On the perturbation methods for some nonlinear Quantum Chemistry models.

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Abstract

The first purpose of this article is to give a sound mathematical foundation to perturbation methods for some nonlinear Quantum Chemistry models. This contributes to the understanding of computations on molecular systems *in situ*, such as solvated molecules or molecules subjected to a uniform external electric field. Our second purpose is to prove in the latter setting a result of non-existence of solutions to the Thomas-Fermi-Von Weizsäcker and to the Hartree-Fock equations, which is the nonlinear counterpart of a result by Avron and Herbst [2].

1 Introduction

The perturbation method is a standard tool in Quantum Mechanics. Its aim is to compute the eigenstates of a Hamiltonian $H_\alpha = H_0 + \alpha W$ from the knowledge of the eigenstates of a reference Hamiltonian H_0. For the reader's convenience, let us briefly describe this method.

Denote u_0 a normalized eigenvector of H_0, associated with the eigenvalue $-\epsilon_0$. Let us consider α as a real parameter. We are looking for two analytic functions $\epsilon(\alpha)$ and $u(\alpha)$ satisfying $\epsilon(0) = \epsilon_0$ and $u(0) = u_0$ and so that for all α, $u(\alpha)$ is a normalized eigenvector of H_α associated with the eigenvalue $-\epsilon(\alpha)$. By inserting the expansions $\epsilon(\alpha) = \sum \frac{\epsilon_k}{k!}\alpha^k$ and $u(\alpha) = \sum \frac{u_k}{k!}\alpha^k$ into the secular equation and the normalization condition $\int |u(\alpha)|^2 = 1$, we get

$$(RS_k) \left\{ \begin{array}{l} (H_0 + \epsilon_0) \cdot u_k = f_k \\ \int u_0^* u_k = a_k \end{array} \right.$$

where f_k and a_k only depend on $(u_j)_{0\leq j\leq k-1}$ and $(\epsilon_j)_{1\leq j\leq k-1}$. When the triangular system $(\mathcal{RS})$, defined as the union of the subsystems $(RS_k)_{k\geq 1}$, has a solution, we get two Taylor series $\sum \frac{\epsilon_k}{k!}X^k$ and $\sum \frac{u_k}{k!}X^k$. Those expansions are called Rayleigh-Schrödinger expansions and abbreviated in the sequel as (RSE). If the convergence radius of each serial is positive then for α small enough, $u(\alpha) = \sum \frac{u_k}{k!}\alpha^k$ is a normalized eigenvector of H_α associated with the eigenvalue $-\epsilon(\alpha) = -\sum \frac{\epsilon_k}{k!}\alpha^k$. In practice, only the first k terms of the expansion are computed, which gives an approximation of $u(\alpha)$ and $\epsilon(\alpha)$. This is called the k-order perturbation method.

The mathematical theory of the perturbation of linear operators, which underlies that method, has been deeply studied since the pioneering works by Rellich on regular perturbation theory [18]. We refer the reader to the reference textbooks [13] and [17].

The main interest of the perturbation method in the early days of Quantum Mechanics was to widely broaden the set of the quantum systems that could be analytically computed. In fact, only very few equations in Quantum Mechanics can be directly solved without resorting to computers. The relevance of the perturbation method in today's Quantum Chemistry is thus not obvious, since one could at first sight argue that, with a computer, the calculation of the eigenstates of the *perturbed* system is a priori neither easier nor more difficult than the calculation of the eigenstates of the *unperturbed* system. Nevertheless, the perturbation methods are still of great interest in Computational Quantum Chemistry. Let us give a few examples.

First, they are commonly used to improve the mean field approximation in the Hartree-Fock models: that is the purpose of Möller Plesset perturbation methods (see [9] for instance) that are implemented in the most widespread Quantum Chemistry calculation programs. We leave this application aside and focus on the following one.

Secondly, perturbation methods allow one to take into account the interactions of the system under consideration with different environments without running a self-consistent calculation for each environment. This method is for instance used in nonlinear optics to compute the response of the molecule to the excitation by an (oscillating) electric field: the so-called coefficients of polarizability of the n-th order are in fact the coefficients of the Taylor series describing the state of the perturbed system. As shown from a chemical and a numerical standpoint in [1], the use of the perturbation methods to study solvated molecules also seems to give satisfactory results.

We also point out that the "good" behavior of a model when it is subjected to a perturbation is a guarantee of stability with respect to numerical approximations.

The first purpose of this article is to give to such computations in a nonlinear setting a sound mathematical foundation.

In Section 2, we present the two nonlinear Quantum Chemistry models we will work on: the spinless real Hartree-Fock model (HF in short), and the Thomas-Fermi-Von-Weizsäcker model (TFW in short). Other models of Quantum Chemistry could be considered but those ones have been chosen for the following reasons: some basic mathematical properties of the former are already known [16], which will make our work easier; besides, this model is very close to other types of Hartree-Fock models commonly used in Computational Chemistry at the present time; the latter is more academic, but it belongs to an important class of models, which, them, are of general use, namely the density functional theory type models (DFT-type models in short), and the present work can be seen as a first step towards their study. We will see how to extend those models to situations when the molecule is no more isolated, but interacts with its environment. For each of the above two models, we will consider the following two environments:

- a solvated molecule,
- a molecule in an external electric field,

both situations being very important as far as the applications are concerned.

For the sake of simplicity, we will treat these two applications separately, but it is possible to study likewise a solvated molecule subjected to an electric field.

In Sections 3, 4 and 5, we study the mathematical foundations of the perturbation method for the HF and the TFW models.

In Section 3, we investigate the case of a so-called regular perturbation of the HF model, a notion that will be made precise there, but that we now define somewhat vaguely as a perturbation which does not modify the domain of definition of the energy functional. In particular, one of the main features of such a perturbation is that its effect decreases fast enough at infinity. Under some assumptions on the local behavior of the unperturbed energy functional in the neighbourhood of the reference state, we prove that RSE can be built at an unperturbed ground state, and that the so-obtained series have positive convergence radii. For this purpose, we use an analytic version of the implicit function theorem.

For the TFW model, considered in Section 4, this method does not allow to conclude because of a lack of analyticity, and we have to show by hand that the RSE are still well defined at the unperturbed ground state. We leave open the questions of convergence of these RSE.

In Section 5, we study a case of a non-regular perturbation, which is very important in practice: the molecule is subjected to a *uniform* external electric field. Again, both the HF and TFW models are studied in this setting. We show in Section 5.1, that RSE are still well defined by a triangular system similar to $(\mathcal{RS})$, but that these expansions are divergent. We obtain the latest point as a corollary of a result

(see the details in Section 5.2) of non-existence of non-trivial solutions to the TFW and HF equations in presence of a uniform external electric field.

This result of non-existence is the second purpose of the present article. It is actually related to the general question of the existence of bound states for Schrödinger operators with potentials that do not vanish at infinity (see Section 5.2.4). It is in particular the nonlinear equivalent of the result of non-existence of bound states for some linear Stark Hamiltonian ([2] and [11]). Our proof mimics the proof of [2].

We conclude this article by some comments on the computations of "Hartree-Fock ground states" of a molecular system subjected to a uniform external electric field, offered by some Quantum Calculation programs.

No attempt will be made here to extend the concept of resonance, which, in the linear case, allows to draw information from the (divergent) Rayleigh-Schrödinger series. We will however give some accesses to the vaste literature devoted to the (linear) resonance theory.

2 Presentation of the models

Let us start from the N-body Hamiltonian

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

which describes the electronic state of an isolated molecule with M nuclei and N electrons, when we follow the Born-Oppenheimer approximation of fixed nuclei and when we neglect the spin terms (all physical constant are set to one). The potential

$$V(x) = -\sum_{k=1}^{M} \frac{z_k}{|x - \overline{x}_k|} \tag{2.1}$$

is here the electrostatic potential created by the point nuclei (z_k is the atomic number of the k-th nucleus and $\overline{x}_k$ its position). The operator H acts on $\mathcal{A} = L^2_a\left((\mathbb{R}^3 \times \{|+\rangle, |-\rangle\})^N, \mathbb{C}\right)$, the vector space of quadratically integrable functions of $(3+1) \times N$ variables of space and spin (3 space real variables and 1 spin boolean variable for each electron), totally antisymetric under exchange of two (space and spin) electron coordinates.

Let us now explain how to take into account the presence of an external electric field or the solvent effect in the solvated case.

It is easy to model the presence of an external electric field: we just have to add its electrostatic potential W_{ef} to the Hamiltonian H,

$$H_{ef} = H + W_{ef}, \tag{2.2}$$

the subscript ef standing for electric field.

On the other hand, the solvated case is more difficult: a precise description of a solvated molecule requires in principle a quantum treatment of each solvent molecule. We would then get an electronic Hamiltonian that would act on much too large a space for the computational means that are available at the present time. Among all the reasonable approaches, one consists in taking into account only the solvent molecules that are located in the neighbourhood of the solute. But that method quickly reaches its limits: the number of nearby solvent molecules fastly increases with the number of atoms of the solute molecule. An alternative approach, much more economic in terms of computational memory and CPU time, consists in replacing the solvent molecules with a continuous dielectric, which covers the entire space but a cavity corresponding to the volume occupied by the solute molecule. This model is called the Polarizable Continuum Model (PCM in short). We refer the reader to an overview of such methods by J. Tomasi and M. Persico [20].

Let us rewrite the electronic Hamiltonian when taking the dielectric medium into account

$$H_s = -\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} V_s(x_i) + \sum_{1\leq i<j\leq N} G_s(x_i, x_j)$$

with

$$V_s(x) = -\sum_{k=1}^{M} G_s(x, \overline{x}_k),$$

where G_s is the Green function on $\mathbb{R}^3$ of the operator $[-\frac{1}{4\pi}\mathrm{div}(\epsilon(x)\nabla\cdot)]$ ($\epsilon(x)$ being the value at x of the dielectric constant and the subscript s standing for solvation). In the traditional versions of PCM, $\epsilon(x)$ is set to one inside the cavity and $\epsilon(x) = \epsilon_s > 1$ outside, ϵ_s being the dielectric constant of the solvent. Here, in order to avoid some technicalities, we assume that $\epsilon(x)$ is a smooth function, everywhere greater than or equal to 1, and constant ($= \epsilon_s > 1$) out of a ball. Other cases of $\epsilon(x)$ including discontinuity surfaces and anisotropies will be studied elsewhere [7]. Under those assumptions, one can easily see that

$$G_s(x, y) = \frac{1}{\epsilon(y)|x-y|} + g_s(x, y), \tag{2.3}$$

where $g_s \in C^0(\mathbb{R}^3\times\mathbb{R}^3)\cap C^\infty((\mathbb{R}^3\times\mathbb{R}^3)\backslash\Delta)\cap L^\infty(\mathbb{R}^3\times\mathbb{R}^3)$ and $\Delta = \left\{(x, x)\ ,\ x \in \mathbb{R}^3\right\}$,

$$\forall y \in \mathbb{R}^3 \qquad G_s(x,y) \underset{x \to \infty}{\sim} \frac{1}{\epsilon_s |x|}, \tag{2.4}$$

$$\forall (x,y) \in (\mathbb{R}^3 \times \mathbb{R}^3) \setminus \Delta \qquad G_s(x,y) = G_s(y,x) > 0. \tag{2.5}$$

In order to emphasize the fact that we consider this model of a solvated molecule as a perturbation of the standard model for a molecule, we write

$$H_s = H + W_{rf}, \tag{2.6}$$

where

$$W_{rf} = \sum_{i=1}^{N} V_{rf}(x_i) + \sum_{1 \le i < j \le N} G_{rf}(x_i, x_j),$$

with

$$V_{rf} = V_s - V$$

and

$$G_{rf}(x,y) = G_s(x,y) - G(x,y),$$

$G(x,y) = \frac{1}{|x-y|}$ being the Green function on $\mathbb{R}^3$ of the operator $[-\frac{1}{4\pi}\Delta]$ (the subscript rf stands for reaction field).

In both cases (2.2) and (2.6), the perturbed Hamiltonian is of the form

$$H_1 = H + W.$$

In order to compute its ground state with a perturbation method, we introduce a real parameter λ and embed H and H_1 into the family of Hamiltonians

$$H_\lambda = H + \lambda W.$$

Remark 1. When the pertubation is an external electric field, letting λ increase from 0 to 1 has a physical counterpart: it means that we increase the voltage inside of the capacitor that creates the field. □

Remark 2. In both cases (2.2) and (2.6), the Hamiltonian H_1 maps the real valued functions of $\mathcal{A}$ on real valued distributions. Therefore, without lost of generality, we may choose a real valued ground state. □

2.1 The spinless real Hartree-Fock model

Minimizing the energy $\langle\psi, H\psi\rangle$ over the manifold $\left\{\psi \in \mathcal{A} \quad / \quad \int |\psi|^2 = 1\right\}$ is only possible in practice for the simplest chemical systems, such as H_2, He or H_2^-. A standard way for dealing with such minimization problems is to look for the minimum of the energy $\langle\psi, H\psi\rangle$ over a subset of $\mathcal{A}$. If the subset is large enough, it is reasonable to think that we will obtain a good approximation of the solution of the original minimization problem. When the subset of $\mathcal{A}$ is chosen as a set of Slater determinants ($\frac{1}{\sqrt{N!}}\det(\phi_i(x_j))$ of N mono-electronic functions (or as a set of finite sums of such determinants in some improvements of this basic idea), the minimization problem is set over much smaller a space (but large enough to keep a physical meaning), but has lost its quadratic nature. These new minimization problems are said to be of the Hartree-Fock type. A review of such models can be found in [9].

We now introduce one of them, on which we will work in the following sections, namely the spinless real Hartree-Fock model.

The spinless Hartree-Fock approximation consists in minimizing $\langle\psi, H\psi\rangle$ over the subset of $\mathcal{A}$ of which the elements read as a Slater determinant of N functions ψ_i on $(\mathbb{R}^3 \times \{|+\rangle, |-\rangle\})$, chosen so that $\forall 1 \leq n \leq N$, $\forall x \in \mathbb{R}^3$,

$$\left\{ \begin{array}{l} \psi_n(x, |+\rangle) = \phi_n(x) \\ \psi_n(x, |-\rangle) = 0 \end{array} \right.$$

with $\forall 1 \leq i, j \leq N$, $\phi_i \in H^1(\mathbb{R}^3)$ and $\int_{\mathbb{R}^3} \phi_i \phi_j^* = \delta_{ij}$. In other words, it forces the N electrons to be in the same spin state. This is of course quite irrelevant from a physical point of view, but the so-obtained model is nevertheless formally very close to the Restricted Hartree-Fock model (see [9]), which, him, is perfectly relevant and commonly used in practice.

Indeed, we come to the following minimization problem

$$\inf \left\{ E^{HF}(\phi) \ , \quad \phi_i \in H^1(\mathbb{R}^3, \mathbb{C}) \quad \int_{\mathbb{R}^3} \phi_{\rm i} \phi_{\rm j}^* = \delta_{\rm ij} \right\}$$

with

$$E^{HF}(\phi) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} V\rho + \frac{1}{2} \sum_{i,j=1}^{N} \left[D(|\phi_i|^2, |\phi_j|^2) - D(\phi_i \phi_j^*, \phi_i^* \phi_j) \right] \quad (2.7)$$

where $\rho = \sum_{i=1}^{N} |\phi_i|^2$ is the total electronic density, and $D(u, v)$ denotes the integral $\int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{u(x)\, v(y)}{|x-y|}\, dx\, dy$. See [9] for instance for the derivation of (2.7).

For technical reasons, we restrict ourselves to real valued ϕ_i. Since we have seen in Remark 2 that the ground state could be chosen real valued, this additional restriction is more natural than that on the spin dependence. Finally we obtain the spinless real Hartree-Fock minimization problem

$$\inf \left\{ E^{HF}(\phi) \ , \quad \phi \in \mathcal{B}^{HF} \right\}$$

with

$$\mathcal{B}^{HF} = \left\{ (\phi_i)_{1 \leq i \leq N} \quad / \quad \phi_i \in H^1(\mathbb{R}^3, \mathbb{R}) \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}.$$

Some existence results are known for this model, in particular for the neutral system (see [16] for instance). To our knowledge, no rigorous result of uniqueness (up to an ortogonal transform) of the ground state has been proved for any Hartree-Fock type model.

