined by:

$$\psi_1^{Z'}(r,\theta,\varphi) = (Z')^{3/2}\,\frac{e^{-Z'r}}{\sqrt{\pi}} \quad \text{and} \quad \psi_2^{Z'}(r,\theta,\varphi) = (Z')^{3/2}\,\frac{\left(1-\frac{Z'r}{2}\right)e^{-\frac{Z'r}{2}}}{\sqrt{8\pi}}. \tag{48}$$

Using the notation (16), we have:

$$\begin{aligned}
\int_{\mathbb{R}^3}|\nabla\psi_1^{Z'}|^2 &= Z'^2,\\
\int_{\mathbb{R}^3}|\nabla\psi_2^{Z'}|^2 &= \frac{Z'^2}{4},\\
-\int_{\mathbb{R}^3}\frac{Z}{|x|}|\psi_1^{Z'}|^2 &= -Z\,Z',\\
-\int_{\mathbb{R}^3}\frac{Z}{|x|}|\psi_2^{Z'}|^2 &= -\frac{Z\,Z'}{4},\\
D(|\psi_1^{Z'}|^2,|\psi_2^{Z'}|^2) &= \frac{17}{81}Z',\\
D(\psi_1^{Z'}\psi_2^{Z'},\psi_1^{Z'}\psi_2^{Z'}) &= \frac{16}{729}Z'.
\end{aligned} \tag{49}$$

Therefore, for any $Z \geq 2$,

$$I = \inf\left\{\int_{\mathbb{R}^3}\left(\frac{1}{2}|\nabla\psi|^2 - \frac{Z}{|x|}\psi^2\right),\ \int_{\mathbb{R}^3}\psi^2 = 1\right\} = \int_{\mathbb{R}^3}\left(\frac{1}{2}|\nabla\psi_1^Z|^2 - \frac{Z}{|x|}|\psi_1^Z|^2\right) = -\frac{Z^2}{2}$$

and, since $(\psi_1^{Z'},\psi_2^{Z'})$ are admissible test functions for $\widetilde{I^{OEP}}$,

$$\widetilde{I^{OEP}} \leq \inf_{Z'>0} E^{HF}(\psi_1^{Z'},\psi_2^{Z'}) = -\frac{5}{8}Z^2 + \eta Z - \frac{2}{5}\eta^2 \tag{50}$$

with $\eta = \frac{137}{729}$. As the RHS of the above inequality is lower that $-\frac{Z^2}{2}$ for any $Z \geq 2$, inequality (47) follows.

Step 2

Let us now consider a minimizing sequence (ϕ_1^n,ϕ_2^n) of the $\widetilde{OEP}$ problem (20). As this sequence is bounded in $H^1(\mathbb{R}^3)$, we can extract a subsequence that weakly converges in $H^1(\mathbb{R}^3)$ to (ϕ_1,ϕ_2). The weak limit (ϕ_1,ϕ_2) satisfies $E^{HF}(\phi_1,\phi_2) \leq \widetilde{I^{OEP}}$ and $(\int_{\mathbb{R}^3}\phi_i\phi_j) \leq (\delta_{ij}), \quad 1 \leq i,j \leq 2$.

Proving that (ϕ_1,ϕ_2) is a minimizer of (20) amounts to proving that (ϕ_1,ϕ_2) also satisfies both conditions

$$\phi_1\Delta\phi_2 - \phi_2\Delta\phi_1 = c\phi_1\phi_2 \quad \text{for some } c \in \mathbb{R} \tag{51}$$

$$\int_{\mathbf{R}^3} \phi_i \phi_j = \delta_{ij}, \qquad 1 \le i, j \le 2. \tag{52}$$

We devote this second step to the proof of (51). For each n, we have some real constant c^n such that

$$\phi_1^n \Delta \phi_2^n - \phi_2^n \Delta \phi_1^n = c^n \phi_1^n \phi_2^n. \tag{53}$$

We multiply by some arbitrary $\psi \in \mathcal{D}(\mathbb{R}^3)$ and integrate to obtain:

$$\int_{\mathbf{R}^3} (\phi_2^n \nabla \phi_1^n - \phi_1^n \nabla \phi_2^n) \nabla \psi = c^n \int_{\mathbf{R}^3} \phi_1^n \phi_2^n \psi. \tag{54}$$

In order to pass to the limit in the left hand side of (54), we remark that (ϕ_1^n, ϕ_2^n) weakly converges to (ϕ_1, ϕ_2) in $(H^1(\mathbb{R}^3))^2$, so (ϕ_1^n, ϕ_2^n) strongly converges to (ϕ_1, ϕ_2) in $(L^2_{loc}(\mathbb{R}^3))^2$ and $(\nabla \phi_1^n, \nabla \phi_2^n)$ weakly converges to $(\nabla \phi_1, \nabla \phi_2)$ in $(L^2(\mathbb{R}^3))^2$. Thus $\phi_2^n \nabla \phi_1^n$ and $\phi_1^n \nabla \phi_2^n$ respectively weakly converge to $\phi_2 \nabla \phi_1$ and $\phi_1 \nabla \phi_2$ in $L^1_{loc}(\mathbb{R}^3)$. This allows to pass to the limit in the left hand side.

For the right hand side of (54) we proceed as follows. If the real sequence c^n is not bounded, we can extract a subsequence, still denoted by c^n, such that $|c^n| \longrightarrow +\infty$. Then necessarily $\phi_1 \phi_2 = 0$, otherwise we may choose $\psi \in \mathcal{D}(\mathbb{R}^3)$ such that $c^n \int_{\mathbf{R}^3} \phi_1^n \phi_2^n \psi \longrightarrow \infty$, and this cannot occur since the left hand side of (54) converges. Next, the fact that $\phi_1 \phi_2 = 0$ and that $\phi_1 \Delta \phi_2 - \phi_2 \Delta \phi_1 = 0$ in the sense of $\mathcal{D}'(\mathbb{R}^3)$, and (51) is trivially satisfied.

Suppose now that c^n is bounded. Then we can extract a subsequence, still denoted by c^n, that converges to some real constant c, and therefore $c^n \phi_1^n \phi_2^n$ converges in $L^1_{loc}(\mathbb{R}^3)$, say. Equation (51) follows. The final two steps are devoted to the proof of the orthonormality condition (52).

Step 3

We here prove, that, up to a rotation, we may always assume without loss of generality that

$$\int_{\mathbf{R}^3} \phi_1 \phi_2 = 0. \tag{55}$$

If the constant c is different from 0 in (51) then we have, integrating this equation over the whole space, $c \int_{\mathbf{R}^3} \phi_1 \phi_2 = 0$ and (55) follows. In order to make this rigorous, since (51) only holds in the sense of distributions, say, we introduce a smooth cut-off function χ_R which has value 1 on the ball B_R, 0 outside the ball B_{R+1} and has values in $[0,1]$ on $B_R^c \cap B_{R+1}$, with $\|\chi_R\|_{C^1} \le 1$. Then we write

$$\begin{aligned} < \phi_2 \Delta \phi_1, \chi_R > &= -\int_{\mathbf{R}^3} \chi_R \nabla \phi_1 \nabla \phi_2 - \int_{\mathbf{R}^3} \phi_2 \nabla \phi_1 \nabla \chi_R \\ &= -\int_{B_R} \nabla \phi_1 \nabla \phi_2 - \int_{B_R^c \cap B_{R+1}} \big(\chi_R \nabla \phi_1 \nabla \phi_2 + \phi_2 \nabla \phi_1 \nabla \chi_R \big). \end{aligned}$$

As R goes to infinity, the first term goes to $\int_{\mathbf{R}^3} \nabla\phi_1 \nabla\phi_2$, while the second one goes to zero using the Cauchy-Schwarz inequality and observing that both ϕ_i are $H^1(\mathbb{R}^3)$ while χ_R is uniformly bounded in C^1.

