

$h - P$ Finite Element Approximation for Full-Potential Electronic Structure Calculations

Yvon MADAY¹

(In honor of the scientific heritage of Jacques-Louis Lions)

Abstract The (continuous) finite element approximations of different orders for the computation of the solution to electronic structures were proposed in some papers and the performance of these approaches is becoming appreciable and is now well understood. In this publication, the author proposes to extend this discretization for full-potential electronic structure calculations by combining the refinement of the finite element mesh, where the solution is most singular with the increase of the degree of the polynomial approximations in the regions where the solution is mostly regular. This combination of increase of approximation properties, done in an a priori or a posteriori manner, is well-known to generally produce an optimal exponential type convergence rate with respect to the number of degrees of freedom even when the solution is singular. The analysis performed here sustains this property in the case of Hartree-Fock and Kohn-Sham problems.

Keywords Electronic structure calculation, Density functional theory, Hartree-Fock model, Kohn-Sham model, Nonlinear eigenvalue problem, $h - P$ version, Finite element method

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1 Introduction

The basic problem in quantum chemistry starts from the postulate of the existence of a time dependent complex function of the coordinates x called the wave function Ψ that contains all possible information about the system we want to consider. The evolution of this wave function depends on its current state through the following equation proposed by Schrödinger: It involves a potential-energy function V that takes into account internal or external interactions as, for instance, those of electrostatic nature; for a single particle, it takes the form

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi \equiv -\frac{\hbar^2}{2m} \nabla_x^2 \Psi + V\Psi.$$

The understanding of what the wave function represents was provided by Born who postulated, after Schrödinger, that $|\Psi(x, t)|^2 dx$ represents the probability density of finding at time t the particle at position x . The wave function Ψ is thus normalized in such a way that the

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¹UPMC University, Paris 06, UMR 7598 LJLL, Paris, F-75005 France; Institut Universitaire de France and Division of Applied Mathematics, Brown University, Providence, RI, USA.

E-mail: maday@ann.jussieu.fr

spatial L^2 norm of Ψ is 1. The strength of the concept comes from the fact that it applies to any system, in particular to molecules; the coordinates x are then the positions of each particle (electrons and nuclei) of the system: hence x belongs to $\mathbb{R}^{3(N+M)}$, where N is the number of electrons and M is the number of nuclei. The Schrödinger’s equations contains all the physical information on the system it is applied to, it does not involve any empirical parameter except some fundamental constants of physics like the Planck constant, the mass and charge of the electrons and nuclei $\dots$. It is thus a fantastic tool to better understand, predict and control the properties of matter from the fundamental background. The very simple Schrödinger equation in appearance is however set in a much too high dimensional framework: $1 + 3(N + M)$, so that it is not tractable for most problems of interest, except that a Quantum Monte Carlo (or QMC for short) approach is used to model and approximate the solutions. These QMC methods allow now to have access to properties other than the energy, including dipole and quadrupole moments, as well as matrix elements between different electronic states. Development and implementation of linear scaling QMC, analytical forces, wave function optimization, and embedding techniques are being pursued (see, e.g., [35–36]).

For direct methods, though, simplifications need to be proposed to make this much too high dimensional problem accessible to numerical discretizations and simulations. Taking into account the time is quite easy from the principle of the separation of variables in case where the potential V does not depend on time. As it is classical in this approach, the problem becomes time independent and takes the form of an eigenvalue problem:

$$-\frac{\hbar^2}{2m}\nabla_x^2\Psi + V\Psi = E\Psi, \quad (1.1)$$

where E has the dimension of an energy.

Through the variation principle, the various solutions to this (linear) eigenproblem, starting by the one associated with the smallest eigenvalue, are associated with a Hamiltonian energy $\langle\Psi|\mathcal{H}\Psi\rangle$, and, the ground state energy of the molecule corresponds to the smallest eigenvalue in (1.1). This interpretation through a variation principle does not simplify the matter but leads to tractable simplified models. The first one—known as the Born Oppenheimer approximation (see [5])—allows to separate the behavior of nuclei and electrons taking into account their large difference of masses. By considering the nuclei as fixed (or moving very slowly), the problem focuses on the behavior of the electrons—in the so-called electronic structure calculation—and is thus related to the wave function Ψ that depends on N variables in $\mathbb{R}^3$ (the position of the electrons) and is parametrized by the position of the M nuclei in the associated Hamiltonian.