Perturbation of the spinless real Hartree-Fock model

A perturbation λW of the N-body Hamiltonian gives rise to an additional term $\lambda \mathcal{W}$ in the HF energy functional. We can easily compute its expression for the two cases we are interested in. In the case of a pertubation by an external electric field, the functional $\mathcal{W}(\phi)$ reads

$$\mathcal{W}_{ef}(\phi) = \int_{\mathbb{R}^3} (\sum_{i=1}^{N} \phi_i^2) \, W_{ef} \, = \int_{\mathbb{R}^3} \rho \, W_{ef}.$$

For a solvated molecule described by PCM, the functional $\mathcal{W}(\phi)$ consists of two terms: a quadratic term corresponding to the modification of the nuclei-electrons interaction

$$\mathcal{W}_{rf}^1(\phi) = \int_{\mathbb{R}^3} (\sum_{i=1}^{N} \phi_i^2) \, V_{rf} \, = \int_{\mathbb{R}^3} \rho \, V_{rf},$$

and a term of the fourth order in the ϕ_i, coming from the modification of the electron-electron interaction

$$\mathcal{W}_{rf}^2(\phi) = \frac{1}{2} \sum_{i,j=1}^{N} D_{rf}(\phi_i^2, \phi_j^2) - \frac{1}{2} \sum_{i,j=1}^{N} D_{rf}(\phi_i \phi_j, \phi_i \phi_j)$$

with $D_{rf}(u,v) = \int_{\mathbb{R}^3 \times \mathbb{R}^3} G_{rf}(x,y) \, u(x) \, v(y) \ dx \, dy$. Notice that in most of the practical calculations, the solvant effect is not taken into account in the exchange energy (ie the second term in the above expression is neglected).

The minimization problem then reads

$$\inf\left\{E_\lambda^{HF}(\phi)\ ,\quad \phi\in\mathcal{B}^{HF}\right\}$$

with

$$E_\lambda^{HF}(\phi)=E^{HF}(\phi)+\lambda\mathcal{W}(\phi).$$

2.2 The Thomas-Fermi-Von Weizsäcker model

We also establish some results concerning the TFW model, in the following sections. This model is a primitive version of the DFT-type models, often used at present time in Quantum Chemistry calculations [8]. The TFW energy reads

$$\overline{E}^{TFW}(\rho)=\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}|^2+\int_{\mathbb{R}^3}V\rho+\frac{3}{5}c_1\int_{\mathbb{R}^3}\rho^{5/3}+\frac{1}{2}D(\rho,\rho),$$

the real constant c_1 being non-negative (the case $c_1=0$ gives the so-called Restricted Hartree model). The density ρ satisfies $\rho\geq 0$, $\int_{\mathbb{R}^3}\rho=N$, and we require that $\sqrt{\rho}\in H^1(\mathbb{R}^3)$ so as the expression above is well defined. It is convenient to express this energy as a function of the square root u of the density ρ. Denote

$$E^{TFW}(u)=\int_{\mathbb{R}^3}|\nabla u|^2+\int_{\mathbb{R}^3}Vu^2+\frac{3}{5}c_1\int_{\mathbb{R}^3}|u|^{10/3}+\frac{1}{2}D(u^2,u^2).$$

Then, E^{TFW} satisfies: $\forall u\in H^1(\mathbb{R}^3)$, $E^{TFW}(u)=E^{TFW}(|u|)=\overline{E}^{TFW}(\rho)$ if $\rho=u^2$.

To find the ground state, we have to compute

$$\inf\left\{E^{TFW}(u),\quad u\in\mathcal{B}^{TFW}\right\}\tag{2.8}$$

where $\mathcal{B}^{TFW}=\left\{u\in H^1(\mathbb{R}^3)\ /\ \int_{\mathbb{R}^3}u^2=N\right\}$. From now on, we assume that in the TFW case, $N\leq\sum z_k$, that is to say that the molecular system is neutral or positively charged. E.H. Lieb has proved that in this case the minimization problem (2.8) has a solution, and that all solutions give the same value for ρ (for the functional $\overline{E}^{TFW}$ is strictly convex with respect to ρ). In particular, (2.8) has a unique non-negative minimizer.

If we perturbate the isolated molecule by tuning on an electric field or by solvating the molecule, its TFW energy reads

$$\overline{E}_\lambda^{TFW}(\rho)=\overline{E}^{TFW}(\rho)+\lambda\overline{\mathcal{W}}(\rho),$$

or, as a function of $u=\sqrt{\rho}$

$$E_\lambda^{TFW}(u) = E^{TFW}(u) + \lambda \mathcal{W}(u).$$

If the perturbation is an external electric field, of potential denoted by W_{ef}, we obtain

$$\mathcal{W}_{ef}(u) = \int_{\mathbb{R}^3} W_{ef}\, u^2 = \int_{\mathbb{R}^3} \rho W_{ef} = \overline{\mathcal{W}}_{ef}(\rho).$$

In the PCM case, the perturbation functional reads

$$\mathcal{W}_{rf}(u) = \int_{\mathbb{R}^3} V_{rf} u^2 + \frac{1}{2} D_{rf}(u^2, u^2) = \int_{\mathbb{R}^3} \rho V_{rf} + \frac{1}{2} D_{rf}(\rho, \rho) = \overline{\mathcal{W}}_{rf}(\rho).$$

We will use in the following the differential $\mathcal{W}'(u)$ of $\mathcal{W}$ at u, which we will identify with an element of H^{-1}, and the second derivative $\mathcal{W}''(u)$ of $\mathcal{W}$ at u, which we will identify with a linear operator mapping H^1 on H^{-1}.

Remark 3. In a more sophisticated DFT-type model taking some exchange terms into account, the term $D_{rf}(u^2, u^2)$ could be replaced by a functional having a more complicated dependence on u. □

3 Regular perturbations of the HF model

In this Section, we only consider some special perturbations of the energy functional that we call regular in the following sense. Denote $D(\mathcal{W})$ the domain of definition of the fonctional $\mathcal{W}$. We say that the perturbation $\mathcal{W}$ of the energy functional E^{HF} is **regular** if

- $(H^1(\mathbb{R}^3, \mathbb{R}))^N \subset D(\mathcal{W})$;
- $\mathcal{W} : (H^1(\mathbb{R}^3, \mathbb{R}))^N \to \mathbb{R}$ has an analytic continuation in $(H^1(\mathbb{R}^3, \mathbb{C}))^N$.

The first condition is essential: it guarantees that the perturbed energy functional is well defined on $\mathcal{B}^{HF}$. The second one is more technical; it is sufficient for our strategy of proof but is not optimal.

Using (2.3) and Hardy inequality, one easily check that the first condition is satisfied for PCM. The second one is also satisfied: $\mathcal{W}_{rf}$ is polynomial with respect to the real functions ϕ_i and its successive derivatives have the required regularity. The perturbation $\mathcal{W}_{rf}$ is therefore regular.

A perturbation by an external electric field of potential W_{ef} so that

$$h \mapsto W_{ef} h \quad \text{is continuous from } H^1(\mathbb{R}^3) \text{ into } H^{-1}(\mathbb{R}^3) \tag{3.9}$$

is clearly regular. This condition is fullfilled for instance if $W_{ef} \in L^\infty$ or if W_{ef} is created by a finite density of charge which has compact support (which is sometimes the case in applied calculations).

On the contrary, a perturbation by a uniform electric field of potential $W_{ef}(x) = (e \cdot x)$ (for some given vector $e \neq 0$ of $\mathbb{R}^3$) is not regular. Indeed, let us consider for example $h(x) = \frac{1}{1+|x|^2}$; $h \in H^1(\mathbb{R}^3)$ but $\int_{\mathbb{R}^3} |(e \cdot x)||h|^2 = +\infty$, which contradicts the condition $(H^1(\mathbb{R}^3, \mathbb{R}))^N \in D(\mathcal{W})$. Section 5 is devoted to the study of this perturbation.

Unless otherwise stated, $\mathcal{W}$ will denote in this section any potential satisfying the two above conditions, in particular $\mathcal{W}_{rf}$ or $\mathcal{W}_{ef}$ with (3.9).

We now consider a minimum ϕ of the unperturbed HF energy functional (2.7)

$$E^{HF}(\phi) = \inf \left\{ E^{HF}(\psi) \ , \quad \psi \in \mathcal{B}^{HF} \right\}. \tag{3.10}$$

Our purpose is to prove that, under some assumptions on the local properties of the energy in the neighbourhood of the minimum ϕ, it is possible to perform a perturbative treatment of any regular perturbation, which in particular gives a sound footing to practical calculations like those in [1]. We mean that the same approach as in the linear case (see Section 1) gives birth to a triangular system similar to $(\mathcal{RS})$, which has a unique solution. Moreover the so-obtained Taylor series have positive convergence radii.

We will prove this result by an application of an analytic version of the implicit function theorem.

Notice that this method does not give any estimation of the convergence radii. If the perturbation has a meaning for small λ, as in the external electric field case, we have nevertheless obtained a physical result: the existence of a solution for weak fields. Otherwise, as in the PCM setting, where only the case $\lambda = 1$ is physically interesting, the obtained mathematical result has no obvious physical counterpart (a direct study of the existence of a solution for the Hartree-Fock model in the PCM setting will be presented elsewhere [7]).

Let us now introduce and discuss the assumptions on the local properties of the energy in the neighbourhood of the minimum ϕ, that we need to prove our result.

We will first suppose that the ϕ_i are eigenvectors of the Fock operator $\mathcal{F}$ associated with the N smallest eigenvalues $-\epsilon_i$ of $\mathcal{F}$. It is always possible to come down to such a case through an orthogonal transform of the ϕ_i (see [9] for instance for more details). We recall

$$\mathcal{F} = -\Delta + V + (\rho \star \frac{1}{|x|}) - \int_{\mathbb{R}^3} \frac{\tau(x,y)}{|x-y|} \bullet (y)\, dy$$

with $\rho(x) = \sum_{i=1}^N \phi_i^2(x)$ et $\tau(x,y) = \sum_{i=1}^N \phi_i(x)\phi_i(y)$. The relations

$$\mathcal{F} \cdot \phi_i = -\epsilon_i \phi_i$$

are the Euler-Lagrange equations of the minimization problem (3.10).

The second-order condition at ϕ reads: for all $U = (u_i) \in (H^1(\mathbb{R}^3))^N$ so that $\int_{\mathbb{R}^3} \phi_i u_j + \phi_j u_i = 0$,

$$\langle U, \tilde{H}^{HF} U \rangle = \sum_{i=1}^N \int_{\mathbb{R}^3} u_i (\tilde{H}^{HF} U)_i \ \geq \ 0$$

with

$$\begin{aligned} (\tilde{H}^{HF} U)_i \quad &= \quad \mathcal{F} u_i + \epsilon_i u_i + 2 \sum_{j=1}^N \left(\phi_j u_j \star \frac{1}{|x|} \right) \phi_i \\ &\quad - \sum_{j=1}^N \left(\phi_i u_j \star \frac{1}{|x|} \right) \phi_j - \sum_{j=1}^N \left(\phi_i \phi_j \star \frac{1}{|x|} \right) u_j. \end{aligned}$$

Denote

$$\mathcal{N} = \left\{ U = \{u_i\}_{1 \leq i \leq N} \quad / \quad u_i \in H^1(\mathbb{R}^3) \quad \int_{\mathbb{R}^3} \phi_i u_j = 0 \quad \forall 1 \leq i,j \leq N \right\}.$$

We now assume that:

1. The N smallest eigenvalues of the Fock operator $\mathcal{F}$ are non-degenerate (ie $-\epsilon_1 < -\epsilon_2 < \cdots < -\epsilon_{N-1} < -\epsilon_N < 0$);
2. $\tilde{H}^{HF}$ is coercive on $\mathcal{N}$.

These two assumptions correspond to the isolated eigenvalue hypothesis introduced in the linear theory (cf Kato-Rellich Theorem, in [17] for instance), which is the foundation of the perturbation method in the non-degenerate case (see any Quantum Mechanics textbook, [14] for instance).

The origin of an eigenvalue degeneracy is often the invariance of the system under the action of a symmetry group. If the molecule does not exhibit any symmetry

(which is usually the case for a molecule consisting of several atoms), assumption 1 therefore seems reasonable.

Assumption 2 (of coercivity) means that ϕ is a strict local minimum of E^{HF} over $\mathcal{B}^{HF}$ up to an orthogonal transform of type (3.12) below.

As for the Unrestricted Hartree-Fock model considered in [3], one can prove that, if $-\epsilon_{N+1}$ denotes the $(N+1)$-th eigenvalue of $\mathcal{F}$, the inequality

$$-\epsilon_N < -\epsilon_{N+1} \tag{3.11}$$

is always satisfied. In reference to the title of [3], it means that "there are no unfilled shell" , or in other words that there is a gap in energy between the highest occupied level and the lowest unoccupied one, in the HF model we are interested in. Notice that (3.11) can also be deduced from assumption 2.

For any one-electron system, the spinless Hartree-Fock model comes down to the linear case. Indeed, in this case, the energy functional is quadratic on $H^1(\mathbb{R}^3)$ and reads

$$E^{HF}(u) = \int_{\mathbb{R}^3} |\nabla u|^2 + \int_{\mathbb{R}^3} V u^2.$$

It is easy to see that both assumptions 1 and 2 are satisfied for this functional at its ground state (which is known to be non-degenerate).

We now state Lemma 1 and Proposition 1, whose proofs are postponed until the end of this section.

Lemma 1. *Suppose that $\mathcal{F}$ and $\tilde{H}^{HF}$ satisfy the assumptions 1 and 2 above. Let $(f_i) \in (H^{-1}(\mathbb{R}^3, \mathbb{C}))^{\mathrm{N}}$ and $(\alpha_i) \in \mathbb{C}^{\mathrm{N}}$. The system*

$$(I) \quad \begin{cases} (\tilde{H}^{HF}U)_i + \mu_i \phi_i = f_i & 1 \le i \le N \\ \int_{\mathbf{R}^3} \phi_i u_i = \alpha_i & 1 \le i \le N \end{cases}$$

has a unique solution $(U = (u_i), (\mu_i))$ in $(H^1(\mathbb{R}^3, \mathbb{C}))^{\mathrm{N}} \times \mathbb{C}^{\mathrm{N}}$. Moreover if the (f_i) are real valued and the (α_i) are real, so are the (u_i) and the (μ_i). □

Proposition 1. *Under assumptions 1 and 2, there exists a range $I =]-\eta_{inf}, +\eta_{sup}[$, $\eta_{inf} > 0$ $\eta_{sup} > 0$ and a neighbourhood Ω of $((\phi_i), (\epsilon_i))$ in $(H^1(\mathbb{R}^3))^N \times \mathbb{R}^N$ so that the set of the solutions $(\lambda, (\psi_i), (\zeta_i))$ in $I \times \Omega$ of the equations*

$$\forall 1 \le i \le N \qquad \mathcal{F}_{(\psi_j)}\psi_i + \frac{\lambda}{2}\frac{\partial \mathcal{W}}{\partial \phi_i}((\psi_j)) + \zeta_i \psi_i = 0,$$

$\mathcal{F}_{(\psi_j)}$ being the Fock operator

$$\mathcal{F}_{(\psi_j)} = -\Delta + V + (\rho_{(\psi_j)} \star \frac{1}{|x|}) - \int_{\mathbb{R}^3} \frac{\tau_{(\psi_j)}(x,y)}{|x-y|} \bullet (y)\, dy$$

with $\rho_{(\psi_j)}(x) = \sum_{j=1}^N \psi_j^2(x)$ *and* $\tau_{(\psi_j)}(x,y) = \sum_{j=1}^N \psi_j(x)\psi_j(y)$, *is a one dimensional curve parameterized by* λ*:*

$$\begin{array}{rcl} I & \rightarrow & \Omega \\ \lambda & \mapsto & ((\phi_i(\lambda)), (\epsilon_i(\lambda))). \end{array}$$

Moreover $\phi_i(\lambda)$ *and* $\epsilon_i(\lambda)$ *are analytic real functions on* I *and verify for all* $1 \leq i \leq N$, $\phi_i(0) = \phi_i$, $\epsilon_i(0) = \epsilon_i$. *In addition, for all* $\lambda \in I$, $\phi(\lambda) = (\phi_i(\lambda))$ *is a local minimum of the energy functional* E_λ^{HF} *operating on* $\mathcal{B}^{HF}$, *unique in a neighbourhood of* ϕ, *up to an orthogonal transform.* $\square$

Let us now expand $\phi_i(\lambda)$ and $\epsilon_i(\lambda)$ in Taylor series around $\lambda = 0$. By analogy with the linear framework, we will call these expansions **Rayleigh-Schrödinger Expansions**.