On the other hand, suppose now $c = 0$ in (51). We then replace (ϕ_1, ϕ_2) by $(\widetilde{\phi_1}, \widetilde{\phi_2})$ defined by:

$$\begin{pmatrix} \widetilde{\phi_1} \\ \widetilde{\phi_2} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

For any θ, the following conditions are satisfied

$$\left\{ \begin{array}{l} \int_{\mathbf{R}^3} \widetilde{\phi_i}^2 \leq 1, \ 1 \leq i, j \leq 2 \\ \widetilde{\phi_1} \Delta \widetilde{\phi_2} - \widetilde{\phi_2} \Delta \widetilde{\phi_1} = 0 \\ E^{HF}(\widetilde{\phi_1}, \widetilde{\phi_2}) = E^{HF}(\phi_1, \phi_2), \end{array} \right. \tag{56}$$

We then choose θ such that we precisely have

$$\int_{\mathbf{R}^3} \widetilde{\phi_1} \widetilde{\phi_2} = 0.$$

In this manner, all the properties satisfied by (ϕ_1, ϕ_2) are shared by $(\widetilde{\phi_1}, \widetilde{\phi_2})$ with in addition orthogonality. From now on, we forget the notation $\widetilde{\phi_i}$ and simply use ϕ_i, considering that (55) is satisfied. We also know that $\int_{\mathbf{R}^3} \phi_i^2 \leq 1$ and there remains now to prove that both ϕ_i are of unit norm.

Step 4

We argue by contradiction and intend to show that

$$\int_{\mathbf{R}^3} \phi_1^2 < 1,$$

say, cannot hold.

For brevity, we denote in this proof by

$$D = D(\phi_1^2, \phi_2^2) - D(\phi_1\phi_2, \phi_1\phi_2),$$

(which, we recall, is a nonnegative quantity), and for $i = 1, 2$,

$$A_i = \frac{1}{2} \int_{\mathbf{R}^3} |\nabla\phi_i|^2 - \frac{Z}{|x|}\phi_i^2$$

and, when it makes sense, $\alpha_i = \dfrac{1}{\sqrt{\int_{\mathbf{R}^3} \phi_i^2}}$. In addition, we recall the notation

$$I = \inf\left\{ \int_{\mathbf{R}^3} \left(\frac{1}{2}|\nabla\psi|^2 - \frac{Z}{|x|}\psi^2 \right), \ \int_{\mathbf{R}^3} \psi^2 = 1 \right\}.$$

With the above notations,

$$E^{HF}(\phi_1, \phi_2) = A_1 + A_2 + D,$$

while the orthonormal family $(\alpha_1\phi_1, \alpha_2\phi_2)$ (in view of (55)) has energy

$$E^{HF}(\alpha_1\phi_1, \alpha_2\phi_2) = \alpha_1^2 A_1 + \alpha_2^2 A_2 + \alpha_1^2\alpha_2^2 D.$$

To begin with, we rule out the case when one, or both, of the ϕ_i is identically zero. Suppose e.g. $\phi_1 \equiv 0$. Then

$$\widetilde{I^{OEP}} \geq E^{HF}(\phi_1, \phi_2) = A_2 \geq \left(\int_{\mathbf{R}^3} \phi_2^2\right) I \geq I,$$

which contradicts (47). We now can suppose that both α_i are well defined. We remark that we have $\alpha_i \geq 1$ and thus, by definition of I, $\alpha_i^2 A_i \geq I$, for $i = 1, 2$.

Suppose we have

$$A_2 + \alpha_1^2 D \geq 0 \text{ or } A_1 + \alpha_2^2 D \geq 0.$$

Then, assuming for instance that the first assertion holds, we have

$$\begin{aligned} E^{HF}(\phi_1, \phi_2) &= A_1 + A_2 + D \\ &\geq A_1 + (1 - \frac{1}{\alpha_1^2}) A_2 \\ &\geq \left(\frac{1}{\alpha_1^2} + \frac{1}{\alpha_2^2}(1 - \frac{1}{\alpha_1^2})\right) I \\ &\geq I, \end{aligned}$$

because $I < 0$ and

$$\frac{1}{\alpha_1^2} + \frac{1}{\alpha_2^2}(1 - \frac{1}{\alpha_1^2}) = \frac{\alpha_1^2 + \alpha_2^2 - 1}{\alpha_1^2\alpha_2^2} \leq 1$$

since $\alpha_i \geq 1$. Clearly, since

$$E^{HF}(\phi_1, \phi_2) \leq \widetilde{I^{OEP}}$$

this contradicts (47). On the other hand, suppose we have

$$A_2 + \alpha_1^2 D < 0 \text{ and } A_1 + \alpha_2^2 D < 0.$$

Then

$$\begin{aligned} E^{HF}(\alpha_1\phi_1, \alpha_2\phi_2) &= \alpha_1^2 A_1 + \alpha_2^2 (A_2 + \alpha_1^2 D) \\ &< \alpha_1^2 A_1 + A_2 + \alpha_1^2 D \\ &\quad \text{since } \alpha_2 \geq 1 \\ &< A_1 + A_2 + D \\ &\quad \text{since } \alpha_1 > 1, \text{and } A_1 + D \leq A_1 + \alpha_2^2 D < 0, \\ &= E^{HF}(\phi_1, \phi_2) \\ &\leq \widetilde{I^{OEP}} \end{aligned}$$

and again we reach a contradiction because $E^{HF}(\alpha_1\phi_1, \alpha_2\phi_2)$ should be greater than or equal to $\widetilde{I^{OEP}}$ for it satisfies the contraints. This concludes the proof. ◊

Proof of Theorem 4.2

We now indicate the slight modifications needed in the arguments of the proof of Theorem 4.1 in order to apply to the minimization problem $\widetilde{J^{OEP}}$.

For Step 1, we only remark that the pair (ψ_1, ψ_2) indeed satisfies all the constraints of problem $\widetilde{J^{OEP}}$, and therefore we have

$$\widetilde{J^{OEP}} < I < 0. \tag{57}$$

In Step 2, considering a minimizing sequence (ϕ_1^n, ϕ_2^n) for $\widetilde{J^{OEP}}$, we may as above assume it weakly converges in H^1 to some (ϕ_1, ϕ_2) which satisfies $E^{HF}(\phi_1, \phi_2) \le \widetilde{J^{OEP}}$ and $(\int_{\mathbb{R}^3} \phi_i \phi_j) \le (\delta_{ij})$, $\quad 1 \le i, j \le 2$. We next pass to the limit in the condition

$$\forall \psi \in \mathcal{D}(\mathbb{R}^3), \ \int_{\mathbb{R}^3} (\phi_1^n)^2 \, |\nabla \psi|^2 \ge c^n \left(\int_{\mathbb{R}^3} \psi^2 \, (\phi_1^n)^2 - \Big(\int_{\mathbb{R}^3} \psi (\phi_1^n)^2\Big)^2 \right), \tag{58}$$

which will conclude the proof of Step 2. For this purpose, we first simply use the fact that ϕ_1^n strongly converges locally, say in L^2_{loc}. So all integrals in (58) converge for ψ fixed. Next, two cases may occur. Either the weak limit ϕ_1 of ϕ_1^n is identically zero, and therefore the condition

$$\forall \psi \in \mathcal{D}(\mathbb{R}^3), \ \int_{\mathbb{R}^3} \phi_1^2 \, |\nabla \psi|^2 \ge c \left(\int_{\mathbb{R}^3} \psi^2 \, \phi_1^2 - \Big(\int_{\mathbb{R}^3} \psi \phi_1^2\Big)^2 \right). \tag{59}$$

is trivially satisfied, for any c. Or, $\phi_1 \not\equiv 0$, and therefore we may find some $\psi \in \mathcal{D}(\mathbb{R}^3)$ such that

$$\int_{\mathbb{R}^3} \psi^2 \, \phi_1^2 - \Big(\int_{\mathbb{R}^3} \psi \phi_1^2\Big)^2 \neq 0.$$

Therefore, we have

$$\limsup c^n \le \frac{\displaystyle\int_{\mathbb{R}^3} \phi_1^2 \, |\nabla \psi|^2}{\displaystyle\int_{\mathbb{R}^3} \psi^2 \, \phi_1^2 - \Big(\int_{\mathbb{R}^3} \psi \phi_1^2\Big)^2},$$

which shows that c^n is a bounded sequence. We thus may assume it converges, to some $c \ge 0$, and pass to the limit in each term of (58) to obtain (59).

