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A general approach for multiconfiguration methods in quantum molecular chemistry

by

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ABSTRACT. – We are concerned with a family of minimization problems arising in Quantum Chemistry for the modelling of the ground state of a molecule. We study the multiconfiguration methods, which are an extension of the well known Hartree-Fock method. We propose a general approach to prove the existence of the ground state in this framework. We apply our approach to two particular cases.

Key words: Hartree-Fock type theories, variational methods.

RÉSUMÉ. – Nous nous intéressons à une classe de problèmes de minimisation issus de la chimie quantique. Nous étudions les méthodes multidéterminants (ou multiconfigurations) de modélisation de l'état fondamental d'une molécule. Dans ce cadre, qui est une extension de la théorie de Hartree-Fock, nous proposons une approche générale pour prouver l'existence de l'état fondamental. A titre d'exemple, nous utilisons cette approche pour l'étude de deux cas particuliers.

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I. INTRODUCTION

One of the most commonly used method for the modelling of the ground state of a molecule is the well known Hartree-Fock method. Let us recall that this method consists in an approximation of the much more complicated following "exact" problem. In order to find the ground state of a molecule with N electrons one solves the minimization problem

$$E = \inf\left\{ \langle H_N \phi, \phi\rangle;\ \phi \in L_a^2(\mathbf{R}^{3N}),\ \int |\phi|^2 = 1 \right\} \tag{1.1}$$

where H_N is the purely Coulombic N-body Hamiltonian

$$H_N = -\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} V(x_i) + \sum_{i<j\leq N} \frac{1}{|x_i - x_j|} \tag{1.2}$$

with

$$V(x) = -\sum_k \frac{z_k}{|x - \tilde{x}_k|} \tag{1.3}$$

and where $L_a^2(\mathbf{R}^{3N})$ is the subspace of $L^2(\mathbf{R}^{3N})$ of antisymmetric functions.

In the Hartree-Fock approximation, instead of considering all the functions belonging to $L_a^2(\mathbf{R}^{3N})$, one only considers functions ϕ of the form

$$\phi = \frac{1}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_N) \tag{1.4}$$

with $\varphi_i \in H^1(\mathbf{R}^3)$ satisfying $\int \varphi_i \varphi_j = \delta_{ij}$.

Therefore one solves the easier problem

$$\begin{aligned} E_{HF} &= \inf\{ \langle H_N \phi, \phi\rangle;\ \phi \text{ of the form } (1.4)\} \\ &= \inf_{\int \varphi_i \varphi_j = \delta_{ij}} \left\{ \sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + \sum_{i=1}^{N} \int V |\varphi_i|^2 \right. \\ &\quad + \frac{1}{2} \int\int \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy \\ &\quad \left. - \frac{1}{2} \int\int \frac{|\rho(x, y)|^2}{|x-y|}\, dx\, dy \right\} \end{aligned} \tag{1.5}$$

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

Let us notice here that, for the sake of simplicity, we shall restrict ourselves in this paper to real-valued functions. Of course, our arguments hold, *mutatis mutandis*, for complex-valued functions. Besides, for the same reason, we do not take the spin variable into account.

From the mathematical point of view, the Hartree-Fock approximation has been studied in [1] and [2]. It turns out that when the total nuclear charge $Z = \sum_k z_k$ satisfies $Z > N - 1$, then every minimizing sequence of the Hartree-Fock problem is relatively compact in $(H^1(\mathbf{R}^3))^N$, and in particular there exists a minimum of (1.5).

Unfortunately in many cases the single determinant Hartree-Fock approximation is not adequate to describe properly the properties of the molecule and chemists have to use some more sophisticated methods to model the ground state. Among these methods stand the multiconfiguration methods (*See*, for instance, [4] for chemical and numerical aspects). The idea of these methods is to minimize over the set of wave functions which are linear combinations of determinants

$$\phi = \sum_k c_k \det(\varphi_1^k, \cdots, \varphi_N^k) \tag{1.6}$$

instead of a single determinant as in the Hartree-Fock method. The associated minimization problem is the following

$$E = \inf\{\langle H_N \phi, \phi\rangle;\ \phi \text{ of the form } (1.6)\}. \tag{1.7}$$

In addition, the φ_i^k appearing in (1.6) are supposed to satisfy some constraints (orthogonality, fixed L^2 norm,...), and the c_k are linked by a constraint that ensures that $\int |\phi|^2 = 1$.

In order to put these methods on a sound mathematical ground, we intend to study in this paper the following family of minimization problems that we formulate somewhat vaguely:

$$E = \inf\Big\{\langle H_N \phi, \phi\rangle;\ \text{is a linear combination of determinants built with the functions } \varphi_i;\ \forall\, i, j \int \varphi_i \varphi_j = \delta_{ij}\Big\}.$$

Of course, the number of φ_i that are involved, and the way the determinants are built with the φ_i depend on the method that one considers.

For instance, we shall study in details in section III the following cases.

Example 1. – *Completely orthogonal determinants.*

The wave functions we consider are

$$\phi = \sum_{k=0}^{K} c_k \frac{1}{\sqrt{N!}} \det(\varphi_{kN+1}, \cdots, \varphi_{kN+N}) \tag{1.9}$$

with

$$\left\{ \begin{array}{l} \int \varphi_i \varphi_j = \delta_{ij}, \; 1 \leqq i \leqq j \leqq N(K+1) \\ \sum_{k=0}^{K} c_k^2 = 1. \end{array} \right\} \tag{1.10}$$

We study the minimization problem with the coefficients $(c_k)_{0 \leqq k \leqq K}$ fixed

$$\begin{aligned} I(c_0, \cdots, c_K) = \inf \Big\{ & \langle H_N \phi, \phi \rangle; \\ & \phi = \sum_{k=0}^{K} c_k \frac{1}{\sqrt{N!}} \det(\varphi_{kN+1}, \cdots, \varphi_{kN+N}) \\ & \times \int \varphi_i \varphi_j = \delta_{ij}, \; 1 \leqq i \leqq j \leqq N(K+1) \Big\} \end{aligned} \tag{1.11}$$

and the global problem

$$I = \inf_{\sum_{k=0}^{K} c_k^2 = 1} I(c_0, \cdots, c_K). \tag{1.12}$$

Example 2. – *Doubly excited configurations.*

In this setting the wave functions are

$$\begin{aligned} \phi = & \frac{\alpha}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N-1}, \varphi_N) \\ & + \frac{\beta}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N+1}, \varphi_{N+2}) \end{aligned} \tag{1.13}$$

with

$$\left\{ \begin{array}{l} \int \varphi_i \varphi_j = \delta_{ij}, \; 1 \leqq i \leqq j \leqq N+2 \\ \alpha^2 + \beta^2 = 1 \end{array} \right\} \tag{1.14}$$

and the minimization problems are

$$I(\alpha, \beta) = \inf \Big\{ \langle H_N \phi, \phi \rangle; \\ \phi = \frac{\alpha}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N-1}, \varphi_N) \\ + \frac{\beta}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N+1}, \varphi_{N+2}) \\ \int \varphi_i \varphi_j = \delta_{ij}\ 1 \leqq i \leqq j \leqq N+2 \Big\} \tag{1.15}$$

and

$$I = \inf_{\alpha^2+\beta^2=1} I(\alpha, \beta). \tag{1.16}$$

From the chemical point of view, the first one of these particular cases may be thought of as a direct generalization of the Hartree-Fock method, and the second one as a way to model a doubly excited configuration. For further information on the chemical background of this family of mathematical problems, we refer the reader to [3], [4] and [5], for instance...

For the family of problem (1.8), the first interesting question is the existence of a minimum. Beyond this existence, it would be very useful, essentially in order to obtain stability properties for numerical algorithms, to know the behaviour of all minimizing sequences. Assuming the existence of a minimum, a third question is of a great chemical interest: is the infimum achieved for a single determinant function, and is the energy at a minimum striclty less than the Hartree-Fock energy? We are going to give here a general approach in order to answer these questions.

Let us now briefly explain the main new difficulty of this class of problems (1.8), in particular compared to the Hartree-Fock problem, and how we manage to overcome it.

A standard way to solve minimization problems like

$$e = \inf \{ \mathcal{E}(\phi);\ J(\phi) = 1 \} \tag{1.17}$$

is to associate to the problem (1.17) the analogous problem with a relaxed constraint

$$e' = \inf \{ \mathcal{E}(\phi);\ J(\phi) \leqq 1 \}. \tag{1.18}$$

and to prove that $e = e'$ (From the viewpoint of the concentration compactness method (*see* [2]), this equality is related to the fact that the so-called problem at infinity is trivial). Then, one takes an arbitrary minimizing sequence of (1.17). Under some reasonable assumptions on $\mathcal{E}$ and J, it is bounded, and thus converges (weakly in H^1), up to an extraction of a subsequence, to a certain ϕ which is a minimum of (1.18). Then one must prove that $J(\phi) = 1$, in which case ϕ is a minimum of (1.17). For this purpose, the strategy is to study the solution ϕ of the Euler-Lagrange equation of the relaxed problem (1.18), and to prove that the Lagrange multiplier do not vanish.

In problems like (1.8), the difficulty comes from the fact that the Euler-Lagrange equation is in fact a n-dimensional system, while the Lagrange multiplier is a matrix of multipliers. In the Hartree-Fock method, which is the simplest method of the general form (1.8), this system can be drastically simplified. Indeed, the relaxed problem is

$$I_{HF} = \inf \left\{ \mathcal{E}_{\mathcal{HF}}(\varphi_1, \cdots, \varphi_n); \left[\int \varphi_i \varphi_j\right] \leqq 1 \right\} \tag{1.19}$$

where the inequality is in the sense of symmetric matrices. Now, thanks to a crucial orthogonal invariance of the energy [if U is a unitary matrix, then $\mathcal{E}_{\mathcal{HF}}(U(\varphi_1, \cdots, \varphi_n)) = \mathcal{E}_{\mathcal{HF}}(\varphi_1, \cdots, \varphi_n)$], one may always assume that a minimum satisfies

$$\int \varphi_i \varphi_j = 0 \qquad \text{for} \quad i \neq j$$

and the Euler-Lagrange equations read

$$\begin{aligned} & -\Delta\varphi_i + V\varphi_i + \left(\rho \star \frac{1}{|x|}\right)\varphi_i \\ & -\left(\int \rho(x, y)\frac{1}{|x-y|}\varphi_i(y)\,dy\right) = \lambda_i \varphi_i. \end{aligned} \tag{1.20}$$

This allows to consider each φ_i as a solution of a single-function problem. In other words, the vector-valued variational problem has split into n less coupled scalar problems. Then one argues as in the scalar case: study the second order condition and obtain a contradiction unless $\int \varphi_i^2 = 1$ which gives the desired result (*see* [2] and [1] for the details).

But when we consider setting involving more than a single determinant function, the orthogonal invariance that makes life simpler does not hold any longer and we have to cope with a "true" n-dimensional strongly coupled system.

The method we are going to present in this paper allows us to overcome this difficulty.

The idea is to solve the minimization problem with completely vector-valued arguments and to take benefit of the quadratic nature of the constraint $\int \varphi_i \varphi_j = \delta_{ij}$. Our argument uses, as in [2] and [1], the fact that the Hamiltonian associated to the second order condition has infinitely many negative eigenvalues, and that this fact will force each of the φ_i to be of norm 1. Technically we have to develop a new approach which do not require any invariance property of the energy. The point actually is that we have to look at the second order condtion in some particular well chosen direction which leads us to a contradiction, unless the constraint $\left[\int \varphi_i \varphi_j\right] \leqq 1$ is completely saturated. In the Hartree-Fock case, this direction happens to be the one that is used in [2] and [1]. We shall detail this method in section II.

In section III, we shall study both of the particular cases (1.9)-(1.10)-(1.11)-(1.12) and (1.13)-(1.14)-(1.15)-(1.16) introduced above and prove the following

THEOREM 1. – (i) *Let K be an integer, and let $c_0, \cdots, c_K \in \mathbf{R} - \{0\}$ such that $\sum_{k=0}^{K} c_k^2 = 1$. We assume that the total nuclear charge $Z = \sum z_k$ satisfies $Z > N - 1$. Then every minimizing sequence of the problem* (1.11) *is relatively compact in $(H^1(\mathbf{R}^3))^{N(K+1)}$, and in particular there exists a minimum.*

(ii) *We have*

$$\inf_{\sum_{k=0}^{K} c_k^2 = 1} I(c_0, \cdots, c_K) = I_{HF}. \tag{1.21}$$

Thus, when $Z > N - 1$, there exists a minimum: $c_0 = 1$, $(\varphi_1, \cdots, \varphi_N)$ minimum for the Hartree-Fock problem.