Denote $\phi_i^{(k)} = \frac{d^k \phi_i}{d\lambda^k}(0)$, $\epsilon_i^{(k)} = \frac{d^k \epsilon_i}{d\lambda^k}(0)$. For all $k \geq 1$, $((\phi_i^{(k)}), (\epsilon_i^{(k)}))$ is a solution of

$$(RS_k^{HF}) \left\{ \begin{array}{ll} (\tilde{H}^{HF}\phi^{(k)})_i + \epsilon_i^{(k)}\phi_i = f_i^{(k)} & 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i \phi_i^{(k)} = \alpha_i^{(k)} & 1 \leq i \leq N \end{array} \right.$$

with

$$f_i^{(k)} = -W_i^{(k)} - \sum_{l=1}^{k-1} \left(\begin{array}{c} k \\ l \end{array} \right) \epsilon_i^{(l)} \phi_i^{(k-l)}$$

$$-\sum_{j=1}^N \sum_{\substack{l_1+l_2+l_3=k \\ 0 \leq l_\nu \leq k-1}} \left(\frac{k!}{l_1! l_2! l_3!} \right) \left[(\phi_j^{(l_1)} \phi_j^{(l_2)} \star \frac{1}{|\mathbf{x}|})\, \phi_i^{(l_3)} - (\phi_i^{(l_1)} \phi_j^{(l_2)} \star \frac{1}{|\mathbf{x}|})\, \phi_j^{(l_3)} \right]$$

and

$$\alpha_i^{(k)} = -\frac{1}{2} \sum_{l=1}^{k-1} \left(\begin{array}{c} k \\ l \end{array} \right) \int_{\mathbb{R}^3} \phi_i^{(l)} \phi_i^{(k-l)}.$$

The term $W_i^{(k)}$ is made up of the coefficients of the terms in λ^{k-1} which arise in the Taylor expansion of $\frac{1}{2}\frac{\partial \mathcal{W}}{\partial \phi_i}(\phi(\lambda))$ and is thus a function of the $(\phi_i^{(l)})$, $1 \leq j \leq N$, $0 \leq l \leq k-1$. The right-hand members $f_i^{(k)}$ and $\alpha_i^{(k)}$ are functions of $((\phi_i^{(j)}),(\epsilon_i^{(j)}))_{0 \leq j \leq k-1}$. The knowledge of the $(k-1)$-order terms thus permits to determine the k-order terms $((\phi_i^{(k)}),(\epsilon_i^{(k)}))$ (in a unique way from Lemma 1). In the following, we will call **Rayleigh-Schrödinger System**, and note $(\mathcal{RS}^{HF})$ the triangular system defined as the union of the subsystems (RS_k^{HF}), $k \geq 1$. Lemma 1 and Proposition 1 show that $(\mathcal{RS}^{HF})$ has a unique solution and that the Taylor series built from the Rayleigh-Schrödinger expansions have positive convergence radii.

Let us now turn to the two applications we are interested in. In both cases, $\mathcal{W}$ is a polynomial, of the second and the fourth degree respectively. The expressions of $W_i^{(k)}$ have thus a simple form: $W_{ef,i}^{(k)} = kW_{ef}\phi_i^{(k-1)}$ and

$$\begin{aligned} W_{rf,i}^{(k)} &= kV_{rf}\phi_i^{(k-1)} \\ &+ \sum_{j=1}^{N} \sum_{\substack{l_1+l_2+l_3=k \\ 0 \leq l_\nu \leq k-1}} \left(\frac{k!}{l_1!l_2!l_3!}\right) \left[\int_{\mathbb{R}^3} G_{rf}(x,y)\phi_j^{(l_1)}(y)\phi_j^{(l_2)}(y)\,dy\right] \phi_i^{(l_3)} \\ &- \sum_{j=1}^{N} \sum_{\substack{l_1+l_2+l_3=k \\ 0 \leq l_\nu \leq k-1}} \left(\frac{k!}{l_1!l_2!l_3!}\right) \left[\int_{\mathbb{R}^3} G_{rf}(x,y)\phi_i^{(l_1)}(y)\phi_j^{(l_2)}(y)\,dy\right] \phi_j^{(l_3)}. \end{aligned}$$

Notice that in the PCM case as well as in the electric field case $\frac{\partial \mathcal{W}}{\partial \phi_i} = 2\Omega_\lambda \cdot \phi_i$. Therefore, the ϕ_i are eigenvectors of the operator $\mathcal{F}_\lambda + \lambda\Omega_\lambda$ (associated with the eigenvalues $-\epsilon_i(\lambda)$). In the electric field case, $\Omega_\lambda = W_{ef}$ (and is then besides independent from λ), and in the PCM case

$$\Omega_\lambda = V_{rf} + \left(\int_{\mathbb{R}^3} G_{rf}(x,y)\rho_\lambda(y)\,dy\right) - \int_{\mathbb{R}^3} G_{rf}(x,y)\tau_\lambda(x,y) \bullet (y)dy.$$

Before we turn to the proofs of Lemma 1 and Proposition 1, we need some elementary algebraic results.

Let us first notice that $\tilde{H}^{HF}$ is clearly self-adjoint. Denote $T_\phi\mathcal{B}^{HF}$ the tangent vector space at u to the submanifold $\mathcal{B}^{HF}$ of $(H^1(\mathbb{R}^3))^N$. We can write

$$T_\phi\mathcal{B}^{HF} = \left\{U = \{u_i\}_{1 \leq i \leq N} \quad / \quad u_i \in H^1(\mathbb{R}^3) \quad \int_{\mathbb{R}^3} \phi_i u_j + \phi_j u_i = 0\right\}.$$

With these notations, the second-order condition at the minimum ϕ of (3.10) reads:

$$\forall U \in T_\phi \mathcal{B}^{HF} \qquad \langle U, \tilde{H}^{HF} U \rangle \geq 0.$$

This quadratic form is degenerate on $T_\phi \mathcal{B}^{HF}$ according to the following invariance

$$\forall O \in O(N),\ \forall \psi \in \mathcal{B}^{HF}, \quad O\psi \in \mathcal{B}^{HF} \quad \text{and} \quad E^{HF}(O\psi) = E^{HF}(\psi) \tag{3.12}$$

where $O(N)$ is the set of orthogonal real $N \times N$ matrices. Denote $A(N)$, $S(N)$ and $S^*(N)$ the sets of the $N \times N$ matrices that are respectively antisymetric, symetric and symetric with their diagonal terms all equal to zero. We recall that $A(N)$ is the Lie Algebra of the group $O(N)$, and that $A(N)$, $S(N)$ and $S^*(N)$ are respectively $\frac{N(N-1)}{2}$, $\frac{N(N+1)}{2}$ and $\frac{N(N-1)}{2}$ dimensional vector subspaces of $\mathcal{M}_N(\mathbb{R})$.

We notice that

$$(H^1(\mathbb{R}^3))^N = S(N)\phi \oplus A(N)\phi \oplus \mathcal{N}, \tag{3.13}$$

$$T_\phi \mathcal{B}^{HF} = A(N)\phi \oplus \mathcal{N}. \tag{3.14}$$

Moreover, for $A = [a_{ij}] \in A(N)$, a straightforward calculation shows that

$$(\tilde{H}^{HF} \cdot A\phi)_i = \sum_{j=1}^{N} (\epsilon_j - \epsilon_i) a_{ij} \phi_j$$

from which we deduce

$$\tilde{H}^{HF}(A(N)\phi) \subset S^*(N)\phi \tag{3.15}$$

$$\langle \psi, \tilde{H}^{HF} A\phi \rangle = 0 \qquad \forall A \in A(N) \quad \forall \psi \in T_\phi \mathcal{B}^{HF} \tag{3.16}$$

and the inclusion in (3.15) is in fact an equality if assumption 1 of non-degeneracy of the N smallest eigenvalues of $\mathcal{F}$ is satisfied.

We can now write the

Proof of Lemma 1:

The (ϕ_i) are real valued and $\tilde{H}^{HF}$ maps real valued functions on real valued distributions. It is therefore possible to split problem (I) into two independent problems (I') and (I''), the former dealing with the real parts and the latter with the imaginary parts. We now come to prove that for (f_i) real valued and (α_i) real, system (I) has a unique solution.

Uniqueness: Let $((u_i),(\mu_i))$ and $((u'_i),(\mu'_i))$ be two solutions of (I) in $(H^1(\mathbb{R}^3,\mathbb{R}))^N \times \mathbb{R}^N$, and $V=(v_i)=(u'_i-u_i)$, $(\nu_i)=(\mu'_i-\mu_i)$. We have

$$\begin{cases} (\tilde{H}^{HF}V)_i + \nu_i\phi_i = 0 & 1\le i\le N \\ \int_{\mathbb{R}^3}\phi_i v_i = 0 & 1\le i\le N. \end{cases}$$

We split up V in accordance with (3.13):

$$V = S\phi + A\phi + V'$$

with $S=[s_{ij}]\in S(N)$, $A=[a_{ij}]\in A(N)$, $V'=(v'_i)\in\mathcal{N}$. Conditions $\int_{\mathbb{R}^3}\phi_i v_i=0$ mean that $S\in S^*(N)$. Let $A'=[a'_{ij}]\in A(N)$.

On the one hand

$$\langle A'\phi, \tilde{H}^{HF}V\rangle = -\sum_{i=1}^N \int_{\mathbb{R}^3}\left(\sum_{j=1}^N a'_{ij}\phi_j\right)\nu_i\phi_i = 0$$

while on the other hand, using (3.14) and (3.16),

$$\begin{aligned} \langle A'\phi, \tilde{H}^{HF}V\rangle &= \langle \tilde{H}^{HF}A'\phi, V\rangle \\ &= \langle \tilde{H}^{HF}A'\phi, S\phi\rangle + \langle \tilde{H}^{HF}A'\phi, A\phi+V'\rangle \\ &= \langle \tilde{H}^{HF}A'\phi, S\phi\rangle \\ &= \sum_{i=1}^N \int_{\mathbb{R}^3}\left(\sum_{j=1}^N a'_{ij}(\epsilon_i-\epsilon_j)\phi_j\right)\left(\sum_{j=1}^N s_{ij}\phi_j\right) \\ &= \sum_{i=1}^N\sum_{j=1}^N (\epsilon_i-\epsilon_j)a'_{ij}s_{ij}. \end{aligned}$$

Using assumption 1 and letting A' varying in $A(N)$, we easily show that $s_{ij}=0$, $\forall i\neq j$. Therefore $S=0$ since we already know that $S\in S^*(N)$. Therefore $V=A\phi+V'\in T_\phi\mathcal{B}^{HF}$.

$$\langle \tilde{H}^{HF}V, V\rangle = -\sum_{i=1}^N\int_{\mathbb{R}^3}\left(\sum_{j=1}^N a_{ij}\phi_j + v'_i\right)\nu_i\phi_i = 0.$$

But $\langle \tilde{H}^{HF}V, V\rangle = \langle \tilde{H}^{HF}V', V'\rangle$ according to (3.16). Thus $\langle \tilde{H}^{HF}V', V'\rangle = 0$, and $V'=0$ since $\tilde{H}^{HF}$ is coercive on $\mathcal{N}$ (assumption 2). Therefore $V=A\phi$ and

$$(\tilde{H}^{HF}V)_i = \sum_{j=1}^{N} a_{ij}(\epsilon_i - \epsilon_j)\phi_j = -\nu_i\phi_i.$$

Thus $\nu_i = 0$ and $a_{ij} = 0$ for all i, j. Finaly $V = 0$, and uniqueness is proved.

Existence: Let $S = [s_{ij}] \in S(N)$ defined by

$$\begin{cases} s_{ii} = \alpha_i & 1 \leq i \leq N \\ s_{ij} = \frac{\langle \phi_i, f_j \rangle - \langle \phi_j, f_i \rangle}{\epsilon_j - \epsilon_i} & 1 \leq i, j \leq N \quad i \neq j. \end{cases}$$

Denote $f' = (f'_i) = (f_i - (\tilde{H}^{HF}S\phi)_i)$. After a straightforward calculation, we obtain

$$\begin{aligned} \langle \phi_j, f'_i \rangle &= \frac{\langle \phi_i, f_j \rangle + \langle \phi_j, f_i \rangle}{2} \\ &\quad - \sum_{k,l=1}^{N} s_{kl} \left[2D(\phi_k\phi_l, \phi_i\phi_j) - D(\phi_i\phi_l, \phi_k\phi_j) - D(\phi_k\phi_i, \phi_l\phi_j) \right]. \end{aligned}$$

Thus, in particular

$$\forall i, j \qquad \langle \phi_j, f'_i \rangle = \langle \phi_i, f'_j \rangle.$$

The self-adjoint operator $\tilde{H}^{HF}$ being coercive on $\mathcal{N}$, the minimization problem

$$\inf_{\psi \in \mathcal{N}} (\langle \tilde{H}^{HF}\psi, \psi \rangle - \langle f', \psi \rangle)$$

has a (unique) solution $U' = (u'_i) \in \mathcal{N}$, and this solution satisfies

$$\begin{cases} (\tilde{H}^{HF}U')_i + \sum_{j=1}^{N} \lambda_{ij}\phi_j = f'_i & 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i u'_j = 0 & 1 \leq i, j \leq N. \end{cases}$$

Let $A' \in A(N)$. As $U' \in \mathcal{N} \subset T_\phi \mathcal{B}^{HF}$, $\langle A'\phi, \tilde{H}^{HF}U' \rangle = 0$. By exploiting the symmetry of the terms $\langle \phi_j, f'_i \rangle$, we get on the other hand

$$\begin{aligned} \langle A'\phi, \tilde{H}^{HF}U' \rangle &= \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\sum_{j=1}^{N} \lambda_{ij}\phi_j + f'_i \right) \left(\sum_{j=1}^{N} a'_{ij}\phi_j \right) \\ &= \sum_{i,j=1}^{N} \lambda_{ij} a'_{ij} \end{aligned}$$

and, with suitable choices of A', we come to $\lambda_{ij} = \lambda_{ji}$, for all (i,j). Denote $\mu_i = \lambda_{ii}$, $a_{ii} = 0$ and $a_{ij} = \frac{\lambda ij}{\epsilon_i - \epsilon_j}$ for $i \neq j$. $A = [a_{ij}] \in A(N)$ and $(\tilde{H}^{HF} A\phi)_i = \sum_{j=1}^N \lambda_{ij}\phi_j$. Let $U = S\phi + A\phi + U'$. We see that $(U, (\mu_i))$ is a solution of (I), which concludes the proof of Lemma 1. $\Box$

We conclude this section with the

Proof of Proposition 1:

In this proof, H^1 and H^{-1} are complex valued distributions. Since $\mathcal{W}$ is regular, $\frac{\partial \mathcal{W}}{\partial \phi_i}$ has an analytic continuation in H^1 (still denoted $\frac{\partial \mathcal{W}}{\partial \phi_i}$) and

$$\begin{array}{rccl} \Phi : & \mathbb{C} \times ((\mathrm{H}^1)^{\mathrm{N}} \times \mathbb{C}^{\mathrm{N}}) & \to & ((H^{-1})^N \times \mathbb{C}^{\mathrm{N}}) \\ & (\lambda, (u_i), (\mu_i)) & \mapsto & \left((\mathcal{F}_{(u_j)} \cdot u_i + \frac{\lambda}{2} \frac{\partial \mathcal{W}}{\partial \phi_i}((u_j)) + \mu_i u_i), (\int_{\mathbb{R}^3} u_i^2 - 1) \right) \end{array}$$

with

$$\mathcal{F}_{(u_j)} \cdot v = -\Delta v + Vv + \sum_{j=1}^N (u_j^2 \star \frac{1}{|x|})v - \sum_{j=1}^N (u_j v \star \frac{1}{|x|})u_j$$

is well defined and analytic and if $c = (0, (\phi_i), (\epsilon_i))$, we have $\Phi(c) = 0$. Besides,

$$d_{(0,(\phi_i),(\epsilon_i))}\Phi \cdot (0, (u_i), (\mu_i)) = \left(((\tilde{H}^{HF} U)_i + \mu_i \phi_i), (\int_{\mathbb{R}^3} \phi_i u_i) \right).$$

Thus, from Lemma 1, $d\Phi|_{\{0\} \times (H^1)^N \times \mathbb{C}^{\mathrm{N}}}$ is an isomorphism from $\{0\} \times (H^1)^N \times \mathbb{C}^{\mathrm{N}}$ on $(H^{-1})^N \times \mathbb{C}^{\mathrm{N}}$.

