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Computing a molecule: A mathematical viewpoint

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We give here an overview of the mathematical results known to this day on the models used in Quantum Chemistry for the numerical computations of molecules. We focus on the problems related to the ground state, in the framework of Hartree–Fock type models and Thomas–Fermi type models. More precisely, we outline the most recent results on the following questions: existence and uniqueness of the minimum, and existence of an optimized geometry for the nuclei. We eventually give a list of open problems.

0. Introduction

The enterprise of trying to put the models used for numerical simulations in quantum molecular chemistry on a sound mathematical ground is a rather new one.

Though a somewhat considerable amount of situations has been considered in say the last twenty years, a lot of questions remain open and the state of the mathematical knowledge is far from being sufficient to cover all the models used in chemistry. Apart from being interesting *per se* since the models used in chemistry give birth to a lot of difficult mathematical problems, we believe that a mathematical study is definitely necessary in order to have a global understanding of a given model. Therefore we find it useful to survey, in this paper principally aimed at chemists, some of the most recent mathematical results on such models. We concentrate on the mathematical aspects belonging to the following field: variational problems associated to nonlinear partial differential equations. We shall be only concerned with the basic questions of existence and uniqueness of a ground state, and of its properties (regularity, symmetry, decreasing at infinity, ...), leaving apart questions like those of asymptotic limits (behavior of the model when the total nuclear charge Z tends to infinity – see, for instance, Lieb [59,62,63], Solovej [89], and references therein –, ...), or any question of algebraic nature. More than being academical, the knowledge of the existence and uniqueness of the ground-state of a system is of practical interest for chemists. For instance, chemical species built from arbitrarily chosen atoms and charges (e.g., NCB^{4-} or $OBCBO^{2-}$!) are nowadays calculated (Pyykkö [77], Scheller and Cederbaum [84,85], Gutowski and Simons [35], Gonzales and Simons [33]) in order to predict their stability and/or geometry prior to be synthetized.

Let us emphasize that we do not pretend to be comprehensive. A lot of models and studies are not included hereafter at least for the two following reasons. The first one because of course there may exist some works we are not aware of; the second one because, on purpose, we chose to present below a synthetic view of the models that are either the most widespread, or the most interesting and the most tractable (or both), emphasizing the mathematical and numerical problems, already solved or still open, they raise. Rather than giving an exhaustive list of the various theories that have been developped so far in Quantum Molecular Chemistry to model the molecular systems and a comprehensive survey of the theoretical works devoted to their mathematical analysis, we therefore prefer to highlight the general mathematical behaviours through some well known examples. Our purpose is to give some insight into the mathematical difficulties. We shall only deal with *ab initio* models, many models, like semi-empirical models, or molecular dynamics models, being not even approached here. In view of the present power of computers, the models we study therefore apply to molecules that do not contain more than an order of magnitude of 10^2 atoms (see for instance Friedman [29], Dixon [18], and Löwdin [67] in order to have an idea on the CPU time and the facilities required for computations in various approaches). But let us at once emphasize that the mathematical results we give here are always valid, independently from the number of atoms contained in the molecule under consideration.

Since we only aim at surveying, no proof will be given. We shall only give the broad outlines of the mathematical ideas, especially when we find they shed light on the deep nature of the model, and refer the interested reader to the bibliography for further information.

Let us finally point out that this article only presents ‘a’ mathematical point of view on the models used in Quantum Chemistry. Other points of view are of course possible. Besides, needless to say, this article does not pretend to compete with reviews made by physicists or chemists on the physical aspects of the subject (see, e.g., Lieb [59], Sprung [90]).

Our article is organized as follows.

In section 1, we first give a synthetic view of the models we are going to consider hereafter. Then we briefly explain the mathematical foundations of these models, describing the general features they share. This first section therefore introduces, in what we hope to be a way as clear as possible, the mathematical tools that will be extensively used in the following sections. Its reading requires only some basic knowledge in topology and real analysis. Of course, readers who are familiar with functional analysis and variational methods may easily skip that part (section 1.2), as well as they may skip the few footnotes that we spread over the text to recall some basic mathematical notions we shall need.

We devote the second section to the Hartree–Fock model, and some related models. Apart from being the most commonly used model, this model is also at the basis of a lot of related ones, as far as the theoretical or the numerical aspects are concerned. We therefore take this opportunity to give details that clearly lie beyond the simple setting of the Hartree–Fock model.

Section 3 deals with the Thomas–Fermi type models. Though these models might seem now a little out-of-date for a computational using, it is however true that the Thomas–Fermi theory can be seen as the first issue of a density functional theory. Besides, it turns out that, mathematically, it gives rise to interesting problems that are moreover close to the problems one probably shall have to understand in the future when dealing with more sophisticated theories.

In the fourth section, we approach the question of the geometry of the molecule. While it is quite customary in a numerical code to optimize the geometry, the theoretical problem of the existence of a set of positions of the nuclei and of an electronic wave function that minimize the total energy of the molecule (kinetic and potential energies of the electrons with respect to the positions of the nuclei plus repulsion of the nuclei) is nevertheless a question of great interest that remains open in particular in the very common Hartree–Fock setting. We briefly outline in that section the proof of this existence in the Hartree and in the Thomas–Fermi–Dirac–von Weizsäcker settings.

We end this article by coming back in the fifth section to a few questions that we believe to be the most interesting ones to tackle, and that are likely to become, to our mind, some of the main challenges in this field in a next future.

1. Generalities

1.1. *Various molecular models*

As said in the introduction, the models we shall deal with in this article are *ab initio* models. In addition, we shall restrict our study to models that share the following features. They are nonrelativistic, time-independent models. Moreover, we assume that the nuclei are points (one may also consider through slight modifications smeared out nuclei), and, in this section and until section 4 below, we assume that they stand at fixed known positions (see on this question the remarks at the beginning of section 4).

Then, finding the electronic ground-state of the molecule and its energy would require to solve the minimization problem:

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

where

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

and

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

In the above formula, and throughout the whole paper, we denote by N the number of electrons, z_k and $\bar{x}_k$ the charge and the position of the kth nucleus, the total nuclear charge being $Z = \sum_k z_k$. For the sake of simplicity, we deal with real-valued functions, and do not explicitely consider the spin variable; we are aware that for the chemical aspects it is not obvious to make such a choice, but, for the mathematical aspects we want to address here, it does not matter and it is more convenient. The vector space associated to physical functions ϕ is that of square integrable functions with respect to the three dimensional measure in the Lebesgue sense, i.e., the Hilbert space $L^2(\mathbf{R}^{3N})$ which is reduced to the subspace $L^2_a(\mathbf{R}^{3N})$ consisting of all antisymmetric functions (this is an arbitrary choice, that is commonly made, but other choices are possible, and the mathematical analysis below will still be valid for these other choices). In addition, in order to give some sense to the first term of H_N, we restrict ourselves to functions ϕ whose partial derivatives are square integrable functions and assume $\phi \in H^1(\mathbf{R}^{3N})$.

This problem turns out to be too difficult to solve numerically, in particular because of two main reasons: the space $L^2_a(\mathbf{R}^{3N})$ is too large, and the nonlinear term

$$\sum_{1 \leqslant i < j \leqslant N} \frac{1}{|x_i - x_j|}$$

leads to overwhelming difficulties.

In order to make a numerically tractable problem, two ways of simplification of the above problem are commonly used, each one corresponding to one of the two above mentioned difficulties. According to this alternative we may suggest to partition the models used in molecular chemistry into two categories. Let us at first emphasize that, by doing so, we only pretend to give a synthetic mathematical view of the models.

On the one hand, the first track used to simplify the above problem consists in restricting oneself to a space of functions smaller than $L^2_a(\mathbf{R}^{3N})$, while keeping the same Hamiltonian. This is what we may call a *rigorous energy / approximated wave function* approach.

If that space of functions is conveniently chosen, it leads at once to easier computations of the terms of the energy (thus there is less CPU time spent in the computations) and an easier representability of the functions by some basis functions (thus a smaller memory is required). But of course there is a price to pay for such a simplification, and the price is an error on the result. Indeed, it follows that we only may hope to obtain an upper bound to the 'true' energy, since the space one minimizes the energy upon is not the entire space.

The typical example of such a model is the Hartree–Fock approximation (see, for instance, among the huge bibliography dealing with the Hartree–Fock approximation, Levine [58], Szabo and Ostlund [94], Wilson [99], Hurley [39,40]): one restricts oneself to the set of functions that are of the form of a determinant

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

where $\int \varphi_i \varphi_j = \delta_{ij}$. Even if spin functions are considered, the φ_i's are spin-orbitals (of the standard α and β Pauli type) and therefore there is an equal number of φ_i's and electrons.