THEOREM 2. – (i) *Let $\alpha, \beta \in \mathbf{R} - \{0\}$ such that $\alpha^2 + \beta^2 = 1$. We assume that the total nuclear charge $Z = \sum z_k$ satisfies $Z \geqq N$. Then every minimizing sequence of the problem* (1.15) *is relatively compact in $(H^1(\mathbf{R}^3))^{N+2}$, and an particular there exists a minimum.*

(ii) *We assume $Z \geqq N$. Then, we have*

$$I = \inf_{\alpha^2+\beta^2=1} I(\alpha, \beta) < I_{HF}. \tag{1.22}$$

Every minimizing sequence $(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2})$ *of the problem I is relatively compact in* $[-1, 1]^2 \times (H^1(\mathbf{R}^3))^{p+2}$, *and in particular there exists a minimum. Because of* (1.22) *no minimum is of the form of a single determinant.*

II. A GENERAL APPROACH

II.0. Notations and preliminaries

Throughout this paper, we shall use the following notations. We denote by $\varphi = (\varphi_1, \cdots, \varphi_n) \in (H^1(\mathbf{R}^3))^n$. The matrix $\left[\int \varphi_i \varphi_j\right]$ is denoted by $M(\varphi)$. Therefore the constraint

$$\left[\int \varphi_i \varphi_j\right] \leqq 1$$

in the sense of the symmetric matrices reads

$$M(\varphi) \leqq 1.$$

The energy $\mathcal{E}(\varphi)$ is defined as

$$\mathcal{E}(\varphi) = \langle H_N \phi, \phi \rangle \tag{2.1}$$

where ϕ is a linear combination of determinants built with the φ_i, with $\int \varphi_i \varphi_j = \delta_{ij}$. We may write $\mathcal{E}(\varphi)$, for φ satisfying $\left[\int \varphi_i \varphi_j\right] = 1$:

Since (2.1) holds, it is straightforward to see, using (1.2) and (1.3), that $\mathcal{E}(\varphi)$ formally reads

$$\mathcal{E}(\varphi) = \sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + \sum_{i=1}^{N} \int V \varphi_i^2 + \sum_{1 \leqq i, j, k, l \leqq n} D(\varphi_i \varphi_j, \varphi_k \varphi_l) \tag{2.2}$$

up to some multiplicative constants. In this formula, we denoted by

$$D(\varphi_i \varphi_j, \varphi_k \varphi_l) = \int\int \frac{\varphi_i(x) \varphi_j(x) \varphi_k(y) \varphi_l(y)}{|x-y|} \, dx \, dy.$$

Beyond this formal representation (2.2), we can give the exact value of $\mathcal{E}(\varphi)$ getting into the detail of ϕ. Indeed, for problems of the type (1.8), the wave function may be written in the following way

$$\phi = \sum c_P \, \varphi_{P(1)}(x_1) \, \varphi_{P(2)}(x_2) \cdots \varphi_{P(N)}(x_N) \tag{2.3}$$

where the sum is taken over the set of applications P from $\{1, \cdots, N\}$ to $\{1, \cdots, n\}$ (n is the number of functions φ_i taken into account).

The values of the coefficients c_P depend on the model one considers.

Thanks to the antisymmetry of ϕ one easily notices that $c_P = -c_Q$, for P, Q satisfying

$$\left.\begin{array}{ll} \exists\,(\alpha, \beta)/P(\alpha) = Q(\beta), & P(\beta) = Q(\alpha), \\ P(\gamma) = Q(\gamma), & \forall \gamma \in \{1, \cdots, N\} - \{\alpha, \beta\}. \end{array}\right\} \tag{2.4}$$

Using the definition (2.1) of $\mathcal{E}(\varphi)$, we may write, for φ such that $M(\varphi) = 1$,

$$\begin{aligned} \mathcal{E}(\varphi) = \sum_{i=1}^{n} \mu_i \int |\nabla \varphi_i|^2 + \sum_{i=1}^{n} \mu_i \int V \varphi_i^2 \\ + \sum_{1 \leqq i, j, k, l \leqq n} c_{ijkl} \, D(\varphi_i \varphi_j, \varphi_k \varphi_l) \end{aligned} \tag{2.5}$$

In (2.5), we have

$$\mu_i = \sum_{P/\exists \alpha;\, P(\alpha) = i} c_P^2.$$

Indeed, the operators $-\Delta$ and V involve the position of one and only one electron at a time (In quantum chemistry, they are called monoelectronic). That is to say for instance

$$\begin{aligned} & -\Delta_{x_1} (\varphi_{P(1)}(x_1) \, \varphi_{P(2)}(x_2) \cdots \varphi_{P(N)}(x_N) \\ & \quad = (-\Delta \varphi_{P(1)}(x_1)) \, \varphi_{P(2)}(x_2) \cdots \varphi_{P(N)}(x_N) \end{aligned}$$

Thus the only terms that do not vanish in $\langle -\Delta\phi, \phi \rangle$ and $\langle V\phi, \phi \rangle$ are those where each of the $N-1$ remaining variables x_j is the argument of the same function φ_i in the left-hand side and in the right-hand side of the bracket (we recall that the φ_i are orthonormal). Therefore we only have square terms. For instance,

$$\begin{aligned} & \langle (-\Delta \, \varphi_{P(1)}(x_1)) \, \varphi_{P(2)}(x_2) \cdots \varphi_{P(N)}(x_N), \\ & \quad \varphi_{P(1)}(x_1) \, \varphi_{P(2)}(x_2) \cdots \varphi_{P(N)}(x_N) \rangle \end{aligned}$$

The situation is a bit more complicated for the terms $D(\varphi_i \varphi_j, \varphi_k \varphi_l)$. The formula (2.5) is formal. In particular, if we do not say anything else, it is not unique, because of the symmetries of $D(\varphi_i \varphi_j, \varphi_k \varphi_l)$ with respect to the indices (i, j, k, l), We do not known much about the coefficients c_{ijkl} because the family (1.8) is very large. However, one may make the above representation unique by deciding

$$c_{ijkl} = 0$$

unless

$$\begin{cases} 1 \leqq i \leqq j \leqq n \\ 1 \leqq k \leqq l \leqq n \\ i \leqq k \end{cases}$$

in which case

$$c_{ijkl} = \sum_{PQ} c_P \, c_Q$$

where the sum is taken over P, Q satisfying the following condition

$$\left.\begin{array}{l} \exists\,(\alpha, \beta) \in \{1, \cdots, N\} / \alpha \neq \beta \\ \quad \{P(\alpha), Q(\alpha)\} = \{i, j\} \\ \quad \{P(\beta), Q(\beta)\} = \{k, l\} \\ \quad P(\gamma) = Q(\gamma), \qquad \forall \gamma \in \{1, \cdots, N\} - \{\alpha, \beta\}. \end{array}\right\} \tag{2.6}$$

The reason why condition (2.6) holds is that the coulombic operator $\dfrac{1}{|x-y|}$ is bi-electronic: the position of two electrons is involved at a time. Therefore the only non zero terms in $\left\langle \dfrac{1}{|x-y|}\,\phi, \phi \right\rangle$ are those where each of the $N-2$ remaining variables x_j is the argument of the same function φ_i (The argument mimics the one we made above for $-\Delta$). And this leads to (2.6).

We now turn to the derivatives of $M(\varphi)$ and

Both functions $M(\varphi)$ and $\mathcal{E}(\varphi)$ are C^2 with respect to φ.

For $\mathbf{h} = (h_1, \cdots, h_n) \in (H^1(\mathbf{R}^3))^n$ a variation at the neighbourhood of φ, we denote respectively by $M'(\varphi) \cdot \mathbf{h}$, $M''(\varphi) \cdot (\mathbf{h}, \mathbf{h})$, and $\mathcal{E}'(\varphi) \cdot \mathbf{h}, \mathcal{E}''(\varphi) \cdot (\mathbf{h}, \mathbf{h})$ their first and second derivatives evaluated on the variation $\mathbf{h}$.

Of course, we have

$$\left.\begin{array}{r} M'(\varphi) \cdot \mathbf{h} = \left[\displaystyle\int \varphi_i \, h_j + \int \varphi_j \, h_i\right] \\ \dfrac{1}{2} M''(\varphi) \cdot (\mathbf{h}, \mathbf{h}) = \left[\displaystyle\int h_i \, h_j\right]. \end{array}\right\} \tag{2.7}$$

We use (2.5) to compute $\mathcal{E}''(\varphi)\cdot(\mathbf{h},\,\mathbf{h})$:

$$\begin{aligned}\frac{1}{2}\,\mathcal{E}''(\varphi)\cdot(\mathbf{h},\,\mathbf{h}) &= \sum_{i=1}^{n}\mu_i\int|\nabla h_i|^2+\sum_{i=1}^{n}\mu_i\int V\,h_i^2\\ &+\sum_{1\leqq i,\,j,\,k,\,l\leqq n} c'_{ijkl}\,D\,(h_i\,h_j,\,\varphi_k\,\varphi_l)\\ &+\sum_{1\leqq i,\,j,\,k,\,l\leqq n} c''_{ijkl}\,D\,(h_i\,\varphi_j,\,h_k\,\varphi_l)\end{aligned}\tag{2.8}$$

where

$$\left.\begin{aligned}c'_{ijkl} &= c_{ijkl}+c_{klij}\\ c''_{ijkl} &= c_{ijkl}+c_{ijkl}+c_{jikl}+c_{jilk}.\end{aligned}\right\}\tag{2.9}$$

II.1. Overview of our strategy of proof

For the family of problems (1.8), the difficulty is to show compactness for the φ_i. Indeed, the coefficients c_k appearing in (1.6) are supposed to be linked by some constraint of the kind

$$\sum_k c_k^2 = 1$$

and thus, without loss of generality, we may assume that they converge. Furthermore, some considerations on the energy, and its comparison to the Hartree-Fock energy for instance, often lead to $c_k \neq 0$ for all k (*see* section III below for details on this point). Therefore we shall assume throughout this section that the c_k are fixed, $c_k \neq 0$, and study the problem (1.8) with φ satisfying $M(\varphi) = 1$, that is:

$$I = \inf\{\,\mathcal{E}(\varphi);\ M(\varphi) = 1\,\}.$$

For such problems, it is standard to prove, using an argument based upon the fact that the potential vanishes at infinity (*see* [2]), that the problem (1.8) coincides with

$$I = \inf\{\,\mathcal{E}(\varphi);\ M(\varphi) \leqq 1\,\}.\tag{2.10}$$

Therefore, taking a minimizing sequence of (1.8), it is easy to see it is bounded thus converges weakly in H^1, up to an extraction, to some φ. We then check that φ is a minimum of (2.10). Proving $M(\varphi) = 1$ amounts to proving the existence of a minimum for (1.8) (then, in a last step, if it is necessary, one obtains the global minimum minimizing over the coefficients c_k).

We argue by contradiction and assume that $M(\varphi) \neq 1$, that is Rank $(1 - M(\varphi)) \geqq 1$.

The first step (II.2) is to find some direction $\mathbf{h}$ for which the second order condition at the minimum φ of (2.10) yields

$$\mathcal{E}''(\varphi) \cdot (\mathbf{h}, \mathbf{h}) \geqq \mathbf{0}. \tag{2.11}$$

We shall see that a convenient choice for $\mathbf{h}$ is given by

$$\mathbf{h} = \sqrt{1 - M(\varphi)}\, \mathbf{f} \tag{2.12}$$

that is $h_i = \sum_j \sqrt{1 - M(\varphi)_{if}}\ f_j$, where $\mathbf{f} = (f_1, \cdots, f_n) \in (\mathrm{H}^1(\mathbf{R}^3))^n$ only satisfies

$$\left.\begin{aligned} &\int f_i \varphi_j \equiv 0, \qquad \forall i, j \\ &\int f_i f_j = \delta_{ij}, \qquad \forall i, j. \end{aligned}\right\} \tag{2.13}$$

Let us emphasize that this first step is basically built upon the quadratic nature of the constraint $M(\varphi)$.

The second step (II.3) consists in proving that (2.11) cannot hold.

For this step, we need to take benefit of the particular form (2.2) of the energy, and to make an assumption on the total nuclear charge Z. In the paragraph II.3, we shall only give the formal scheme of the argument, and explain how it must be applied to any problem of the family (1.8). Of course, the argument will be detailed in each particular case we study here (*see* section III).

Roughly speaking, the contradiction comes from the fact that $\mathcal{E}''(\varphi)$ cannot be positive on such a class of $\mathbf{h}$, because it is too often negative (Think of the Hartree-Fock case, where the Hamiltonian has infinitely many negative eigenvalues). In order to reach the contradiction, we shall build some appropriate spherically symmetric functions f_i, use a scaling argument, and prove that, if Z is large enough, the corresponding $\mathbf{h}$ [with (2.11)] satisfies

$$\mathcal{E}''(\varphi) \cdot (\mathbf{h}, \mathbf{h}) < \mathbf{0}.$$

The argument we make here is an extension of the proof of lemma II.1 and II.3 in [2].

II.2 First step: Construction of h such that $\mathcal{E}''(\varphi)\cdot(\mathbf{h}\cdot\mathbf{h}) \geqq 0$

Let us write a small perturbation of the constraint M in the neighbourhood of φ.