We may now apply the implicit function theorem (analytic version): there exist a neighbourhood ω of 0 in $\mathbb{C}$, a neighbourhood Ω of $((\phi_i), (\epsilon_i))$ in $(H^1(\mathbb{R}^3, \mathbb{C}))^{\mathrm{N}} \times \mathbb{R}^{\mathrm{N}}$ and $2\,N$ analytic functions $\phi_i : \omega \to H^1$, $\epsilon_i : \omega \to \mathbb{C}$, $1 \leq i \leq N$, so that the only solutions of $\Phi = 0$ in $\omega \times \Omega$ are $\{(\lambda, (\phi_i(\lambda)), (\epsilon_i(\lambda))), \quad \lambda \in \omega\}$. Since they are analytic on ω, we can expand these functions in Taylor series at $\lambda = 0$. By inserting the expansions $\sum \frac{\phi_i^{(k)}}{k!}\lambda^k$ and $\sum \frac{\epsilon_i^{(k)}}{k!}\lambda^k$ into the equation $\Phi((\lambda, (\phi_i(\lambda)), (\epsilon_i(\lambda))) = 0$, we see that their coefficients $(\phi_i^{(k)}, \epsilon_i^{(k)})_{k \geq 1}$ are a solution of the system $(\mathcal{RS}^{HF})$ and Lemma 1 proves that this solution is unique and that $(\phi_i^{(k)})$ are real valued and $(\epsilon_i^{(k)})$ are real for all k. Denote I the larger real range (neighbourhood of 0 in $\mathbb{R}$) so that the above expansions are valid. If we restrict $\phi_i(\lambda)$ and $\epsilon_i(\lambda)$ to the range I, we obtain $2\,N$ analytic real functions defined on I, verifying $\phi_i(0) = \phi_i$ and $\epsilon_i(0) = \epsilon_i$, and so that for all $\lambda \in I$, $\phi(\lambda) = (\phi_i(\lambda))$ is the unique critical point of E_λ^{HF} over $\mathcal{B}^{HF}$ in the neighbourhood of ϕ (as usual up to the rotational invariance). At last, does mean restraining I, $\phi_i(\lambda)$ is a strict local minimum for all $\lambda \in I$: the second-order quadratic form at ϕ is coercive on

$\mathcal{N}$; thus, by continuity, the second-order quadratic form at $\phi(\lambda)$ is also coercive on $\mathcal{N}_\lambda = \left\{ U = \{u_i\}_{1\le i\le N} \quad / \quad u_i \in H^1(\mathbb{R}^3) \quad \int_{\mathbb{R}^3} \phi_i(\lambda) u_j = 0 \quad \forall ij \right\}$ for λ small enough. □

4 Perturbations of the TFW model

The method used in the proof of Proposition 1 requires the analyticity of the unperturbed energy functional, at least in the neighbourhood of the ground state under consideration. This condition is not satisfied in general for DFT-type models [8]: for instance, a standard approximation brings a term in $\rho^{4/3}$. In this section, we show, on the simple example of the TFW functional, that we can nevertheless get some results, and notably existence and uniqueness results for the Rayleigh-Schrödinger expansions. However we are not able to show that the radii of convergence of these expansions are positive.

In this section, we will limit ourselves to the situations when the perturbation is either

$$\mathcal{W}(u) = \mathcal{W}_{rf}(u) = \int_{\mathbb{R}^3} V_{rf} u^2 + \frac{1}{2} D_{rf}(u^2, u^2)$$

or

$$\mathcal{W}(u) = \mathcal{W}_{ef}(u) = \int_{\mathbb{R}^3} W_{ef} u^2.$$

In the latter case, the assumption (3.9) is not sufficient to prove the existence result in Proposition 2 below. For this purpose, we need moreover some additional conditions on the regularity and on the behaviour at infinity of the electrostatic potential W_{ef}. We require here for instance,

$$W_{ef} = \rho \star \frac{1}{|x|}$$

where $\rho = \rho_+ - \rho_-$ with ρ_+ and ρ_- being bounded non-negative measures with compact supports, and so that $\rho_+(\mathbb{R}^3) = \rho_-(\mathbb{R}^3)$. These assumptions are certainly not optimal, but they cover in particular the case of a capacitor of finite size. The behaviour of W_{ef} at infinity is well known. We have indeed

$$\lim_{x\to\infty} W_{ef}(x) = 0$$

$$[W_{ef}]_+(x) \underset{x \to \infty}{\in} o\left(\frac{1}{|x|}\right),$$

where $[W_{ef}]_+$ denotes the non-negative part of the spherical average of W_{ef}. In order to avoid some technicalities, we assume moreover that W_{ef} is smooth everywhere. This condition can be easily suppressed: only local regularity results established in Proposition 2 will cease to be true at the points where W_{ef} is not smooth.

Proposition 2. *For all $\lambda \in [0,1]$, the minimization problem*

$$\inf \left\{ \overline{E}_\lambda^{TFW}(\rho)\,, \quad \rho \geq 0 \;\; \sqrt{\rho} \in H^1(\mathbb{R}^3) \;\; \int_{\mathbb{R}^3} \rho = N \right\} \tag{4.17}$$

has a unique solution $\rho(\lambda)$. The function $u(\lambda) = \sqrt{\rho(\lambda)}$ belongs to $H^2(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{\overline{x}_k\})$, is positive on $\mathbb{R}^3$ and satisfies

$$-\Delta u(\lambda) + Vu(\lambda) + c_1 u(\lambda)^{7/3} + \frac{\lambda}{2}\mathcal{W}'(u(\lambda)) + (u(\lambda)^2 \star \frac{1}{|\mathbf{x}|})u(\lambda) + \mu(\lambda)u(\lambda) = 0.$$

Moreover $\mu(\lambda) > 0$ and $(u(\lambda), \mu(\lambda))$ is the only pair $(u,\mu) \in H^1(\mathbb{R}^3) \times \mathbb{R}$ satisfying

$$\left\{ \begin{array}{l} -\Delta u + Vu + c_1|u|^{4/3}u + \frac{\lambda}{2}\mathcal{W}'(u) + (u^2 \star \frac{1}{|\mathbf{x}|})u + \mu u = 0 \\ \int_{\mathbb{R}^3} u^2 = N \\ u \geq 0. \end{array} \right. \tag{4.18}$$

□

Proposition 3. *The functions*

$$\begin{array}{rccc} \mathcal{U}\;: & [0,1] & \to & H^2 \\ & \lambda & \mapsto & u(\lambda) \end{array} \qquad \begin{array}{rccc} \mathcal{M}\;: & [0,1] & \to & \mathbb{R} \\ & \lambda & \mapsto & \mu(\lambda) \end{array}$$

are C^∞ and their successive derivatives at $\lambda \in [0,1]$, $u^{(k)}(\lambda) = \frac{d^k\mathcal{U}}{d\lambda^k}(\lambda)$ and $\mu^{(k)}(\lambda) = \frac{d^k\mathcal{M}}{d\lambda^k}(\lambda)$ are obtained in a univoque way by solving the triangular Rayleigh-Schrödinger system $(\mathcal{RS}^{TFW}(\lambda))$ consisting of the subsystems

$$(RS_k^{TFW}(\lambda)) \left\{ \begin{array}{l} \tilde{H}^{TFW}(\lambda)\cdot u^{(k)}(\lambda) + \mu^{(k)}(\lambda)u(\lambda) = f^{(k)}(\lambda) \\ \int_{\mathbb{R}^3} u(\lambda)u^{(k)}(\lambda) = \alpha^{(k)}(\lambda) \end{array} \right.$$

where

$$\begin{aligned} \tilde{H}^{TFW}(\lambda)\cdot v \;\; = \;\; & -\Delta v + Vv + \frac{7}{3}c_1 u(\lambda)^{4/3}v + (u^2(\lambda) \star \frac{1}{|\mathbf{x}|})v \\ & +2(u(\lambda)v \star \frac{1}{|\mathbf{x}|})u(\lambda) + \frac{\lambda}{2}\mathcal{W}''(u(\lambda))\cdot v + \mu(\lambda)v \end{aligned}$$

$$
\begin{aligned}
f^{(k)}(\lambda) &= -W^{(k)}(\lambda) - \sum_{j=1}^{k-1} \mu^{(k-j)}(\lambda) u^{(j)}(\lambda) \\
&- \sum_{\substack{j_1+j_2+j_3=k \\ 0 \le j_i \le k-1}} \frac{k!}{j_1! j_2! j_3!} (u^{(j_1)}(\lambda) u^{(j_2)}(\lambda) \star \frac{1}{|\mathbf{x}|}) u^{(j_3)}(\lambda) \\
&- \sum_{l=2}^{k} \left(\begin{array}{c} 7/3 \\ l \end{array} \right) \sum_{\substack{j_1+\cdots+j_l=k \\ 0 \le j_i \le k-1}} \frac{k!}{j_1! \cdots j_l!} u^{(j_1)}(\lambda) \cdots u^{(j_l)}(\lambda) u(\lambda)^{7/3-l}
\end{aligned}
$$

$$
\alpha^{(k)}(\lambda) = -\frac{1}{2} \sum_{j=1}^{k-1} \left(\begin{array}{c} k \\ j \end{array} \right) \int_{\mathbb{R}^3} u^{(j)}(\lambda) u^{(k-j)}(\lambda)
$$

with $W_{ef}^{(k)}(\lambda) = k W_{ef} u^{(k-1)}(\lambda)$ *and*

$$
\begin{aligned}
W_{rf}^{(k)}(\lambda) &= k V_{rf} u^{(k-1)}(\lambda) \\
&+ \sum_{\substack{j_1+j_2+j_3=k \\ 0 \le j_i \le k-1}} \frac{k!}{j_1! j_2! j_3!} \left(\int_{\mathbb{R}^3} G_{rf}(x,y) u^{(j_1)}(\lambda)(y) u^{(j_2)}(\lambda)(y)\, dy \right) u^{(j_3)}(\lambda).
\end{aligned}
$$

□

Proposition 3 shows in particular that the Rayleigh-Schrödinger system ($\mathcal{RS}^{TFW}(0)$) has a unique solution and that this solution is the set of the successive derivatives of $u(\lambda)$ and $\mu(\lambda)$ at 0. But we cannot conclude that the Taylor series thus obtained have or do not have positive convergence radii.

The case $\mathcal{W} = \mathcal{W}_{ef}$ being simpler, we carry out the proofs of Propositions 2 and 3 with $\mathcal{W} = \mathcal{W}_{rf}$.

Proof of Proposition 2:

The uniqueness result is a consequence of the strict convexity of the functional $\overline{E}_\lambda^{TFW}(\rho)$, that can be written

$$
\begin{aligned}
\overline{E}_\lambda^{TFW}(\rho) &= \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + \int_{\mathbb{R}^3} [(1-\lambda)V + \lambda V_s]\, \rho \\
&\quad + \frac{3}{5} c_1 \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1-\lambda}{2} D(\rho,\rho) + \frac{\lambda}{2} D_s(\rho,\rho).
\end{aligned}
$$

This property comes from (2.5) (the positivity of the Green function $G_s(x,y)$ implies that $f \mapsto D_s(f,f) > 0$ for all $f \neq 0$ regular enough).

The proof of the existence of a solution in the non-perturbed case established by E.H. Lieb [15] still allows to conclude in this framework. Indeed, we assume that the dielectric constant $\epsilon(x)$ is constant out of a ball: the behavior at infinity (2.4) is thus the same as if $\epsilon(x)$ is constant in the whole space. More precisely, using (2.3), we have, for all $u \in H^1(\mathbb{R}^3)$

$$\begin{aligned} \left| \int_{\mathbb{R}^3} V_s u^2 \right| &\leq \|g_s\|_{L^\infty} \|u\|_{L^2}^2 + \left| \int_{\mathbb{R}^3} V u^2 \right| \\ &\leq \|g_s\|_{L^\infty} \|u\|_{L^2}^2 + C \|u\|_{L^2} \|\nabla u\|_{L^2}. \end{aligned}$$

Moreover (as in [15]), we can prove with (2.3) and (2.4) that, if $u_n \rightharpoonup u$ in H^1 weak, then $\int_{\mathbb{R}^3} V_s u_n^2 \to \int_{\mathbb{R}^3} V_s u^2$.

Thanks to the results above, we are able to conclude (see [15] for more details) that the minimization problem with relaxed constraint

$$\inf \left\{ E_\lambda^{TFW}(u) \ , \quad u \in H^1(\mathbb{R}^3) \ \int_{\mathbb{R}^3} u^2 \leq N \right\} \tag{4.19}$$

has a solution $u(\lambda)$. Besides, it is straightforward to see with a scaling argument that $u(\lambda)$ cannot be identically equal to zero. Let us next write the Euler-Lagrange equation of problem (4.19). We have

$$-\Delta u(\lambda) + \mathcal{V}_\lambda u(\lambda) + \mu(\lambda) u(\lambda) = 0, \tag{4.20}$$

with

$$\mathcal{V}_\lambda = (1-\lambda)V + c_1 u(\lambda)^{4/3} + (1-\lambda)(u(\lambda)^2 \star \frac{1}{|\mathbf{x}|}) + \lambda W_s, \tag{4.21}$$

where W_s satisfies

$$-\mathrm{div}(\epsilon \nabla W_s) = -\sum_{k=1}^{M} z_k \, \delta_{\overline{x}_k} + u(\lambda)^2. \tag{4.22}$$

Using (2.3) and Hardy inequality we deduce that

- $\mathcal{V}_\lambda \, u(\lambda) \in L^2(\mathbb{R}^3)$, and thus $u(\lambda) \in H^2(\mathbb{R}^3)$;
- $\mathcal{V}_\lambda \in L^q_{loc}$ for some $q > \frac{3}{2}$. Therefore $u(\lambda) > 0$ by Harnack inequality.

Using Sobolev injection $H^2(\mathbb{R}^3) \hookrightarrow C^{0,1/2}$ and a bootstrap argument on the system ((4.20), (4.21), (4.22)) based on Schauder elliptic regularity results, we obtain $u(\lambda) \in C^\infty(\mathbb{R}^3 \setminus \{\overline{x}_k\})$.

It remains to prove that the constraint $\int_{\mathbb{R}^3} u^2 \leq N$ is saturated. If we suppose $\int_{\mathbb{R}^3} u^2 < N$, there comes $\mu(\lambda) = 0$. Thus, $u(\lambda) > 0$ is a C^2 function in the domain $D = \{x \,/\, |x| > a\}$ and $u(\lambda)$ satisfies $(-\Delta + \mathcal{V}_\lambda)u(\lambda) = 0$ on D. Denote $[\mathcal{V}_\lambda]$ the spherical average of $\mathcal{V}_\lambda$ and $[\mathcal{V}_\lambda]_+ = \max([\mathcal{V}_\lambda], 0)$. Let $b \geq a$ so that $\epsilon(x) = \epsilon_s$ in B_b^c. We have, in B_b^c,

$$[\mathcal{V}_\lambda] = (1-\lambda)[V + u(\lambda)^2 \star \frac{1}{|\mathbf{x}|}] + \lambda[W_s] + c_1[u(\lambda)^{4/3}].$$

By an application of the Gauss theorem, we obtain, for all $x \in B_b^c$,

$$[V + u(\lambda)^2 \star \frac{1}{|\mathbf{x}|}](x) = \frac{-Z + \int_{B_{|x|}} u^2}{|x|} < 0, \qquad [W_s](x) = \frac{-Z + \int_{B_{|x|}} u^2}{\epsilon_s |x|} < 0.$$

Thus in B_b^c, $[\mathcal{V}_\lambda]_+ \leq c_1[u(\lambda)^{4/3}]$. As $c_1[u(\lambda)^{4/3}]$ is in $L^{3/2}(B_b^c)$, so is $[\mathcal{V}_\lambda]_+$. Lemma 7.18 in [15] enables us to conclude that $u(\lambda) \notin L^2(B_b^c)$, which is a contradiction. The existence of a solution of the minimization problem (4.17) is thus proved. With the same argument, we also obtain $\mu(\lambda) \neq 0$. Fixing λ and considering N as a real parameter, we conclude as in [15] that $\mu(\lambda) > 0$. □

Proof of Proposition 3:

First step

Let $\lambda \in [0, 1]$. We begin by proving that $(\mathcal{RS}^{TFW}(\lambda))$ has a unique solution.