In order to comply with the Pauli principle of exclusion, the electronic wave function has to be antisymmetric with respect to the electron positions. The electronic problem thus consists in the minimization of the Schrödinger’s Hamiltonian over all L^2 normalized, antisymmetric wave functions. By minimizing instead on a smaller set of functions provides a tractable problem at the price of yielding to a larger ground state energy. This is the matter of the Hartree Fock problem that consists in minimizing the actual Schrödinger’s energy over all wave functions that are written as a so-called Slater determinant, i.e., a determinant: $\det[\phi_i(x_j)]$, where the one electron orbitals ϕ_i ($i = 1, \dots, N$) are unknown functions over $\mathbb{R}^3$. The minimization problem over such Slater determinants leads to a minimization problem involving a new energy.

Let us describe this model associated to a so-called closed-shell system with an even number

$\mathcal{N} = 2N$ of electrons, the electronic state is described by N orbitals $\Phi = (\phi_1, \dots, \phi_N)^T \in (H^1(\mathbb{R}^3))^N$ satisfying the orthonormality conditions

$$\int_{\mathbb{R}^3} \phi_i \phi_j dx = \delta_{ij},$$

and the associated electronic density

$$\rho_\Phi(x) := 2 \sum_{i=1}^N |\phi_i(x)|^2.$$

The factor 2 in the above expression accounts for the spin. In closed-shell systems, each orbital is indeed occupied by two electrons, one with spin up and one with spin down.

We then introduce the admissible space for molecular orbitals

$$\mathcal{M} = \left\{ \Phi = (\phi_1, \dots, \phi_N)^T \in (H^1_\#(\Gamma))^N \mid \int_{\Gamma} \phi_i \phi_j dx = \delta_{ij} \right\}.$$

In the case where the molecular system we consider is in vacuo and consists of M nuclei of charges $(z_1, \dots, z_M) \in (\mathbb{N} \setminus \{0\})^M$ located at the positions $(R_1, \dots, R_M) \in (\mathbb{R}^3)^M$ of the physical space, and of N pairs of electrons, the so-called Hartree Fock problem reads: Find Φ^0 such that

$$\mathcal{I}_N^{\text{HF}}(V^{\text{nuc}}) \equiv \mathcal{E}^{\text{HF}}(\Phi^0) = \inf \{ \mathcal{E}^{\text{HF}}(\Phi), \Phi \in \mathcal{M} \} \quad (1.2)$$

with

$$\begin{aligned} \mathcal{E}^{\text{HF}}(\{\phi_i\}) &= \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 dx + \int_{\mathbb{R}^3} V^{\text{nuc}} \rho_\Phi dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Phi(x) \rho_\Phi(x')}{|x - x'|} dx dx' \\ &\quad - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\tau_\Phi(x, x')|^2}{|x - x'|} dx dx', \end{aligned} \quad (1.3)$$

$$\tau_\Phi(x, x') = 2 \sum_{i=1}^N \phi_i(x) \phi_i(x'), \quad \rho_\Phi(x) = 2 \sum_{i=1}^N |\phi_i(x)|^2,$$

$$V^{\text{nuc}}(x) = - \sum_{k=1}^M \frac{z_k}{|x - R_k|}. \quad (1.4)$$

An alternative formalism, different in nature but that ends up to a similar mathematical problem, is based on the key result of Hohenberg and Kohn [30] that shows that ground state properties of a system is fully described by the electronic density. This led to the density functional theory, with the instrumental approach of Kohn and Sham [31]. Indeed, from [30] the existence of an energy functional of the electronic density was established, this result is weakened however by the lack, even as of today, of knowledge of its proper functional form. It follows from the Hohenberg-Kohn theorem (see [30, 37–38, 56]), that there exists an exact functional, that is a functional of the electronic density ρ that provides the ground state electronic energy and density of the $\mathcal{N}$ -body electronic Schrödinger equation. The work of Kohn and Sham addressed this issue by providing approximations of the energy functional and laid the foundations for the practical application of DFT to materials systems.