Because of the quadratic nature of M, there is no term of order larger than 2 in the Taylor series, and we have obviously

$$M(\varphi + t\,\mathbf{h}) = M(\varphi) + t\,M'(\varphi)\cdot\mathbf{h} + \frac{1}{2}\,t^2\,M''(\varphi)\cdot(\mathbf{h},\,\mathbf{h}). \tag{2.14}$$

We now fix an arbitrary $\mathbf{f} = (f_1, \ldots, f_n) \in (\mathrm{H}^1(\mathbf{R}^3))^n$ such that

$$\left.\begin{aligned} &\int f_i\,\varphi_j \equiv 0, && \forall\, 1 \leqq i,\, j \leqq n \\ &\int f_i\,f_j = \delta_{ij}, && \forall\, 1\, i,\, j \leqq n \end{aligned}\right\} \tag{2.15}$$

and we define

$$\mathbf{h} = \sqrt{1 - M(\varphi)}\,\mathbf{f}. \tag{2.16}$$

[(2.16) stands for $h_i = \sum_j \sqrt{1 - M(\varphi)_{ij}}\; f_j$,] $\forall\, 1 \leqq i \leqq n$.]

We claim that, for these $\mathbf{h}$, (2.14) yields

$$M(\varphi + t\,\mathbf{h}) \leqq 1, \qquad \forall |t| \leqq 1. \tag{2.17}$$

Indeed, let us first notice that $\sqrt{1 - M(\varphi)}$ is well defined, as the square root of the symmetric positive matrix $1 - M(\varphi)$. Moreover, since the $(f_i)_{1 \leqq i \leqq n}$ are an orthonormal family, and since we have assumed from the beginning that Rank $(1 - M(\varphi)) \geqq 1$, the set of $\mathbf{h}$ defined by (2.16) is not trivial.

In view of (2.15), (2.16) and (2.7), we have

$$M'(\varphi)\cdot\mathbf{h} = 0$$

since $\int \varphi_i\, f_i \equiv 0$, and

$$\begin{aligned} \frac{1}{2} M''(\varphi)\cdot(\mathbf{h},\,\mathbf{h}) &= \left[\int \Big(\sum_k \sqrt{1 - M(\varphi)_{ik}}\; f_k\Big)\Big(\sum_l \sqrt{1 - M(\varphi)_{jl}}\; f_l\Big)\right] \\ &= \left[\sum_k \sqrt{1 - M(\varphi)_{ik}}\;\sqrt{1 - M(\varphi)_{jk}}\right] \\ &= 1 - M(\varphi) \end{aligned}$$

since $\int f_i\, f_j = \delta_{ij}$.

Therefore (2.14) yields

$$M(\varphi + t\,\mathbf{h}) = M(\varphi) + 0 + \frac{1}{2}\, t^2 (1 - M(\varphi))$$
$$\leqq M(\varphi) + 1 - M(\varphi) = 1$$

in the sense of symmetric matrices, as soon as $|t| \leqq 1$. That is (2.17).

It follows from (2.17) that, for $|t| \leqq 2$, $\varphi + t\,\mathbf{h}$ satisfies

$$\mathcal{E}(\varphi + t\,\mathbf{h}) \geqq \mathcal{E}(\varphi)$$

by definition of the minimum φ on the set $M \leqq 1$. Hence $\mathcal{E}'(\varphi)\cdot\mathbf{h} = 0$ and

$$\mathcal{E}''(\varphi)\cdot(\mathbf{h},\, \mathbf{h}) \geqq 0.$$

This concludes step 1.

II.3. Second step: Reaching a contradiction

We now turn to the heart of our proof. Whereas the previous step was based on the quadratic nature of the constraint $M(\varphi)$, this one is based on the properties of the energy $\mathcal{E}(\varphi) = \langle H_N\, \phi,\, \phi \rangle$. Since this step is long and crucial, we first give an outline of it.

In the paragraph II.3.1, we are going to compute $\mathcal{E}''(\varphi)\cdot(\mathbf{h},\, \mathbf{h})$ for some arbitrary $\mathbf{h}$ given by $\mathbf{h} = \sqrt{1 - \mathrm{M}(\varphi)}\, \mathbf{f}$. Then we shall scale $\mathbf{h}$ [*i.e.* change $\mathbf{h}$ into $\mathbf{h}_\sigma = \sigma^{-(3/2)}\, \mathbf{h}\left(\frac{\cdot}{\sigma}\right)$] and evaluate $\mathcal{E}''(\varphi)\cdot(\mathbf{h}_\sigma,\, \mathbf{h}_\sigma)$.

In the paragraph II.3.2., we shall prove that the n quantities

$$A_i = -\Big(\sum_k \mu_k\, a_{ki}^2\Big) Z + \sum_{1 \leqq k,\, l \leqq n} \Big(\sum_{jm} c'_{mjkl}\, a_{ji}\, a_{mi}\Big) \int \varphi_k\, \varphi_l \tag{2.18}$$

satisfy

$$A_i \geqq 0. \tag{2.19}$$

In (2.18) we recall that μ_k, and c'_{mjkl} are respectively given by (2.5) and (2.9), and we denote by $a_{ij} = \sqrt{1 - M(\varphi)_{ij}}$. From (2.19) we shall deduce *a fortiori*

$$\sum_{i=1}^{n} A_i \geqq 0. \tag{2.20}$$

In order to prove (2.19), we shall argue by contradiction and assume that some of the A_i, say A_1, is strictly negative. Following the idea of

P. L. Lions in the proof of lemma II.1 in [2], we shall then find some σ_0 large enough, and build some convenient family of spherically symmetric functions $(f_1, \cdots, f_n)$, such that both following facts hold. On the one hand

$$\mathcal{E}''(\varphi) \cdot (\mathbf{h}_{\sigma_0}, \mathbf{h}_{\sigma_0}) < 0$$

because, when σ tends to infinity, $\mathcal{E}''(\varphi) \cdot (\mathbf{h}_\sigma, \mathbf{h}_\sigma)$ behaves like

$$\frac{1}{\sigma} \sum_i A_i \int \frac{f_i^2}{|x|}$$

and we shall show that this quantity is negative in this case.

On the other hand

$$\mathcal{E}''(\varphi) \cdot (\mathbf{h}_{\sigma_0}, \mathbf{h}_{\sigma_0}) \geqq 0$$

in view of step 1. This will lead to a contradiction and thus proves (2.19) and (2.20).

In the paragraph II.3.3, we shall see that (2.20) implies the following inequality

$$Z \leqq \frac{\displaystyle\sum_{1 \leqq j, k, l, m \leqq n} c'_{mjkl} \left(\delta_{jm} - \int \varphi_j \varphi_m\right) \int \varphi_k \varphi_l}{\displaystyle\sum_{k=1}^{n} \mu_k \left(1 - \int \varphi_k^2\right)} \tag{2.21}$$

We shall then explain why (2.21) cannot hold when Z is large enough. That is to say we shall prove the existence of some Z_c depending only on the parameters of the model and of the number of electrons, such that, if $Z \geqq Z_c$ then (2.21) cannot hold, thus our assumption $Rank\,(1 - M(\varphi)) \geqq 1$ is false, thus $M(\varphi) = 1$ and there exist a minimum for (1.8). In this section we shall give an upper bound to Z_c for the general case (1.8). But let us recall what we announced in II.1. This step remains a bit formal; we only give here the general scheme of the argument, and explain what makes it work. The argument has to be detailed in each particular case. In each of the examples we shall treat in section III, a much better value of Z_c will be found.

II.3.1.

We take an arbitrary $\mathbf{f} = (f_1, \cdots, f_n)$ such that $\int f_1 f_j = \delta_{ij}$, and put

$$\mathbf{h} = \sqrt{1 - M(\varphi)}\, \mathbf{f}$$

that is $h_i = \sum_j a_{ij} f_j$ with a $a_{ij} = \sqrt{1 - M(\varphi)_{ij}}$.

(2.8) yields

$$
\begin{aligned}
\frac{1}{2} \mathcal{E}''(\varphi) \cdot (\mathbf{h}, \mathbf{h}) = & \sum_{i,j} (\sum_k \mu_k a_{ki} a_{kj}) \int |\nabla f_i|^2 \\
& + \sum_{ij} (\sum_k \mu_k a_{ki} a_{kj}) \int V f_i f_j \\
& + \sum_{1 \leqq i, j, k, l \leqq n} d'_{ijkl} D(f_i f_j, \varphi_k \varphi_l) \\
& + \sum_{1 \leqq i, j, k, l \leqq n} d''_{ijkl} D(f_i \varphi_j, f_k \varphi_l)
\end{aligned}
\tag{2.22}
$$

with in particular (we shall see below why it suffices to compute this particular coefficient)

$$
d'_{iikl} = \sum_{jm} c'_{mjkl} a_{ji} a_{mi}. \tag{2.23}
$$

We now scale the functions f_i, that is to say we change each f_i into $f_{i\sigma} = \sigma^{-(3/2)} f_i \left(\frac{\cdot}{\sigma}\right)$ where $\sigma > 0$ will be chosen later on. (2.22) reads

$$
\begin{aligned}
\frac{1}{2} \mathcal{E}''(\varphi) \cdot (\mathbf{h}_\sigma, \mathbf{h}_\sigma) = & \frac{1}{\sigma^2} \sum_{i=1}^{n} (\sum_k \mu_k a_{ki}^2) \int |\nabla f_i|^2 \\
& + \frac{1}{\sigma^2} \sum_{i \neq j} (\sum_k \mu_k a_{ki} a_{kj}) \int \nabla f_i \cdot \nabla f_j \\
& + \sum_{i=1}^{n} (\sum_k \mu_k a_{ki}^2) \int f_{i\sigma}^2 \\
& + \sum_{i \neq j}^{n} (\sum_k \mu_k a_{ki} a_{kj}) \int V f_{i\sigma} f_{j\sigma} \\
& + \sum_{1 \leqq i, k, l \leqq n} d'_{iikl} D(f_{i\sigma}^2, \varphi_k \varphi_l) \\
& + \sum_{1 \leqq i \neq j, k, l \leqq n} d'_{ijkl} D(f_{i\sigma} f_{j\sigma}, \varphi_k \varphi_l) \\
& + \sum_{1 \leqq i, j, k, l \leqq n} d''_{ijkl} D(f_{i\sigma} \varphi_j, f_{k\sigma} \varphi_l).
\end{aligned}
\tag{2.24}
$$

If we now assume that the $(f_i)_{1 \leqq i \leqq n}$ have compact supports and that these supports are disjoints, (2.24) may be simplified into

$$\begin{aligned} \frac{1}{2}\,\mathcal{E}''(\varphi)\cdot(\mathbf{h}_\sigma,\,\mathbf{h}_\sigma) = {} & \frac{1}{\sigma^2}\sum_{i=1}^{n}(\sum_k \mu_k\,a_{ki}^2)\int|\nabla f_i|^2 \\ & + \sum_{i=1}^{n}(\sum_k \mu_k\,a_{ki}^2)\int V\,f_{i\sigma}^2 \\ & + \sum_{1\leqq i,\,k,\,l\leqq n} d''_{iikl}\,D\,(f_{i\sigma}^2,\,\varphi_k\,\varphi_l) \\ & + \sum_{1\leqq i,\,j,\,k,\,l\leqq n} d''_{ijkl}\,D\,(f_{i\sigma}\,\varphi_j,\,f_{k\sigma}\,\varphi_l). \end{aligned} \tag{2.25}$$

II.3.2.

We now turn to the proof of (2.19), that is

$$\forall\, 1 \leqq i \leqq n, \qquad A_i \geqq 0.$$

As mentioned above, we argue by contradiction and assume $A_1 < 0$. We are going to build some particular family $(f_i)_{1\leqq i\leqq n}$. Let

$$R = \mathrm{MAX}\left(2,\ -1 + 4\sum_{i=2}^{n}\frac{|A_i|}{-A_1}\right). \tag{2.26}$$

For $1 \leqq i \leqq n$, we take a function f_i satisfying the following conditions

$$\left.\begin{array}{l} f_i \text{ spherically symmetric} \\ f_i \text{ is supported in the annulus } [(i-1)\,R+1,\ (i-1)\,R+2] \\ f_i \in H^1(\mathbf{R}^3) \\ \displaystyle\int f_i^2 = 1 \end{array}\right\} \tag{2.27}$$

In particular, the family $(f_i)_{1\leqq i\leqq n}$ satisfies

$$\left.\begin{array}{ll} \displaystyle\int f_i\,f_j = \delta_{ij} & \\ \displaystyle\int \nabla f_i\,\nabla f_j = 0 & \text{for } \ i \neq j \\ \displaystyle\int \frac{1}{|x|}\,f_i\,f_j = 0 & \text{for } \ i \neq j \end{array}\right\} \tag{2.28}$$

We now set

$$\mathbf{h}_\sigma = \sqrt{1 - M(\varphi)}\,\mathbf{f}_\sigma.$$

We claim that

$$\frac{1}{2}\,\mathcal{E}''(\varphi)\cdot(\mathbf{h}_\sigma, \mathbf{h}_\sigma) = \frac{1}{\sigma}\sum_i A_i \int \frac{f_i^2}{|x|} + o\left(\frac{1}{\sigma}\right) \tag{2.29}$$

where the remainder $o\left(\frac{1}{\sigma}\right)$ does not depend on the choice of the $(f_i)_{1 \leqq i \leqq n}$ but only on R (*i.e.* on the A_i), and on the norms $\|f_i\|_{L^\infty}$, $\|f_i\|_{H^1}$.

Let us assume for the moment that (2.29) holds and conclude the proof of (2.19).