This leads to the following minimization problem:

$$\begin{aligned} I^{\mathrm{HF}} &= \inf\left\{\langle H_N\phi, \phi\rangle;\ \phi \text{ of the form (1.4)};\ \int \varphi_i\varphi_j = \delta_{ij}\right\} \\ &= \inf\Bigg\{E^{\mathrm{HF}}(\varphi_1, \dots, \varphi_N) = \sum_{i=1}^{N} \int |\nabla\varphi_i|^2 + \sum_{i=1}^{N} \int V|\varphi_i|^2 \\ &\qquad + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y - \frac{1}{2}\iint \frac{|\rho(x,y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y; \\ &\qquad \varphi_i \in H^1(\mathbf{R}^3),\ \int \varphi_i\varphi_j = \delta_{ij}\Bigg\}, \end{aligned} \tag{1.5}$$

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

We shall come back to this problem in the next section.

On the other hand, one may simplify the above problem by following what we call here a *rigorous density / approximated energy* approach.

Basically, it consists in minimizing some approximated energy functional on the set of electronic densities ρ that are functions of only three space variables. In view of a fundamental result by Hohenberg and Kohn [38] (see section 3.4), there is in fact no loss of generality, as far as the ground state is concerned. In addition, the electronic repulsion which is the most delicate term to deal with is often simplified, for instance replaced by some averaged local field the electrons are subjected to. But then, the choice of the approximated energy requires great attention, since all the imperfections of the model and the inadequacy in comparison with the expected results will come from it.

The simplest example of such an approximation is the Thomas–Fermi theory (Levine [58], March [69], Dreizler and Gross [19], ...). It consists in finding the solution to the following minimization problem:

$$I^{\mathrm{TF}} = \inf\left\{E^{\mathrm{TF}}(\rho);\ \rho \geqslant 0,\ \rho \in L^1 \cap L^{5/3},\ \int_{\mathbf{R}^3} \rho = N\right\}, \tag{1.6}$$

where

$$E^{\mathrm{TF}}(\rho) = \int_{\mathbf{R}^3} \rho^{5/3} + \int_{\mathbf{R}^3} V\rho + \frac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y, \tag{1.7}$$

$$V(x) = -\sum_k \frac{z_k}{|x - \bar{x}_k|}. \tag{1.8}$$

Of course, this approximation is *per se* too crude and many improvements of the energy functional $E^{\mathrm{TF}}(\rho)$ are necessary (we shall come back to these improvements below).

But the general feature is, for the most part, already contained in the Thomas–Fermi problem (1.6)–(1.8).

In each of the two strategies described above, we have just seen that the approximation may be not accurate enough. Therefore, some improvements are necessary.

In the first approach, the inaccuracy lies in the fact that the space of functions is too small. Thus there remains to enlarge this space, considering more functions. This gives rise to the so called multiconfiguration methods, such as for instance the Configuration Interaction method, or the Multi Configuration Self Consistent Field method, where one considers functions that are convenient sums of determinants.

In the second approach, a lot of better approximation of the energy functional are available: Thomas–Fermi–von Weizsäcker model, Thomas–Fermi–Dirac–von Weizsäcker model, models issued from the Density Functional theory (Kohn–Sham approach, Local density approximation), ... Several density functionals for molecules have been reviewed in 1990 by Clementi and Chakraverty [16] or [17].

Each of these models leads to a new mathematical minimization problem, that it is worthwhile to study. Thus, we shall see below the mathematical properties of each of these methods, but we prefer to come back now to the general mathematical setting of these approximations.

1.2. Mathematical background

In all the models we introduced above, the mathematical fundation is the following abstract problem ($\mathcal{P}$):

($\mathcal{P}$) *Define the energy functional* $E(\phi)$ *on a set* X *of functions* ϕ *(the set of all the possible states of the molecule).*

Then find a function $\phi_0 \in X$ *(the ground-state) satisfying some given constraint* $J(\phi_0) = \lambda$ *(which means that the number of electrons is fixed) and minimizing the energy* E *on the convenient set of states, namely*

$$I_\lambda = E(\phi_0) = \inf \big\{ E(\phi);\ \phi \in X,\ J(\phi) = \lambda \big\}.$$

(I_λ *is the ground-state energy*.)

(In order to make this abstract problem more concrete, think to the Thomas–Fermi model (1.6)–(1.7).)

Let us consider this problem ($\mathcal{P}$) from the mathematical viewpoint.

1.2.1. Existence of a minimum: the possible loss of compactness

First, the existence of a minimum ϕ_0 is not obvious.

Indeed, in all interesting situations, there is not enough compactness in the model to ensure that a minimum exists *a priori*. Let us briefly explain what we mean by this fundamental notion of compactness.

Let ϕ^n be a minimizing sequence of the problem $(\mathcal{P})$, that is a sequence satisfying

$$\begin{cases} \phi^n \in X, \\ J(\phi^n) = \lambda, \\ E(\phi^n) \overset{n\to\infty}{\longrightarrow} I_\lambda. \end{cases}$$

(Clearly, such a sequence exists as soon as $\{\phi \in X,\ J(\phi) = \lambda\}$ is nonempty.)

A natural guess is to hope that, under suitable conditions, the sequence ϕ^n converges, in some sense to be precised later, to some ϕ_0 that belongs to the set X, that satisfies at once $J(\phi_0) = \lambda$ and $E(\phi_0) = I_\lambda$, thus is a minimum of the problem $(\mathcal{P})$.

However, from the rigorous mathematical viewpoint, the above fact is not obvious and one faces the following difficulty.

Assume that the problem is well-posed, which means that the energy functional $E(\phi)$ is bounded from below on the set $\{\phi \in X;\ J(\phi) = \lambda\}$, and that any minimizing sequence is bounded for some well chosen norm. It is then always possible to weaken the topology of X in order to make the sequence ϕ^n converge to some $\phi_0 \in X$ in a weak sense, but then for the functional E, and for the functional J, there is not enough information in order to pass to the limit and the convergence may be so weak that it is not easy to prove that $E(\phi^n) \overset{n\to\infty}{\longrightarrow} E(\phi_0)$ (which yields $E(\phi_0) = I_\lambda$) and $J(\phi_0) = \lambda$.

Indeed, the weaker the topology, the more numerous the compact sets (thus the more numerous the convergent sequences). In a reflexive Banach space (e.g., a space like $L^p(\mathbf{R}^3)$, $1 < p < \infty$, or $H^1(\mathbf{R}^3)$), any bounded sequence is, up to an extraction, convergent for the weak topology[1]. This presents the interest of creating a limit, which is a good candidate to be a minimum for problem $(\mathcal{P})$; But there remains next to prove that this limit is indeed a minimum. For all these mathematical notions (and the others we shall approach below), we refer the interested reader to the following books: Adams [1], Reed and Simon [81], Gilbarg and Trudinger [30].

In order to illustrate this difficulty in a simple way, we consider the so-called Thomas–Fermi–von Weizsäcker model, which is an improvement of the basic Thomas–Fermi model (1.6)–(1.7),

$$I_\lambda^{\mathrm{TFW}} = \inf\left\{E^{\mathrm{TFW}}(\phi);\ \phi \in H^1(\mathbf{R}^3),\ \int_{\mathbf{R}^3} \phi^2 = \lambda\right\}, \tag{1.9}$$

$$E^{\mathrm{TFW}}(\phi) = \int_{\mathbf{R}^3} |\nabla\phi|^2 + \int_{\mathbf{R}^3} \phi^{10/3} + \int_{\mathbf{R}^3} V\phi^2 + \frac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\phi^2(x)\phi^2(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y, \tag{1.10}$$

with V given by (1.8).

For a minimizing sequence ϕ^n of the above problem (1.9)–(1.10), it is easy to prove (see Lieb [59], Lieb and Simon [61]) that ϕ^n converges up to an extraction

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[1] Recall that the weak topology is defined in such a space by: $f_n \in X$ weakly converges to $f \in X$ if and only if $\langle g, f_n\rangle \to \langle g, f\rangle$ for all g in the dual space X' of X, that is the space of all continuous linear maps from X to $\mathbf{R}$. Recall also that *convergent up to an extraction* means that there exists some subsequence of the given sequence that converges.

to some $\phi_0 \in H^1(\mathbf{R}^3)$, for the weak topology of $H^1(\mathbf{R}^3)$, and that $E^{\mathrm{TFW}}(\phi^n) \overset{n\to\infty}{\longrightarrow} E^{\mathrm{TFW}}(\phi_0)$. Nevertheless, without further condition (Lieb [59], Lieb–Simon [61]), we can only claim that $\int_{\mathbf{R}^3} \phi_0^2 \leqslant \lambda$ and not that $\int_{\mathbf{R}^3} \phi_0^2 = \lambda$. We say that there is a possible loss of compactness at infinity. In other words, some charge among the total charge λ may have escaped at infinity (think for instance to the sequence $\phi^n(x) = 1$ if $x \in [n, n+1]$, 0 otherwise, in $L^2(\mathbf{R})$, that weakly converges to $\phi_0 = 0$ when n tends to infinity, but satisfies $\int |\phi^n|^2 = 1$ for all n).