In addition, we may also pass to the limit in the commutation condition to obtain

$$\phi_2 \Delta \phi_1 - \phi_1 \Delta \phi_2 = c \phi_1 \phi_2.$$

This concludes Step 2.

For Step 3, we only make the following additionnal comment.

When $c \neq 0$, we have as above, by integration, $\int_{\mathbb{R}^3} \phi_1 \phi_2 = 0$, and Step 3 is completed. In the case $c = 0$, condition (59) is indeed empty, as the integral of a nonnegative function is always nonnegative. Therefore, (ϕ_1, ϕ_2) may be replaced by $(\widetilde{\phi_1}, \widetilde{\phi_2})$, so that $\displaystyle\int_{\mathbb{R}^3} \widetilde{\phi_1} \widetilde{\phi_2} = 0$, keeping the property that (59) is satisfied, again with $c = 0$.

For Step 4, we remark the following. If condition (59) is satisfied by ϕ_1 for some $c \geq 0$, then $\alpha_1 \phi_1$ also satifies it, whenever $\alpha_1 \geq 1$. Indeed, it suffices to remark that

$$\begin{aligned}
\alpha_1^2 \int_{\mathbf{R}^3} \phi_1^2 \, |\nabla \psi|^2 &\geq c\, \alpha_1^2 \Big(\int_{\mathbf{R}^3} \psi^2 \, \phi_1^2 - \big(\int_{\mathbf{R}^3} \psi \phi_1^2 \big)^2 \Big) \\
&\geq c \, \Big(\int_{\mathbf{R}^3} \psi^2 \, (\alpha_1 \phi_1)^2 - \frac{1}{\alpha_1^2} \big(\int_{\mathbf{R}^3} \psi (\alpha_1 \phi_1)^2 \big)^2 \Big) \\
&\geq c \, \Big(\int_{\mathbf{R}^3} \psi^2 \, (\alpha_1 \phi_1)^2 - \big(\int_{\mathbf{R}^3} \psi (\alpha_1 \phi_1)^2 \big)^2 \Big)
\end{aligned}$$

since $\alpha_1 \geq 1$. Therefore we can make use of the same argument as in Step 4 of the proof of Theorem 4.1 without modification. ◊

5 Penalized form of the OEP problem

The weak forms of the OEP problems (8) and (17) introduced above in (20) and (26) may be considered, from a certain point of view, as too *weak*. We shall see in Section 6 that, at least formally and in the simple radial case, they can be shown to be "equivalent" (note the quotes !) to the original problem in the "strong" form. Nevertheless, it remains that from a rigorous viewpoint we are not able to show the equivalence and therefore other tracks for giving a sense (8) and (17) may be pursued. One of such track is a penalization strategy, where one introduces a control on the potential W in order to be able to pass to the limit in minimizing sequences. From the computational standpoint, such a strategy is not surprising and is efficient in many other settings.

In view of the above motivation, we introduce, for any $\varepsilon > 0$, the following penalized version of problem (8)

$$\begin{aligned}
I_\varepsilon^{OEP} \;=\; & \inf \{ E^{HF}(\phi_1, \phi_2) \,+\, \varepsilon \left(\|\mu\|_X + \|V\|_Y \right), \int_{\mathbf{R}^3} \phi_i \phi_j = \delta_{ij} \;,\; 1 \leq i, j \leq 2, \\
& \phi_i \in H^1(\mathbb{R}^3), \;\; \text{such that for some } \lambda_1, \lambda_2 \in \mathbb{R},\, \mu \in X,\, V \in Y \\
& (-\frac{1}{2} \Delta - \frac{Z}{|x|} + \mu \star \frac{1}{|x|} + V) \, \phi_i = \lambda_i \phi_i \text{ in the sense of } \mathcal{D}'(\mathbb{R}^3) \, \},
\end{aligned} \tag{60}$$

In this definition, the functional space X is, for instance, chosen to be L^p for some $1 \leq p < 3/2$ and the functional space Y as L^q for, say, $q = 3/2$. Of course, our choice is arbitrary, and other functional spaces could be chosen, provided they satisfy some technical assumptions that allow for the arguments that will follow in this section. However, we do not want to enter such technicalities. Our purpose is only to show that such a penalized problem is well posed. The point is that the class of potentials W (according to the notation of (8)) that we have chosen, namely $-\dfrac{Z}{|x|} + \mu \star \dfrac{1}{|x|} + V$, with such μ and V, contains some reasonable potentials, relevant from the application viewpoint, so far as we can judge. Of course, such a form is reminiscent of the form of the Fock potential.

The same penalization technique can be applied to (17) and it leads to the formulation

$$\begin{aligned}
J_\varepsilon^{OEP} \;=\; & \inf\{E^{HF}(\phi_1,\phi_2) + \varepsilon\left(\|\mu\|_X + \|V\|_Y\right), \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}\ ,\ 1 \le i,j \le 2, \\
& \phi_i \in H^1(\mathbb{R}^3), \quad \text{such that } (\phi_1,\lambda_1)(\text{resp. } (\phi_2,\lambda_2)) \\
& \text{is the first (resp. a second) eigenvector/eigenvalue of the operator} \\
& -\frac{1}{2}\Delta - \frac{Z}{|x|} + \mu\star\frac{1}{|x|} + V \ \text{ for some } \mu \in X,\ V \in Y\},
\end{aligned} \tag{61}$$

Like in the previous sections, the minimizations problems $I_{r,\varepsilon}^{OEP}$, $I_\varepsilon^{OEP,\mathbb{C}}$, $I_{r,\varepsilon}^{OEP,\mathbb{C}}$, $J_{r,\varepsilon}^{OEP}$, $J_\varepsilon^{OEP,\mathbb{C}}$, $J_{r,\varepsilon}^{OEP,\mathbb{C}}$, with self-explanatory notations, can be defined accordingly.

In this section, we begin by studying the problem I_ε^{OEP}. For all the other "usual" problems $I_{r,\varepsilon}^{OEP}$, $I_\varepsilon^{OEP,\mathbb{C}}$, $I_{r,\varepsilon}^{OEP,\mathbb{C}}$, the proofs basically follow the same lines and the result of Theorem 5.1 below holds *mutatis mutandis*. For brevity, we skip all of them. Next, we study problem J_ε^{OEP}. Our proof can be extended (but we do not do so) to the complex valued case $J_\varepsilon^{OEP,\mathbb{C}}$, and the radial cases $J_{r,\varepsilon}^{OEP}$, $J_{r,\varepsilon}^{OEP,\mathbb{C}}$.

Theorem 5.1 *For $Z \ge 2$ (neutral atom or positive ion), the minimization problem (60) admits a minimizer.*

Proof of Theorem 5.1

The proof mimicks that of Theorem 4.1, so we will only give an outline of it and detail the differences.
Step 1 consists in showing that

$$I_\varepsilon^{OEP} < I, \tag{62}$$

as defined by the right-hand side of (47), and this property is a straightforward consequence of the fact that (ψ_1,ψ_2) defined by (48) satifies the constraints of (60) (with $\mu = V = 0$), and $E^{HF}(\psi_1,\psi_2) < I$ as shown in (50).