We first check that the right-hand side of (2.29) is negative for σ large. Indeed, we have $\int \frac{f_1^2}{|x|} \geqq \frac{1}{2}\int f_1^2 = \frac{1}{2}$ because f_i is supported on the annulus [1, 2], and $\int \frac{f_i^2}{|x|} \leqq \frac{1}{R+1}\int f_i^2 = \frac{1}{2}$ for $2 \leqq i \leqq n$ because, for such i, f_i is supported outside the ball of radius $R+1$. Therefore

$$\begin{aligned}\sum_i A_i \int \frac{f_i^2}{|x|} &\leqq \frac{1}{2}\,A_1 + \sum_{i=2}^{n} \frac{1}{R+1}|A_i| \\ &\leqq \frac{1}{2}\,A_1 - \frac{1}{4}\,A_1 = \frac{1}{4}\,A_1 < 0\end{aligned}$$

in view of (2.26).

Using (2.29), we fix some σ_0 large enough such that

$$\mathcal{E}''(\varphi)\cdot(\mathbf{h}_{\sigma_0}, \mathbf{h}_{\sigma_0}) < 0$$

and we emphasize that σ_0 does not depend on the choice of the $(f_i)_{1 \leqq i \leqq n}$ but only on their norms and on R. For this σ_0, using a trivial dimension argument (In an infinite dimension space, the intersection of a ball and any given vectorial subspace of finite codimension has infinite dimension), we are able to choose $(f_i)_{1 \leqq i \leqq n}$ satisfying (2.27) and

$$\int f_i\,\varphi_j\,(\sigma_0 \cdot) = 0, \qquad \forall\, 1 \leqq i,\, j \leqq n. \tag{2.30}$$

In other words,

$$\int f_{i\sigma_0}\,\varphi_j = 0, \qquad \forall\, 1 \leqq i,\, j \leqq n.$$

Hence the conditions (2.13) are satisfied by $f_{i\sigma_0}$ and we may apply the result of step 1 to $\mathbf{h}_{\sigma_0}$. We obtain

$$\mathcal{E}''(\varphi)\cdot(\mathbf{h}_{\sigma_0}, \mathbf{h}_{\sigma_0}) \geqq 0.$$

This gives the desired contradiction, thus (2.19) holds. And of course (2.20) follows.

There remains to prove (2.29)

We go back to the expression (2.24) $\mathcal{E}''(\varphi)\cdot(\mathbf{h}_\sigma, \mathbf{h}_\sigma)$ which may be simplified for our f_i into (2.25) that is

$$\begin{aligned}\frac{1}{2}\mathcal{E}''(\varphi)\cdot(\mathbf{h}_\sigma, \mathbf{h}_\sigma) = {} & \frac{1}{\sigma^2}\sum_{i=1}^{n}\Big(\sum_k \mu_k a_{ki}^2\Big)\int |\nabla f_i|^2 \\ & + \sum_{i=1}^{n}\Big(\sum_k \mu_k a_{ki}^2\Big)\int V f_{i\sigma}^2 \\ & + \sum_{1\leqq i,j,k,l\leqq n} d''_{iikl}\, D(f_{i\sigma}^2, \varphi_k\varphi_l) \\ & + \sum_{1\leqq i,j,k,l\leqq n} d''_{ijkl}\, D(f_{i\sigma}\varphi_j, f_{k\sigma}\varphi_l).\end{aligned}$$

In order to prove (2.29), we are going to look at each term of the right-hand side and study its behaviour when σ goes to infinity. The idea is, roughly speaking, that, if m is a bounded measure, then $D(m, f_\sigma^2)$ behaves like $\frac{1}{\sigma}\int m \int \frac{f^2}{|x|}$, thus the right-hand side of (2.25) behaves like

$$\frac{1}{\sigma}\sum_i\Big(-\Big(\sum_k \mu_k a_{ki}^2\Big)Z + \sum_{1\leqq k,l\leqq n} d'_{iikl}\int \varphi_k\varphi_l\Big)\int \frac{f_i^2}{|x|}.$$

We first show that

$$D(f_{i\sigma}^2, \varphi_k\varphi_l) = \frac{1}{\sigma}\int \frac{f_i^2}{|x|}\int \varphi_k\varphi_l + o\Big(\frac{1}{\sigma}\Big). \tag{2.31}$$

For this purpose, we remark that

$$\begin{aligned} D(f_{i\sigma}^2\,\varphi_k\varphi_l) &= \int f_{i\sigma}^2\Big(\varphi_k\varphi_l \star \frac{1}{|x|}\Big) \\ &= \int f_{i\sigma}^2\Big\langle\Big(\varphi_k\varphi_l\star\frac{1}{|x|}\Big)\Big\rangle \\ &= \int f_{i\sigma}^2\Big(\Big\langle\varphi_k\varphi_l\Big\rangle\star\frac{1}{|x|}\Big) \\ &= \int\int \frac{f_i(x)^2\langle\varphi_k\varphi_l\rangle(y)}{\max(|\sigma x|, |y|)}\,dx\,dy\end{aligned}$$

using Newton's theorem, and denoting by $\langle\cdot\rangle$ the spherical average.

Now, we notice that

$$\sigma \frac{f_i(x)^2\langle\varphi_k\varphi_l\rangle(y)}{\max(|\sigma x|, |y|)} \to \frac{f_i(x)^2\langle\varphi_k\varphi_l\rangle(y)}{|x|}$$

almost everywhere when σ goes to infinity, thus, from Lebesgue's theorem, we obtain

$$\sigma D(f_{i\sigma}^2, \varphi_k\varphi_l) \to \int \frac{f_i^2}{|x|}\int \varphi_k\varphi_l.$$

Moreover, we may bound the rest as follows

$$\begin{aligned}
&\left| D(f_{i\sigma}^2, \varphi_k\varphi_l) - \frac{1}{\sigma}\int\frac{f_i^2}{|x|}\int\varphi_k\varphi_l\right| \\
&\leqq \frac{2}{\sigma}\int\int_{|y|\geqq\sigma x|} \frac{f_i(x)^2\langle\varphi_k\varphi_l\rangle(y)}{|x|}\,dx\,dy \\
&\leqq \frac{2}{\sigma}\int\int_{|y|\geqq\sigma} f_i(x)^2|\langle\varphi_k\varphi_l\rangle(y)|\,dx\,dy \\
&\leqq \frac{2}{\sigma}\int\int_{|y|\geqq\sigma} |\varphi_k\varphi_l|\,dy
\end{aligned}$$

using the fact that f_i is supported on $|x|\geqq 1$. This shows (2.31) with a remainder $o\left(\frac{1}{\sigma}\right)$ that does not depend on the choice of f_i.

Following the same argument, one can show

$$\int V f_{i\sigma}^2 = -\frac{1}{\sigma} Z \int \frac{f_i^2}{|x|} \tag{2.32}$$

as soon as $\sigma \geqq \max(|\bar{x}_k|)$.

We now deal with

$$\sum_{1\leqq i,j,k,l\leqq n} d''_{ijkl}\, D(f_{i\sigma}\varphi_j, f_{k\sigma}\varphi_l).$$

Arguing as in the proof of lemma II.3 in [2], and using the fact that the f_i have their supports between the spheres of radius 1 and $\rho=(n-1)R+2$, one can see that each term $D(f_{i\sigma}\varphi_j, f_{k\sigma}\varphi_l)$ may be bounded as follows

$$\begin{aligned}
\left| D(f_{i\sigma}\varphi_j, f_{k\sigma}\varphi_l)\right| &\leqq \frac{1}{\sigma} C\|f_i\|_{L^\infty}\|f_k\|_{L^\infty} \\
&\times\left(\int_{\sigma\leqq|y|\leqq\rho\sigma}\varphi_j^2\right)^{1/2}\left(\int_{\sigma\leqq|y|\leqq\rho\sigma}\varphi_l^2\right)^{1/2}.
\end{aligned} \tag{2.33}$$

With (2.31), (2.32), (2.33), we obtain, for $\sigma \geqq \max(|\bar{x}_k|)$,

$$\left| \frac{1}{2} \mathcal{E}''(\varphi) \cdot (\mathbf{h}_\sigma, \mathbf{h}_\sigma) - \frac{1}{\sigma} \sum_i A_i \int \frac{f_i^2}{|x|} \right|$$

$$\leqq \frac{C}{\sigma} \left(\frac{1}{\sigma} \sum_i \|\nabla f_i\|_{L^2}^2 + \sum_{kl} \int_{|y| \geqq \sigma} |\varphi_k \varphi_l| dy \right.$$

$$+ \sum_{ijkl} \|f_i\|_{L^\infty} \|f_k\|_{L^\infty} \left(\int_{\sigma \leqq |y| \leqq \rho\sigma} \varphi_j^2 \right)^{1/2}$$

$$\left. \times \left(\int_{\sigma \leqq |y| \leqq \rho\sigma} \varphi_l^2 \right)^{1/2} \right)$$

where the constant C only depends on the parameters of the model and on the φ_i. This yields (2.29), and thus concludes the proof of (2.19)-(2.20).

II.3.3

Let us detail (2.20)

$$\sum_{i=1}^n A_i = -\Big(\sum_{i=1}^n (\sum_k \mu_k a_{ki}^2)\Big) Z + \sum_{i=1}^n \sum_{1 \leq k, l \leq n} d'_{iikl} \int \varphi_k \varphi_l.$$

Now we remark that by definition of $a_{ij} = \sqrt{1 - M(\varphi)_{ij}}$ we have

$$\sum_{i=1}^n (\sum_k \mu_k a_{ki}^2) = \sum_{k=1}^N \mu_k (\sum_i a_{ki}^2) = \sum_{k=1}^n \mu_k \left(1 - \int \varphi_k^2\right)$$

where we have $\mu_k = \sum_{P/\exists\alpha;\, P(\alpha)=k} c_P^2 > 0$, because there is at least one appropriate P.

Moreover, we have assumed that $Rank(1 - M(\varphi)) \geqq 1$, thus at least one of the φ_k satisfyies $1 - \int \varphi_k^2 > 0$. It follows that

$$\sum_{k=1}^n \mu_k \left(1 - \int \varphi_k^2\right) > 0.$$

Besides, since $d'_{iikl} = \sum_{jm} c'_{mjkl} \sqrt{1 - M(\varphi)_{ji}} \sqrt{1 - M(\varphi)_{mi}}$, we have

$$\sum_{1 \leqq i,\, k,\, l \leqq n} d'_{iikl} \int \varphi_k \varphi_l = \sum_{1 \leqq j,\, k,\, l,\, m \leqq n} c'_{mjkl} \left(\delta_{jm} - \int \varphi_j \varphi_m \right) \int \varphi_k \varphi_l.$$

Therefore, with (2.20), we obtain

$$Z \leqq \frac{\displaystyle\sum_{1 \leqq j,\, k,\, l,\, m \leqq n} c'_{mjkl} \left(\delta_{jm} - \int \varphi_j \varphi_m \right) \int \varphi_k \varphi_l}{\displaystyle\sum_{k=1}^{n} \mu_k \left(1 - \int \varphi_k^2 \right)} \tag{2.34}$$

where we recall the value of the coefficients

$$\mu_k = \sum_{P / \exists \alpha;\, P(\alpha) = k} c_P^2$$

$$c'_{ijkl} = c_{ijkl} + c_{klij}. \tag{2.35}$$

In the second assertion, it is possible, as we have seen in II.0, to take

$$c_{ijkl} = \sum_{PQ \text{ satisfying } (2.6)} c_P \, c_Q$$

for

$$\begin{cases} 1 \leqq i \leqq j \leqq n \\ 1 \leqq k \leqq l \leqq n \\ i \leqq k \end{cases}$$

We shall reach a contradiction as soon as we shall be able to give conditions that imply that (2.34) cannot hold.

We claim that this may be made with a condition of the kind

$$Z > Z_c$$

where Z_c depends on the number of electrons N, and on the coefficients c_P of the model.

Indeed, in (2.34) we may bound the integrals $\int \varphi_k \varphi_l$ by

$$\left| \int \varphi_k \varphi_l \right| \leqq \operatorname{Min} \left(\sqrt{\left(1 - \int \varphi_k^2 \right) \left(1 - \int \varphi_l^2 \right)}, \right.$$

$$\left. \sqrt{\left(\int \varphi_k^2 \right) \left(\int \varphi_l^2 \right)} \right) \tag{2.36}$$

on the one hand, because $1 - M(\varphi) \geqq 0$, and, on the other hand, because of Cauchy-Schwarz inequality.

Thus, considering the particular value (2.35) of the coefficients of the model, we may bound the right hand side of (2.34), and obtain some critical value Z_c.

Why does such a Z_c exist?

This is not obvious *a priori* since one could imagine a situation where the denominator of (2.34) tends to vanish.

We are going to see that Z_c exists and that we may find a general upper bound to it:

$$Z_c \leqq (2n - 1)\, n^3 \tag{2.37}$$

where we recall that n is the number of functions φ_i involved.