It is to be emphasized here that this kind of phenomenon of course would not happen if the problem was posed over a bounded domain $\Omega \subset \mathbf{R}^3$ instead of over $\mathbf{R}^3$ itself. Actually, the minimization problems we consider here are called *locally compact problems* in the following sense: if they were posed on a bounded domain, these problems would be easily solvable by standard techniques. The most obvious simplification in the bounded case is the following. Replace the problem (1.9)–(1.10) by

$$I_\lambda^{\mathrm{TFW}}(\Omega) = \inf\left\{ E_\Omega^{\mathrm{TFW}}(\phi);\ \phi \in H_0^1(\Omega),\ \int_\Omega \phi^2 = \lambda \right\}, \tag{1.9'}$$

$$E_\Omega^{\mathrm{TFW}}(\phi) = \int_\Omega |\nabla\phi|^2 + \int_\Omega \phi^{10/3} + \int_\Omega V\phi^2 + \frac{1}{2}\iint_{\Omega\times\Omega} \frac{\phi^2(x)\phi^2(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y, \tag{1.10'}$$

where $H_0^1(\Omega) = \{\phi \in L^2(\Omega);\ \phi = 0 \text{ on } \partial\Omega,\ \nabla\phi \in (L^2(\Omega))^3\}$.

Then, using the compact embedding of $H_0^1(\Omega)$ into $L^p(\Omega)$, for all $1 \leqslant p < 6$, we know that, extracting a subsequence if necessary, any arbitrary minimizing sequence ϕ^n converges strongly in $L^p(\Omega)$, thus $\int_\Omega \phi_0^2 = \lambda$.

1.2.2. Existence of a minimum: How to prove it

In order to prevent the loss of compactness in the unbounded case, we have to make a more detailed study. Though it is not our purpose in this work to describe in details the study of all kinds of possible loss of compactness in this family of minimization problem (we refer the interested reader to Lions [64] or [65] where the concentration compactness approach is extensively explained), we still wish to make a few general comments here. Next we shall explain why and how one is able to avoid a complicated analysis in the simple Thomas–Fermi–von Weizsäcker case, and find some simple condition that ensures that a minimum exists.

In this family of problems, some charge may escape at infinity in order to obtain a lower energy. Roughly speaking, a minimizing sequence ϕ^n for the problem I_λ may for instance split into two parts ϕ_1^n and ϕ_2^n such that ϕ_1^n is a minimizing sequence for some subproblem I_{λ_1} and ϕ_2^n is a minimizing sequence for some subproblem at infinity $I_{\lambda-\lambda_1}^\infty$ (i.e., the same problem as $I_{\lambda-\lambda_1}$ but with $V \equiv 0$). In order to prevent such a splitting, it is enough (and actually the two facts are equivalent) to check the following inequality, which is called a strict subadditivity condition,

$$I_\lambda < I_{\lambda_1} + I_{\lambda-\lambda_1}^\infty,$$

for all possible $0 < \lambda_1 < \lambda$. Proving such a condition amounts to proving the compactness. It is to be outlined that this mathematical formulation truly fits in with the physical reality: think to the splitting of a minimizing sequence with $\lambda_1 = \lambda - 1$, as an escape of an electron, namely a ionization or at least an excitation. Likewise, in another framework, quantum chemists speak of coulombian explosure of dications. Such species are metastable, i.e., they can be observed via spectroscopic methods but the corresponding geometry is a secondary minimum of their potential surface which is separated from the true minimum by a very large energy barrier (through which tunneling is very low), see Levasseur et al. [57].

Let us now turn to the simpler case of the Thomas–Fermi–von Weizsäcker problem.

It turns out that ϕ_0, the weak limit of the arbitrary minimizing sequence ϕ^n we consider, is the minimum of the so-called problem with relaxed constraint

$$\tilde{I}_\lambda^{\mathrm{TFW}} = \inf\left\{E^{\mathrm{TFW}}(\phi);\ \phi \in H^1(\mathbf{R}^3),\ \int_{\mathbf{R}^3} \phi^2 \leqslant \lambda\right\}. \tag{1.11}$$

(The reason is essentially that the potential V given by (1.8) vanishes at infinity, see Lieb [59], Lieb and Simon [61]; hence the problem at infinity, in the sense we defined above, is trivial.)

Next, it follows that ϕ_0 satisfies the Euler–Lagrange equation associated to the minimization problem (1.11), which is a nonlinear elliptic partial differential equation of the second order, namely

$$\left(-\Delta + V + \frac{5}{3}\phi_0^{4/3} + \phi_0^2 \star \frac{1}{|x|}\right)\phi_0 = -\mu\phi_0. \tag{1.12}$$

A straightforward argument shows that it suffices to show that the Lagrange multiplier μ cannot vanish in order to prove that ϕ_0 is a minimum of (1.9). Let us emphasize this point: the existence of a minimum is a mathematical problem that is closely related to the fact that 0 is or not an eigenvalue of some Schrödinger operator (here $-\Delta + V + (5/3)\phi_0^{4/3} + \phi_0^2 \star (1/|x|)$). Note that 0 actually is the bottom of the continuous spectrum of this operator.

Here, in the Thomas–Fermi–von Weizsäcker case, a theoretical result (see Lieb [59]) allows to conclude that $\mu > 0$ as soon as $Z \geqslant \lambda$, and we then obtain that ϕ_0 is a minimum of the problem, and that it satisfies (1.12) (remark that $\mu > 0$ corresponds to the strict subbaditivity condition $I_\lambda < I_{\lambda_1}$ for all $0 < \lambda_1 < \lambda$ in the terminology of the concentration compactness approach).

It is important to note here that the strategy of proof we explained above does not only show that a minimum exists, but also that any minimizing sequence converges, up to an extraction, to a minimum. It is not always possible to show that latter fact directly (see the example of the atomic gradient expansion of the exchange energy in Le Bris [56]). The property that any arbitrary minimizing sequence converges to a minimum is of course interesting, in particular in view to numerical purposes. By the way, note, thinking to situations where the uniqueness of the minimum is known, that if all arbitrary convergent subsequences of some given sequence living in a compact set converge to the same limit, then the whole sequence itself converges to this limit.

On the example of the Thomas–Fermi–von Weizsäcker model, we have seen an example of the possible noncompactness of the abstract problem ($\mathcal{P}$).

However, one can see on (1.10) that the Thomas–Fermi–von Weizsäcker energy functional is (strictly) convex with respect to ϕ^2. This leads to a simplification of the minimization problem (see below). Indeed, ϕ_0 is the only solution to the Euler–Lagrange equation (1.12) satisfying $\int \phi^2 = \lambda$. (More precisely, if $\int \phi^2$ is fixed, the pair (μ, ϕ_0) is unique (up to a sign for ϕ_0).) Thinking to the numerical aspects, this is an important fact, since solving (1.12) will be equivalent to solving (1.9)–(1.10). And let us already remark, though we shall come back to the question of uniqueness below, that the strict convexity implies the uniqueness of the minimizing density ϕ_0^2.

Nevertheless, most of interesting problems are not convex, and the properties we just mentioned are not true. In particular, we want to emphasize here that, when the energy functional is not convex, it may admit critical points that are not the desired minimum, but for instance local minima or saddle points, and thus the resolution of the Euler–Lagrange equation, even the most accurate, does not necessarily lead *a priori* to the minimizing density.

1.2.3. What else about a minimum?

The above remarks give us a transition to the next question we want to briefly address here: once the existence of a minimum is proved, what else can we say about it?

In particular because of the fact that a minimum is a solution to the Euler–Lagrange equation of the minimization problem, further information on this minimum is in many cases available (see, e.g., the study by Ahlrichs [2] for the Schrödinger equation).

First of all, the Euler–Lagrange equation yields regularity on the minimum. We send the reader to Lieb [59] for instance.