Step 2. We consider a minimizing sequence (ϕ_1^n,ϕ_2^n), associated with functions μ^n and V^n respectively in $X = L^p$ and $Y = L^q$. As the Hartree-Fock energy is bounded from above, we may assume (ϕ_1^n,ϕ_2^n) weakly converges to a limit (ϕ_1,ϕ_2) in $(H^1)^2$. In addition, due to the penalty term, the functions μ^n and V^n may also be assumed to weakly converge in X and Y respectively. In view of the eigenvalue equation

$$(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \mu^n\star\frac{1}{|x|} + V^n)\,\phi_i^n = \lambda_i^n\phi_i^n,$$

the eigenvalues

$$\lambda_i^n = \frac{1}{2}\int_{\mathbb{R}^3}|\nabla\phi_i^n|^2 - \int_{\mathbb{R}^3}\frac{Z}{|x|}(\phi_i^n)^2 + \int_{\mathbb{R}^3}(\mu^n\star\frac{1}{|x|})(\phi_i^n)^2 + \int_{\mathbb{R}^3}V_n(\phi_i^n)^2$$

are also bounded (each of the last three terms of the right-hand side can indeed be treated by Hölder type inequalities, the conditions $1 \le p < 3/2$ and $q = 3/2$ playing here a role), and therefore may be assumed to also converge, to some λ_i, as n goes to infinity. By Solobev compact imbeddings, we have the local strong convergences of ϕ_i^n in L^r (at least) for $1 \leq r < 6$, and therefore it is then easy to pass to the limit locally in the equations to obtain

$$(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \mu \star \frac{1}{|x|} + V)\,\phi_i = \lambda_i \phi_i. \tag{63}$$

As a consequence of the weak convergence in H^1, we have $\int_{\mathbf{R}^3} \phi_i \phi_j \leq 1$ in the sense of symmetric matrices, and there now remains to prove the orthonormality constraint on (ϕ_1, ϕ_2) to conclude the proof.

Step 3 is exactly the same as that in the proof of Theorem 4.1, $\lambda_2 - \lambda_1$ playing the role of c, of course.

Step 4 also is in the same vein. Indeed, the only three ingredients that are used are (a) the orthogonality $\int_{\mathbf{R}^3} \phi_1 \phi_2 = 0$ as produced by Step 3, (b) the property that

$$I_\varepsilon^{OEP} \geq E^{HF}(\phi_1, \phi_2) + \varepsilon \left(\|\mu\|_X + \|V\|_Y \right)$$

due to the weak convergences at hand, and (c) the fact that $I_\varepsilon^{OEP} < I$ as remarked in Step 1. Note also that the penalty term, being nonnegative and independent of the norm of ϕ_i does not perturbate the various inequalities involved in the argument. This concludes the proof. $\diamondsuit$

Remark 5.2 *It is unfortunately not known whether*

$$\lim_{\varepsilon \longrightarrow 0} I_\varepsilon^{OEP} = \widetilde{I^{OEP}}. \tag{64}$$

We now turn to the proof of

Theorem 5.3 *For $Z \geq 2$ (neutral atom or positive ion), the minimization problem J_ε^{OEP} defined by (61) admits a minimizer.*

Proof of Theorem 5.3

We again refer to the 4 steps of the proof of Theorem 4.1. Step 1 is of course unchanged as $(\psi_1^{Z'}, \psi_2^{Z'})$ are the first two eigenfunctions of $-\Delta - \frac{Z'}{|x|}$. Next, we need to make some slight modifications of the argument. Consider a miminizing sequence denoted as above. Since ϕ_1^n is the first eigenfunction of the operator $-\Delta + W^n$, where for brevity we denote by

$$W^n = -\frac{Z}{|x|} + \mu^n \star \frac{1}{|x|} + V^n, \tag{65}$$

we may assume (in view of the regularity of W^n, which is in $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$), that $\phi_1^n > 0$ everywhere. In addition, we use the argument of Section 2, formula (24), to claim that, λ_2^n being the second eigenvalue of $-\Delta + W^n$, we have

$$\big((-\frac{1}{2}\Delta + W^n)\theta, \theta\big) - \lambda_1^n \int_{\mathbf{R}^3} \theta^2 \geq (\lambda_2^n - \lambda_1^n) \left(\int_{\mathbf{R}^3} \theta^2 - \big(\int_{\mathbf{R}^3} \theta \phi_1^n \big)^2 \right) \tag{66}$$

for any function $\theta \in \mathcal{D}(\mathbb{R}^3)$.

This being done, we pass to the weak limits in the minimizing sequence to obtain some μ, V, ϕ_i, λ_i (as in Step 3) such that

$$(-\frac{1}{2}\Delta + W)\,\phi_i = \lambda_i \phi_i \tag{67}$$

where of course $W = -\dfrac{Z}{|x|} + \mu \star \dfrac{1}{|x|} + V$. Moreover, we have $\phi_1 \geq 0$ as a consequence of $\phi_1^n > 0$, and, for any $\theta \in \mathcal{D}(\mathbb{R}^3)$,

$$((-\frac{1}{2}\Delta + W)\theta, \theta) - \lambda_1 \int_{\mathbf{R}^3} \theta^2 \geq (\lambda_2 - \lambda_1)\left(\int_{\mathbf{R}^3} \theta^2 - \big(\int_{\mathbf{R}^3} \theta\phi_1\big)^2\right) \tag{68}$$

as a consequence of (66). We then rule out the case when one the ϕ_i is identically zero using $J_\varepsilon^{OEP} < I$ and arguing as above. Therefore, we deduce $\phi_1 > 0$ by Harnack inequality on (67), and thus ϕ_1 is the ground state of $-\dfrac{1}{2}\Delta + W$ (as $W \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, the ground state is non-degenerate). We now turn to λ_2 and ϕ_2, which we know is not zero. We know $\lambda_2 \geq \lambda_1$. Suppose $\lambda_2 = \lambda_1$. Then $\phi_2 = \alpha\phi_1$ for some constant α, because of again the nondegeneracy of the ground state. In fact, $\alpha \neq 0$ because $\phi_2 \not\equiv 0$. The fact that $\displaystyle\int_{\mathbf{R}^3} \phi_i\phi_j \leq 1$ in the sense of symmetric matrices writes

$$\left(1 - \int_{\mathbf{R}^3} \phi_1^2\right)\left(1 - \int_{\mathbf{R}^3} \phi_2^2\right) \geq \left(\int_{\mathbf{R}^3} \phi_1\phi_2\right)^2,$$

in general and thus in the present case

$$1 - (1+\alpha^2)\int_{\mathbf{R}^3} \phi_1^2 \geq 0.$$

On the other hand, the Hartree-Fock energy then takes the particular form

$$\begin{aligned} E^{HF}(\phi_1, \phi_2) &= E^{HF}(\phi_1, \alpha\phi_1) \\ &= (1+\alpha^2)\left(\frac{1}{2}\int_{\mathbf{R}^3} |\nabla\phi_1|^2 - \frac{Z}{|x|}\phi_1^2\right) \\ &\geq (1+\alpha^2)\left(\int_{\mathbf{R}^3} \phi_1^2\right) I \\ &\geq I. \end{aligned}$$

We reach a contradiction since by weak convergence $E^{HF}(\phi_1, \phi_2) \leq J_\varepsilon^{OEP} < I$. Therefore, we necessarily have the situation when $\lambda_2 > \lambda_1$ and ϕ_2 is a (possibly not normalized) eigenstate associated to λ_2. It then follows using (68) and the argument of Section 2 that λ_2 is the second eigenvalue. It also follows that $\displaystyle\int_{\mathbf{R}^3} \phi_1\phi_2 = 0$ and then we enter Step 4 directly. The proof can then be pursued. $\diamondsuit$

6 Do the weak formulations $\widetilde{\text{OEP}}$ allow to recover the OEP problems?

We present in this final section an argument that shows that the minimizer (ϕ_1, ϕ_2) of the weakly formulated problem $\widetilde{J^{OEP}}$ indeed satisfies the "strong constraints" stated in (17), in some sense at least. Unfortunately, our proof only applies to the *radial* case (i.e. to problem $\widetilde{J_r^{OEP}}$, together with its complex valued analogue, that we do not detail here for brevity).