Actually, we shall also see that we may improve (2.37) with

$$Z_c \leqq (2n - 1)\, n\, \alpha(n) \tag{2.38}$$

where $\alpha(n)$ is the number of integrals $\int \varphi_i \varphi_j$ which do not vanish. Of course, $\alpha(n) \leqq n^2$, and the case $\alpha(n) = n^2$ may occur *a priori*. However, in some cases where one can use some orthogonal invariance, and thus assume without loss of generality that some of the $\int \varphi_i \varphi_j$, $i \neq j$ are zero, (2.38) may be much better than (2.37).

Before giving the proof of (2.37), let us study the situation where one may assume $\int \varphi_i \varphi_j = 0$ for $i \neq j$. Of course, this case is not very interesting since it is precisely the case for which our approach is not necessary. However we believe it illuminates the nature of (2.34), and helps to understand why (2.34) cannot hold any longer for Z large enough. To some extent, this is the best case one may find: the critical value Z_c is small.

We claim that, in this particular case,

$$Z_c \leqq n - 1. \tag{2.39}$$

Indeed, if $\int \varphi_i \varphi_j = 0$ for $i \neq j$, (2.34) reads

$$Z \leqq \frac{\sum\limits_{1 \leqq j,\, k \leqq n} c'_{jjkk} \left(1 - \int \varphi_j^2\right) \int \varphi_k^2}{\sum\limits_{k=1}^{n} \mu_k \left(1 - \int \varphi_k^2\right)}. \tag{2.40}$$

Now, with (2.5) and the expression of c_{ijkl}, we have

$$c'_{jjkk} = \sum_{PQ} c_P\, c_Q$$

where the sum is taken over PQ satifying

$$\begin{aligned} &\exists\,(\alpha,\,\beta)/\alpha \neq \beta\\ &\qquad P(\alpha) = Q(\alpha) = j\\ &\qquad P(\beta) = Q(\beta) = k\\ &\qquad P(\gamma) = Q(\gamma), \qquad \forall\,\gamma \in \{1,\,\cdots,\,N\} - \{\alpha,\,\beta\}\end{aligned}$$

That is to say

$$c'_{jjkk} = \sum_{P} c_P^2$$

where the sum is taken over P satisfying

$$\exists\,(\alpha,\,\beta)/\alpha \neq \beta, \qquad P(\alpha) = j, \qquad P(\beta) = k.$$

Therefore

$$\begin{cases} c'_{jjkk} = 0 & \text{for} \quad j = k,\\ |c'_{jjkk}| \leqq \mu_j & \text{for} \quad j \neq k.\end{cases}$$

Then (2.40) yields

$$Z \leqq \frac{\displaystyle\sum_{1 \leqq j \neq k \leqq n} \mu_j \left(1 - \int \varphi_j^2\right) \int \varphi_k^2}{\displaystyle\sum_{k=1}^{n} \mu_k \left(1 - \int \varphi_k^2\right)} \leqq n - 1$$

since $\displaystyle\int \varphi_k^2 \leqq 1$. And we obtain a contradiction as soon as $Z > n - 1$.

We now come back to the general case and to the proof of (2.37)-(2.38).

We are going to bound the coefficients c'_{mjkl}.

Let us first deal with c'_{kkjl}. One can see that, since (2.6) holds, we have

$$
\begin{aligned}
|c'_{jjkl}| &\leqq \sum_{PQ \text{ satisfying } (2.6)} |c_P\, c_Q| \\
&\leqq \sum_{PQ/\exists\alpha;\, P(\alpha)=Q(\alpha)=j} |c_P\, c_Q| \\
&\leqq \Big(\sum_{P/\exists\alpha;\, P(\alpha)=j} |c_P| \Big)^2 \\
&\leqq n \sum_{P/\exists\alpha;\, P(\alpha)=j} |c_P|)^2 = n\, \mu_j .
\end{aligned}
$$

Therefore

$$
\begin{aligned}
&\Big| \sum_{1 \leqq j,\, k,\, l \leqq n} c'_{jjkl} \Big(1 - \int \varphi_1^2\Big) \int \varphi_k\, \varphi_l \Big| \\
&\quad \leqq n \Big(\sum_{1 \leqq j \leqq n} \mu_j \Big(1 - \int \varphi_j^2\Big)\Big) \sum_{1 \leqq k,\, l \leqq n} \Big| \int \varphi_k\, \varphi_l \Big| \\
&\quad \leqq n\, \alpha(n) \sum_{1 \leqq j \leqq n} \mu_j \Big(1 - \int \varphi_j^2\Big).
\end{aligned} \tag{2.41}
$$

On the other hand, for $m \neq j$, we may bound the coefficient c'_{mjkl} as follows

$$
\begin{aligned}
|c'_{mjkl}| &\leqq \sum_{PQ/\exists\, \alpha;\, \{P(\alpha), Q(\alpha)\} = \{m, j\}} |c_P\, c_Q| \\
&\leqq 2 \Big(\sum_{P/\exists\alpha;\, P(\alpha)=m} |c_P| \Big) \Big(\sum_{Q/\exists\alpha;\, Q(\alpha)=j} |c_Q| \Big) \\
&\leqq 2\, n \sqrt{\mu_m\, \mu_j} .
\end{aligned}
$$

Thus, using successively (2.36) and Cauchy-Schwarz inequality,

$$
\begin{aligned}
&\Big| \sum_{1 \leqq m \neq j,\, k,\, l \leqq n} c'_{mjkl} \int \varphi_m\, \varphi_j \int \varphi_k\, \varphi_l \Big| \\
&\quad \leqq 2\, n \Big(\sum_{1 \leqq m \neq j \leqq n} \sqrt{\mu_m\, \mu_j} \Big| \int \varphi_m\, \varphi_j \Big| \Big) \times \Big(\sum_{1 \leqq k,\, l \geqq n} \Big| \int \varphi_k\, \varphi_l \Big| \Big) \\
&\quad \leqq 2\, n \Big(\sum_{1 \leqq m \neq j \leqq n} \sqrt{\mu_m\, \mu_j} \sqrt{\Big(1 - \int \varphi_m^2\Big) \Big(1 - \int \varphi_j^2\Big) \alpha(n)} \\
&\quad \leqq 2\, n\, (n-1)\, \alpha(n) \sum_{1 \leqq j \leqq n} \mu_j \Big(1 - \int \varphi_j^2\Big).
\end{aligned} \tag{2.42}
$$

With (2.34), (2.41), and (2.42), we obtain

$$Z \leqq n\alpha(n) + 2n(n-1)\alpha(n) = (2n-1)n\alpha(n)$$

and reach therefore a contradiction as soon as $Z > (2n-1)n\alpha(n)$, whence we deduce (2.38), and (2.37).

Let us make a few comments on (2.37).

Of course, though it shows the existence of a critical value Z_c (and gives an upper bound of it) whatever the problem (1.8) may be, (2.37) [and (2.39) to a less extent] is not very satisfactory.

There are two main reasons.

First, it depends on the number n of functions φ_i involved, which may be much larger than the number N of electrons. Secondly, it depends on n at the fourth order, and, for physical reasons in particular, a growth of order 1 is expected [For this second point, (2.39) is much better since it depends on n^1 and $n \geqq N$, but we must use an extra hypothesis]. But let us recall that our point in this section is just to prove that (2.34) necessarily leads to a contradiction for Z large enough. As far as the exact value of the critical Z is concerned, there is room for improvement in the above argument, because we did not specify any further property of the general problem (1.8). In the next section, taking benefit of the particular form of each example we study, and using (2.36) in a more accurate way, we shall considerably improve (2.37)-(2.38). For our examples, we shall see $Z_c = N - 1$ [with $n = K(N+1)$] and $Z_c = N$ (with $n = N + 2$). Unfortunately we are not able to improve (2.37) in the general case.

Let us now conclude this section with a few remarks.

Remarks. – 1) It may be interesting to see what our approach means on the classical Hartree-Fock case. Thanks to the above mentioned orthogonal invariance, we may always assume that $\int \varphi_i \varphi_j = 0$ for $i \neq j$. Thus the matrix $1 - M(\varphi)$ is diagonal. Assuming that $Rank(1 - M(\varphi)) \geqq 1$ is assuming that at least of the φ_i satisfies $\left(1 - \int \varphi_i^2\right) > 0$.

The choice (2.12) of the direction $\mathbf{h}$ is actually.

$$h_i = \left(1 - \int \varphi_i^2\right) f_i$$

which is interesting only for the indices i for which $\left(1 - \int \varphi_i^2\right) > 0$. Once more we observe that the vector-valued problem has degenerated into n scalar problems. The direction h_i is the one that is classically used to reach a contradiction.

In this direction, we obtain (2.34)-(2.35), which may be written in the Hartree-Fock case

$$Z \leq \frac{\sum_{i \neq k} \left(1 - \int \varphi_i^2\right) \int \varphi_k^2}{\sum_{k=1}^{n} \left(1 - \int \varphi_k^2\right)} \leq \frac{\sum_{i \neq k} \left(1 - \int \varphi_i^2\right)}{\sum_{k=1}^{n} \left(1 - \int \varphi_k^2\right)} = N - 1$$

because we have here

$$n = N$$
$$c_P = \frac{1}{\sqrt{N\,!}} \varepsilon(P)$$
$$\mu_k = 1$$
$$c_{iikl} = \frac{1}{2} (1 - \delta_{ik}) \, \delta_{kl}$$
$$d'_{iikl} = \delta_{kl} \left(1 - \int \varphi_i^2\right)$$

where we denoted by $\varepsilon(P)$ the signature of the permutation P.

Therefore, as soon as $Z > N - 1$ we obtain the desired contradiction. This is what we expected.

Of course, we could also have ignored the orthogonal invariance and obtain the same result. In the next section, when we treat the case of $K + 1$ orthogonal determinants, the case $K = 0$ is actually the Hartree-Fock case, and we shall obtain also $Z > N - 1$.

2) In step 2, one can remark that we did not use the particular form of the potential created by the nucleii, but only the fact that is was a convolution with some bounded measure $(\sum_k z_k \, \delta_{\bar{x}k})$ with total mass Z.

A straightforward extension of our work is to consider the case of smeared nucleii.

$$V = \sum_k m_k \star \frac{1}{|x|}$$

(m_k is bounded measure).

The argument will be the same, and the condition on Z arising at the end of step will be replaced by

$$\int \Delta V > C$$

for a certain constant C depending on N, and on the model.

III. TWO EXAMPLES

III.1. Linear combination of completely orthogonal determinants

We fix $N \geqq 3$ (N is the number of electrons, see the remark at the end of this paragraph for the case $N = 2$), and $K \geqq 0$ ($K + 1$ is the number of determinants).

A natural idea in order to extend the Hartree-Fock model is to study the problem (1.11)-(1.12), that we recall here

$$I = \inf \left\{ \langle H_N \phi, \phi \rangle ;\ \phi = \sum_{k=0}^{K} c_k \frac{1}{\sqrt{N!}} \det(\varphi_{kN+1}, \cdots, \varphi_{kN+N}) \right.$$
$$\left. \times \int \varphi_i \varphi_j = \delta_{ij},\ 1 \leqq i \leqq j \leqq N(K+1) \sum_{k=0}^{K} c_k^2 = 1 \right\}. \tag{3.1}$$

We denote by

$$\mathcal{E}(c_0, \cdots, c_K, \varphi_1, \cdots, \varphi_{N(K+1)}) = \langle H_N \phi, \phi \rangle$$

for ϕ as in (3.1).

For $N \geqq 3$, it is easy to see that we have

$$\mathcal{E}(c_0, \cdots, c_K, \varphi_1, \cdots, \varphi_{N(K+1)}) = \sum_{k=0}^{K} c_k^2 \, \mathcal{E}_{HF}(\varphi_{k+1}, \cdots, \varphi_{k+N}) \tag{3.2}$$

where we recall that $\mathcal{E}_{\mathcal{HF}}$ is given by

$$\mathcal{E}_{HF}(\varphi_1, \cdots, \varphi_N) = \sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + \sum_{i=1}^{N} \int V |\varphi_i|^2 + \frac{1}{2} \sum_{i \neq j} (D(\varphi_i^2, \varphi_j^2) - D(\varphi_i \varphi_j, \varphi_i \varphi_j)).$$

Indeed, since $\int \varphi_i \varphi_j = \delta_{ij}$, any term of the kind

$$\langle H_N \det(\varphi_{iN+1}, \cdots, \varphi_{iN+N}), \det(\varphi_{jN+1}, \cdots, \varphi_{iN+N}) \rangle$$

is zero for $i \neq j$. In such terms, since H_N is at most bi-electronic and $N \geqq 3$, there always remain at least one integral of the kind $\int \varphi_i \varphi_j$ with $i \neq j$; and this integral is zero.

It follows from (3.2) that

$$I = I_{HF}.$$

Therefore, the general problem (3.1) [or (1.12)] is of no chemical interest (as far as the energy is concerned).

However, as far as we known, the problem (1.11), that is

$$I(c_0, \cdots, c_K) = \inf \Big\{ \langle H_N \phi, \phi \rangle; \\ \phi = \sum_{k=0}^{K} c_k \frac{1}{\sqrt{N!}} \det(\varphi_{kN+1}, \cdots, \varphi_{kN+N}) \\ \times \int \varphi_i \varphi_j = \delta_{ij}, 1 \leqq i \leqq j \leqq N(K+1) \Big\}$$

where $(c_0, \cdots, c_K)$ is given such that

$$\begin{cases} \sum_{k=0}^{K} c_k^2 = 1 \\ c_k \neq 0, \qquad 0 \leqq k \leqq K \end{cases}$$

has never been considered from the mathematical point of view.