But the best example to our mind is the question of the behaviour of the density near the nuclei, or at infinity (that is when $|x|$ tends to infinity). Take for instance the minimum ϕ_0 of the Thomas–Fermi–von Weizsäcker problem we obtained above. At least when $\lambda \leqslant Z$, we saw that the Lagrange multiplier μ appearing in (1.12) is positive (it is actually true for all $0 \leqslant \lambda < \lambda_c$ with $\lambda_c > Z$). It follows from a standard mathematical argument that the density has an exponential decay at infinity, that one may even precise (see Lieb [59]; see also Ishida and Ohno [41] for the same question in the Hartree–Fock setting). In the same way, the behaviour near the nuclei is well known. We shall come back to these aspects when we deal with the Thomas–Fermi type models in section 3.

Unfortunately, questions of uniqueness are much more difficult.

We saw above that the strict convexity of the energy functional is a way to insure the uniqueness of the minimum. Actually it is the only systematic way to prove a minimum is unique, all questions of uniqueness being difficult. Indeed, recall that the Euler Lagrange equation is most of the time a nonlinear partial differential equation. Proving it admits at most one solution is a difficult task. We shall see below in the course of our article that for most of the interesting models the uniqueness of the minimizing density is still an open question.

Often related to the question of uniqueness is the question of the symmetry of the minimizing density in view of a given symmetry of the geometry of the nuclei. Apart from some very simple cases that might be of poor interest from the practical point of view, nothing can be said (see below, in particular in section 3).

Yet, since the symmetry is of great chemical interest, we briefly reproduce here an argument from Lieb [59] that shows that in the pure Thomas–Fermi atomic case, the density is a radially symmetric function, that is moreover nonincreasing with respect to the radius r.

Let ρ be the minimizing density of the atomic Thomas–Fermi problem, and denote by $\rho^\star$ the symmetric decreasing rearrangement of ρ. Assume by contradiction that $\rho \neq \rho^\star$. By standard arguments, $\int \rho^{\star 5/3} \leqslant \int \rho^{5/3}$ and, since $\int \rho \leqslant Z$,

$$-\int \frac{Z}{|x|}\rho^\star(x)\,\mathrm{d}x + \iint \frac{\rho^\star(x)\rho^\star(y)}{|x-y]} \leqslant -\int \frac{Z}{|x|}\rho(x)\,\mathrm{d}x + \iint \frac{\rho(x)\rho^\star(y)}{|x-y|}.$$

Hence,

$$0 \geqslant E^{\mathrm{TF}}(\rho) - E^{\mathrm{TF}}(\rho^\star) \geqslant \frac{1}{2}\iint \frac{(\rho(x)-\rho^\star(x))(\rho(y)-\rho^\star(y))}{|x-y]} > 0.$$

It follows that $\rho = \rho^\star$.

We are going to end here this section devoted to the general mathematical aspects of the problem of finding a minimum. As announced above, we shall come back in the next sections to all the questions raised here, then in a more specific way giving details on each of the studied models.

2. Hartree–Fock and related models

2.1. *The Hartree–Fock approximation*

Let us first recall the minimization problem corresponding to the famous Hartree–Fock approximation

$$\begin{aligned} I^{\mathrm{HF}} &= \inf\left\{\langle H_N\phi,\phi\rangle;\ \phi \text{ of the form (1.4)};\ \int \varphi_i\varphi_j = \delta_{ij}\right\} \\ &= \inf\left\{E^{\mathrm{HF}}(\varphi_1,\dots,\varphi_N) = \sum_{i=1}^{N}\int |\nabla\varphi_i|^2 + \sum_{i=1}^{N}\int V|\varphi_i|^2\right. \\ &\qquad + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y - \frac{1}{2}\iint \frac{|\rho(x,y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y; \\ &\qquad \left.\varphi_i \in H^1(\mathbf{R}^3),\ \int \varphi_i\varphi_j = \delta_{ij}\right\}, \end{aligned} \tag{2.1}$$

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

Although this approximation is at the basis of a huge number of numerical codes that are used daily in laboratories, the proof of the existence of a minimum in this setting is rather recent and may be found in Lieb and Simon [60] and Lions [64] (under the condition that $N - 1 < Z = \sum_k z_k$). As explained in section 1, the difficulty lies in the possible loss of compactness at infinity.

Roughly speaking, one argues as follows.

One first checks that the minimizing sequences of (2.1), that is sequences $(\varphi_1^n, \ldots, \varphi_N^n)$ satisfying $\int \varphi_i^n \varphi_j^n = \delta_{ij}$ and

$$E^{\mathrm{HF}}(\varphi_1^n, \ldots, \varphi_N^n) \overset{n\to\infty}{\longrightarrow} I^{\mathrm{HF}},$$

are bounded, thus converge in a weak sense to some $(\varphi_1, \ldots, \varphi_N)$. One next shows that

$$E^{\mathrm{HF}}(\varphi_1, \ldots, \varphi_N) = I^{\mathrm{HF}}.$$

Proving the existence of a minimum for I^{HF} amounts to proving that $\int \varphi_i \varphi_j = \delta_{ij}$. Then, one follows the general framework given in section 1 for such problems dealing with functions defined on the whole space $\mathbf{R}^3$, the constraint $\int |\varphi_i^n|^2 = 1$ may be lost when n tends to infinity. In other words, in order to minimize the energy, charge has escaped at infinity, and the weak limit may only satisfy $\int |\varphi_i|^2 < 1$. This phenomenon does not occur here, essentially because $(\varphi_1, \ldots, \varphi_N)$ is the minimum of the problem with relaxed constraint $[\int \varphi_i \varphi_j] \leqslant [\delta_{ij}]$ (in the sense of nonnegative symmetric matrices), and therefore satisfies $\int |\varphi_i|^2 = 1$ (see Lieb and Simon [60] and Lions [64]). Following the above strategy of proof, one shows the existence of a minimum, and also the compactness (up to a subsequence) of any minimizing sequence of (2.1), which may be useful thinking to numerical purposes.

Let us note here that the minimum of the Hartree–Fock energy satisfies (up to an orthogonal transform) the following well-known Hartree–Fock equations

$$-\Delta\varphi_i + V\varphi_i + \left(\rho \star \frac{1}{|x|}\right)\varphi_i - \int \frac{\rho(x,y)}{|x-y|}\varphi_i(y)\,\mathrm{d}y = -\varepsilon_i\varphi_i, \tag{2.2}$$

where the Lagrange multipliers are actually the N lowest eigenvalues of the elliptic operator appearing in the left-hand side of (2.2).

It is useful to remark that the numerical codes solve this equation (2.2), that is the Euler–Lagrange equation of the minimization problem (2.1), but not the problem (2.1) itself.

It is not our purpose here to present the methods used in the numerical computations to solve the Hartree–Fock equations, a thick literature being devoted to the subject (see Szabo and Ostlund [94], Levine [58], Hehre et al. [36], …). But we wish to take this opportunity to mention that a recent method consisting of a formulation of these equations in a position-momentum space (obtained through a wavelet transform) is studied in Fischer and Defranceschi [25–27] (see also references therein).

Let us add that, actually, the numerical codes available for molecules (and even for atoms) do not solve (2.2) as a partial differential equation but as a linear system of equations equivalent to it which is obtained by expanding the φ_i's with respect to a (finite!) set of fixed basis sets (i.e., introducing the so-called LCAO-MO approximation). It has been shown (Klahn and Bingel [46,47], Kutzelnigg [52]) that the LCAO expansion converges towards the expected solutions for the energies as well as the functions provided the basis are appropriated (for instance Slater or Gauss type orbitals).

The existence of a minimum is of course not the only interesting question that the Hartree–Fock approximation raises. Unfortunately it is almost the only one solved at this day. In particular the uniqueness of the minimizing $(\varphi_1, \ldots, \varphi_N)$ (up to an orthogonal transform) or the uniqueness of ρ is an open question.

Symmetry questions are also open. For instance, consider an atom ($\bar{x}_k \equiv 0$ for all k). The question whether the minimum density ρ has a spherical symmetry is open. For a general discussion on the questions of symmetry in this kind of problems, we refer to Lions [66] where it is shown that some symmetry breaking does appear in an analogous problem in nuclear physics.

We finally mention that the existence of infinitely many excited states in the Hartree–Fock setting is proved in Lions [64]. However, these excited states obtained from the ground-state are not directly related to the physical excited states observed by spectroscopy. On the other hand, the one-electron energies ε_i of the occupied orbitals and the corresponding wave functions φ_i obtained for the ground-state can be related to the ionization potential thanks to the Koopmans approximation which provides them a somewhat physical reality (Turner et al. [96]).

2.2. *Beyond the Hartree–Fock approximation*

Beyond the Hartree–Fock approximation stand the multiconfiguration methods (Configuration Interaction, Multi Configuration Self Consistent Field method) that are very useful because the single determinant approximation is often not adequate enough to describe the properties of a molecule.