First of all, we show that $\tilde{H}^{TFW}(\lambda)$ is coercive on $T_{u(\lambda)}\mathcal{B}^{TFW} = u(\lambda)^{\perp_{L^2}}$. We already know that $\forall h \in H^1$

$$\begin{aligned} \langle h, \tilde{H}^{TFW}(\lambda)h\rangle &= \langle h, (-\Delta + \mathcal{V}_\lambda + \mu(\lambda))h\rangle \\ &\quad +2(1-\lambda)D(u(\lambda)h, u(\lambda)h) + 2\lambda D_s(u(\lambda)h, u(\lambda)h) \\ &\geq \langle h, (-\Delta + \mathcal{V}_\lambda + \mu(\lambda))h\rangle. \end{aligned}$$

The Euler-Lagrange equation (4.20) shows that $u(\lambda)$ is an eigenvector of the Hamiltonian operator $-\Delta + \mathcal{V}_\lambda$. As $u(\lambda) > 0$ on $\mathbb{R}^3$, $u(\lambda)$ is in fact a ground state. With (2.1), (2.3), we can see furthermore that $\mathcal{V}_\lambda^+ \in L^1_{loc}$ and that $\mathcal{V}_\lambda^- \in L^\infty + L^{3/2}$. A result by Faris and Simon mentioned in [17], enables us to conclude that the ground state $u(\lambda)$ is non-degenerate. It follows that if $h \in T_{u(\lambda)}\mathcal{B}^{TFW}$, then

$$\langle h, (-\Delta + \mathcal{V}_\lambda + \mu(\lambda))h\rangle \geq \beta \|h\|^2_{L^2}, \tag{4.23}$$

the real constant β being the (positive) gap between $-\mu(\lambda)$ and the second eigenvalue of $-\Delta+\mathcal{V}_\lambda$. Let us now show that there exists $\gamma>0$ so that $\forall h\in T_{u(\lambda)}\mathcal{B}^{TFW}$,

$$\langle h,(-\Delta+\mathcal{V}_\lambda+\mu(\lambda))h\rangle\geq\gamma\,\|h\|_{H^1}^2.$$

Let us assume that there exists a sequence (h_n) of elements of $T_{u(\lambda)}\mathcal{B}^{TFW}$ so that $\|h_n\|_{H^1}=1$ and $\langle h_n,(-\Delta+\mathcal{V}_\lambda+\mu(\lambda))h_n\rangle\to 0$. Inequality (4.23) proves that $h_n\to 0$ in L^2. From Hardy inequality, the sequence $(\mathcal{V}_\lambda h_n)_{n\in\mathbb{N}}$ is bounded in $L^2(\mathbb{R}^3)$. Therefore, with Schwarz inequality $\int_{\mathbb{R}^3}\mathcal{V}_\lambda h_n^2\to 0$. Thus $\int_{\mathbb{R}^3}|\nabla h_n|^2=\langle h_n,(-\Delta+\mathcal{V}_\lambda+\mu(\lambda))h_n\rangle-\int_{\mathbb{R}^3}\mathcal{V}_\lambda h_n^2-\mu(\lambda)\int_{\mathbb{R}^3}h_n^2\to 0$. Therefore $\|h_n\|_{H^1}\to 0$, which contradicts $\|h_n\|_{H^1}=1$. Coercivity is proved.

We now prove the following inequalities: $\forall(\gamma,\Gamma)\ /\ \gamma<\sqrt{\mu(\lambda)}<\Gamma\quad\exists\,0<c<C\ /$

$$\forall x\in\mathbb{R}^3\qquad c\,e^{-\Gamma|x|}\ \leq\ u(\lambda)(x)\ \leq\ C\,e^{-\gamma|x|}. \tag{4.24}$$

Let $\epsilon>0$. As $\mathcal{V}_\lambda$ tends to zero at infinity, we can find $R\geq 1+\max(|\overline{x}_k|)$ so that $\forall x\in B_R^c$, $|\mathcal{V}_\lambda(x)|\leq\epsilon$. The function $u(\lambda)$ is in $C^\infty(B_R^c)$, goes to 0 at infinity and satisfies the following inequalities on B_R^c

$$-\Delta u(\lambda)+(\mu(\lambda)-\epsilon)u(\lambda)\leq 0\leq-\Delta u(\lambda)+(\mu(\lambda)+\epsilon)u(\lambda).$$

Consider $f_{\alpha,\omega}(x)=\alpha\frac{R}{|x|}e^{-\omega(|x|-R)}$, which is in $C^\infty(B_R^c)$ and satisfies for $\omega>0$

$$\begin{cases}-\Delta f_{\alpha,\omega}+\omega^2 f_{\alpha,\omega}=0 & \text{in } B_R^c\\ f_{\alpha,\omega}=\alpha & \text{on } S_R\\ f_{\alpha,\omega}=0 & \text{at infinity.}\end{cases}$$

By comparing $u(\lambda)$ first with f_{α_1,ω_1} where $\alpha_1=\sup_{S_R}u(\lambda)$ and $\omega_1=\mu(\lambda)-\epsilon$, then with f_{α_2,ω_2} where $\alpha_2=\inf_{S_R}u(\lambda)$ and $\omega_2=\mu(\lambda)+\epsilon$, we show that on B_R^c

$$(\inf_{\partial B_R^c}u(\lambda))\frac{R}{|x|}e^{-\sqrt{\mu(\lambda)+\epsilon}(|x|-R)}\leq u(\lambda)(x)\leq(\sup_{\partial B_R^c}u(\lambda))\frac{R}{|x|}e^{-\sqrt{\mu(\lambda)-\epsilon}(|x|-R)}. \tag{4.25}$$

Since $u(\lambda)$ is bounded from above and from below on the compact $\overline{B}_R$ by a positive number, inequalities (4.24) are a consequence of (4.25).

To show existence and uniqueness of $\left((u^{(k)}(\lambda),\mu^{(k)}(\lambda))\right)_{k\geq 0}$, we argue by induction on the following hypothesis:

$(\mathcal{H}_k)$ *There exists a unique solution* $\left((u^{(j)}(\lambda),\mu^{(j)}(\lambda))\right)_{0\leq j\leq k}$ *of the system* $\left((RS_0^{TFW}(\lambda)\right),\ \cdots,\ (RS_k^{TFW}(\lambda))\big)$, *In addition* $u^{(j)}(\lambda)\in H^2(\mathbb{R}^3)\cap C^\infty(\mathbb{R}^3\setminus\{\overline{x}_k\})$ and satisfies

$$\forall j\leq k\quad\forall\alpha<\sqrt{\mu(\lambda)}\quad\exists C_{j,\alpha}\quad/\quad\forall x\in\mathbb{R}^3\quad|u^{(j)}(\lambda)(x)|\leq C_{j,\alpha}e^{-\alpha|x|}.$$

We denote by $(RS_0^{TFW}(\lambda))$ the system (4.18). The results established above show that $(\mathcal{H}_0)$ is true. Let us assume that $(\mathcal{H}_{k-1})$ is satisfied. Using inequalities (4.24) and the induction hypothesis $(\mathcal{H}_{k-1})$, we claim that $f = f^{(k)}(\lambda)$ is in $L^2(\mathbb{R}^3)$. In fact, $u^j(\lambda) \in H^2(\mathbb{R}^3)$ for all $0 \leq j \leq k-1$. Thus the more delicate terms are those of the form $u^{(j_1)}(\lambda) \dots u^{(j_l)}(\lambda) u^{7/3-l}(\lambda)$ $(0 \leq j_i \leq k-1)$ with $l \geq 3$. Let $\epsilon > 0$ small enough so that $\beta = l\sqrt{\mu(\lambda) - \epsilon} + (\frac{7}{3} - l)\sqrt{\mu(\lambda) + \epsilon} \geq \sqrt{\mu(\lambda)}$. From (4.24) and hypothesis $(\mathcal{H}_{k-1})$, we can choose $c_0 > 0$ and $c_{j_i} \geq 0$ so that for all $x \in \mathbb{R}^3$, $u(\lambda)(x) \geq c_0 e^{-\sqrt{\mu(\lambda)+\epsilon}|x|}$ and $|u^{(j_i)}(\lambda)(x)| \leq c_{j_i} e^{-\sqrt{\mu(\lambda)-\epsilon}|x|}$. Denote $C = c_0^{7/3-l} c_{j_1} \dots c_{j_l}$. We have $|u^{(j_1)}(\lambda)(x) \dots u^{(j_l)}(\lambda)(x) u^{7/3-l}(\lambda)(x)| \leq C e^{-\sqrt{\mu(\lambda)}|x|}$ for all $x \in \mathbb{R}^3$, which implies in particular that the left hand member of the inequality is in $L^2(\mathbb{R}^3)$.

The pair (u, μ) is a solution of $(RS_k^{TFW}(\lambda))$ in $(H^1 \times \mathbb{R})$ if and only if $v = u - \alpha^{(k)}(\lambda) u(\lambda)$ is a solution of the Euler-Lagrange equation of the minimization problem

$$\inf \left\{ \langle v, \tilde{H}^{TFW}(\lambda) \cdot v \rangle - \langle f, v \rangle \ , \quad v \in T_{u(\lambda)} \mathcal{B}^{TFW} \right\}$$

and μ is the Lagrange multiplier associated with the constraint $v \in T_{u(\lambda)} \mathcal{B}^{TFW}$. The coercivity result established above proves that this minimization problem has a unique solution. It follows that $(RS_k^{TFW}(\lambda))$ has a unique solution $(u^{(k)}(\lambda), \mu^{(k)}(\lambda))$ in $(H^1 \times \mathbb{R})$.

Denote $f = u^{(k)}(\lambda)$ (in order to simplify notations). f satisfies the equation

$$-\Delta f + \mathcal{V}_\lambda f + \mu(\lambda) f = g \tag{4.26}$$

with $g \in L^2(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{\overline{x}_k\})$ and so that

$$\forall \alpha < \sqrt{\mu(\lambda)} \quad \exists\, C_\alpha \quad / \quad \forall x \in \mathbb{R}^3 \quad |g(x)| \leq C_\alpha \, e^{-\alpha|x|}.$$

By a bootstrap argument on equation (4.26), we get $f \in H^2(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{\overline{x}_k\})$. Let $0 < \alpha < \sqrt{\mu(\lambda)}$ and $\epsilon = \mu(\lambda) - \alpha^2$. Let $R \geq 1 + \max(|\overline{x}_k|)$ so that $|\mathcal{V}_\lambda| \leq \epsilon$ in B_R^c. Denote $L = \Delta - \alpha^2$, $B = \sup_{S_R} |u|$ and

$$v(x) = \frac{C_\alpha}{4\alpha^2} \left(1 + \alpha|x| - \frac{\alpha R^2 + R}{|x|} \right) e^{-\alpha|x|} + \frac{BR}{r} e^{-\alpha(r-R)}.$$

The function $v(x)$ satisfies $Lv = -C_\alpha e^{-\alpha|x|}$, $v = B$ on S_R and $v \to 0$ at infinity. Let $w = v - |u|$ and $I = \inf_{B_R^c}(w)$. Let us assume $I < 0$. As w goes to zero at infinity and $w \geq 0$ on S_R, I is achieved at $x_0 \in \overset{\circ}{B^c}_R$. We have $|u(x_0)| > v(x_0) > 0$. We conclude that $|u|$ is C^∞ in a neighbourhood of x_0, and so is w. Besides, $\Delta w(x_0) \geq 0$,

and therefore, as $w(x_0) = I < 0$, we have $Lw(x_0) > 0$. On the other hand, using Kato inequality, we get on B_R^c

$$\begin{aligned} Lw &= Lv - \Delta|u| + \alpha^2|u| \\ &\leq Lv - sgn(u)\Delta u + \alpha^2|u| \\ &= -C_\alpha e^{-\alpha|x|} - sgn(u)(\mathcal{V}_\lambda u + \mu(\lambda)u - g) + \alpha^2|u| \\ &\leq -(C_\alpha e^{-\alpha|x|} - |g|) - (\epsilon - |\mathcal{V}_\lambda|)|u| \\ &\leq 0. \end{aligned}$$

We reach a contradiction. Thus $I = 0$, ie $|u| \leq v$. Finaly, $(\mathcal{H}_k)$ is satisfied.

Second step

Let us now show that $\mathcal{U}$ and $\mathcal{M}$ are C^∞ and that their successive derivatives at λ are solutions of $(\mathcal{RS}^{TFW}(\lambda))$. Let us consider

$$\begin{array}{rccl} \Phi_0 \ : & \mathbb{R} \times (H^2 \times \mathbb{R}) & \to & (L^2 \times \mathbb{R}) \\ & (\lambda, u, \mu) & \mapsto & (-\Delta u + V u + c_1|u|^{4/3}u + \frac{\lambda}{2}\mathcal{W}'(u) + (u^2 \star \frac{1}{|x|})u + \mu u, \\ & & & \int_{\mathbb{R}^3} u^2 - N). \end{array}$$

To check that Φ_0 is C^1, it is enough showing that so is $F \ : \ u \mapsto |u|^{4/3}u$. Let $u \in H^2$. Let us consider the linear operator $G(u) \ : \ h \mapsto \frac{7}{3}|u|^{4/3}h$ from H^2 into L^2. Let $\epsilon > 0$. We have $u \in L^\infty$ and the real function $t \mapsto |t|^{4/3}t$ is C^2 on $\mathbb{R}$. Thus there exists $\eta > 0$ so that

$$\forall x \in \mathbb{R}^3 \quad \forall |t| \leq \eta \quad \left| |u(x) + t|^{4/3}(u(x) + t) - |u(x)|^{4/3}u(x) - \frac{7}{3}|u(x)|^{4/3}t \right| \leq \epsilon.$$

Let $\zeta > 0$ so that $\|h\|_{H^2} \leq \zeta \ \Rightarrow \ \|h\|_{L^\infty} \leq \eta$. We have

$$\forall h \in H^2 \ , \ \|h\|_{H^2} \leq \zeta \qquad \|F(u+h) - F(u) - G(u) \cdot h\|_{L^2} \leq \epsilon \|h\|_{L^2} \leq \epsilon \|h\|_{H^2}$$

Thus F is differentiable at u and $F'(u) = G(u)$. We easily check that $u \mapsto G(u)$ is continuous from H^2 into $\mathcal{L}(H^2, L^2)$, which proves that F is C^1.

Let $\lambda \in [0, 1]$ and $c = (\lambda, u(\lambda), \mu(\lambda))$. We have $\Phi_0(c) = 0$ and $d_c\Phi_0|_{\{0\} \times H^2 \times \mathbb{R}}$ is an isomorphism from $\{0\} \times H^2 \times \mathbb{R}$ into $L^2 \times \mathbb{R}$. We can thus use the implicit function theorem in a neighbourhood of λ (for all $\lambda \in [0, 1]$) and conclude that $\mathcal{U}$ and $\mathcal{M}$ are C^1 and that their derivatives satisfy

$$\frac{\partial \Phi_0}{\partial \lambda}(\lambda, u(\lambda), \mu(\lambda)) + \frac{\partial \Phi_0}{\partial (u, \mu)}(\lambda, u(\lambda), \mu(\lambda)) \cdot (\frac{du}{d\lambda}(\lambda), \frac{d\mu}{d\lambda}(\lambda)) = 0. \tag{4.27}$$

From (4.27) we draw that $(\frac{du}{d\lambda}(\lambda), \frac{d\mu}{d\lambda}(\lambda))$ is a solution of $(RS_1^{TFW}(\lambda))$ in $(H^1 \times \mathbb{R})$. Since this system has a unique solution: $(u^{(1)}(\lambda), \mu^{(1)}(\lambda)))$, we conclude that $\mathcal{U}$ and $\mathcal{M}$ are C^1 and that $\frac{d^j\mathcal{U}}{d\lambda^j} = u^{(j)}$, $\frac{d^j\mathcal{M}}{d\lambda^j} = \mu^{(j)}$, for $0 \leq j \leq 1$.