Of course, $I(c_0, \cdots, c_K) \geqq I_{HF}$, but the question of the existence of a minimum was open. In this paragraph, we answer this question, proving theorem 1, that we mentioned in the introduction.

Let us give now its proof.

Proof of theorem 1. – Of course, point (ii) is a straightforward consequence of (3.2). The difficulty is point (i).

We take a minimizing sequence of (1.11). By classical arguments (*see* II.2 in [2] and use the fact that none of the c_k vanishes), this sequence is bounded in $(H^1(\mathbf{R}^3))^{N(K+1)}$, thus converges in weak-H^1, up to an extraction, to a certain φ, which is a minimum of the problem

$$I(c_0, \cdots, c_K) = \inf \Big\{ \mathcal{E}(c_0, \cdots, c_K, \varphi_1, \cdots, \varphi_{N(K+1)}) \Big/ \\ \Big[\int \varphi_i \varphi_j\Big] \leqq 1 \Big\}. \tag{3.3}$$

And we obtain a problem contained in the general framework of section II. We mimic the argument we made there.

We have (3.2):

$$\begin{aligned}
&\mathcal{E}(c_0, \cdots, c_K, \varphi_1, \cdots, \varphi_{N(K+1)}) \\
&\quad = \sum_{k=0}^{K} c_k^2 \, \mathcal{E}_{\mathcal{HF}}(\varphi_{kN+1}, \cdots, \varphi_{kN+N}) \\
&\quad = \sum_{k=0}^{K} \Bigg[\sum_{i=1}^{N} \int |\nabla \varphi_{kN+i}|^2 + \sum_{i=1}^{N} \int V |\varphi_{kN+i}|^2 \\
&\qquad + \frac{1}{2} \sum_{1 \leqq i \neq j \leqq N} \left(D(\varphi_{kN+i}^2, \varphi_{kN+j}^2) - D(\varphi_{kN+i}\varphi_{kN+j}, \varphi_{kN+i}\varphi_{kN+j}) \right) \Bigg].
\end{aligned}$$

To compute the second derivative, we only have to sum up the second derivatives of the Hartree-Fock energy. We take $\mathbf{h}$ as in (2.12). The terms that give the behaviour of $\mathcal{E}''(\varphi) \cdot (\mathbf{h}_\sigma, \mathbf{h}_\sigma)$ for σ large are

$$\begin{aligned}
\sum_{k=0}^{K} c_k^2 \Bigg[&\sum_{i=1}^{N} \sum_{j=1}^{K(N+1)} a_{kN+i,j}^2 \int V |f_j|^2 \\
&+ \sum_{1 \leqq i \neq j \leqq N} \sum_{l=1}^{K(N+1)} \left(a_{kN+j,l}^2 D(\varphi_{kN+i}^2, f_l^2) \right. \\
&\left. - a_{kN+i,l}\, a_{kN+j,l}\, D(\varphi_{kN+i}\varphi_{kN+j}, f_l^2) \right) \Bigg]
\end{aligned}$$

where we recall our notation $a_{ij} = \sqrt{1 - M(\varphi)_{ij}}$.

Therefore (2.34) takes the particular form

$$\begin{aligned}
&- Z \left(\sum_{k=0}^{K} c_k^2 \sum_{i=1}^{N} \sum_{j=1}^{K(N+1)} a_{kN+i,j}^2 \right) \\
&\quad + \sum_{k=0}^{K} c_k^2 \sum_{1 \leqq i \neq j \leqq N} \sum_{l=1}^{K(N+1)} \\
&\quad \times \left(a_{kN+j,l}^2 \int \varphi_{kN+i}^2 - a_{kN+i,l}\, a_{kN+j,l} \int \varphi_{kN+i}\varphi_{kN+j} \right)
\end{aligned}$$

i. e.

$$
\begin{aligned}
&- Z\left(\sum_{k=0}^{K} c_k^2 \sum_{i=1}^{N}\left(1-\int \varphi_{kN+i,j}^2\right)\right)\\
&+\sum_{k=0}^{K} c_k^2 \sum_{1\leqq i\neq j\leqq N}\left(\left(1-\int \varphi_{kN+j}^2\right)\int \varphi_{kN+i}^2\right.\\
&\left.+\left(\int \varphi_{kN+i}\,\varphi_{kN+j}\right)^2\right). \qquad (3.4)
\end{aligned}
$$

In terms of the coefficients μ_i and c'_{ijkl} introduced in section II in formulae (2.5)-(2.8), we have

$$\mu_k = c_i^2 \quad \text{for} \quad Ni \leqq k \leqq Ni + K \qquad (3.5)$$

and

$$
c'_{mjkl} = \left\{\begin{array}{ll}
- c_{[j/N]}, & \text{for} \quad j = k,\ m = l,\ k \neq l,\ \left[\dfrac{j}{N}\right] = \left[\dfrac{m}{N}\right];\\
c_{[j/N]}, & \text{for} \quad k = l, j = m,\ j \neq k,\ \left[\dfrac{j}{N}\right] = \left[\dfrac{k}{N}\right];\\
0 & \text{otherwise.}
\end{array}\right\} \qquad (3.6)
$$

It follows from (3.4)-(3.5)-(3.6) that

$$
Z \leqq \frac{\left\{\begin{array}{l}\displaystyle\sum_{k=0}^{K} c_k^2 \sum_{1\leqq i\neq j\leqq N}\left[\left(1-\int \varphi_{j+kN}^2\right)\int \varphi_{i+kN}^2\right.\\ \qquad\qquad \left.+\left(\int \varphi_{i+kN}\,\varphi_{j+kN}\right)^2\right]\end{array}\right\}}{\displaystyle\sum_{k=0}^{K} c_k^2 \sum_{i=1}^{N}\left(1-\int \varphi_{j+kN}^2\right)} \qquad (3.7)
$$

Now, using (2.36), we have, for $i \neq j$,

$$\left(1-\int \varphi_{j+kN}^2\right)\int \varphi_{i+kN}^2 + \left(\int \varphi_{i+kN}\,\varphi_{j+kN}\right)^2 \leqq 1 - \int \varphi_{j+kN}^2.$$

Thus (3.7) yields

$$Z \leqq \frac{\sum_{k=0}^{K} c_k^2 \sum_{1 \leqq i \neq j \leqq N} \left(1 - \int \varphi_{j+kN}^2\right)}{\sum_{k=0}^{K} c_k^2 \sum_{i=1}^{N} \left(1 - \int \varphi_{i+kN}^2\right)} = N - 1.$$

If we assume

$$Z > N - 1$$

we reach a contradiction, and thus we prove (i) of theorem 1. ◊

Remarks. – 1) From the beginning of this paragraph, we have assumed $N \geqq 3$. It has been useful in the computation of the energy (3.2).

The case $N = 2$ is special, because in that case there exists triangle terms of the kind

$$\langle H_N \det(\varphi_{i+1}, \varphi_{i+2}), \det(\varphi_{j+1}, \varphi_{j+2})\rangle$$

for $i \neq j$. The situation is therefore rather different. The case of two determinants for $N = 2$ is actually a particular case of the case studied in next paragraph. We shall see there that the condition on Z is $Z \geqq 2$, and not $Z > 1$ as one should have expected if this case were close to the one studied here.

2) The case $K = 0$ is the Hartree-Fock case.

3) Let us point out that we do not know if any minimum of the problem (1.12) is of the form

$$\begin{cases} c_{k_0} = 1 \\ c_k = 0, \qquad \forall k \neq k_0 \\ (\varphi_{k_0 N+1}, \cdots, \varphi_{k_0 N+N}) \text{ minimum for the Hartree–Fock problem} \end{cases}$$

In other words, it might be possible (even if it is unlikely), as far as we know, to find two minima for the Hartree-Fock problem $(\varphi_1, \cdots, \varphi_N)$ and $(\varphi_{N+1}, \cdots, \varphi_{N+N})$ such that

$$\forall 1 \leqq i \leqq N, \quad \forall N+1 \leqq j \leqq 2N, \qquad \int \varphi_i \varphi_j = 0,$$

and then any

$$\begin{cases} c_0 \dfrac{1}{\sqrt{N!}} \det(\varphi_1, \cdots, \varphi_N) + c_1 \dfrac{1}{\sqrt{N!}} \det(\varphi_{N+1}, \cdots, \varphi_{N+N}) \\ c_0^2 + c_1^2 = 1 \end{cases}$$

III.2. Doubly excited configuration

A major drawback of the previous example is that there is no coupling of two different determinants for the energy. Therefore, one does not really see the interest of our approach.

We choose here to study what we may call a strongly coupled problem. This is (1.15)-(1.16):
is a minimum for (1.12).

$$\begin{aligned} I = \inf \{ \langle H_N \phi, \phi \rangle; \\ \phi = \frac{\alpha}{\sqrt{N!}} \det (\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N-1}, \varphi_N) \\ + \frac{\beta}{\sqrt{N!}} \det (\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N+1}, \varphi_{N+2}) \\ \times\ \alpha^2 + \beta^2 = 1 \int \varphi_i \varphi_j = \delta_{ij},\ 1 \leqq i \leqq j \leqq N+2 \Big\}. \end{aligned} \tag{3.8}$$

For this problem, one may see, after a tedious computation, that

$$\begin{aligned} \mathcal{E} (\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2}) = \alpha^2 \mathcal{E}_{HF} (\varphi_1, \cdots, \varphi_N) \\ + \beta^2 \mathcal{E}_{HF} (\varphi_1, \cdots, \varphi_{N-2}, \varphi_{N+1}, \varphi_{N+2}) \\ + 2\alpha\beta [D (\varphi_{N-1}, \varphi_{N+1}, \varphi_N \varphi_{N+2}) \\ - D (\varphi_{N-1} \varphi_{N+2}, \varphi_N \varphi_{N+1})]. \end{aligned} \tag{3.9}$$

We claim that, for $Z > N - 1$, (3.9) implies

$$I < I_{HF}. \tag{3.10}$$

Indeed, if we take $(\varphi_1, \cdots, \varphi_N)$ the minimum for the Hartree-Fock problem, we claim that we may choose φ_{N+1} and φ_{N+2} in $\text{Vect}\,(\varphi_1, \cdots, \varphi_N)^\perp$ such that, for instance,

$$D (\varphi_{N-1} \varphi_{N+1}, \varphi_N \varphi_{N+2}) - D (\varphi_{N-1} \varphi_{N+2}, \varphi_N \varphi_{N+1}) > 0.$$

Let us argue by contradiction, and assume that (φ_1, φ_2) being given such that $\int \varphi_1^2 = 1$, $\int \varphi_2^2 = 1$, $\int \varphi_1 \varphi_2 = 0$, we have

$$D (\varphi_1 \varphi_3, \varphi_2 \varphi_4) - D (\varphi_1 \varphi_4, \varphi_2 \varphi_3) = 0$$

for all (φ_3, φ_4) such that $\int \varphi_3^2 = 1$, $\int \varphi_4^2 = 1$, $\int \varphi_3 \varphi_4 = \int \varphi_1 \varphi_3 = \int \varphi_2 \varphi_3 = \int \varphi_1 \varphi_4 = \int \varphi_2 \varphi_4 = 0$. Then we have

$$\int \left[\left(\varphi_1 \varphi_3 \star \frac{1}{|x|} \right) \varphi_2 - \left(\varphi_2 \varphi_3 \star \frac{1}{|x|} \right) \varphi_1 \varphi_4 = 0$$

for all $\varphi_4 \in \text{Vect}(\varphi_1, \varphi_2, \varphi_3)^\perp$.