From the mathematical point of view, these methods share the following features.

Since the energy $\langle H_N\phi, \phi\rangle$ has been minimized on a too small subspace of $L^2_a(\mathbf{R}^{3N})$, namely the set of functions that are of the form of a single determinant, the Hartree–Fock energy is only an upper bound to the true energy, and the density is not the good one. Therefore, there remains to enlarge the subspace one minimizes the energy upon in order to obtain a more accurate result. The corresponding mathematical setting is the following: minimize $\langle H_N\phi, \phi\rangle$ on a set of functions ϕ that are linear combinations of determinants:

$$\phi = \sum_k c_k \det\bigl(\varphi_1^k, \ldots, \varphi_N^k\bigr). \tag{2.3}$$

At this point, it is worth stressing that the determinants introduced in order to better describe the ground-state have nothing to see with the physical excited states of the system.

In the configuration interaction method (Shavitt [86]), the columns φ_i^k of the determinants are prescribed, and one only optimizes the coefficients c_k of the combination, while in the Multi Configuration Self Consistent Field method (Shepard [87], Wahl and Das [97], Werner and Meyer [98], Hinze [37]) one optimizes both the coefficients and the functions involved in each determinant.

In order to make a mathematically tractable problem, the above problems are formalized by considering in Le Bris [55] the following family of minimization problems:

$$E = \inf \biggl\{ \langle H_N\phi, \phi\rangle;\ \phi \text{ linear combination of determinants}$$
$$\text{built with the functions } \varphi_i;\ \forall i, j \int \varphi_i\varphi_j = \delta_{ij} \biggr\}. \tag{2.4}$$

In Le Bris [55], a general strategy to prove the existence of a minimum in this setting is described, therefore answering partially to the questions asked in Fonte [28]. This strategy draws its inspiration from the proof in the Hartree–Fock case. It basically follows the same patterns, the only difference lying in tedious technical difficulties.

Indeed, the soon complicated Hartree–Fock equations are here replaced by a much more strongly coupled system of partial differential equations.

Heuristically, it is quite natural to some extent that in the Hartree–Fock case and in the multiconfiguration case the existence of a minimum can be proved by the same mathematical techniques. It emphasizes the fact that they are problems sharing the same deep mathematical fundations since they are nothing but successive degrees of approximation of the one and only problem (1.1). The strategy of Le Bris [55] allows us to prove (for $N \leqslant Z$) the existence of a minimum (and the compactness up to an extraction of all minimizing sequences), in particular for the following cases, that might have poor sense from the chemical viewpoint, but are, mathematically, two examples of contrasting situations:

Example 1: Consider the space consisting of the functions

$$\phi = \sum_{k=0}^{K} c_k \frac{1}{\sqrt{N!}} \det\bigl(\varphi_{kN+1}, \ldots, \varphi_{kN+N}\bigr) \tag{2.5}$$

with $\int \varphi_i\varphi_j = \delta_{ij}$, $1 \leqslant i \leqslant j \leqslant N(K+1)$, and $\sum_{k=0}^{K} c_k^2 = 1$, and set the corresponding (2.4) problem.

Example 2: Consider the space consisting of the functions

$$\phi = \frac{\alpha}{\sqrt{N!}} \det(\varphi_1, \ldots, \varphi_{N-2}, \varphi_{N-1}, \varphi_N)$$
$$+ \frac{\beta}{\sqrt{N!}} \det(\varphi_1, \ldots, \varphi_{N-2}, \varphi_{N+1}, \varphi_{N+2}) \tag{2.6}$$

with $\int \varphi_i\varphi_j = \delta_{ij}$, $1 \leqslant i \leqslant j \leqslant N+2$, and $\alpha^2 + \beta^2 = 1$, and set the corresponding (2.4) problem.

Moreover, for the second problem, it is shown in Le Bris [55] that the infimum energy I satisfies $I < I_{\mathrm{HF}}$, therefore proving that the Hartree–Fock minimum was not the right minimum and that the Hartree–Fock energy was not the right energy either. This result justifies in a rigorous way the interest of the methods involving many determinants.

Of course, the questions of uniqueness and symmetry are also open for the multiconfiguration models.

3. Thomas–Fermi type models

3.1. *The primitive Thomas–Fermi model*

We recall that basically the Thomas–Fermi approach consists in finding the solution to the following minimization problem:

$$I^{\mathrm{TF}} = \inf\left\{E^{\mathrm{TF}}(\rho);\ \rho \geqslant 0,\ \rho \in L^1 \cap L^{5/3},\ \int_{\mathbf{R}^3} \rho = N\right\}, \tag{3.1}$$

where for the simplest Thomas–Fermi model,

$$E^{\mathrm{TF}}(\rho) = \int_{\mathbf{R}^3} \rho^{5/3} + \int_{\mathbf{R}^3} V\rho + \frac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y, \tag{3.2}$$

$$V(x) = -\sum_k \frac{z_k}{|x-\bar{x}_k|}. \tag{3.3}$$

In (3.2), the term $\int_{\mathbf{R}^3} \rho^{5/3}$, which comes from the theory of uniform electron gas, models the kinetic energy of the electrons, while the integral

$$\frac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y$$

is an approximation of the Coulomb repulsion between the electrons (see, for instance, March [69,68], Parr and Yang [73], Levine [58]). In the computations, all terms of (3.2), and terms of correction that will be incorporated below, are multiplied by various coefficients that depend in particular on the physical unities of charge and mass and on the nature of the studied molecule (see, e.g., Dreizler and Gross [19] for a discussion on the choice of these coefficients). Yet, we forget all these coefficients here because they do not change the mathematical arguments.

The model (3.1)–(3.2) leads to a well-posed mathematical problem, in the sense that, under adequate conditions ($N \leqslant Z$), a minimum exists, and is unique. In addition, it has reasonable properties: for instance it has the spherical symmetry for an atom ($\bar{x}_k \equiv 0$ in (3.3)).

However this model suffers from a lot of drawbacks.

Since the above approximation (3.2) of the energy is too crude, the result one obtains is often unsatisfactory. First because the numerical result for the ground-state energy is not accurate enough, but above all because the model presents a number of aspects that can be in contradiction with the physical admissibility and the theoretical prevision (see the discussion in Pan Hui-Yun and Zhao Zu Sen [100] and Koga and Thakkar [48] on the properties a wave function must have). For instance, in the Thomas–Fermi setting (3.1)–(3.2), the density ρ is not bounded from above in the neighborhood of the point nuclei (it behaves like $1/|x-\bar{x}_k|^{3/2}$); it decays too slowly at infinity (when $|x| \to \infty$, $\rho(x)$ decays like $1/|x|^4$); and, last but not least, Teller's no-binding theorem prevents any molecular system from existing in the model (3.1)–(3.3) (the energy of two systems S_1 and S_2 taken together is always strictly greater than the sum of the energies of the two systems taken at an infinite distance from each other).

As a matter of fact, there exists a lot of corrections to the Thomas–Fermi energy (3.2). We shall not review here all the mathematical results known on them in detail. We refer to the comprehensive review in Lieb [59], and prefer to summarize here the mathematical difficulties, and mention the most recent results (thus not included in Lieb [59]).

3.2. The Thomas–Fermi–Dirac–von Weizsäcker model

Let us consider an improved form of (3.2), namely the Thomas–Fermi–Dirac–von Weizsäcker model

$$I_N^{\mathrm{TFDW}} = \inf\left\{\mathcal{E}^{\mathrm{TFDW}}(\psi);\ \psi \in H^1,\ \int_{\mathbf{R}^3} \psi^2 = N\right\}, \tag{3.4}$$

$$\begin{aligned}\mathcal{E}^{\mathrm{TFDW}}(\psi) = {} & c_0 \int_{\mathbf{R}^3} |\nabla\psi|^2 + \int_{\mathbf{R}^3} V\psi^2 + c_1 \int_{\mathbf{R}^3} |\psi|^{10/3} - c_2 \int_{\mathbf{R}^3} |\psi|^{8/3} \\ & + \frac{1}{2} \iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\psi(x)^2\psi(y)^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y.\end{aligned} \tag{3.5}$$

With such a model ($c_0 \neq 0$), the main drawbacks of the Thomas–Fermi model that we mentioned above disappear: the density $\rho = |\psi|^2$ is bounded, it decays in an exponential way at infinity, and Teller's theorem does not hold any longer (these improvements are essentially due to the gradient term $\int_{\mathbf{R}^3} |\nabla\psi|^2$). Moreover, the numerical results obtained for the energy are better (see, e.g., Stich et al. [93] for a numerical solution of the Thomas–Fermi–Dirac–von Weizsäcker problem).