The Kohn-Sham approach reduces the many-body problem of interacting electrons into an equivalent problem of non-interacting electrons in an effective mean field that is governed by

the electron density. It is formulated in terms of an unknown exchange-correlation term that includes the quantum-mechanical interactions between electrons. Even though this exchange-correlation term is approximated and takes the form of an explicit functional of electron density, these models were shown to predict a wide range of materials properties across various materials systems. The development of increasingly accurate and computationally tractable exchange-correlation functionals is still an active research area in electronic structure calculations.

In the Kohn-Sham model, also described in the closed-shell configuration, the ground state is obtained by solving the minimization problem: Find Φ^0 such that

$$\mathcal{I}_N^{KS}(V) \equiv \mathcal{E}^{KS}(\Phi^0) = \inf \{ \mathcal{E}^{KS}(\Phi), \Phi \in \mathcal{M} \}, \quad (1.5)$$

where the Kohn-Sham energy functional reads

$$\mathcal{E}^{KS}(\Phi) := \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 dx + \int_{\mathbb{R}^3} V^{\text{nuc}} \rho_{\Phi} dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(x) \rho_{\Phi}(x')}{|x - x'|} dx dx' + E_{\text{xc}}(\rho_{\Phi}). \quad (1.6)$$

The first term models the kinetic energy of Φ , the second term models the interactions between nuclei and electrons, and the third term models the interaction between electrons. The fourth term, called the exchange-correlation functional actually collects the errors made in the approximations of the kinetic energy and of the interactions between electrons by the first and third terms of the Kohn-Sham functional, respectively, as follows from the Hohenberg-Kohn theorem. The lack of precise knowledge for the Kohn-Sham functional is localized on this exchange-correlation term only. It therefore has to be approximated in practice. The local density approximation (or LDA for short) consists in approximating the exchange-correlation functional by

$$\int_{\mathbb{R}^3} e_{\text{xc}}^{\text{LDA}}(\rho(x)) dx,$$

where $e_{\text{xc}}^{\text{LDA}}(\bar{\rho})$ is an approximation of the exchange-correlation energy per unit volume in a uniform electron gas with density $\bar{\rho}$. The resulting Kohn-Sham LDA model is well understood from a mathematical viewpoint (see [1, 33]). On the other hand, the existence of minimizers for Kohn-Sham models based on more refined approximations of the exchange-correlation functional, such as generalized gradient approximations (see [1]) or exact local exchange potentials (see [12]) in the general case, is still an open problem.

Note that the Kohn-Sham problem can be split-up into two problems of minimization, with one among them being stated as a pure density problem. We first define the set of admissible densities:

$$\mathcal{R}_N = \left\{ \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho dx = N \right\}, \quad (1.7)$$

then we propose the first problem

$$\begin{aligned} T_{KS}(\rho) = \inf \left\{ \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 dx, \Phi = (\phi_i)_{i=1, \dots, N}, \forall i, j = 1, \dots, N, \right. \\ \left. \int_{\mathbb{R}^3} \phi_i \phi_j dx = \delta_{i,j}, \rho = \rho_{\Phi} \right\} \end{aligned} \quad (1.8)$$

followed by the pure density functional problem

$$\mathcal{I}_N^{KS}(V) = \inf \left\{ \mathcal{F}(\rho) = T_{KS}(\rho) + \int_{\mathbb{R}^3} V^{\text{nuc}} \rho dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(x')}{|x - x'|} dx dx' + E_{\text{xc}}(\rho) \right\}. \quad (1.9)$$

There are a lot of variations on the frame of the simulation of these equations. First we may be interested in simulating a molecule alone, small or big, the molecule may also have neighbors, and these can be taken into account exactly or in an average manner like for molecules in solvation (see [52]). When there are many molecules, these can be arranged in a periodic array that is exactly periodic or contains some local defects then the simulation will be done on a very large box composed of many cells, one of them containing the defect. In this case, the simulation domain, sometimes referred to as the supercell, is no longer the whole space $\mathbb{R}^3$, as in (1.5); it is the unit cell Γ of some periodic lattice of $\mathbb{R}^3$. In the periodic Kohn-Sham framework, the periodic boundary conditions are imposed to the Kohn-Sham orbitals (Born-von Karman PBC). Imposing PBC at the boundary of the simulation cell is the standard method to compute condensed phase properties with a limited number of atoms in the simulation cell, hence at a moderate computational cost.