Therefore, there exists (α, β, γ) such that

$$\left(\varphi_1 \varphi_3 \star \frac{1}{|x|} \right) \varphi_2 - \left(\varphi_2 \varphi_3 \star \frac{1}{|x|} \right) \varphi_1 = \alpha\varphi_1 + \beta\varphi_2 + \gamma\varphi_3.$$

By multiplying successively this equation by $\varphi_1, \varphi_2, \varphi_3$, we obtain

$$\alpha = \int \varphi_3 \psi_1$$
$$\beta = \int \varphi_3 \psi_2$$
$$\gamma = 0$$

where we denote by

$$\psi_1 = \left(\varphi_1 \varphi_2 \star \frac{1}{|x|} \right) \varphi_1 - \left(\varphi_1^2 \star \frac{1}{|x|} \right) \varphi_2$$
$$\psi_2 = \left(\varphi_2^2 \star \frac{1}{|x|} \right) \varphi_1 - \left(\varphi_1 \varphi_2 \star \frac{1}{|x|} \right) \varphi_2.$$

In terms of (ψ_1, ψ_2) we have

$$\begin{aligned} \int \frac{1}{|x-y|} [\varphi_1(y)\varphi_2(x) - \varphi_1(x)\varphi_2(y)]\varphi_3(y)\,dy \\ - \int \varphi_1(x)\psi_1(y)\varphi_3(y)\,dy \\ - \int \varphi_2(x)\psi_2(y)\varphi_3(y)\,dy = 0 \end{aligned}$$

for all $x \in \mathbf{R}^3$, and $\varphi_3 \in \text{Vect}(\varphi_1, \varphi_2)^\perp$. Thus there exists two functions $\alpha(x)$ and $\beta(x)$ such that

$$\begin{aligned} \frac{1}{|x-y|} [\varphi_1(y)\varphi_2(x) - \varphi_1(x)\varphi_2(y)] - \varphi_1(x)\psi_1(y) - \varphi_2(x)\psi_2(y) \\ = \alpha(x)\varphi_1(y) + \beta(x)\varphi_2(y). \end{aligned}$$

Changing x into y and vice-versa, we obtain another equation that we substract to the above equation. This yields

$$\begin{aligned}
&2\,\frac{1}{|x-y|}\,[\varphi_1(y)\,\varphi_2(x)-\varphi_1(x)\,\varphi_2(y)]\\
&=\left[\left(\varphi_1\,\varphi_2\star\frac{1}{|x|}\right)(y)-\left(\varphi_1\,\varphi_2\star\frac{1}{|x|}\right)(x)\right]\\
&\quad\times\,[\varphi_1(x)\,\varphi_1(y)-\varphi_2(x)\,\varphi_2(y)]\\
&\quad+\left[\left(\varphi_1^2\star\frac{1}{|x|}\right)(y)+\left(\varphi_2^2\star\frac{1}{|x|}\right)\times(x)\right]\\
&\quad\times\,[\varphi_2(x)\,\varphi_1(y)-\varphi_1(x)\,\varphi_2(y)]\\
&\quad+[\alpha(x)\,\varphi_1(y)-\alpha(y)\,\varphi_1(x)]\,[\beta(x)\,\varphi_2(y)-\beta(y)\,\varphi_2(x)].
\end{aligned}$$

This implies that

$$\forall\,(x,\,y)\in\mathbf{R}^3\times\mathbf{R}^3,\qquad \varphi_1(y)\,\varphi_2(x)=\varphi_1(x)\,\varphi_2(y).$$

[Study the limit $y\to x$: the right-hand side tends to 0, thus $\varphi_1(y)\,\varphi_2(x)-\varphi_1(x)\,\varphi_2(y)=o(|x-y|)$, which only happens when $\varphi_1(y)\,\varphi_2(x)-\varphi_1(x)\,\varphi_2(y)\equiv 0$].

And of course we reach a contradiction because this yields, for all $x\in\mathbf{R}^3$,

$$\varphi_1(x)=\int\varphi_1(x)\,\varphi_2^2(y)\,dy=\int\varphi_2(x)\,\varphi_1(y)\,\varphi_2(y)\,dy=0.$$

Therefore we may take

$$D(\varphi_{N-1}\,\varphi_{N+1},\,\varphi_N\,\varphi_{N+2})-D(\varphi_{N-1}\,\varphi_{N+2},\,\varphi_N\,\varphi_{N+1})>0.$$

We now take

$$\alpha=1-\varepsilon^2$$
$$\beta=-\sqrt{1-\alpha^2}$$

and send $\mathcal{E}$ to 0 in (3.9). We get

$$\begin{aligned}
&\mathcal{E}(\alpha,\,\beta,\,\varphi_1,\,\cdots,\varphi_{N+2})\\
&\quad=(1-2\,\varepsilon^2)\,I_{HF}+2\,\varepsilon^2\,\mathcal{E}_{\mathrm{HF}}(\varphi_1,\,\cdots,\,\varphi_{N-2},\,\varphi_{N+1},\,\varphi_{N+2})\\
&\qquad-\varepsilon\sqrt{8}\,[D(\varphi_{N-1}\,\varphi_{N+1},\,\varphi_N\,\varphi_{N+2})-D(\varphi_{N-1}\,\varphi_{N+2},\,\varphi_N\,\varphi_{N+1})]\\
&\qquad+o(\varepsilon)\\
&\quad=I_{HF}\\
&\qquad-\varepsilon\sqrt{8}\,[D(\varphi_{N-1}\,\varphi_{N+1},\,\varphi_N\,\varphi_{N+2})-D(\varphi_{N-1}\,\varphi_{N+2},\,\varphi_N\,\varphi_{N+1})]\\
&\qquad+o(\varepsilon)\\
&\quad<I_{HF}\qquad\text{for}\quad\varepsilon>0\quad\text{small,}
\end{aligned}$$

whence we deduce (3.10).

(3.10) shows the interest of the model. As a step towards the study of problem (3.8), we introduce in a classical way the problem (1.15) at (α, β) fixed. We are going to prove in this paragraph Theorem 2, that we stated in the introduction.

Proof of theorem 2. – (i) Let $(\varphi_1, \cdots, \varphi_{N+2})_n$ be a minimizing sequence of (1.15).

We are first going to prove that $(\varphi_1, \cdots, \varphi_{N+2})_n$ is bounded in $(H^1(\mathbf{R}^3))^{N+2}$.

For this purpose, we notice that

$$\begin{aligned} &D(\varphi_{N-1}\varphi_{N+1}, \varphi_N \varphi_{N+2}) - D(\varphi_{N-1}\varphi_{N+2}, \varphi_N \varphi_{N+1}) \\ &\quad = \frac{1}{2}\int\int \frac{1}{|x-y|}(\varphi_{N-1}(x)\varphi_N(y) - \varphi_{N-1}(y)\varphi_N(x)) \\ &\qquad \times (\varphi_{N+1}(x)\varphi_{N+2}(y) - \varphi_{N+1}(y)\varphi_{N+2}(x))\,dx\,dy \end{aligned}$$

thus, by Cauchy-Schwarz inequality,

$$\begin{aligned} &|D(\varphi_{N-1}\varphi_{N+1}, \varphi_N \varphi_{N+2}) - D(\varphi_{N-1}\varphi_{N+2}, \varphi_N \varphi_{N+1})| \\ &\quad \leqq \frac{1}{2}\left(\int\int \frac{(\varphi_{N-1}(x)\varphi_N(y) - \varphi_{N-1}(y)\varphi_N(x))^2}{|x-y|}\right)^{1/2} \\ &\qquad \times \left(\int\int \frac{(\varphi_{N+1}(x)\varphi_{N+2}(y) - \varphi_{N+1}(y)\varphi_{N+2}(x))^2}{|x-y|}\right)^{1/2} \\ &\quad = [D(\varphi_{N-1}^2, \varphi_N^2) - D(\varphi_{N-1}\varphi_N, \varphi_{N-1}\varphi_N)]^{1/2} \\ &\qquad \times [D(\varphi_{N+1}^2, \varphi_{N+2}^2) - D(\varphi_{N+1}\varphi_{N+2}, \varphi_{N+1}\varphi_{N+2})]^{1/2}. \end{aligned}$$

Therefore

$$\begin{aligned} &|2\alpha\beta(D(\varphi_{N-1}\varphi_{N+1}, \varphi_N \varphi_{N+2}) - D(\varphi_{N-1}\varphi_{N+2}, \varphi_N \varphi_{N+1}))| \\ &\quad \leqq \alpha^2[D(\varphi_{N-1}^2, \varphi_N^2) - D(\varphi_{N-1}\varphi_N, \varphi_{N-1}\varphi_N)] \\ &\quad + \beta^2[D(\varphi_{N+1}^2, \varphi_{N+2}^2) - D(\varphi_{N+1}\varphi_{N+2}, \varphi_{N+1}\varphi_{N+2})]. \end{aligned}$$

It follows from the definition of the energy (3.9) and from the above inequality that

$$
\begin{aligned}
\mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2}) \geqq \alpha^2 & \left[\sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + \sum_{i=1}^{N} \int V|\varphi_i|^2\right] \\
& + \beta^2 \left[\sum_{i=1, \cdots, N-1, N+1, N+2} \int |\nabla \varphi_i|^2 \right. \\
& \left. + \sum_{i=1, \cdots, N-1, N+1, N+2} \int V|\varphi_i|^2\right] \qquad (3.11)
\end{aligned}
$$

where we remark that each term of the right-hand side is bounded below by $J = \inf_{\int \psi^2 = 1} \left\{ \int |\nabla \psi|^2 + \int V|\psi|^2 \right\} > -\infty$ (which proves in particular that $I > -\infty$).

We now come back to our minimizing sequence $(\varphi_1, \cdots, \varphi_{N+2})_n$.

(3.11) and the remark above show that the sequences $\varphi_{i,n}$ for $1 \leqq i \leqq N+2$ are bounded in H^1. Therefore they weakly converge (up to an extraction) to some φ_i.

We claim that $\varphi = (\varphi_1, \cdots, \varphi_{N+2})$ satisfies

$$\mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2}) = I(\alpha, \beta).$$

It suffices to prove that

$$\mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2}) \leqq \liminf \mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2})_n.$$

For this purpose, we study each term of (3.9).

The terms $\int |\nabla \varphi_i|^2$ and $\int V \varphi_i^2$ are standard, and we have

$$\int |\nabla \varphi_i|^2 \leqq \liminf \int |\nabla \varphi_{i,n}|^2$$

$$\int V \varphi_i^2 = \lim \int V \varphi_{i,n}^2$$

Besides, since positive definite quadratic forms are non-increasing under weak limits (*see* [1] and reference therein), and since

$$
\begin{aligned}
D(\varphi_i^2, \varphi_j^2) - D(\varphi_i \varphi_j, \varphi_i \varphi_j) = \frac{1}{2} \Big\langle & \frac{1}{|x-y|} (\varphi_i(x) \varphi_j(y) \\
& - \varphi_i(y) \varphi_j(x)), (\varphi_i(x) \varphi_j(y) - \varphi_i(y) \varphi_j(x)) \Big\rangle
\end{aligned}
$$

we have

$$D(\varphi_i^2, \varphi_j^2) - D(\varphi_i \varphi_j, \varphi_i \varphi_j)$$
$$\leqq \liminf D(\varphi_{i,n}^2, \varphi_{j,n}^2) - D(\varphi_{i,n} \varphi_{j,n}, \varphi_{i,n} \varphi_{j,n}).$$

We use this result for $1 \leqq i \leqq j \leqq N$, and $1 \leqq i \leqq N-2$, $j = N-1$, N, $N+1$, $N+2$.

We remark now that

$$\begin{aligned}&\alpha^2 [D(\varphi_{N-1}^2, \varphi_N^2) - D(\varphi_{N-1} \varphi_N, \varphi_{N-1} \varphi_N)]\\&\quad + \beta^2 [D(\varphi_{N+1}^2, \varphi_{N+2}^2) - D(\varphi_{N+1} \varphi_{N+2}, \varphi_{N+1} \varphi_{N+2})]\\&\quad + 2\alpha\beta [D(\varphi_{N-1}, \varphi_{N+1}, \varphi_N \varphi_{N+2}) - D(\varphi_{N-1} \varphi_{N+2}, \varphi_N \varphi_{N+1})]\\&\quad = \left\langle \frac{1}{|x-y|} \psi, \psi \right\rangle\end{aligned}$$

where

$$\begin{aligned}\psi = &\frac{\alpha}{\sqrt{2}} (\varphi_{N-1}(x) \varphi_N(y) - \varphi_{N-1}(y) \varphi_N(x))\\&+ \frac{\beta}{\sqrt{2}} (\varphi_{N+1}(x) \varphi_{N+2}(y) - \varphi_{N+1}(y) \varphi_{N+2}(x)).\end{aligned}$$

Therefore, for the same reason as above, this term is non-increasing under weak limits.

It follows that

$$\mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2}) \leqq \liminf \mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2})_n.$$

Thus φ is a minimum of the problem with relaxed constraints.

We closely follow the general scheme given in section II.