But the price to pay for these improvements is a large increase of the mathematical complexity of the model. On the form (3.5), the reader may read the mathematical difficulties of this family of models: the model is nonlinear, non convex with respect to the density, and deals with functions defined on the whole space $\mathbf{R}^3$. When at least one of the two coefficients c_0 or c_2 vanishes, the situation is simpler: when

$c_2 = 0$, the model (then called the Thomas–Fermi–von Weizsäcker model) is convex[2], when $c_0 = 0$ (Thomas–Fermi–Dirac model), it can be studied with a mathematical trick (see Lieb [59]). But the full Thomas–Fermi–Dirac–von Weizsäcker model is delicateto treat. Preliminary results were obtained by Lieb [59]. In [64], Lions proved the existence of a minimum when $N \leqslant Z$. The main difficulty is that the so-called problem at infinity (see Lions [65,64]), that is the problem (3.4)–(3.5) where $V \equiv 0$, is not trivial (as it is for instance in the Thomas–Fermi–von Weizsäcker case).

In Le Bris [53], the second of us continues the study, proving first that a minimum exists for every $N \leqslant N_c$ for some $N_c > Z$. It must be emphasized that it is an open mathematical problem to know if $N_c < \infty$: it is not known in this model if the maximum number of electrons that a given number of nuclear charges may bound is finite.

Then it is proved that the Thomas–Fermi–Dirac–von Weizsäcker model is not far from the Thomas–Fermi–Dirac–von Weizsäcker model when the coefficient c_2 is small in the following sense: the minimum is then unique (up to a sign), and the ground-state energy is a strictly convex function of the number of electrons when $N \leqslant Z$.

3.3. Further improvements

Further improvements of the Thomas–Fermi–Dirac–von Weizsäcker are possible. In this section we consider the ones resulting from a better approximation of the exchange term since it turns out that the Dirac exchange functional $c_2 \int \rho^{4/3}$ may not be accurate enough in some situations and has to be modified. Though they are not commonly used models, some of them bring new mathematical difficulties that may be found elsewhere. We shall thus give a brief overview on the results obtained about them (see Le Bris [56] for the details).

A general form for these models is the following:

$$I_N = \inf \left\{ E(\rho);\ \rho \geqslant 0,\ \sqrt{\rho} \in H^1,\ \int_{\mathbf{R}^3} \rho = N \right\} \tag{3.6}$$

with

$$E(\rho) = \int_{\mathbf{R}^3} |\nabla \sqrt{\rho}|^2 + \int_{\mathbf{R}^3} V\rho + c_1 \int_{\mathbf{R}^3} \rho^{5/3} - K(\rho) + \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, \mathrm{d}x\, \mathrm{d}y, \tag{3.7}$$

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[2] By saying the model is convex, we mean here that the energy is a convex function with respect to the density $\rho = \psi^2$. It turns out that when the energy $E(\phi)$ is a convex function of ϕ, the mathematical problem ($\mathcal{P}$) defined in its whole generality in section 1.2 above, is much simpler. Indeed, assuming that the energy is continuous for the strong topology, which is usually the case, one easily deduces that the weak limit ϕ of a minimizing sequence ϕ^n satisfies $E(\phi) \leqslant \liminf E(\phi^n) = I_\lambda$ (this is equivalent to saying that a convex function that is continuous for the strong topology is lower semi-continuous for the weak topology); it follows that ϕ satifies $E(\phi) = I_\lambda$. There remains next to show that $J(\phi) = \lambda$ (therefore that ϕ is a minimum), which is usually true at least for λ small enough (see the details, e.g., in [59]). Another simplification, soon mentioned in section 1.2, is that, for a convex energy, any solution to the Euler–Lagrange equation is a minimum of the energy.

where the functional $K(\rho)$ is an improved form of $\int \rho^{4/3}$.

One can use the so called Gunnarsson–Lundqvist functional (March [68], Parr and Yang [73], Gunnarsson and Lundqvist [34]), that is

$$\begin{aligned} K(\rho) = {} & c_e \int \rho^{4/3} \\ & + c_p \int \rho \left[\left(1 + \frac{a^3}{\rho}\right) \operatorname{Log}\left(1 + \frac{\rho^{1/3}}{a}\right) + \frac{1}{2} a \rho^{-1/3} - a^2 \rho^{-2/3} - \frac{1}{3} \right] \end{aligned} \tag{3.8}$$

with $c_e > 0$, $c_p > 0$, $a > 0$.

But one may also use the gradient expansion of the exchange energy (Parr and Yang [73], Shih et al. [88]) which leads at the second order to the following form:

$$K(\rho) = \alpha \int \rho^{4/3} + \beta \int \frac{|\nabla \rho|^2}{\rho^{4/3}} \tag{3.9}$$

with $\alpha > 0$, $\beta > 0$.

Dealing with atoms (that is to say $\bar{x}_i \equiv 0$), a third possibility is to use the following functional, known to be 'better' than (3.9) (see March [68], Parr and Yang [73], Bartolotti [4]):

$$K(\rho) = \left(a + bN^{-2/3}\right) \int \rho^{4/3} - cN^{-2/3} \int |x|^2 \rho^{-2/3} |\nabla \rho|^2 \tag{3.10}$$

with $a > 0$, $b > 0$, $c > 0$.

The model (3.8) is very close to the Thomas–Fermi–Dirac–von Weizsäcker model because we only have subtracted to it a functional $\tilde{K}(\rho)$ which is a C^2 function of $\sqrt{\rho}$, which is nonnegative, less than $\int \rho^{4/3}$, and convex. It follows from these properties that the model is actually contained in the general framework defined by Lions in [64]. Therefore the minimizing sequences are compact up to a subsequence, and there exists a minimum at least for $N \leqslant Z$, satisfying some of the properties also satisfied by a TFDW minimum: it decays in an exponential way at infinity, it is a radially symmetric decreasing function in the atomic case, … .

Secondly, the model (3.9) leads to an energy which is not bounded from below. Another correction that heightens this energy is therefore necessary. This correction may for instance appear in a better modelling of the kinetic energy: gradient expansion

$$\gamma \int \rho^{1/3} \left[\left(\frac{\Delta \rho}{\rho}\right)^2 - \frac{9}{8} \frac{\Delta \rho}{\rho} \left(\frac{\nabla \rho}{\rho}\right)^2 + \frac{1}{3} \left(\frac{\nabla \rho}{\rho}\right)^4 \right]$$

(the corresponding problem has not been studied yet), Kohn–Sham approach (see below), … .

Eventually, the model (3.10) is more compact[3] than the Thomas–Fermi–Dirac–von Weizsäcker model because the functional $|x|^2\rho^{-2/3}|\nabla\rho|^2$ plays the role of a potential that tends to infinity at infinity. We have however to face some difficulties because this functional is not a derivable function of $\sqrt{\rho}$. We prove in Le Bris [56] the existence of a minimum (and again the compactness of all minimizing sequences up to an extraction), using a technique of regularization of the energy (3.10). We do not know if a minimum is a radially symmetric function.

3.4. *Density functional theory*

As we remarked earlier, the mathematical study of the Thomas–Fermi type models may also be considered as a first step towards the mathematical understanding of rather new models like those issued from the density functional theory.

Let us briefly recall the basis of the density functional theory. It turns out, which is not obvious, that the properties of the stationary non-relativistic ground state depend only on the one-particle density ρ, and thus that the ground state may be calculated using a variational principle that involves only the density, and that we formulate somewhat vaguely by

$$I = \inf E(\rho). \tag{3.11}$$

The proof of the above fact is due to Hohenberg and Kohn [38]. We shall not discuss the mathematical foundations of the density functional theory, to which a substantial literature is devoted, and we refer the reader to Dreizler and Gross [19], March [68], Parr and Yang [73], Jones and Gunnarsson [42], amongst others, for further information. We prefer to focus here on a practical application of the density functional theory, namely the Kohn–Sham approach [49]. Once the general form (3.11) of the minimization problem is known, there remains indeed to construct an explicit energy functional, that will approximate the exact energy functional as accurately as possible. The first difficulty lying in a good representation of the kinetic energy, Kohn and Sham have introduced an equivalent orbital picture that provides a convenient form of the kinetic energy. Their model gives birth to an interesting minimization problem that we are going to consider now, in order to give a rough idea of the mathematical difficulties one has to overcome when dealing with such models. To some extent, as far as the variational aspects are concerned, the Kohn–Sham approach is a kind of mixing between the Hartree–Fock approximation and a Thomas–Fermi type model. Indeed the minimization problem is the following:

$$I^{\mathrm{KS}} = \inf\left\{E^{\mathrm{KS}}(\phi_1,\ldots,\phi_N);\ \rho=\sum_{i=1}^{N}|\phi_i|^2,\ \phi_i\in H^1\bigl(\mathbf{R}^3\bigr),\ \int_{\mathbf{R}^3}\phi_i\phi_j=\delta_{ij}\right\} \tag{3.12}$$

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[3] i.e., a minimum is more likely to exist in this setting. A minimization problem of the family $(\mathcal{P})$ is said *compact* if it admits a minimum.

with

$$E^{\mathrm{KS}}(\phi_1,\ldots,\phi_N)=\sum_{i=1}^{N}\int_{\mathbf{R}^3}|\nabla\phi_i|^2+\int_{\mathbf{R}^3}V\rho + \frac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y-K(\rho). \tag{3.13}$$

In (3.13), $K(\rho)$ is of the form $c\int_{\mathbf{R}^3}\rho^{4/3}$ or of any convenient form such as the above improvements of the exchange energy made in the framework of the Thomas–Fermi theory on the exchange energy (3.8)–(3.10) or even else.