Both minimization problems (1.2)–(1.5) lead to the resolution of a nonlinear eigenvalue problem, where the eigensolutions are atomic orbitals, function over $\mathbb{R}^3$, that thus become tractable to numerical simulations. In order to formulate these eigenproblems, we have to introduce the Hamiltonian for the Hartree-Fock or Kohn-Sham energies:

$$\mathcal{H}_{\Phi}^{\text{HF}} = -\frac{1}{2}\Delta + (V^{\text{nuc}} + V_{\rho\Phi}^{\text{Coulomb}} - V_{\tau\Phi}^{\text{Exchange}}) = h + \mathcal{V}_{\Phi},$$

where

$$h = -\frac{1}{2}\Delta + V^{\text{nuc}}, \quad \mathcal{V}_{\Phi} = V_{\rho\Phi}^{\text{Coulomb}} - V_{\tau\Phi}^{\text{Exchange}}, \quad (1.10)$$

where V^{Coulomb} and V^{Exchange} are defined for any ψ by

$$V_{\rho}^{\text{Coulomb}}\psi(x) = \left(\rho \star \frac{1}{|x|}\right)\psi(x), \quad V_{\tau}^{\text{Exchange}}\psi(x) = \int_{\mathbb{R}^3} \frac{\tau(x, y)}{|x - y|} \psi(y) dy, \quad \forall x \in \mathbb{R}^3. \quad (1.11)$$

We notice that $\mathcal{E}^{\text{HF}'}(\Phi^0) = 4\mathcal{H}_{\Phi^0}^{\text{HF}}\Phi^0$ and thus the Euler equations associated with the minimization problem (1.2) read

$$\mathcal{H}_{\Phi^0}^{\text{HF}}\phi_i^0 = \sum_{j=1}^N \lambda_{ij}^0 \phi_j^0, \quad \forall 1 \leq i \leq N, \quad (1.12)$$

where the $N \times N$ matrix $\Lambda_N^0 = (\lambda_{ij}^0)$, which is the Lagrange multiplier of the matrix constraint $\int_{\Gamma} \phi_i \phi_j dx = \delta_{ij}$, is symmetric.

In fact, the problem (1.2) has an infinity of minimizers since any unitary transform of the Hartree-Fock orbitals Φ^0 is also a minimizer of the Hartree-Fock energy. This is a consequence of the following invariance property:

$$U\Phi \in \mathcal{M} \quad \text{and} \quad \mathcal{E}^{\text{HF}}(U\Phi) = \mathcal{E}^{\text{HF}}(\Phi), \quad \forall \Phi \in \mathcal{M}, \quad \forall U \in \mathcal{U}(N), \quad (1.13)$$

where $\mathcal{U}(N)$ is the group of the real unitary matrices:

$$\mathcal{U}(N) = \{U \in \mathbb{R}^{N \times N} \mid U^T U = 1_N\},$$

1_N denoting the identity matrix of rank N . This invariance can be exploited to diagonalize the matrix of the Lagrange multipliers of the orthonormality constraints (see, e.g., [18]), yielding the existence of a minimizer (still denoted by Φ^0), such that

$$\mathcal{H}_{\Phi^0}^{\text{HF}}\phi_i^0 = \epsilon_i^0 \phi_i^0 \quad (1.14)$$

for some $\epsilon_1^0 \leq \epsilon_2^0 \leq \dots \leq \epsilon_N^0$.

Similarly, for the Kohn Sham problem, we introduce the associated Hamiltonian

$$\mathcal{H}_\Phi^{\text{KS}} = -\frac{1}{2}\Delta + \left(V^{\text{nuc}} + V_{\rho_\Phi}^{\text{Coulomb}} + \frac{de_{\text{xc}}^{\text{LDA}}}{d\rho}(\rho_\Phi) \right) = h + \mathcal{V}_{\rho_\Phi},$$

where h is the same as above and

$$\mathcal{V}_\rho = V_\rho^{\text{Coulomb}} + \frac{de_{\text{xc}}^{\text{LDA}}}{d\rho}(\rho). \quad (1.15)$$

The same analysis leads to an eigenvalue problem. By using again the invariance through unitary transforms (1.13), that still holds for the Kohn-Sham problem, we get the existence of a minimizer with a set of molecular orbitals still denoted as Φ^0 , such that

$$\mathcal{H}_{\Phi^0}^{\text{KS}} \phi_i^0 = \epsilon_i^0 \phi_i^0 \quad (1.16)$$

for some $\epsilon_1^0 \leq \epsilon_2^0 \leq \dots \leq \epsilon_N^0$.