Let us briefly describe our purpose. A pair (ϕ_1, ϕ_2) that satifies the commutation condition

$$\phi_2 \Delta \phi_1 - \phi_1 \Delta \phi_2 = c \phi_1 \phi_2$$

formally satisfies the set of "equations"

$$\left\{ \begin{array}{rcl} -\frac{1}{2}\Delta\phi_1 + \left(\frac{\phi_1\Delta\phi_1 + \phi_2\Delta\phi_2 + c\phi_2^2}{2(\phi_1^2+\phi_2^2)}\right)\phi_1 & = & 0 \\ -\frac{1}{2}\Delta\phi_2 + \left(\frac{\phi_1\Delta\phi_1 + \phi_2\Delta\phi_2 + c\phi_2^2}{2(\phi_1^2+\phi_2^2)}\right)\phi_2 & = & c\phi_2 \end{array} \right. \tag{69}$$

and thus formally is a pair of eigenvectors of the same Schrödinger type operator $-\frac{1}{2}\Delta + W$ with $W = \dfrac{\phi_1\Delta\phi_1 + \phi_2\Delta\phi_2 + c\phi_2^2}{2(\phi_1^2+\phi_2^2)}$. The difficulty to give a rigorous sense to this formal statement is twofold. First, we have to prove we may legitimately divide by the density $\rho = \phi_1^2 + \phi_2^2$, and second that the potential W is regular enough for the product $W\phi_1$ and $W\phi_2$ to be given a sense. The two facts are of course closely intertwinned as any information on W gives information on the set of zeros of the ϕ_i.

In the case of the $\widetilde{I^{OEP}}$ problem, we are not able to reach this goal. On the other hand, we can provide rigorous arguments for the $\widetilde{J^{OEP}}$ problem (at least in the radial case) by making use of inequality (23). For technical reasons, our proof is limited to the cases when $Z \geq 4$, but our result probably holds true for $Z = 2$ and $Z = 3$.

We begin by stating three lemmas, the proofs of which are postponed until the statement of our main result in Proposition 6.4 below.

Lemma 6.1 *Let us assume that $Z \geq 4$ and consider a minimizer (ϕ_1, ϕ_2) of $\widetilde{J_r^{OEP}}$ (the existence of which is stated in Theorem 4.2). The non negative constant c arising in conditions (19) and (23) is positive.*

Lemma 6.2 *For any minimizer (ϕ_1, ϕ_2) of $\widetilde{J_r^{OEP}}$ such that the constant c arising in conditions (19) and (23) is positive, the functions ϕ_1 and ϕ_2 are continuous (except possibly at the origin) and the set of points $\{x \in \mathbb{R}^3, \, / \, \phi_1(x) \neq 0\}$ is connex.*

As ϕ_1 is radially symmetric and continuous, the support of ϕ_1 therefore is either the whole space $\mathbb{R}^3$, or a ball, or the complement of a ball, or a hollow ball. It also follows from Lemma 6.2 that ϕ_1 does not change its sign, and therefore we may suppose that ϕ_1 is positive. Our second lemma asserts that we may always assume, without loss of generality, that ϕ_2 is also supported in $\mathrm{Supp}\,\phi_1$.

Lemma 6.3 *Let us assume that $Z \geq 4$ (or that $Z = 2$ or $Z = 3$ and that there exists a minimizer of $\widetilde{J_r^{OEP}}$ for which the constant c arising in conditions (19) and (23) is positive). Then there exists a solution of $\widetilde{J_r^{OEP}}$, still denoted by (ϕ_1, ϕ_2), such that $\phi_1 \geq 0$ and $\mathrm{Supp}\,\phi_2 \subset \mathrm{Supp}\,\phi_1$.*

Collecting these three lemmas, we show

Proposition 6.4 *(Radial case). Let us assume that $Z \geq 4$ (or that $Z = 2$ or $Z = 3$ and that there exists a minimizer of $\widetilde{J_r^{OEP}}$ for which the constant c arising in conditions (19) and (23) is positive). Let (ϕ_1, ϕ_2) be a solution $\widetilde{J_r^{OEP}}$ satisfying the properties set in Lemma 6.3. Let us denote by $\rho(x) = \phi_1(x)^2 + \phi_2(x)^2$ the electronic density and by $\Omega = \left\{x \in \mathbb{R}^3,\ \rho(x) > 0\right\}$. Then the potential*

$$W = \left| \begin{array}{ll} \dfrac{\phi_1 \Delta \phi_1 + \phi_2 \Delta \phi_2 + c\phi_2^2}{2\rho} & \text{on } \Omega \\ +\infty & \text{elsewhere} \end{array} \right.$$

is in $H^{-1}(\omega)$ for any open set $\omega \subset\subset \Omega$, and so are the products $W\phi_1$ and $W\phi_2$. In this sense, the system

$$\left\{ \begin{array}{l} -\dfrac{1}{2}\Delta \phi_1 + W\phi_1 = 0 \\ -\dfrac{1}{2}\Delta \phi_2 + W\phi_2 = \dfrac{c}{2}\phi_2 \end{array} \right.$$

holds in $\omega \subset\subset \Omega$.

As we shall only work in this section with radially symmetric functions, say ϕ, we shall often make the slight abuse of notations consisting in denoting by $\phi(r)$ the single value $\phi(x)$ for any $x \in \mathbb{R}^3$ such that $|x| = r$.

Proof of Lemma 6.1. Assume that $c = 0$. For $k = 1, 2$, let us denote by $\left\{\Omega_i^k\right\}_{i \in \mathcal{I}_k}$ the family of the connex components of the open set $\phi_k \neq 0$ (the functions ϕ_k are continuous except possibly at the origin). Of course, the domains Ω_i^k are radially symmetric for so are the functions ϕ_k. The relation $\phi_2 \Delta \phi_1 - \phi_1 \Delta \phi_2 = 0$ involves that $\phi_2 \nabla \phi_1 - \phi_1 \nabla \phi_2$ is divergence-free and therefore that $\phi_2 \nabla \phi_1 - \phi_1 \nabla \phi_2 = 0$ since we deal with radial symmetric functions. Therefore, ϕ_1 and ϕ_2 are proportional on each domain one of them at least has no zero. It follows that for any $(i_1, i_2) \in \mathcal{I}_1 \times \mathcal{I}_2$, either $\Omega_{i_1}^1 \cap \Omega_{i_2}^2 = \emptyset$ or $\Omega_{i_1}^1 = \Omega_{i_2}^2$. Let us denote by $\{\Omega_i\}_{i \in \mathcal{I}}$ the family obtained by merging the two families $\{\Omega_i^1\}_{i \in \mathcal{I}_1}$ and $\{\Omega_i^2\}_{i \in \mathcal{I}_2}$. For any $i \in \mathcal{I}$, there exists a function $\psi_i \in H_0^1(\Omega_i)$ and two real constants α_i and β_i such that $\int_{\Omega_i} \psi_i^2 = 1$, and $\phi_1 = \alpha_i \psi_i$, $\phi_2 = \beta_i \psi_i$ on Ω_i. A simple calculation shows that