The analogous models where the constraint $\int\phi_i\phi_j=\delta_{ij}$ has been changed into $\int\phi_i^2=1$, $\forall 1\leqslant i\leqslant N$, may also be considered for mathematical purposes:

$$J=\inf\left\{E^{\mathrm{KS}}(\phi_1,\ldots,\phi_N);\ \rho=\sum_{i=1}^{N}|\phi_i|^2,\ \phi_i\in H^1(\mathbf{R}^3),\ \int_{\mathbf{R}^3}\phi_i^2=1\right\}. \tag{3.14}$$

Like in the Hartree–Fock approximation, one has to deal with N functions ϕ_i appearing in the energy through gradient dependent terms and a L^2 constraint $\int_{\mathbf{R}^3}\phi_i\phi_j=\delta_{ij}$, or $\int\phi_i^2=1$. It follows that the Euler–Lagrange equation is a system of coupled partial differential equations. Besides, like in the Thomas–Fermi model, the other terms of the energy are functions of the density ρ. Therefore the mathematical study we made in the Thomas–Fermi case turns out to be very instructive now. In other words, the mathematical difficulties are at least the sum of the ones soon faced in the Hartree–Fock case on the one hand, and in the Thomas–Fermi case on the other hand. In Le Bris [56], we prove the existence of a minimum for the Kohn–Sham model, with $K(\rho)=c\int_{\mathbf{R}^3}\rho^{4/3}$, using the same techniques as in the Thomas–Fermi–Dirac–von Weizsäcker case.

From the chemical viewpoint, note that, in the Kohn–Sham framework, it is impossible to connect the Kohn–Sham orbitals and the standard orbital picture of the LCAO approximation to which chemists are customed to interpret electronic spectra (e.g., photoelectron spectroscopy), or chemical reactivity (e.g., Woodward Hoffman rules).

Besides, it is worth stressing that all densities ρ are not 'v-representable' which means that for a given ρ there is not necessarily a $K(\rho)$ associated to the fundamental state of the hamiltonian.

For various reasons, the density functional approach seems to raise up a great interest (see Dreizler and Gross [19], Parr and Yang [73]). Current research in chemistry is directed towards finding the best form of the energy, or at least a reasonable approximation of it. It is here and now clear that, once the form chosen, the problem will not be closed from the variational point of view. There will remain to answer all the questions we are interested in, as questions of existence, uniqueness, … in this new setting.

4. Geometry optimization

So far we have only optimized the energy of the electronic wave function (in a more or less simplified form of the function or of the energy), considering the positions of the nuclei $\bar{x}_k$ as given parameters. These positions are for instance the experimentaly observed ones.

By this mean, we of course have made a drastic simplification since the wave function of the molecule actually is *stricto sensu* a function not only of the positions of the N electrons, but also of the positions of the K nuclei. And the Hamiltonian takes the nucleus–nucleus repulsion into account.

A direct attack of the full minimization problem is clearly out of reach now, and is likely to remain so within the next decades. However, in view of the ratio of mass, it is quite reasonable to consider the nuclei as fixed, according to the Born-Oppenheimer approximation, and ignore the coupling terms between the various resulting types of motion: translation, rotation, vibration and electron motion. Therefore the minimization problem one has to solve is the following:

$$I = \inf\left\{E(\bar{x}_1,\dots,\bar{x}_K) + \sum_{i<j} V(\bar{x}_i,\bar{x}_j);\ (\bar{x}_1,\dots,\bar{x}_K)\in \mathbf{R}^{3K}\right\}, \tag{4.1}$$

$$E(\bar{x}_1,\dots,\bar{x}_K) = \inf\left\{E_{\bar{x}_i}(\phi);\ \phi \text{ electronic wave function}\right\},$$

where $E_{\bar{x}_i}(\phi)$ is the energy of ϕ with the nuclei at the positions $\bar{x}_i$, and where $V(\bar{x}_i,\bar{x}_j)$ is the nuclear repulsion (for instance for point nuclei $V(\bar{x}_i,\bar{x}_j) = z_i z_j/|\bar{x}_i - \bar{x}_j|$).

It is obvious that, for $K \geqslant 2$, an additional difficulty has arisen in (4.1).

In the numerical codes, the search for a minimizing configuration of nuclei is done through more or less sophisticated techniques (see for instance the analytical derivative method in Pulay [76], or also the diffusion equation method for clusters of atoms in Kostrowicki et al. [50,51], Piela et al. [75]). But from the theoretical viewpoint, the question of the existence of a minimum remains. Consider the Hartree–Fock approximation and take point nuclei for the sake of simplicity. Then our new problem is

$$I = \inf\left\{E^{\mathrm{HF}}(\bar{x}_1,\dots,\bar{x}_K) + \sum_{i<j}\frac{z_i z_j}{|\bar{x}_i - \bar{x}_j|};\ (\bar{x}_1,\dots,\bar{x}_K)\in \mathbf{R}^{3K}\right\}, \tag{4.2}$$

where $E^{\mathrm{HF}}(\bar{x}_1,\dots,\bar{x}_K)$ is the Hartree–Fock energy with the nuclei at the positions $\bar{x}_i$. The existence of a minimum $(\bar{x}_1,\dots,\bar{x}_K,\phi)$ for the problem (4.2) is an open problem.

However, in the Hartree case

$$\begin{aligned} I^{\mathrm{H}} = \inf\Bigg\{ & E^{\mathrm{H}}(\bar{x}_1,\dots,\bar{x}_K,\varphi_1,\dots,\varphi_N) = \sum_{i=1}^{N}\int|\nabla\varphi_i|^2 - \sum_{k=1}^{K}\sum_{i=1}^{N} z_k\int\frac{|\varphi_i|^2}{|x-\bar{x}_k|} \\ & + \frac{1}{2}\iint\sum_{i\neq j}\frac{|\varphi_i(x)|^2|\varphi_j(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y + \sum_{i<j}\frac{z_i z_j}{|\bar{x}_i-\bar{x}_j|};\ \int|\varphi_i|^2 = 1\Bigg\}, \end{aligned} \tag{4.3}$$

the existence of a minimizing $(\bar{x}_1, \ldots, \bar{x}_K, \varphi_1, \ldots, \varphi_N)$ is due to Catto and Lions [11–14]. The proof is long, technical and difficult. It is outlined in Catto and Lions [15].

One first shows (Catto and Lions [11–13]) that the existence of a minimum is guaranteed as soon as the system cannot split into two subneutral or neutral subsystems (that is two systems where the number of electrons is at most equal to the nuclear charge). It means

$$I_N(S) < I_p\big(S^1\big) + I_{N-p}\big(S^2\big), \quad \forall 1 \leqslant p \leqslant N-1,$$

for all S^i such that $S = S^1 \cup S^2$, $Z(S^1) \geqslant p$, and $Z(S^2) \geqslant N-p$, where $I_k(\Sigma)$ is the optimized energy (4.3) of the system Σ consisting of k electrons and $Z(\Sigma)$ total nuclear charges (actually, in the Hartree setting, it is not obvious and has to be proved mathematically that it is sufficient to check such a condition for physical subsystems, that is subsystems where the 'number' of electrons is an integer, see the details in Catto and Lions [11–13]).

In particular, for a neutral system like a molecule, the existence of the ground state is equivalent to the binding of all neutral subsystems, namely

$$I_N(S) < I_p\big(S^1\big) + I_{N-p}\big(S^2\big), \quad \forall 1 \leqslant p \leqslant N-1,$$

for all S^i such that $S = S^1 \cup S^2$, $Z(S^1) = p$, and $Z(S^2) = N-p$.