2 About Numerical Methods

2.1 Generalities

For problems set in a periodic framework (analysis of crystals), the approximation by plane waves (Fourier) has traditionally been one of the popular approaches used for solving the Kohn-Sham problem since it allows for an efficient computation of the electrostatic interactions through Fourier transforms. In addition the plane waves (Fourier) approximation is a high order method that is fully deployed if the solutions to be approximated are very regular. Unfortunately, for full potential electronic structure calculations, the nuclear potential is not smeared out and induces singularities in the solutions (atomic orbitals and density) at the level of the nuclei, more precisely cusps in place of the nuclei and rapidly varying wave functions in their vicinity (see [24, 29]). Another drawback of these methods lies in the nonlocality of the basis set that leads to a uniform spatial resolution which can be useless e.g. for materials systems with defects, where higher basis resolution is required in some spatial regions and a coarser resolution suffices elsewhere. In practice of such discretizations, the singular nuclear potential V^{nuc} defined by (1.4) is usually replaced with a smoother potential V^{ion} ; this amounts to replacing point nuclei with smeared nuclei. Not surprisingly, the smoother the potential, the faster the convergence of the planewave approximation to the exact solution of (1.2) or (1.5) (see [8]). The nuclear potential V^{nuc} is replaced by a pseudopotential modeling the Coulomb interaction between the valence electrons on the one hand, and the nuclei and the core electrons on the other hand. The pseudopotential consists of two terms: a local component V_{local} (whose associated operator is the multiplication by the function V_{local}) and a nonlocal component. As a consequence, the second term in the Kohn-Sham energy functional (1.6) is replaced by

$$\int_{\Gamma} \rho_\Phi V_{\text{local}} dx + 2 \sum_{i=1}^N \langle \phi_i | V_{\text{nl}} | \phi_i \rangle.$$

The pseudopotential approximation gives satisfactory results in most cases, but sometimes fails. Note that a mathematical analysis of the pseudopotential approximation is still lacking. Moreover, the core electrons need sometimes be considered since they are responsible for intricate

properties. The full-potential/all-electron calculation is thus sometimes necessary. In order to overcome the convergence difficulties of the plane wave approximations, resulting from the cusp singularities one can augment the plane waves bases set as done in the augmented plane wave (or APW for short) method (see [42, 50]), which is among the most accurate methods for performing electronic structure calculations for crystals. We refer to [16] for the numerical analysis of the convergence based on the careful analysis of the properties of the cusp that we shall recall in Section 2.2. These APWs provide very good results, at the price however of two remaining drawbacks. The first one is that of the periodic framework that does not fit for single molecules or molecules in solvent. The second one is that the basis come from two different families and the locality of the plane waves (orthonormal basis) is lost.

For efficient computations in the case of all-electron calculations on a large materials system, approximation methods based on Gaussian basis are among the other most classical methods. An example is using the Gaussian package (see [25]). These approaches initially introduced on Hartree-Fock problem, have been developed both for reasons of accuracy and easiness of implementation due to the fact that product of these basis functions arising in nonlinear terms of the potential are easy to evaluate through analytical expressions. The basis functions are centered at each nuclei and are fitted so as to represent well the behavior of the atomic orbital at the level of the cusp and at infinity. There exist a large amount of know how in these methods, that benefit from highly optimized Gaussian basis functions on many molecules. When this expertise does not exist, the approximation properties of the Gaussian expansion are more questionable. We refer e.g. to [9–10] for the presentation and numerical analysis in this context.

Due to the large nonlinearities encountered in the energies involved in advanced Kohn-Sham models, the complexity of the computations, when it turns to implement the methods, scales as $\mathcal{O}(N^d)$, where N is the number of degrees of freedom, and d can be pretty large ($d \geq 3$). One way is to “squeeze” at most the numerical scheme, performing, at the mathematical level, what computational experts in simulations for electronic structure calculations design when they propose ad-hoc discrete basis (e.g. contracted Gaussian bases sets). The expertise here is based on the mathematical arguments involved in model reduction techniques (the reduced basis approximation), and we refer to [11, 40] for a presentation of these techniques. They are based on adapted (not universal) discretizations and are shown to provide good approximations, but are still in their infancy.