$$\begin{aligned} E^{HF}(\phi_1, \phi_2) &\geq \frac{1}{2} \int_{\mathbf{R}^3} |\nabla \phi_1|^2 + \frac{1}{2} \int_{\mathbf{R}^3} |\nabla \phi_2|^2 - \int_{\mathbf{R}^3} \frac{Z}{|x|} \phi_1^2 - \int_{\mathbf{R}^3} \frac{Z}{|x|} \phi_2^2 \\ &= \sum_{i \in \mathcal{I}} (\alpha_i^2 + \beta_i^2) \left(\frac{1}{2} \int_{\Omega_i} |\nabla \psi_i|^2 - \int_{\Omega_i} \frac{Z}{|x|} \psi_i^2 \right) \\ &\geq \sum_{i \in \mathcal{I}} (\alpha_i^2 + \beta_i^2) \lambda_1 (H_Z^{\Omega_i}) \end{aligned}$$

where $\lambda_1(H_Z^{\Omega_i})$ denotes the ground state of the self-adjoint operator defined on $H^2(\Omega_i) \cap H_0^1(\Omega_i)$ by $H_Z^{\Omega_i} \phi = -\frac{1}{2} \Delta \phi - \frac{Z}{|x|} \phi$. In addition the constraints $\int_{\mathbf{R}^3} \phi_i \phi_j = \delta_{ij}$ now read $\sum_{i \in \mathcal{I}} \alpha_i^2 = 1$, $\sum_{i \in \mathcal{I}} \beta_i^2 = 1$, $\sum_{i \in \mathcal{I}} \alpha_i \beta_i = 0$. It is a straightforward consequence of the Courant-Fischer formulae that $\Omega \subset \Omega'$ involves $\lambda_1(H_Z^{\Omega}) \geq \lambda_1(H_Z^{\Omega'})$; in addition, it is well known that any eigenvector of $H_Z^{\Omega_i}$ which is positive on Ω_i is the ground state. It follows that the restriction to B_{r_0} (resp. to $\overline{B}_{r_0}^c$) with $r_0 = 2/Z$ of the second radial eigenvector of $H_Z^{\mathbf{R}^3}$ (which takes the value 0 for $r = r_0$ only) is the ground state of $H_Z^{B_{r_0}}$ (resp. of $H_Z^{\overline{B}_{r_0}^c}$); thus $\lambda_1(H_Z^{B_{r_0}}) = \lambda_1(H_Z^{\overline{B}_{r_0}}) = -Z^2/8$.

Let us first examine the situation when $\phi_1(r_0) = \phi_2(r_0) = 0$. In this case, for any $i \in \mathcal{I}$, either $\Omega_i \subset B_{r_0}$ or $\Omega_i \subset \overline{B}_{r_0}^c$ and therefore $\lambda_1(H_Z^{\Omega_i}) \geq -Z^2/8$. Consequently, in virtue of inequality (57),

$$E^{HF}(\phi_1, \phi_2) \geq -\frac{Z^2}{4} > -\frac{Z^2}{2} = I > \widetilde{J^{OEP}}.$$

We reach a contradiction. Therefore, there exists $i_0 \in \mathcal{I}$ such that the sphere $|x| = r_0$ belongs to Ω_{i_0}, and as Ω_{i_0} is radial symmetric, there exist two constants $0 \leq a < b \leq +\infty$ such that $\Omega_{i_0} = B_b \cap \overline{B_a}^c$. By convention $\lambda_1(H_Z^{B_0}) = +\infty$ and $\lambda_1(H_Z^{\overline{B_{+\infty}}^c}) = 0$. For any $i \in \mathcal{I}$, either $\Omega_i \subset B_a$ or $\Omega_i \subset \overline{B_b}^c$. Therefore

$$E^{HF}(\phi_1, \phi_2) \geq (\alpha_{i_0}^2 + \beta_{i_0}^2) \lambda_1(\Omega_{i_0}) + (2 - (\alpha_{i_0}^2 + \beta_{i_0}^2)) \min \left(\lambda_1(H_Z^{B_a}), \lambda_1(H_Z^{\overline{B_b}^c}) \right).$$

Both $\lambda_1(H_Z^{B_a})$ and $\lambda_1(H_Z^{\overline{B_b}^c})$ being greater than $-Z^2/8$, it is necessary that $\lambda_1(\Omega_{i_0}) < -Z^2/8$ (otherwise $E^{HF}(\phi_1, \phi_2) \geq -Z^2/4$ and (ϕ_1, ϕ_2) cannot be a minimizer of $\widetilde{J^{OEP}}$). As

$$\max_{\sum_{i \in \mathcal{I}} \alpha_i^2 = 1,\, \sum_{i \in \mathcal{I}} \beta_i^2 = 1,\, \sum_{i \in \mathcal{I}} \alpha_i \beta_i = 0} (\alpha_{i_0}^2 + \beta_{i_0}^2) = 1$$

we obtain

$$\begin{aligned} E^{HF}(\phi_1, \phi_2) &\geq \lambda_1(\Omega_{i_0}) + \min \left(\lambda_1(H_Z^{B_a}), \lambda_1(H_Z^{\overline{B_b}^c}) \right) \\ &= \min \left(\lambda_1(\Omega_{i_0}) + \lambda_1(H_Z^{B_a}), \lambda_1(\Omega_{i_0}) + \lambda_1(H_Z^{\overline{B_b}^c}) \right) \\ &\geq \min \left(\lambda_1(H_Z^{\overline{B_a}^c}) + \lambda_1(H_Z^{B_a}), \lambda_1(B_b) + \lambda_1(H_Z^{\overline{B_b}^c}) \right). \end{aligned}$$

for $\Omega_{i_0} \subset \overline{B_a}^c$ and $\Omega_{i_0} \subset B_b$. Finally,

$$E^{HF}(\phi_1, \phi_2) \geq \min\left(F_Z(a), F_Z(b)\right).$$

where the function F_Z is defined as $F_Z(R) = \lambda_1(H_Z^{B_R}) + \lambda_1(H_Z^{\overline{B_R}^c})$. By a scaling argument, it is easy to check that $F_Z(R) = Z^2 F_1(ZR)$; thus

$$E^{HF}(\phi_1, \phi_2) \geq Z^2 \min\left(F_1(Za), F_1(Zb)\right).$$

By making use of the inequality

$$\inf_{0 \leq R \leq +\infty} F_1(R) > A = -\frac{5}{8} + \frac{\eta}{4} - \frac{\eta^2}{40} \tag{70}$$

with $\eta = \dfrac{137}{729}$ (see Remark 6.5 below), we obtain that for any $Z \geq 4$,

$$E^{HF}(\phi_1, \phi_2) \geq Z^2 \inf_{0 \leq R \leq +\infty} F_1(R) > -\frac{5}{8} Z^2 + \eta Z - \frac{2}{5}\eta^2 \geq \widetilde{J^{OEP}}.$$

We again reach a contradiction and the proof of the Lemma is completed. ◊

Remark 6.5 *We have to point out that inequality (70) has been established* numerically. *Denoting by r_n (resp. R_n) the lowest (resp. the highest) zero of the n-th radial eigenfunction of the operator $-\frac{1}{2}\Delta - \frac{1}{|x|}$ on $L^2(\mathbb{R}^2)$, we have for any $R \leq r_n$, $\lambda_1(H_1^{B_R}) \geq \lambda_n\left(-\frac{1}{2}\Delta - \frac{1}{|x|}\right) = -\frac{1}{2n^2}$, and for any $R \geq R_n$, $\lambda_1(H_1^{\overline{B_R}^c}) \geq \lambda_n\left(-\frac{1}{2}\Delta - \frac{1}{|x|}\right) = -\frac{1}{2n^2}$. Therefore*

$$\forall R \notin [r_n, R_n], \quad F_1(R) \geq -\frac{1}{2} - \frac{1}{2n^2}.$$