Nevertheless, even if this condition is not fulfilled, other physical states can exist where the system S is stable. An example is given by the H_3O molecule which ground-state is unstable compared to its dissociation products (H_2O + H or OH + H^2). However, H_3O is stable in its excited Rydberg state as it has been shown recently (Talbi and Saxon [95]).

Next one shows (Catto and Lions [14]) that the above strict subadditivity condition holds. This last step cannot unfortunately be adapted to the Hartree–Fock case (because of the orthonormality constraint $\int \varphi_i \varphi_j = \delta_{ij}$ appearing in the Hartree–Fock setting).

The result of existence and the above outlined proof also hold *mutatis mutandis*, in the Thomas–Fermi–Dirac–von Weizsäcker case (see Catto and Lions [11–14] again).

5. Future trends in molecular quantum chemistry

We give in this last section a list of open problems, that we have hardly or not at all addressed in the above sections, and that we believe to be the most interesting ones. The reason why we come back to them or introduce them is that we want to emphasize that there are still a lot of facts that are far from being proved in a rigorous way, although they might seem straightforward at first sight.

Let us begin with questions that concern the electronic ground-state of the isolated molecule.

Though the existence of a minimum is now known for a lot of models (at least in the neutral case), it is to be noted that, in many models, we only give a sufficient condition (a condition involving N and Z, typically $N \leqslant Z$), in order to insure this existence. As noticed in Lions [64], it is an important open question to know the best condition on N. In some cases, this best condition is known (for instance in the Thomas–Fermi, or in the Thomas–Fermi–Dirac model: it is actually $N \leqslant Z$, see Lieb [59]). In some other cases, it has been established that there is a critical number of electrons N_c until which there exists a minimum and above which no minimum exists any longer; in addition, a bound from above and a bound from below on this N_c are known (for instance in the Thomas–Fermi–von Weizsäcker model for an atom, $Z < N_c < Z + 1$, see Benguria and Lieb [5] and Solovej [89]). But for a model like the famous Hartree–Fock model or for the Thomas–Fermi–Dirac–von Weizsäcker model, the question is open. So, in the Thomas–Fermi–Dirac–von Weizsäcker model, it is not known whether this critical number N_c exists (it is possible that $N_c = \infty$, which would mean that a given number of positive charges may bound an arbitrary large number of electrons in this setting), nor even if the set of numbers N for which there exists a minimum is an interval. One could imagine a peculiar situation where for some N large enough, there is no ground state with N electrons, while there is some with $N + 1$ electrons!

For instance, a minimum has been found numerically (Pyykkö [80]) for NCB^{4-}, a system which is isoelectronic of a very familiar compound, namely CO_2! For the moment, the chemical intuition makes up for the lack of definite mathematical statement concerning anions. Presently a problem of interest for quantum chemists is to know how many negative charges a given arrangement of atoms can support (Pyykkö and Zhao [80]).

When the existence of a minimum is insured, the next natural question is uniqueness. For a huge list of models, this uniqueness is not known: Hartree–Fock, Multi-Configuration models, Thomas–Fermi–Dirac–von Weizsäcker model (with a coefficient c_2 in (3.5) that is not small), $\ldots$.

A question that is close to uniqueness is the question of a symmetry for the density. Once more, it is open in most cases.

Once the ground state is determined in a given geometry, we saw above that the optimal geometry is still to be found. The existence of this geometry in the Hartree–Fock setting is not proven yet. It is at once a difficult and interesting study to lead.

But, in addition to these questions about the ground state of the isolated molecule, what we believe to be one of the main challenges in the next years certainly is how to take into account some environmental effects on the state of the molecule.

Take first the influence of a magnetic field or an electric field. While in the numerical practice the standard technique is to use a perturbation method to compute the variations of the characteristic parameters of the molecule with respect to the outside perturbation (think for instance to the quantum computations used in nonlinear optics, nuclear magnetic resonance, electron spin resonance), it is interesting for theoretical purposes to go beyond this approach and consider the full problem of the minimization of the perturbed energy. This has been made in a rather academical situation, in a particular Thomas–Fermi setting (namely the Thomas–Fermi model with the Fermi–

Amaldi correction), by Le Bris [54,56] (see also the related studies by Benguria et al. [6,7], Goldstein and Rieder [31], Brézis [9], and more recently Goldstein et al. [32]), and, in the Hartree–Fock setting, by Esteban and Lions [20]. But a lot of work remains to be done in this field. It is here and now clear that, as shown by the still preliminary studies we quoted above, the main difficulty is how to deal with an external potential that does not vanish at infinity. Indeed, for a molecule alone in the space, the only potential (in addition to their own Coulomb self-repulsion potential) the electrons are subjected to is the Coulomb attraction of the nuclei. This potential tends to 0 as $1/|x|$ when $|x|$ tends to infinity. But, when the molecule is subjected for instance to an external electric field, some term of the kind $\int V_{\mathrm{elec}}(x)\rho(x)\,\mathrm{d}x$ appears in the energy, with some $V_{\mathrm{elec}}(x)$ that does not necessarily tend to 0 as $|x|$ tends to infinity. Giving some sense to such a term and understanding its influence on the compactness of the problem is a mathematical and chemical question of interest.

Take also what one may consider as a close problem, the problem of the condensed phase. Indeed, while most of the calculations deal with isolated molecules, it is necessary to compare the numerical results with experimental data that are obtained through studies in condensed phase. Therefore any improvement of the theoretical model taking into account the fact that the molecule is not alone is a great progress.

Consider first the solid phase. It seems clear that in a crystal the state of a given molecule is highly influenced by the surrounding molecules. Any modelling of this effect leads to a new minimization problem that we think interesting to consider. As far as we know, only a few mathematical studies exist. See for instance the study of the Thomas–Fermi model for solids in Lieb [59] and Lieb and Simon [61], and a forthcoming study by Catto, Le Bris and Lions [10] of a Thomas–Fermi–von Weizsäcker model for solids. Such studies may also be considered as a first stage in the understanding of the following problem: how to pass from the microscopic scale to the macroscopic scale. Starting from a quantum molecular model for the molecule alone, one first obtains a quantum model for the solid, and next a true macroscopic model.

Likewise, in the liquid phase a solvated molecule is subjected to outside effects that certainly modify its state. A modelling and numerical codes are available: see Onsager [72] for the original model, and Jortner [43], Jortner and Coulson [44], Rivail and Rinaldi [83], Rinaldi et al. [82], Miertiuš et al. [70], Persico and Tomasi [74] (and other references therein) for theoretical as well as numerical considerations. A rough description of such a model is as follows. One considers a molecule in a cavity (most of the time a spherical one, but sophisticated models with ellipsoidal cavities exist). The continuum within the cavity is a vacuum. The cavity is surrounded by a dielectric. The electrostatic field an electron of the molecule is subjected to is then the usual Coulomb repulsion of the other electrons, plus the interaction field between the electrons and the dielectric. A new minimization problem therefore arises. So far as we know, no mathematical work deals with such a model, while it must certainly provide some interesting framework.

Of course, all the questions that are of some interest as far as the ground-state of the molecule is concerned may be asked as well for the excited states. In this field, we are not aware of any mathematical work. A starting point could for instance be Katriel [45].

Another interesting track for a mathematical research is the relativistic correction. It is well known that when the nuclear charge Z becomes large, the Hartree–Fock approximation gets less and less accurate, essentially because the electrons that are close to the nuclei tend to have relativistic velocities. The Hartree–Fock equations have then to be replaced by the Dirac–Fock equations (Bethe and Salpeter [8]; for a recent review see Pyykkö and Desclaux [79], or Pyykkö [78]). The existence of solutions to equations describing the electron in a relativistic environment is being investigated (Esteban and Séré [21,22], Esteban et al. [23]).

Let us end this paper by mentioning a whole field that, as far as we know, has not been much explored: the algorithms used in the numerical codes certainly deserve some mathematical interest. There must lie here a lot of interesting questions of numerical analysis, like questions about the convergence of the algorithm used to solve the equations (see, e.g., Stanton [91,92], and Facelli and Contreras [24] on numerical tricks overcoming convergence failures in the standard numerical treatment of Hartree–Fock equations, see also Auchmuty and Wenyao Jia [3] for the study of an iterative method in the Hartree setting), or the convergence of the sequence of solutions with respect to the size of the basis of functions (see Morgan [71] for a study of the influence of the choice of the basis), and to the number of determinants in the multi-configuration methods, or questions about *a priori* error estimates, … .

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