To prove the result at order k, we also argue by induction. Let us suppose that we have shown that $\mathcal{U}$ and $\mathcal{M}$ were C^k and $\frac{d^j\mathcal{U}}{d\lambda^j} = u^{(j)}$, $\frac{d^j\mathcal{M}}{d\lambda^j} = \mu^{(j)}$, for $0 \leq j \leq k$. We resume the processes above with

$$\begin{array}{rccl} \Phi_k \ : & \mathbb{R} \times (H^2 \times \mathbb{R}) & \to & (L^2 \times \mathbb{R}) \\ & (\lambda, u, \mu) & \mapsto & (\tilde{H}^{TFW}(\lambda)u + \mu u(\lambda) - f^{(k)}(\lambda), \int_{\mathbb{R}^3} u(\lambda)u - \alpha^{(k)}(\lambda)) \end{array}$$

which is C^1 (as the reader can check) and so that $\forall \lambda \in \mathbb{R}$, $\Phi_k(\lambda, u^{(k)}(\lambda), \mu^{(k)}(\lambda)) = 0$ and $d_{(\lambda, u^{(k)}(\lambda), \mu^{(k)}(\lambda))}\Phi_k\big|_{\{0\}\times H^2 \times \mathbb{R}}$ is an isomorphism from $\{0\} \times H^2 \times \mathbb{R}$ into $L^2 \times \mathbb{R}$. Using the implicit function theorem, we claim that $u^{(k)}(\lambda)$ and $\mu^{(k)}(\lambda)$ are C^1 and that their derivatives satisfy

$$\frac{\partial \Phi_k}{\partial \lambda}(\lambda, u^{(k)}(\lambda), \mu^{(k)}(\lambda)) + \frac{\partial \Phi_k}{\partial (u, \mu)}(\lambda, u^{(k)}(\lambda), \mu^{(k)}(\lambda)) \cdot (\frac{du^{(k)}}{d\lambda}(\lambda), \frac{d\mu^{(k)}}{d\lambda}(\lambda)) = 0.$$

After a simple manipulation of that equality, we can see that $(\frac{du^{(k)}}{d\lambda}(\lambda), \frac{d\mu^{(k)}}{d\lambda}(\lambda))$ is a solution of system $(RS^{TFW}_{k+1}(\lambda))$ in $(H^1 \times \mathbb{R})$. Since this system has a unique solution: $(u^{(k+1)}(\lambda), u^{(k+1)}(\lambda))$, we conclude that $\mathcal{U}$ and $\mathcal{M}$ are C^{k+1} and that $\frac{d^j\mathcal{U}}{d\lambda^j} = u^{(j)}$, $\frac{d^j\mathcal{M}}{d\lambda^j} = \mu^{(j)}$, for $0 \leq j \leq k+1$. The induction goes on. □

Remark 4. In the case of a perturbation by an external electric field, Propositions 2 and 3 are true for $\lambda \in \mathbb{R}$. □

Remark 5. By resuming the proof of Proposition 1, we recover the analyticity of $\mathcal{U}$ and $\mathcal{M}$ for $c_1 = 0$, that is to say for the Restricted Hartree functional. □

5 Molecule in a uniform external electric field

We now put the molecule in a uniform external electric field of modulus $\mathcal{E} > 0$ oriented along Ox. The electrostatic potential of the field reads $W_{ef}(x, y, z) = -\mathcal{E}x$. From a mathematical point of view, this situation is radically different from those considered previously in Section 3 and 4 (in which the electric potential satisfies (3.9)), since here, the potential becomes infinite in some directions. Let us take for instance the simple example of the hydrogen atom ($M = 1$, $N = 1$) in a uniform electric field of modulus $\mathcal{E} > 0$ oriented as Ox. Its Hamiltonian reads

$$H_{\mathcal{E}} = H_0 - \mathcal{E}x = -\Delta - \frac{1}{r} - \mathcal{E}x$$

and operates on $L^2(\mathbb{R}^3)$. It is known (see [2]) that $H_{\mathcal{E}}$ is essentially self-adjoint and that the pure point spectrum of its closure is empty and that its essential spectrum is equal to $\mathbb{R}$.

The operator $H_{\mathcal{E}}$ has thus no eigenvalue: there exists no stationary state.

However, from a physical point of view (see [14]), the eigenstates have not completely disappeared: for small values of $\mathcal{E}$, experiments confirm that there exist some metastable states, also called long-life states, closed to non-perturbed stationary states, whose evolution by the time-dependent Schrödinger equation $i\,\partial\psi/\partial t = H_{\mathcal{E}} \cdot \psi$ is "slow". The "energies" of those states can be computed quite precisely using the perturbation method (stopping after the first terms since the serial diverges); their life-times can also been estimated with a WKB calculus of tunneling through a potential barrier. The relative shift of the energies of metastable states can be observed by spectroscopy: it is the Stark effect.

Attempts to give a mathematical sense to these calculations lead up to the notion of resonance. This theory enables us to understand how the Rayleigh-Schrödinger serial, which is not summable in a usual sense, can nevertheless be summed in a more sophisticated way to compute the "energies" and the life-times of the metastable states. We refer the reader to the original article by E. Balslev and J.M. Combes [4] on dilation analyticity and to the article by I. Herbst [10] to see the application of this tool for the study of Stark Hamiltonians. We refer also to [12], and to [6] for a more physical point of view.

Let now come back to the nonlinear settings of the HF and TFW models. For the TFW model, we first notice that for all $\mathcal{E} > 0$,

$$\inf \left\{ E^{TFW}(u) - \mathcal{E} \int_{\mathbb{R}^3} xu^2 \,, \quad u \in \mathcal{D}(\mathbb{R}^3) \,, \quad \int_{\mathbb{R}^3} u^2 = 1 \right\} = -\infty.$$

Indeed, let $u \in \mathcal{D}(\mathbb{R}^3)$ so that $\int_{\mathbb{R}^3} u^2 = 1$ and $u_n(\cdot) = u(\cdot - n\mathcal{E}\vec{e}_x)$, where $\vec{e}_x$ is the unit vector associated with the direction Ox. It is straightforward to see that $E^{TFW}(u_n) \to -\infty$. The standard definition of the ground state as the state which minimizes the energy, has no more a meaning. We even show in Section 5.2 that the TFW equation has no non-null solution in $H^1(\mathbb{R}^3)$ as soon as a uniform external electric field is turned on. Same conclusions can be drawn for the spinless real Hartree-Fock model.

On the other hand, we will see in Section 5.1, that Rayleich-Schrödinger expansions are still perfectly defined as solutions of the system $(\mathcal{RS}^{HF})$ (resp. $(\mathcal{RS}^{TFW}(0))$) when the perturbation is a uniform electric field. But, the so-obtained Taylor series (at least some of them) have convergence radii equal to zero, and thus are not summable in a usual sense, even if $\mathcal{E}$ is small.

5.1 Rayleigh-Schrödinger expansions

Proposition 4: *The Rayleigh-Schrödinger system $(\mathcal{RS}^{HF})$ (resp. $(\mathcal{RS}^{TFW}(0))$) still has a unique solution in presence of a uniform electric field. But at least one of the so-obtained Taylor series has a convergence radius equal to zero.* □

Proof:

For the TFW model, existence and uniqueness can be proved as in Proposition 3 with $\lambda = 0$ and $\mathcal{W}(u) = -\mathcal{E}\int_{\mathbb{R}^3} xu^2$: just notice that $x\,v$ is in $L^2(\mathbb{R}^3)$ if v decays exponentially.

For the HF model, we can prove this result as in Proposition 3 by arguing by induction on

($\mathcal{H}_k$) *There exists a unique solution* $\left(((\phi_i^{(j)}),(\epsilon_i^{(j)}))\right)_{0\le j\le k}$ *of the system* $\left((RS_1^{HF}),\right.$ $\left.\cdots,\ (RS_k^{HF})\right)$ *with, moreover:*

$$\forall i \quad \forall j \le k \quad \exists \mu_{i,j} > 0 \quad \exists C_{i,j} \quad / \quad \forall x \in \mathbb{R}^3 \quad |\phi_i^{(j)}(x)| \le C_{i,j} e^{-\mu_{i,j}|x|}.$$

The exponential decay of the ϕ_i is already known [16]. At the order k, we show the exponential decay of the ϕ_i^k as follows: denote $h_i = \phi_i^k$ to simplify the notations. We have

$$-\Delta h_i + (V + \rho \star \frac{1}{|y|})h_i + \epsilon_i h_i - \sum_{j=1}^{N} (\phi_i\phi_j \star \frac{1}{|y|})h_j = r_i$$

with

$$r_i = -2\sum_{j=1}^{N}(\phi_j h_j \star \frac{1}{|y|})\phi_i + \sum_{j=1}^{N}(\phi_j h_i \star \frac{1}{|y|})\phi_j + \sum_{j=1}^{N}(\phi_i h_j \star \frac{1}{|y|})\phi_j + f_i^k.$$

We easily deduce from the induction hypothesis ($\mathcal{H}_{k-1}$) that there exists $C \ge 0$ and $\lambda > 0$ so that $|r_i(x)| \le Ce^{-\lambda|x|}$ for all $x \in \mathbb{R}$ and $1 \le i \le N$. Denote $g = \sum_{i=1}^{N} h_i^2$. We have

$$\begin{aligned} -\Delta g &= -2\sum_{i=1}^{N} h_i\Delta h_i - 2\sum_{i=1}^{N}|\nabla h_i|^2 \\ &\le -2(V + \rho\star\frac{1}{|x|})g - 2\sum_{i=1}^{N}\epsilon_i h_i^2 + 2\sum_{i,j=1}^{N}(\phi_i\phi_j\star\frac{1}{|x|})h_ih_j + 2\sum_{i=1}^{N} r_ih_i. \end{aligned}$$

We know that $h_i \in H^2 \subset L^\infty$. Thus there exists a constant C so that $|2\sum_{i=1}^{N} r_ih_i| \le Ce^{-\lambda|x|}$. On the other hand $|\sum(\phi_i\phi_j \star \frac{1}{|x|})h_ih_j| \le (\rho\star\frac{1}{|x|})g$. It comes

$$-\Delta g + c(x)g + \epsilon_N g \le Ce^{-\lambda|x|}$$

with $c(x) = 2V(x) \to 0$ when x goes to infinity. As in the proof of Proposition 3, we conclude that there exists $\alpha > 0$ so that $g(x) \le C\,e^{-\alpha|x|}$. Thus for all i, $|h_i(x)| \le Ce^{-\frac{\alpha}{2}|x|}$.

To prove that one at least of the Taylor series obtained with the Rayleigh-Schrödinger system has a convergence radius equal to zero, it is enough to prove that equation (5.32) (resp. (5.45)) below has no solution as soon as $\mathcal{E} > 0$ (in fact, if all the Taylor series were convergent for some $\mathcal{E} > 0$, they would give birth to solutions of equation (5.32) (resp. (5.45)). This non-existence result is the purpose of the following section. □

5.2 Non-existence of non-trivial solutions to the TFW and HF equations

We prove here the non-existence of non-trivial solutions to the TFW and HF equations in $H^1(\mathbb{R}^3)$ and $(H^1(\mathbb{R}^3))^N$ respectively in presence of a uniform electric field chosen oriented along Ox. We take, as in Section 5.1, $W_{ef}(x, y, z) = -\mathcal{E}x$ with $\mathcal{E} > 0$.

To establish this non-existence result, we will follow the method used by Avron and Herbst [2] in the linear case. This method extends to higher dimensions the following simple idea in one dimension. Let us consider the equation

$$-v''(x) - \mathcal{E}xv(x) + V(x)v(x) + \mu v(x) = 0 \tag{5.28}$$

on $\mathbb{R}$ with the following assumptions: $x \mapsto V(x)$ is C^1 and

$$\limsup_{x \to +\infty} |V'(x)| < \mathcal{E}. \tag{5.29}$$

Then $v = 0$ is the unique solution of equation (5.28) in $H^1(\mathbb{R})$.

Indeed, denote $v \in H^1(\mathbb{R})$ a solution of (5.28). Let us define

$$G(x) = -v'(x)^2 + (-\mathcal{E}x + V(x) + \mu)v(x)^2. \tag{5.30}$$

The first derivative of G reads

$$G'(x) = -(\mathcal{E} - V'(x))v(x)^2.$$

Thus, according to assumption (5.29), G is decreasing for x large enough and has a finite limit at $+\infty$ (because G' is in $L^1(]1, +\infty[)$). As $\frac{G(x)}{x}$ is in $L^1(]1, +\infty[)$, this limit is zero. Thus $G(x)$ decreases to zero when x goes to $+\infty$. On the other hand, also in accordance with hypothesis (5.29), $-\mathcal{E}x + V(x) + \mu < 0$ for $x \geq x_0$, x_0 large enough. Therefore $G(x) = 0$ for $x \geq x_0$, and thus $v(x) = v'(x) = 0$ for $x \geq x_0$. The unique continuation principle (or the linear Cauchy-Lipschitz theorem, since we work in one dimension) enables us to conclude that $v = 0$.

We first establish the non-existence for the TFW model, which needs a more careful adaptation of the proof by Avron and Herbst. Then, we will prove this result for the HF model.

5.2.1 Notations

For $v \in H^1(\mathbb{R}^3)$, denote T_v the function from $\mathbb{R}$ into $L^2(\mathbb{R}^2)$ which, with all $x_0 \in \mathbb{R}$ associates the trace of v on the plane $x = x_0$.

$$\begin{array}{rccl} T_v(x_0) & : & \mathbb{R}^2 & \to \mathbb{C} \\ & & (y,z) & \mapsto v(x_0,y,z). \end{array}$$

We will use the following results, which are proved in the appendix:

- If $v \in H^1(\mathbb{R}^3)$, $T_v \in C^0(\mathbb{R}, L^2(\mathbb{R}^2))$.
- If $v \in H^2(\mathbb{R}^3)$, $T_v \in C^1(\mathbb{R}, L^2(\mathbb{R}^2)) \cap C^0(\mathbb{R}, H^1(\mathbb{R}^2))$ and

$$T_v' = T_{\frac{\partial v}{\partial x}} \qquad \frac{\partial}{\partial y}(T_v(x_0)) = T_{\frac{\partial v}{\partial y}}(x_0) \qquad \frac{\partial}{\partial z}(T_v(x_0)) = T_{\frac{\partial v}{\partial z}}(x_0). \tag{5.31}$$

Let $\alpha \in \mathbb{R}$ and $\Omega_\alpha =]\alpha, +\infty[\times \mathbb{R}^2$. We will also use the Banach spaces:

$$H^k_{x-loc}(\Omega_\alpha) \stackrel{\text{def}}{=} \left\{ v \in H^k_{loc}(\Omega_\alpha) \quad / \quad h(x)v(x,y,z) \in H^k(\Omega_\alpha) \quad \forall h \in D(]\alpha, +\infty[) \right\}$$

The function T_v is continuous on $]\alpha, +\infty[$ for all $v \in H^1_{x-loc}(\Omega_\alpha)$ and equalities (5.31) still hold for $v \in H^2_{x-loc}(\Omega_\alpha)$ and $x_0 \in]\alpha, +\infty[$.

From now on, we denote by $H = L^2(\mathbb{R}^2)$ and for $(v,w) \in H \times H$, $\|v\|_H = (\int_{\mathbb{R}^2} |v|^2)^{1/2}$ and $\langle v, w \rangle_H = \int_{\mathbb{R}^2} v^* w$.