The RHS of the above inequality is greater than A for any integer $n \geq 3$. Therefore, $F_1(R) > A$ for $R \notin [r_3, R_3]$. In the range $[r_3, R_3]$ we have used a numerical evaluation of the function $F_1(R)$; we have first sampled the range $[1.9, 7.1]$ ($r_3 \simeq 1.902$ and $R_3 \simeq 7.098$) with a length step 0.001, then search for the global minimum around the point $R \simeq 4.566$ by dichotomy; the numerical evaluation of the function $F_1(R)$ for a given value of R was obtained by solving the eigenvalue equation $-v''(r) - \frac{v(r)}{r} = \lambda v(r)$ first on $H_0^1(0, R)$ to get $\lambda_1(H_1^{B_R})$, then on $H_0^1(R, R_{Max})$ with $R_{Max} = 200$ to get $\lambda_1(H_1^{\overline{B_R}^c})$ (the value for R_{Max} has been chosen such that the value of the ground state of $H_1^{\overline{B_{R_3}}^c}$, which is known analytically, vanishes at the machine precision for $r \geq R_{max}$); for this purpose we have used a spectral Galerkin approximation in the Fourier basis with 10^3 elements. We have obtained $F_1(R) > -0.5681$ and $A < -0.5789$. Although the Galerkin approximation provides upper bounds of the eigenvalues whereas lower bounds are needed, it is reasonable to be confident in the numerical lower bound since the numerical values of $\lambda_1(H_1^{B_R})$ at the check points $R = r_2 = 2$ and $R = r_3 = 9/2 - 3/2\sqrt{3}$ and of $\lambda_1(H_1^{\overline{B_R}^c})$ at $R = R_2 = 2$ and $R = R_3 = 9/2 + 3/2\sqrt{3}$ are equal to the analytical ones up to 10^{-6}.

Proof of Lemma 6.2. Since ϕ_i is a radially symmetric function in $H^1(\mathbb{R}^3)$, ϕ_i is continuous except maybe at the origin. Clearly, since $\phi_1 \not\equiv 0$ we may consider some x_0 such that $\phi_1(x_0) \neq 0$, and, say, $\phi_1(x_0) > 0$. Let $r_0 = |x_0|$. By continuity, we may consider the largest $0 < \alpha \leq r_0$ and the largest $0 < \beta \leq +\infty$ such that $\phi_1 > 0$ on $B^c_{r_0-\alpha} \cap B_{r_0+\beta}$. Clearly, if $r_0 - \alpha > 0$ then $\phi_1(r_0 - \alpha) = 0$, and if $\beta < +\infty$ then $\phi_1(r_0 + \beta) = 0$. Suppose that $r_0 - \alpha > 0$ and $r_0 + \beta < +\infty$ (otherwise the following proof is even simpler, since no cut-off is needed at the origin, and/or the cut-off at infinity can be treated likewise). The idea is to consider a sequence of radially symmetric functions $\psi_n \in \mathcal{D}(\mathbb{R}^3)$ such that ψ_n goes to the characteristic function of $B^c_{r_0-\alpha} \cap B_{r_0+\beta}$. This can easily be done for instance by setting $\psi_n(r) = 0$ for any $r \leq r_0 - \alpha$ or $r \geq r_0 + \beta$, $\psi_n(r) = 1$ for any $r_0 - \alpha + \frac{1}{n} \leq r \leq r_0 + \beta - \frac{1}{n}$, $0 \leq \psi_n(r) \leq 1$ for $r_0 - \alpha \leq r \leq r_0 - \alpha + \frac{1}{n}$ or $r_0 + \beta - \frac{1}{n} \leq r \leq r_0 + \beta$, and $\frac{1}{n}\|\psi_n\|_{C^1}$ uniformly bounded with respect to n. Then we pass to the limit in

$$\int_{\mathbf{R}^3} \phi_1^2 \, |\nabla \psi_n|^2 \geq c \left(\int_{\mathbf{R}^3} \psi_n^2 \, \phi_1^2 - \big(\int_{\mathbf{R}^3} \psi_n \phi_1^2 \big)^2 \right), \tag{71}$$

in order to obtain

$$0 \geq c \left(\int_{B^c_{r_0-\alpha} \cap B_{r_0+\beta}} \phi_1^2 - \big(\int_{B^c_{r_0-\alpha} \cap B_{r_0+\beta}} \phi_1^2 \big)^2 \right), \tag{72}$$

which clearly implies, since $c > 0$ (cf. Lemma 6.1),

$$\int_{B^c_{r_0-\alpha} \cap B_{r_0+\beta}} \phi_1^2 = 1,$$

and therefore concludes the proof: the total mass of ϕ_1^2 being one, ϕ_1 is therefore supported in the connex set $B^c_{r_0-\alpha} \cap B_{r_0+\beta}$.

In order to go from (71) to (72), we simply have to remark that for any function such as ϕ_1 in $H^1_r(\mathbb{R}^3)$, we have

$$\begin{aligned}
|\phi_1(a+t) - \phi_1(a)| &= \left| \int_a^{a+t} \frac{\partial \phi_1}{\partial r} \, dr \right| \\
&\leq \left(\frac{1}{4\pi} \int_{B_{a+t} \cap B^c_a} |\nabla \phi_1|^2 \right)^{1/2} \left(\int_a^{a+t} \frac{dr}{r^2} \right)^{1/2} \\
&= \left(\frac{1}{4\pi} \int_{B_{a+t} \cap B^c_a} |\nabla \phi_1|^2 \right)^{1/2} \frac{1}{a} O(\sqrt{t}),
\end{aligned}$$

and therefore, applying this to $a = r_0 - \alpha$ and $t = 1/n$,

$$\begin{aligned}
\int_{r_0-\alpha}^{r_0-\alpha+\frac{1}{n}} \phi_1^2 \, |\nabla \psi_n|^2 &\leq C\, n^2 \int_{r_0-\alpha}^{r_0-\alpha+\frac{1}{n}} \phi_1^2 \\
&\leq C\, n^2 \left(\frac{1}{4\pi} \int_{B_{r_0-\alpha+1/n} \cap B^c_{r_0-\alpha}} |\nabla \phi_1|^2 \right)^{1/2} O(\frac{1}{n^2}) \\
&= o(1),
\end{aligned}$$

indeed goes to zero as n goes to infinity. The same applies to the cut-off at $r_0 + \beta$ and the proof of the Lemma is completed. $\diamondsuit$

Proof of Lemma 6.3. We now intend to show that we may always assume, without loss of generality, that ϕ_2 is also supported in $\operatorname{Supp}\phi_1$, that we henceforth denote by $\overline{B_{r_2}} \cap B^c_{r_1}$ where $r_1 = \inf\{r,\ \phi_1(r) > 0\}$ and $r_2 = \sup\{r,\ \phi_1(r) > 0\}$, where we recall that r_1 may be zero, and r_2 may be $+\infty$. We for instance show that we may always assume $\phi_2(r) = 0$, when $r \geq r_2$ and $r_2 < +\infty$ (the same arguments can be used to show that we can assume that $\phi_2(r) = 0$, when $r \leq r_1$ and $r_1 > 0$).

To begin with, we make some remarks.

By definition of r_2, we know that $\phi_1(r) \equiv 0$ for $r \geq r_2$. Changing ϕ_2 into $-\phi_2$ if necessary, we may always assume $\phi_2(r_2) \geq 0$. Moreover, we may then change ϕ_2 into the function, still denoted by ϕ_2,

$$\phi_2(r) = \begin{cases} \phi_2(r), & \text{when } r \leq r_2, \\ |\phi_2|(r), & \text{when } r \geq r_2, \end{cases} \tag{73}$$

without changing anything in the properties of the pair (ϕ_1, ϕ_2). If $\phi_2 = 0$ on $[r_2, +\infty[$, the proof is finished; so we henceforth assume that $\phi_2 \not\equiv 0$, $\phi_2 \geq 0$ on $[r_2, +\infty[$.