Let us first look at the second derivative of (3.9). The second derivative of the Hartree-Fock energy being well known, the only on standard term comes from

$$2\alpha\beta [D(\varphi_{N-1} \varphi_{N+1}, \varphi_N \ \varphi_{N+2}) - D(\varphi_{N-1} \varphi_{N+2}, \varphi_N \ \varphi_{N+1})].$$

In the analogue formula of (2.34), this term gives rise to the following contribution

$$2\,\alpha\beta\left[\sum_i a_{N-1,\,i}\,a_{N+1,\,i}\int \varphi_N\,\varphi_{N+2}+\sum_i a_{Ni}\,a_{N+2,\,i}\int \varphi_{N-1}\,\varphi_{N+1}\right.$$
$$-\sum_i a_{N-1,\,i}\,a_{N+2,\,i}\int \varphi_N\,\varphi_{N+1}$$
$$\left.-\sum_i a_{N-1,\,i}\,a_{N+2,\,i}\int \varphi_{N-1}\,\varphi_{N+2}\right]$$

where we still denote by $a_{ij}=\sqrt{1-M(\varphi)_{ij}}$. That is to say

$$4\,\alpha\beta\left[\int \varphi_{N-1}\,\varphi_{N+2}\int \varphi_N\,\varphi_{N+1}-\int \varphi_{N-1}\,\varphi_{N+1}\int \varphi_N\,\varphi_{N+2}\right].$$

Gathering with the terms coming from the Hartree-Fock energies, we obtain the particular form of (2.34):

$$Z \leqq (N-1) + \frac{4\,\alpha\beta\left\{\left[\int \varphi_{N-1}\,\varphi_{N+2}\int \varphi_N\,\varphi_{N+1} - \int \varphi_{N-1}\,\varphi_{N+1}\int \varphi_N\,\varphi_{N+2}\right]\right\}}{\left\{\sum_{1\leqq i\leqq N-2}\left(1-\int \varphi_i^2\right) + \alpha^2\left(2-\int \varphi_{N-1}^2-\int \varphi_N^2\right) + \beta^2\left(2-\int \varphi_{N+1}^2-\int \varphi_{N+2}^2\right)\right\}} \tag{3.12}$$

We claim that

$$\left|4\,\alpha\beta\left[\int \varphi_{N-1}\,\varphi_{N+2}\int \varphi_N\,\varphi_{N+1} - \int \varphi_{N-1}\,\varphi_{N+1}\int \varphi_N\,\varphi_{N+2}\right]\right| \leqq \alpha^2\left(2-\int \varphi_{N-1}^2-\int \varphi_N^2\right) + \beta^2\left(2-\int \varphi_{N+1}^2-\int \varphi_{N+2}^2\right). \tag{3.13}$$

Indeed, by Cauchy-Schwarz inequality we have

$$\begin{aligned}\left|\int \varphi_{N-1}\varphi_{N+2}\int \varphi_N\varphi_{N+1} - \int \varphi_{N-1}\varphi_{N+1}\int \varphi_N\varphi_{N+2}\right| \\ \leqq \left[\left(\int \varphi_{N-1}\varphi_{N+2}\right)^2 + \left(\int \varphi_{N-1}\varphi_{N+1}\right)^2\right]^{1/2} \\ \times \left[\left(\int \varphi_N\varphi_{N+1}\right)^2 + \left(\int \varphi_N\varphi_{N+2}\right)^2\right]^{1/2}.\end{aligned}$$

Using now (2.36), we obtain

$$\begin{aligned}&\left|\int \varphi_{N-1}\varphi_{N+2}\int \varphi_N\varphi_{N+1} - \int \varphi_{N-1}\varphi_{N+1}\int \varphi_N\varphi_{N+2}\right| \\ &\quad \leqq \frac{1}{2}\,\mathrm{MIN}\left(\left(2 - \int \varphi_{N-1}^2 - \int \varphi_N^2\right)\right. \\ &\quad \times \left(2 - \int \varphi_{N+1}^2 - \int \varphi_{N+2}^2\right), \\ &\quad \times \left.\left(\int \varphi_{N-1}^2 + \int \varphi_N^2\right)\left(\int \varphi_{N+1}^2 + \int \varphi_{N+2}^2\right)\right). \qquad (3.14)\end{aligned}$$

To obtain (3.13) from (3.14), we use the following technical lemma whose proof is postponed until the end of our argument.

LEMMA. – *Let* $\alpha > 0$, $\beta > 0$ *such that* $\alpha^2 + \beta^2 = 1$. *Then*

$$\begin{aligned}&\max_{0\leqq a\leqq 2,\, 0\leqq b\leqq 2} \mathrm{Min}\left(\frac{(2-a)(2-b)}{\alpha^2(2-a)+\beta^2(2-b)}, \frac{\mathrm{ab}}{\alpha^2(2-a)+\beta^2(2-b)}\right) \\ &\quad = \frac{2}{(\alpha+\beta)^2}.\end{aligned}$$

Applying the lemma above to $|\alpha|$, $|\beta|$, $= \int \varphi_{N-1}^2 + \int \varphi_N^2$, $b = \int \varphi_{N+1}^2 + \int \varphi_{N+2}^2$, and noticing that $\frac{2}{(|\alpha| + |\beta|)^2} \leqq \frac{1}{2|\alpha\beta|}$, we obtain (3.13).

It follows from (3.13) that (3.12) implies

$$
\begin{aligned}
Z \leqq &\ (N-1) \\
&+ \frac{\left\{ \begin{array}{l} \alpha^2 \left(2 - \int \varphi_{N-1}^2 - \int \varphi_N^2\right) \\ \quad + \beta^2 \left(2 - \int \varphi_{N+1}^2 - \int \varphi_{N+2}^2\right) \end{array} \right\}}{\left\{ \begin{array}{l} \sum_{1 \leqq i \leqq N-2} \left(1 - \int \varphi_i^2\right) \\ \quad + \alpha^2 \left(2 - \int \varphi_{N-1}^2 - \int \varphi_N^2\right) \\ \quad + \beta^2 \left(2 - \int \varphi_{N+1}^2 - \int \varphi_{N+2}^2\right) \end{array} \right\}} \\
\leqq &\ N - 1 + 1 = N
\end{aligned}
\tag{3.15}
$$

and, as soon as $Z > N$, we obtain a contradiction.

Actually, we can do a little better, because if $Z = N$ we also reach a contradiction.

Indeed, in this case, (3.15) implies $\int \varphi_i^2 = 1$ for all $1 \leqq i \leqq N - 2$. Moreover, (3.13) and (3.14) are equalities and one can see that this can only occur if the φ_i, $N-1 \leqq i \leqq N+2$ are colinear (case of equality in Cauchy-Schwarz inequalities), and this leads first to $\varphi_{N-1} = \varphi_N = \varphi_{N+1} = \varphi_{N+2}$ and then to $\int \varphi_i^2 = 1$ for all i, which cannot hold.

To conclude the proof of (i), there remains to prove the lemma above.

Since $(2 - a)(2 - b) \leqq ab$ for $a + b \geqq 2$, we have

$$
\text{Min} = \begin{cases} \dfrac{(2-a)(2-b)}{\alpha^2 (2-a) + \beta^2 (2-b)}, & \text{for} \quad a + b \geqq 2; \\[2ex] \dfrac{ab}{\alpha^2 (2-a) + \beta^2 (2-b)}, & \text{for} \quad a + b \leqq 2. \end{cases}
$$

Now, it is straighforward to see that

$$
\max_{a \leqq 2,\, b \leqq 2,\, a+b \geqq 2} \frac{(2-a)(2-b)}{\alpha^2 (2-a) + \beta^2 (2-b)} = \frac{2}{(\alpha + \beta)^2}
$$

and

$$\max_{0 \leqq a,\, 0 \leqq b,\, a+b \leqq 2} \frac{ab}{\alpha^2 (2-a) + \beta^2 (2-b)} = \frac{2}{(\alpha+\beta)^2}.$$

And one can remark that the equality only occurs on the line $a + b = 2$.

(ii) Let $(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2})_n$ be a minimizing sequence of the global problem.

It is clear that we may assume without loss of generality that α_n and β_n converge to some α, β such that $\alpha^2 + \beta^2 = 1$. Proving that neither α nor β vanishes amounts to proving (ii).

We argue by contradiction and assume that, for instance, $\beta = 0$ and $\alpha = 1$.

(3.11) shows that the sequences $\alpha_n \varphi_{i,n}$ $(1 \leqq i \leqq N)$, and $\beta_n \varphi_{i,n}$ $(1 \leqq i \leqq N-2,\ i = N+1,\ i = N+2)$ are bounded, thus weakly convergent in H^1. It follows that $\varphi_{i,n}$ weakly converges to φ_i for $1 \leqq i \leqq N$, and $\beta_n \varphi_{i,n}$ weakly converges to 0 for $i = N+1,\ N+2$ (because, for such i, $\beta^2 \int \varphi_i^2 \leqq \liminf \beta_n^2 \int \varphi_{i,n}^2 \leqq \liminf \beta_n^2 = 0$).

We are going to see, passing to the weak limit in (3.9), that this implies

$$I_{HF} \leqq \liminf \mathcal{E}(\alpha, \beta, \varphi_1, \cdots, \varphi_{N+2})_n = I \tag{3.16}$$

which contradicts (3.10). The point is to pass to the weak limit in the term

$$2\,\alpha\beta\,[D(\varphi_{N-1}\varphi_{N+1},\ \varphi_N\,\varphi_{N+2}) - D(\varphi_{N-1}\varphi_{N+2},\ \varphi_N\,\varphi_{N+1})]$$

because we do not know that $\varphi_{N+1,n}$ and $\varphi_{N+2,n}$ are weakly convergent. We argue as follows. We clearly have

$$\begin{aligned}
&\sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + \sum_{i=1}^{N} \int V\,|\varphi_i|^2 \\
&\qquad + \frac{1}{2} \sum_{i \neq j\ \&\ \{i,j\} \neq \{N-1,N\}} (D(\varphi_i^2,\ \varphi_j^2) - D(\varphi_i\varphi_j,\ \varphi_i\varphi_j)) \\
&\qquad \leqq \liminf \alpha_n^2 \Bigg[\sum_{i=1}^{N} \int |\nabla \varphi_{i,n}|^2 + \sum_{i=1}^{N} \int V |\varphi_{i,n}|^2 \\
&\qquad + \frac{1}{2} \sum_{i \neq j\ \&\ \{i,j\} \neq \{N-1,N\}} \\
&\qquad \times (D(\varphi_{i,n}^2,\ \varphi_{j,n}^2) - D(\varphi_{i,n}\varphi_{j,n},\ \varphi_{i,n}\varphi_{j,n})) \Bigg]
\end{aligned} \tag{3.17}$$

since $\varphi_{i,n}$ is weakly convergent for $1 \leqq i \leqq N$, and

$$0 = \leqq \liminf \beta_n^2 \left[\sum_{i=1}^{N-2} \int |\nabla \varphi_{i,n}|^2 + \sum_{i=1}^{N-2} \int V - 2\varphi_{i,n}|^2 \right.$$
$$+ \frac{1}{2} \sum_{i \neq j \,\&\, \{i,j\} \neq \{N+1, N+2\}}$$
$$\left. \times \left(D(\varphi_{i,n}^2, \varphi_{j,n}^2) - D(\varphi_{i,n}\varphi_{j,n}, \varphi_{i,n}\varphi_{j,n}) \right) \right] \tag{3.18}$$

because all the terms $D(\varphi_{i,n}^2, \varphi_{j,n}^2) - D(\varphi_{i,n}\varphi_{j,n}, \varphi_{i,n}\varphi_{j,n})$ are nonnegative. There remains to study the term

$$\alpha_n^2 [D(\varphi_{N-1,n}^2, \varphi_{N,n}^2) - D(\varphi_{N-1,n}\varphi_{N-1,n}, \varphi_{N,n})]$$
$$\beta_n^2 [D(\varphi_{N+1,n}^2, \varphi_{N+2,n}^2) - D(\varphi_{N+1,n}\varphi_{N+2,n}, \varphi_{N+1,n}\varphi_{N+2,n})]$$
$$+ 2\alpha_n \beta_n [D(\varphi_{N-1,n}\varphi_{N+1,n}, \varphi_{N,n}\varphi_{N+2,n})$$
$$- D(\varphi_{N-1,n}\varphi_{N+2,n}, \varphi_{N,n}\varphi_{N+1,n})].$$

We introduce

$$\psi_n = \frac{\alpha_n}{\sqrt{2}} (\varphi_{N-1,n}(x)\varphi_{N,n}(y) - \varphi_{N-1,n}(y)\varphi_{N,n}(y))$$
$$+ \frac{\beta_n}{\sqrt{2}} (\varphi_{N+1,n}(x)\varphi_{N+2,n}(y) - \varphi_{N+1,n}(y)\varphi_{N+2,n}(y))$$

and we claim it is weakly convergent in $H^1(\mathbf{R}^6)$. Indeed, the first term is easy, and, for the second, we remark that the sequences $\varphi_{N+1,n}$ and $\varphi_{N+2,n}$ are bounded in $L^2(\mathbf{R}^3)$ and $\beta_n \to 0$. Thus $\left\langle \frac{1}{|x-y|} \psi_n, \psi_n \right\rangle$ is nonincreasing under the weak limit. That is to say

$$[D(\varphi_{N-1}^2, \varphi_N^2) - D(\varphi_{N-1}\varphi_N, \varphi_{N-1}\varphi_N)] + 0 + 0$$
$$\leqq \liminf \alpha_n^2 [D(\varphi_{N-1,n}^2, \varphi_{N,n}^2) - D(\varphi_{N-1,n}\varphi_{N,n}, \varphi_{N-1,n}\varphi_{N,n})]$$
$$\times \beta_n^2 [D(\varphi_{N+1,n}^2 \varphi_{N+2,n}^2) - D(\varphi_{N+1,n}\varphi_{N+2,n}, \varphi_{N+1,n}\varphi_{N+2,n})]$$
$$+2\alpha_n \beta_n [D(\varphi_{N-1,n}\varphi_{N+1,n}, \varphi_{N,n}\varphi_{N+2,n})$$
$$-[D(\varphi_{N-1,n}\varphi_{N+2,n}, \varphi_{N,n}\varphi_{N+1,n}]. \tag{3.19}$$

Therefore, gathering (3.17), (3.18) and (3.19), we pass to the weak limit in (3.9) and we obtain (3.16).

This contradicts (3.10), thus neither α nor β vanishes. Therefore the sequence $(\varphi_1, \cdots, \varphi_{N+2})_n$ is actually a minimizing sequence of $I(\alpha, \beta)$ and we apply the result of (i). $\diamondsuit$

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