5.2.2 The Thomas-Fermi-Von Weizsäcker case

In presence of a uniform electric field of modulus $\mathcal{E} > 0$ oriented along Ox, the TFW equation reads

$$-\Delta u + Vu + c_1 |u|^{4/3} u + (|u|^2 \star \frac{1}{|\mathbf{x}|}) u - \mathcal{E} x u + \mu u = 0 \tag{5.32}$$

where μ is the Lagrange multiplier associated with the constraint $\int_{\mathbb{R}^3} u^2 = N$. Our purpose is to show

Proposition 5. *For all $\mathcal{E} > 0$ and $\mu \in \mathbb{R}$, the unique solution u to (5.32) in $H^1(\mathbb{R}^3)$ is $u = 0$.* □

Remark 6: We emphasize that the above result states the non-existence on non-trivial solutions to equation (5.32) in a functional set which is far larger than the set

$\left\{u \in H^1(\mathbb{R}^3)\ ,\quad \int_{\mathbb{R}^3} |x|\, u^2 < +\infty\right\}$ which gives a sense to the energy $E^{TFW}(u) - \int_{\mathbb{R}^3} xu^2$ formally associated with (5.32).

Remark 7: The reader will check that if the energy functional contains terms of the form $c \int_{\mathbb{R}^3} |u|^p$ $(2 \leq p \leq 6)$, the following proof will apply if and only if $c \geq 0$. The case of the Thomas-Fermi-Dirac-Von Weizsäcker functional (see [16]) is therefore still open.

Proof:

Let $\mu \in \mathbb{R}$. Denote u a solution to (5.32) in $H^1(\mathbb{R}^3)$. We want to prove that $u = 0$. As in the 1-dimension case treated above, we look at the region where x goes to infinity. For this purpose, we consider the function

$$g(x) = \int_{\mathbb{R}^2} u^2(x, y, z)\, dy\, dz = \|T_u(x)\|^2.$$

By analogy with (5.30), we define a function $G(x)$, which enables us to reach a contradiction if we assume $g(x)$ non-identically equal to zero for large x.

First step

We first need some regularity results. Denote $a = 1 + \max(|\overline{x}_k|)$. By a bootstrap argument, we see that u is in $H^3_{x-loc}(\Omega_a)$.

We now split up the effective potential $(V + (u^2 \star \frac{1}{|\mathbf{x}|}) + c_1|u|^{4/3})$ into two parts: the first one regroups the terms that go to zero at infinity as well as their first derivatives with respect to x; we put the other terms in the second part. Notice that if we had supposed $u \in H^3(\mathbb{R}^3)$, the three terms in the effective potential would have their first derivatives with respect to x going to zero at infinity (for in this case both u and ∇u are continuous and go to zero at infinity) and it would not have been necessary to resort to this split.

Therefore we define the operator

$$W(x) = W_1(x) + W_2(x),$$

with on the one hand,

$$\begin{array}{rccl} W_1(x) & : & H & \to & H \\ & & v(y,z) & \mapsto & (V + u^2 \star \frac{1}{|\mathbf{x}|})(x,y,z)v(y,z), \end{array}$$

and on the other hand

$$\begin{array}{rccl} W_2(x) & : & H & \to & H \\ & & v(y,z) & \mapsto & c_1|u|^{4/3}(x,y,z)v(y,z). \end{array}$$

Since $u \in H^3_{x-loc}(\Omega_a)$, the operator $W_1(x)$ is well defined if $x > a$ and the function $x \mapsto W_1(x)$ is in $C^1(]a, +\infty[, \mathcal{L}(H))$. Moreover its derivative satisfies

$$\begin{array}{rccl} W_1'(x) & : & H & \to & H \\ & & v(y,z) & \mapsto & (\frac{\partial V}{\partial x} + 2u\frac{\partial u}{\partial x} \star \frac{1}{|\mathbf{x}|})(x,y,z)v(y,z). \end{array}$$

As

$$\lim_{x \to +\infty} \sup_{(y,z) \in \mathbb{R}^2} \left| V + (u^2 \star \frac{1}{|\mathbf{x}|}) \right| (x,y,z) = 0,$$

and

$$\lim_{x \to +\infty} \sup_{(y,z) \in \mathbb{R}^2} \left| \frac{\partial V}{\partial x} + 2(u\frac{\partial u}{\partial x} \star \frac{1}{|\mathbf{x}|}) \right| (x,y,z) = 0,$$

we have

$$\lim_{x \to +\infty} \|W_1(x)\|_{\mathcal{L}(H)} = 0$$

and

$$\lim_{x \to +\infty} \|W_1'(x)\|_{\mathcal{L}(H)} = 0.$$

Let $0 < \delta < \mathcal{E}$ and $x_0 \geq a$ so that

$$\forall x \geq x_0 \quad , \quad \|W_1'(x)\|_{\mathcal{L}(H)} \leq \mathcal{E} - \delta. \tag{5.33}$$

As for W_2, its derivative is

$$\begin{array}{rccl} W_2'(x) & : & H & \to & H \\ & & v(x,y) & \mapsto & \frac{4}{3}c_1(|u|^{1/3}sgn(u)\frac{\partial u}{\partial x})(x,y,z)v(y,z) \end{array}$$

and we cannot say how $W_2'(x)$ behaves when x goes to $+\infty$. The key point that enables us to overcome this difficulty is that $c_1|u|^{4/3}$ is everywhere non-negative.

In order to simplify the notations, we denote by

$$\phi(x) = T_u(x).$$

For all $x \geq x_0$, we define, by analogy with (5.30), the function

$$G(x) = -\|\phi'(x)\|_H^2 + \langle \phi(x), (p_\perp^2 - \mathcal{E}x + \mu + W(x)) \cdot \phi(x) \rangle_H$$

with $p_\perp^2 = -\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$. For all $x \geq x_0$,

$$
\begin{aligned}
G'(x) &= -\langle \phi(x), (\mathcal{E} - W'(x)) \cdot \phi(x) \rangle_H \\
&= -\langle \phi(x), (\mathcal{E} - W_1'(x)) \cdot \phi(x) \rangle_H + \frac{2}{5} c_1 \frac{d}{dx} \left(\int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\, dy\, dz \right).
\end{aligned}
$$

Thus, $\forall x_0 \leq x \leq x'$,

$$
\begin{aligned}
&\left(G(x) - \tfrac{2}{5} c_1 \textstyle\int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\, dy\, dz\right) - \left(G(x') - \tfrac{2}{5} c_1 \textstyle\int_{\mathbb{R}^2} |u|^{10/3}(x',y,z)\, dy\, dz\right) \\
&= \textstyle\int_x^{x'} \langle \phi(t), (\mathcal{E} - W_1'(t)) \cdot \phi(t) \rangle_H \, dt.
\end{aligned}
$$

From (5.33), we conclude that the integral in the right hand side converges when x' goes to $+\infty$. Therefore $G(x') - \frac{2}{5} c_1 \int_{\mathbb{R}^2} |u|^{10/3}(x',y,z)\, dy\, dz$ has a finite limit at $+\infty$ and this limit must be zero because $\frac{1}{x}(G(x) - \frac{2}{5} \int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\, dy\, dz)$ is in $L^1(]x_0, +\infty[)$. Thus for $x \geq x_0$

$$
G(x) = \int_x^{+\infty} \langle \phi(t), (\mathcal{E} - W_1'(t)) \cdot \phi(t) \rangle_{H \times H} \, dt + \frac{2}{5} c_1 \int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\, dy\, dz. \quad (5.34)
$$

The point is to remark that in (5.34), the nonlinear term appears with a positive sign. Using (5.33), we have for all $x \geq x_0$,

$$
G(x) \geq \delta \int_x^{+\infty} g(t)\, dt. \quad (5.35)
$$

From now on, the proof is almost the same as in [2]. However, we reproduce it here in full for the convenience of the reader.

The result of (5.35) is that for all $x \geq x_0$:

$$
g''(x) = 4 \|\phi'(x)\|_H^2 + 2G(x) \geq 0. \quad (5.36)
$$

The function g is a positive convex function integrable on $]x_0, +\infty[$. Thus $g'(x) \leq 0$ on $]x_0, +\infty[$, and $\lim_{x \to +\infty} g(x) = \lim_{x \to +\infty} g'(x) = 0$, which allows us to write, for all $x \geq x_0$,

$$
g(x) = \int_x^{+\infty} dt_1 \int_{t_1}^{+\infty} dt_2 \; g''(t_2),
$$

and with Fubini Theorem

$$
g(x) = \int_x^{+\infty} (x' - x)\, g''(x')\, dx'.
$$

As $g''(x') \geq 2G(x') \geq 2\delta \int_{x'}^{+\infty} g(t)\,dt$, we obtain after another application of Fubini Theorem,

$$g(x) \geq \delta \int_x^{+\infty} (x'-x)^2 g(x')\,dx'. \tag{5.37}$$

We have also, with (5.35) and Fubini Theorem,

$$\begin{aligned} 2\|\phi'(x)\|^2 + G(x) &\geq G(x) \\ &\geq \delta \int_x^{+\infty} g(t)\,dt \\ &= \delta \int_x^{+\infty} \frac{(x'-x)^2}{2} g''(x')\,dx', \end{aligned}$$

and therefore with (5.36),

$$2\|\phi'(x)\|^2 + G(x) \geq \delta \int_x^{+\infty} (x'-x)^2 (2\|\phi'(x')\|^2 + G(x'))\,dx'. \tag{5.38}$$

We refer the reader to [2] for the proof of the following result: if a real valued function h satisfies

- $0 \leq h(x) < +\infty \quad$ a.e. on $[x_0, +\infty[$
- $\forall x \geq x_0 \quad h(x) \geq \delta \int_x^{+\infty} (x'-x)^2 h(x')dx'$,

then $h(x)$ also satisfies for all γ so that $\gamma^3 < 2\delta$:

$$\int_{x_0}^{+\infty} e^{\gamma x} h(x)dx < +\infty.$$

Therefore, from (5.37) and (5.38) we obtain for all γ so that $\gamma^3 < 2\delta$,

$$\int_{x_0}^{+\infty} e^{\gamma x} g(x)\,dx < +\infty, \tag{5.39}$$

and

$$\int_{x_0}^{+\infty} e^{\gamma x} (2\|\phi'(x)\|^2 + G(x))\,dx < +\infty.$$

and the latter can also be written as

$$\int_{x_0}^{+\infty} e^{\gamma x} [(\|\phi'(x)\|^2 + \langle \phi(x), p_\perp^2 \cdot \phi(x) \rangle_H + c_1 \int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\,dy\,dz)$$

$$+ (\langle \phi(x), W_1(x) \cdot \phi(x) \rangle_H - \mathcal{E} x g(x) + \mu g(x))] \, dx < +\infty.$$

Using (5.39), it is easy to see that or all γ so that $\gamma^3 < 2\delta$,

$$\int_{x_0}^{+\infty} e^{\gamma x} \left(|\langle \phi(x), W_1(x) \cdot \phi(x) \rangle_H| + |\mathcal{E} x| g(x) + |\mu| g(x)) \right) \, dx < +\infty \tag{5.40}$$

Therefore, each of the following integrals of non-negative functions converges:

$$\int_{x_0}^{+\infty} e^{\gamma x} \|\phi'(x)\|^2 \, dx < +\infty \tag{5.41}$$

$$\int_{x_0}^{+\infty} e^{\gamma x} \langle \phi(x), p_\perp^2 \cdot \phi(x) \rangle_H \, dx < +\infty \tag{5.42}$$

$$\int_{x_0}^{+\infty} e^{\gamma x} \left(c_1 \int_{\mathbb{R}^2} |u|^{10/3}(x, y, z) \, dy \, dz \right) \, dx < +\infty \tag{5.43}$$

Second Step

For $\lambda \geq 0$, $0 < \epsilon < 1$ and $x \geq a$, let us denote

$$\phi_{\lambda,\epsilon}(x) = e^{\lambda x^{1-\epsilon}} \phi(x),$$

$$W_{\lambda,\epsilon}(x) = \lambda \epsilon (1-\epsilon) x^{-1-\epsilon} + \lambda^2 (1-\epsilon)^2 x^{-2\epsilon},$$

and

$$G_{\lambda,\epsilon}(x) = -\|\phi'_{\lambda,\epsilon}(x)\|_H^2 + \langle \phi_{\lambda,\epsilon}(x), (p_\perp^2 - \mathcal{E} x + \mu + W(x) - W_{\lambda,\epsilon}(x)) \cdot \phi_{\lambda,\epsilon}(x) \rangle_H.$$

We see that

$$\begin{aligned} G_{\lambda,\epsilon}(x) &= e^{2\lambda x^{1-\epsilon}} [G(x) - \lambda(\epsilon(1-\epsilon) x^{-1-\epsilon} g(x) + 2(1-\epsilon) x^{-\epsilon} \langle \phi(x), \phi'(x) \rangle_H) \\ &\quad - \lambda^2 (2(1-\epsilon)^2 x^{-2\epsilon} g(x))] \end{aligned} \tag{5.44}$$

and

$$\begin{aligned} \tfrac{d}{dx} & \left(G_{\lambda,\epsilon}(x) - \tfrac{2}{5} c_1 e^{2\lambda x^{1-\epsilon}} \textstyle\int_{\mathbb{R}^2} |u|^{10/3}(x, y, z) \, dy \, dz \right) \\ = \; & -4\lambda(1-\epsilon) x^{-\epsilon} \|\phi'_{\lambda,\epsilon}(x)\|_H^2 - e^{2\lambda x^{1-\epsilon}} \langle \phi_{\lambda,\epsilon}(x), (\mathcal{E} - W_1'(x)) \cdot \phi_{\lambda,\epsilon}(x) \rangle_H \\ & - W'_{\lambda,\epsilon}(x) g(x) - \tfrac{4}{5} c_1 \lambda (1-\epsilon) x^{-\epsilon} e^{2\lambda x^{1-\epsilon}} (\textstyle\int_{\mathbb{R}^2} |u|^{10/3}(x, y, z) \, dy \, dz). \end{aligned}$$

Let us assume there exists $x_1 \geq x_0$ so that $g(x_1) \neq 0$. Equation (5.44) shows that we can choose λ_0 large enough to have $\forall \epsilon \in]0, 1/2[$, $G_{\lambda_0,\epsilon}(x_1) < 0$. Let us now fix $0 < \epsilon_0 < 1/2$ so that $0 \leq -W'_{\lambda_0,\epsilon_0}(x_1) \leq \delta/2$. The convex function W_{λ_0,ϵ_0} also satisfies $\forall x \geq x_1$, $0 \leq -W'_{\lambda_0,\epsilon_0}(x) \leq \delta/2$, which implies

$$\frac{d}{dx}\left(G_{\lambda,\epsilon}(x) - \frac{2}{5}c_1 e^{2\lambda x^{1-\epsilon}} \int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\,dy\,dz\right) \leq 0$$

on $]x_1, +\infty[$. As furthermore $G_{\lambda,\epsilon}(x_1) - \frac{2}{5}c_1 e^{2\lambda x_1^{1-\epsilon}} \int_{\mathbb{R}^2} |u|^{10/3}(x_1,y,z)\,dy\,dz < 0$, we get

$$\int_{x_1}^{+\infty} \left(G_{\lambda,\epsilon}(x) - \frac{2}{5}c_1 e^{2\lambda x^{1-\epsilon}} \int_{\mathbb{R}^2} |u|^{10/3}(x,y,z)\,dy\,dz\right) dx = -\infty.$$

This result is in contradiction with inequalities (5.39) to (5.43). Thus $g(x) = 0$ if $x \geq x_0$, ie $u = 0$ on $[x_0, +\infty[\times\mathbb{R}^2$. By unique continuation, $u = 0$ in the whole space. □

5.2.3 The Hartree-Fock case

In presence of the same electric field, the HF equations read

$$-\Delta\phi_i + V\phi_i + (\sum_{j=1}^{N} \phi_i^2 \star \frac{1}{|x|})\phi_i - \sum_{j=1}^{N} (\phi_i\phi_j \star \frac{1}{|x|})\phi_j - \mathcal{E}x\phi_i + \epsilon_i\phi_i = 0. \qquad (5.45)$$

Proposition 6. *If $\mathcal{E} > 0$, for all $(\epsilon_i) \in \mathbb{R}^N$, the unique solution to (5.45) in $(H^1(\mathbb{R}^3))^N$ is the trivial solution.* □

Proof:

Denote

$$\Phi_i(x) = T_{\phi_i}(x) \qquad g(x) = \sum_{i=1}^{N} \|\Phi_i(x)\|_H^2.$$

We define the operators

$$\begin{array}{rccl} W(x) & : & H & \to & H \\ & & v(y,z) & \mapsto & (V + (\sum_{j=1}^{N} \phi_i^2 \star \frac{1}{|x|}))(x,y,z)v(y,z) \end{array}$$

and

$$\begin{array}{rccl} W_{i,j}(x) & : & H & \to & H \\ & & v(y,z) & \mapsto & -(\phi_i\phi_j \star \frac{1}{|x|})(x,y,z)v(y,z). \end{array}$$

The functions $x \mapsto W(x)$ and $x \mapsto W_{i,j}(x)$ are in $C^1(]a,+\infty[, L(H))$ and their respective derivatives $W'(x)$ and $W'_{i,j}(x)$ tend to 0 in norm when $x \mapsto +\infty$. Let $0 < \delta < 2\mathcal{E}/3$ and $x_0 \geq a$ so that $\|W(x)\|_{\mathcal{L}(H)} \leq \mathcal{E} - 3\delta/2$ and $\|W_{i,j}(x)\|_{\mathcal{L}(H)} \leq \delta/2$ for all (x,i,j), $x \geq x_0$.