On the set $r > r_2$, we have the Euler-Lagrange equation

$$-\frac{1}{2}\Delta\phi_2 - \frac{Z}{|x|}\phi_2 + (\phi_1^2 \star \frac{1}{|x|})\phi_2 = -\lambda_2\phi_2. \tag{74}$$

Equation (74) can be obtained directly on the minimization problem by considering variations of ϕ_2 only on the set $r > r_2$ that keep c fixed (the constraints (19) and (23) do not play any role for $\phi_1 \equiv 0$ on this open set). It follows from (74) that $\Delta\phi_2 \in L^2(B^c_{r_2})$ and that, together from the nonnegativity of ϕ_2 on the same set, we have

$$\phi_2(r) > 0, \text{ when } r > r_2,$$

by Harnack inequality.

Clearly, two cases may occur: $\phi_2(r_2) = 0$ or $\phi_2(r_2) > 0$.

We first show that necessarily $\phi_2(r_2) = 0$. Let us argue by contradiction and assume $\phi_2(r_2) > 0$. Then the strict positivity of ϕ_2, already true for $r > r_2$ can be slightly extended around r_2, by continuity of ϕ_2. More precisely, we may find an interval $[r_2 - \eta, r_2 + \eta]$, $\eta > 0$, where ϕ_2 is bounded below, away from zero by a constant $a > 0$. On such an interval (upon which $\phi_2 \geq a > 0$), we may write the commutation condition as

$$-\text{div}\,(\phi_2^2\,\nabla f) + c\phi_2^2\, f = 0$$

with $f = \dfrac{\phi_1}{\phi_2} \geq 0$. We are now allowed to use Harnack inequality to conclude that

$$\sup_{[r_2-\eta/4, r_2]} f \leq \alpha \inf_{[r_2-\eta/4, r_2]} f$$

for some positive constant α. As we have assumed $\phi_2(r_2) > 0$, $f(r_2) = 0$ and then $f = 0$ on $[r_2 - \eta/4, r_2]$, which contradicts the definition of r_2 as $\sup\{r,\ \phi_1(r) > 0\}$.

We are now in the situation when $\phi_2(r_2) = 0$, and of course, for $r > r_2$, $\phi_1(r) = 0$ and $\phi_2(r) > 0$. Let us decompose the Hartree-Fock energy of (ϕ_1, ϕ_2) as follows

$$E^{HF}(\phi_1, \phi_2) = A_1 + A_{r_2} + A_{r_2^c} + D, \tag{75}$$

with

$$A_1 = \frac{1}{2}\int_{\mathbf{R}^3} |\nabla\phi_1|^2 - \frac{Z}{|x|}\phi_1^2$$

$$A_{r_2} = \frac{1}{2}\int_{B_{r_2}} |\nabla\phi_2|^2 - \frac{Z}{|x|}\phi_2^2$$

$$A_{r_2^c} = \frac{1}{2}\int_{B_{r_2^c}} |\nabla\phi_2|^2 - \frac{Z-1}{|x|}\phi_2^2$$

(note the $\frac{(Z-1)}{|x|}$ instead of the $\frac{Z}{|x|}$ because the potential generated by ϕ_1 is accounted for), and

$$D = \iint_{B_{r_2}\times B_{r_2}} \frac{\phi_1^2(x)\phi_2^2(y)}{|x-y|} - \iint_{B_{r_2}\times B_{r_2}} \frac{\phi_1(x)\phi_2(x)\phi_1(y)\phi_2(y)}{|x-y|}.$$

We recall that $\phi_2 > 0$ on $\overline{B_{r_2}}^c$; thus we have $\int_{B^c_{r_2}} \phi_2^2 > 0$, and we may introduce $\mu = \frac{\int_{B_{r_2}} \phi_2^2}{\int_{B^c_{r_2}} \phi_2^2}$.

We next consider pairs of the form $(\phi_1, \widetilde{\phi_2} = \alpha\phi_2|_{B_{r_2}} + \beta\phi_2|_{B^c_{r_2}})$ which automatically satisfy the constraints of problem $\widetilde{J_r^{OEP}}$ as soon as we impose

$$\alpha^2\int_{B_{r_2}} \phi_2^2 + \beta^2\int_{B^c_{r_2}} \phi_2^2 = 1.$$

We have

$$\begin{aligned} E^{HF}(\phi_1,\widetilde{\phi_2}) &= A_1 + \alpha^2 A_{r_2} + \beta^2 A_{r_2^c} + \alpha^2 D \\ &= E^{HF}(\phi_1,\phi_2) + (\alpha^2-1)(A_{r_2} + D - \mu A_{r_2^c}). \end{aligned}$$

The case when $\int_{B^c_{r_2}} \phi_2^2 = 1$ can be excluded for it involves that ϕ_2 is entirely supported in $B^c_{r_2}$, and therefore that $\phi_2\Delta\phi_1 - \phi_1\Delta\phi_2 = 0$; this is not possible in virtue of Lemma 6.1. Thus, we may now choose α first such that $\alpha^2 - 1 > 0$, and next such that $\alpha^2 - 1 < 0$ (note both cases are possible precisely when $0 < \int_{B^c_{r_2}} \phi_2^2 < 1$). This shows that necessarily $A_{r_2} + D - \mu A_{r_2^c} = 0$, otherwise we would contradict the fact that (ϕ_1,ϕ_2) is a minimizer. But then this shows that, for any α and β we have $E^{HF}(\phi_1,\widetilde{\phi_2}) = E^{HF}(\phi_1,\phi_2)$, and therefore in particular we may choose $\beta = 0$, and leave the Hartree-Fock energy unchanged. Consequently, it is indeed possible to assume that ϕ_2 vanishes outside B_{r_2}. $\diamondsuit$

Proof of Proposition 6.4. Let $\omega \subset\subset \Omega$. As $\rho > 0$ on Ω, there exists some positive constant a such that $\rho \geq a$ on ω. It follows that $f_1 = \frac{\phi_1}{\rho}$ belongs to $H^1(\omega)$; indeed, $f_1 \in L^2(\omega)$ and

$$\begin{aligned} |\nabla f_1| &\leq \frac{|\nabla\phi_1|}{a} + \frac{|2\phi_1^2\nabla\phi_1 + 2\phi_1\phi_2\nabla\phi_2|}{\rho^2} \\ &\leq \frac{3}{a}|\nabla\phi_1| + \frac{1}{a}|\nabla\phi_2|. \end{aligned}$$

The same results holds for $f_2 = \dfrac{\phi_2}{\rho}$. Therefore

$$W = \frac{1}{2}\left(f_1\Delta\phi_1 + f_2\Delta\phi_2 + c\frac{\phi_2^2}{\rho}\right) \in H^{-1}(\omega).$$

Moreover, $f_1\phi_1$ and $f_2\phi_1$ also are in $H^1(\omega)$, since a simple calculation shows that

$$|\nabla(f_1\phi_1)| \leq \frac{4}{\sqrt{a}}|\nabla\phi_1| + \frac{1}{\sqrt{a}}|\nabla\phi_2|, \quad |\nabla(f_2\phi_1)| \leq \frac{3}{2\sqrt{a}}\left(|\nabla\phi_1| + |\nabla\phi_2|\right).$$

The product $W\phi_1$ then is well defined in $H^{-1}(\omega)$. Similarly, $W\phi_2 \in H^{-1}(\omega)$. ♢

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