Denote this time

$$\begin{aligned} G(x) &= \sum_{i=1}^{N} \left(-\|\Phi'_i(x)\|_H^2 + \langle \Phi_i(x), (p_\perp^2 - \mathcal{E}x + \epsilon_i + W(x)) \cdot \Phi_i(x) \rangle_H \right) \\ &\quad + \sum_{i,j=1}^{N} \langle W_{i,j}(x) \cdot \Phi_i(x), \Phi_j(x) \rangle_H. \end{aligned}$$

We have

$$-G'(x) = \sum_{i=1}^{N} \langle \Phi_i(x), (\mathcal{E} - W'(x)) \cdot \Phi_i(x) \rangle_H - \sum_{i,j=1}^{N} \langle W'_{i,j}(x) \cdot \Phi_i(x), \Phi_j(x) \rangle_H.$$

There comes

$$\forall x \geq x_0 \qquad -G'(x) \geq \delta \; g(x)$$

and thus

$$\forall x \geq x_0 \qquad G(x) \geq \delta \int_x^{+\infty} g(x)\, dx + c$$

As $\frac{G(x)}{x} \in L^1(]x_0,+\infty[)$, $c = 0$ and therefore

$$\forall x \geq x_0 \qquad G(x) \geq \delta \int_x^{+\infty} g(x)\, dx$$

which enables us to resume the proof by Avron and Herbst (cf [2] and Section 5.2.2). □

The extension of this proof to some other classical real or complex Hartree-Fock type models is straightforward.

5.2.4 Remarks on the non-existence proof

We wish to make a few comments on the above result. Let us come back to the equation considered by Avron and Herbst:

$$-\Delta u + Vu - xu = 0.$$

The proof of non-existence of bound states, that we have mimicked above, makes use of the behaviour of the *derivative* of the potential V with respect to the coordinate x along the electric field: if for instance V is bounded but $\frac{\partial V}{\partial x}$ has large deviations, the above proof does nos allow to conclude. For example, let us consider $V(x,y,z) = \frac{\sin(x^2)}{\sqrt{1+|x|}}$. This potential does not fall into the scope of our proof. Unfortunately, we do not know how to extend the proof by Avron and Herbst to cover such situations. However, we wish to draw the reader's attention on the following point. If we restrict ourselves to considering positive solutions, then it is possible to prove a non-existence result that covers much a wider class of potentials that the ones considered so far. Indeed a variational argument allows us to prove

Lemma 2. *Let us consider the system*

$$(II) \begin{cases} -\Delta u + \mathcal{V} u = 0 & \text{on } \mathbb{R}^3 \\ u > 0 & \text{on } \mathbb{R}^3 \end{cases}$$

with $\mathcal{V} \in L^q_{loc}$ for some $q \geq 6/5$ and so that

$$\exists\,(R_n) \quad R_n > 0 \quad \exists\,(y_n) \quad / \qquad R_n^2 \operatorname*{ess\,sup}_{B_{R_n}(y_n)} \mathcal{V} \to -\infty. \tag{5.46}$$

Then the system (II) has no solution in $H^1_{loc}(\mathbb{R}^3)$. □

Before we give the simple proof of this lemma, we would like to mention that, so far as we know, results of non-existence of positive solutions are rather seldom. Here we consider a rather simple case when the potential (at least in some well chosen areas of $\mathbb{R}^3$) goes to $-\infty$ as $|x| \to +\infty$, and we obtain that the only positive solution is trivial, only by assuming the local integrability of the solution and its first derivative. If the potential does not go to $-\infty$, but still does not go fast enough to zero at infinity, the situation is less simple, and a standard result is that if $\mathcal{V} \in L^{3/2}(\mathbb{R}^3)$ there is no solution u to (II) (see [19]). Also in the framework of Quantum Mechanics we refer the reader to [5], where various conditions on the behaviour of the potential at infinity are considered. More generally, this question is connected to the interesting and difficult question of existence of bound states for Schrödinger operators with a potential that does not vanish at infinity.

Remark 8: Note that when we get rid of the assumption $u \geq 0$, results of non-existence are even more seldom: we only are aware of the result by Avron and

Herbst [2] (and its extension to the N-body problem in [11]) and of the Virial Theorem (see [17]).

Proof of Lemma 2:

Denote $\lambda_1 > 0$ the first eigenvalue of the operator $-\Delta$ on $B_1(0)$ with the Dirichlet condition $u = 0$ on the boundary $S_1(0)$. Let $\phi_1 > 0$ be the positive eigenvector associated with λ_1. As a consequence of the strong maximum principle, ϕ_1 also satisfies $\frac{\partial \phi_1}{\partial \nu} < 0$ on $S_1(0)$ (ν denotes the outward pointing normal). Denote $\phi_1^{(n)}(x) = \phi_1((x - y_n)/R_n)$. The function $\phi_1^{(n)}$ is the first eigenvector of the operator $-\Delta$ on $B_{R_n}(y_n)$ with the Dirichlet condition $u = 0$ on the boundary $S_{R_n}(y_n)$ associated with the eigenvalue λ_1/R_n^2. Suppose that there exists a solution $u \in H^1_{loc}$ of (II). As $\phi_1^{(n)}$ and u are positive on $B_{R_n}(y_n)$, we have

$$\begin{aligned} 0 &= \int_{B_{R_n}(y_n)} (-\Delta u + \mathcal{V} u)\phi_1^{(n)} \\ &\leq \int_{B_{R_n}(y_n)} (-\Delta \phi_1^{(n)})u + \int_{S_{R_n}(y_n)} \frac{\partial \phi_1^{(n)}}{\partial \nu} u + \int_{B_{R_n}(y_n)} \mathcal{V} u \phi_1^{(n)} \\ &\leq \frac{1}{R_n^2}(\lambda_1 + R_n^2 \operatorname*{ess\,sup}_{B_{R_n}(y_n)} \mathcal{V})(\int_{B_{R_n}(y_n)} \phi_1^{(n)} u) \end{aligned}$$

and thus $\lambda_1 \geq -R_n^2$ ess $\sup_{B_{R_n}(y_n)} \mathcal{V}$, which contradicts hypothesis (5.46). □

5.3 On "states" computed by Quantum Calculation programs

All Quantum Calculation programs offer to compute the "Hartree-Fock ground-state" of a molecular system subjected to a uniform external electric field. Having regard to our result of non-existence, that seems, at first sight, irrelevant.

We can easily understand the reason why these programs may converge, for they actually minimize the Hartree-Fock energy over the unit ball of a *finite dimensional* vector space (of linear combinations of Slater or Gaussian functions). This problem is obviously compact in the usual sense, and the minimum is thus always achieved. The question is that of the intrinsic nature of the result obtained by such a calculation. On the one hand, it is clear that the computed energy can be made as low as one wish by choosing an appropriate finite basis. On the other hand, it is reasonable to think, though this is not proved at the present time, that the particular finite basis function sets considered by the chemists, which consist of Slater or Gaussian functions that are centered on the nuclei (or on "chemical bonds"), force the electrons to stay close to the nuclei, and prevent them from tunnelling through the potential barrier separating the potential wells created by the nuclei from the regions of large x where the electrostatic potential is highly negative. The

so-obtained numerical result may therefore have an intrinsic nature which might be related to some resonance state.

We underline that our non-existence result that claims that, for Hartree-Fock models, it is impossible to bind nuclei and electrons together under a uniform external electric field, is only in *apparent* contradiction with the calculations performed by the Chemists. It only shows that an additional mathematical study is necessary to make the situation clear.

6 Appendix

Let $v \in H^1(\mathbb{R}^3)$. Let us prove that $x \mapsto T_v(x)$ is continuous (and even Lipschitz) from $\mathbb{R}$ into $H = L^2(\mathbb{R}^2)$. Let $v \in S(\mathbb{R}^3)$ and $(x_1, x_2) \in \mathbb{R} \times \mathbb{R}$. Denote $\hat{v}^1$ the Fourier transform of v with respect to the first coordinate. It comes

$$\begin{aligned}
&\|T_v(x_2) - T_v(x_1)\|^2_{L^2(\mathbb{R}^2)} \\
&= \int_{\mathbb{R}^2} (v(x_2, y, z) - v(x_1, y, z))^2 \, dy \, dz \\
&= \int_{\mathbb{R}^2} \left(\int_{-\infty}^{+\infty} \hat{v}^1(\xi, y, z)(e^{i\xi x_2} - e^{i\xi x_1}) \, d\xi \right)^2 dy \, dz \\
&= \int_{\mathbb{R}^2} \left(\int_{-\infty}^{+\infty} \hat{v}^1(\xi, y, z)(1 + |\xi|^2)^{1/2} (\tfrac{e^{i\xi x_2} - e^{i\xi x_1}}{(1+|\xi|^2)^{1/2}}) \, d\xi \right)^2 dy \, dz \\
&\leq \left(\int_{\mathbb{R}^3} |\hat{v}^1|^2(\xi, y, z)(1 + |\xi|^2) \, d\xi \, dy \, dz \right) \left(\int_{-\infty}^{+\infty} \tfrac{|e^{i\xi x_2} - e^{i\xi x_1}|^2}{1+\xi^2} \, d\xi \right) \\
&\leq \|v\|^2_{H^1(\mathbb{R}^3)} \left(\int_{-\infty}^{+\infty} \tfrac{sin^2 t}{t^2} \, dt \right) |x_2 - x_1|^2.
\end{aligned}$$

Thus there exists $A > 0$ so that $\forall v \in S(\mathbb{R}^3)$ $\forall (x_1, x_2) \in \mathbb{R} \times \mathbb{R}$,

$$\|T_v(x_2) - T_v(x_1)\| \leq A \|v\|_{H^1(\mathbb{R}^3)} |x_2 - x_1|.$$

As for x fixed, $v \mapsto T_v(x)$ is continuous from $H^1(\mathbb{R}^3)$ into H, and as $S(\mathbb{R}^3)$ is dense in $H^1(\mathbb{R}^3)$, we conclude that

$$\forall v \in H^1(\mathbb{R}^3) \; \forall (x_1, x_2) \in \mathbb{R} \times \mathbb{R} \; \|T_v(x_2) - T_v(x_1)\| \leq A \|v\|_{H^1(\mathbb{R}^3)} |x_2 - x_1|.$$

Let us now consider $v \in H^2(\mathbb{R}^3)$. We will prove that $T_v \in C^1(\mathbb{R}, L^2(\mathbb{R}^2))$ and $T'_v = T_{\frac{\partial v}{\partial x}}$.
Let $v \in S(\mathbb{R}^3)$ and $(x_1, x_2) \in \mathbb{R} \times \mathbb{R}$ with $x_1 \neq x_2$.

$$
\begin{aligned}
&\| \tfrac{1}{x_2-x_1}(T_v(x_2)-T_v(x_1)) - T_{\frac{\partial v}{\partial x}}(x_1)\|_H^2 \\
&= \int_{\mathbb{R}^2} \left(\tfrac{v(x_2,y,z)-v(x_1,y,z)}{x_2-x_1} - \tfrac{\partial v}{\partial x}(x_1) \right)^2 dy\,dz \\
&= \int_{\mathbb{R}^2} \left(\int_{-\infty}^{+\infty} \hat{v}^1(\xi,y,z)(\tfrac{e^{i\xi x_2}-e^{i\xi x_1}}{x_2-x_1} - i\xi e^{i\xi x_1})\,d\xi \right)^2 dx\,dy \\
&= \int_{\mathbb{R}^2} \left(\int_{-\infty}^{+\infty} \hat{v}^1(\xi,y,z)(1+\xi^2)(\tfrac{\frac{e^{i\xi x_2}-e^{i\xi x_1}}{x_2-x_1} - i\xi e^{i\xi x_1}}{1+\xi^2})\,d\xi \right)^2 dx\,dy \\
&\leq \left(\int_{\mathbb{R}^3} |\hat{v}^1|^2(\xi,y,z)(1+\xi^2)^2\,d\xi\,dy\,dz \right) \left(\int_{-\infty}^{+\infty} \tfrac{|\frac{e^{i\xi x_2}-e^{i\xi x_1}}{x_2-x_1} - i\xi e^{i\xi x_1}|^2}{(1+|\xi|^2)^2}\,d\xi \right) \\
&\leq \alpha^2(x_1,x_2)\ \|v\|^2_{H^2(\mathbb{R}^3)}
\end{aligned}
$$

with

$$
\alpha(x_1,x_2) = \left(\int_{-\infty}^{+\infty} \frac{|\frac{e^{i\xi x_2}-e^{i\xi x_1}}{x_2-x_1} - i\xi e^{i\xi x_1}|^2}{(1+|\xi|^2)^2}\,d\xi \right)^{1/2}.
$$

For x fixed, $v \mapsto (T_v(x), T_{\frac{\partial v}{\partial x}}(x))$ is continuous from $H^2(\mathbb{R}^3)$ on $H \times H$. Besides $S(\mathbb{R}^3)$ is dense in $H^2(\mathbb{R}^3)$. Therefore

$\forall v \in H^1(\mathbb{R}^3) \quad \forall (x_1,x_2) \in \mathbb{R}\times\mathbb{R} \ / \ x_1 \neq x_2,$

$$
\| \frac{1}{x_2-x_1}(T_v(x_2)-T_v(x_1)) - T_{\frac{\partial v}{\partial x}}(x_1)\|_H \leq \alpha(x_1,x_2)\|v\|_{H^2(\mathbb{R}^3)}.
$$

There remains to prove that for $x_1 \in \mathbb{R}$, $\alpha(x_1,x_2)$ tends to zero as x_2 goes to x_1. Let $x_1 \in \mathbb{R}$. Let us consider a real sequence $(x_2^{(n)})_{n\in\mathbb{N}}$ which converges to x_1. Denote

$$
f_n(\xi) = \frac{\left| \frac{e^{i\xi x_2^{(n)}}-e^{i\xi x_1}}{x_2^{(n)}-x_1} - i\xi e^{i\xi x_1} \right|^2}{(1+|\xi|^2)^2}.
$$

We see that

- $\forall \xi \in \mathbb{R} \quad \lim_{n\to+\infty} f_n(\xi) = 0,$
- $\forall \xi \in \mathbb{R} \quad |f_n(\xi)| \leq \frac{4}{1+\xi^2}.$

By dominated convergence $\lim_{n\to+\infty} \alpha(x_1,x_2^n) = 0$.

Finally if $v \in H^2(\mathbb{R}^3)$, it is clear that for all $x_0 \in \mathbb{R}$, $\frac{\partial}{\partial y}(T_v(x_0)) = T_{\frac{\partial v}{\partial y}}(x_0)$ and that $\frac{\partial}{\partial z}(T_v(x_0)) = T_{\frac{\partial v}{\partial z}}(x_0)$ (it is true for $v \in D(\mathbb{R}^3)$; we conclude with a density argument).

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