There is thus room for the development of more robust approaches for electronic structure calculations, like for example finite element approximation of low or high order that, in other contexts (fluid mechanics, structure mechanics, wave, $\dots$), are of classical use. There has been already quite a lot of experiences in the domain of quantum chemistry even though the relative number of contributions is still small. We refer to [2, 6, 21, 34, 39, 43, 45–47, 51, 53–55, 58–59] and the references therein for an overview of the contributions in this direction.

In order to be competitive with respect to plane-wave basis or Gaussian type basis, though, the full knowledge and expertise in the finite element machinery has to be requested, indeed, as appears in e.g. [6, 28], the accuracy required for electronic structure calculation involves of the order of 100, 000 basis functions per atom for $\mathbb{P}_1$ finite elements, which is far too expensive and the use of higher-order finite element methods is thus the only viable way. However, the use

of high-order finite elements has some consequences on the complexity of the implementation, indeed these require the use of higher-order accurate numerical quadrature rules with larger stencils of points and leads also to increase in the bandwidth of the stiffness matrices that grow cubically with the order of the finite-element, with a mass matrix that, contrarily to what happens for plane wave approximation, is not diagonal. In addition, using high order methods in regions where the solution presents singularities is a waste of resources.

The right question to raise is thus not accuracy with respect to number of degrees of freedom but accuracy with respect to run time. In this respect, the publication [57] analyses in full details on a variety of problems and regularity of solutions, the accuracy achieved by low to high order finite element approximations as a function of the number of degrees of freedom and of the run time. It appears, with respect to this second argument that the use of degrees between 5 and 8 is quite competitive. Of course, the answer depends on the implementation of the discretization method and the exact properties of the solution to be approximated but this indicates a tendency that is confirmed, both by the numerical analysis and by implementation on a large set of other applications.

A recent investigation in the context of orbital-free DFT indicates that the use of higher-order finite elements can significantly improve the computational efficiency of the calculations (see [44, 51]). For instance, a 100 to 1000 fold computational advantage was reported by using a fourth to sixth order finite element in comparison to a linear finite element. This involves a careful implementation of various numerical and computational techniques: (i) an a priori mesh adaption technique to construct a close to optimal finite element discretization of the problem; (ii) an efficient solution strategy for solving the discrete eigenvalue problem by using spectral finite elements in conjunction with Gauss-Lobatto quadrature, and a Chebyshev acceleration technique for computing the occupied eigenspace (see [44]).

As far as we are aware of, the current implementations of the finite element method involve uniform degree of the polynomial approximation. This results in an improved accuracy-per-node ratio that is still polynomial in the number of degrees of freedom. This is actually a bit disappointing since, as is explained in a series of papers by Fournais, Sørensen, Hoffmann-Ostenhof, and Hoffmann-Ostenhof [22–24, 29] the solution is analytic (with exponential convergence to zero at infinity on unbounded domains) at least away from the position of the nuclei, where, if exact singular potential are used, the knowledge on singular behavior of the solution is rather well known (this one being of the shape $e^{-\frac{Zr}{2}}$), which results that the solution is not better than $H^{\frac{5}{2}}$ around the singularities.

In the finite element culture, such behavior — very regular except at some point where the behavior of the pointwise singularity is known — is known to allow for an exponential convergence with respect to the number of degrees of freedom. Indeed, in a series of papers written by Babuška and co-authors [3, 26–27], a careful analysis is performed that leads to the conclusion that the $h - P$ version of the finite element method allows for an exponential rate of convergence when solving problems with piecewise analytic data. In particular, in the three papers [3, 26–27], the authors focus on the approximation of the function $(x - \xi)_+^\alpha$ over $(0, 1)$ for $\xi \in (0, 1)$, this simple function is a prototype of pointwise singular behavior that can be present in the solution of regular problems in geometries with corners or edges, or for problems with nonregular coefficients. It is straightforward to check that when

- (1) $\alpha > -\frac{1}{2}$ then the function is in $L^2(0, 1)$,
- (2) $\alpha > \frac{1}{2}$ then the function is in $H^1(0, 1)$,
- (3) $\alpha > \frac{3}{2}$ then the function is in $H^2(0, 1)$,
- (4) $\alpha > \frac{5}{2}$ then the function is in $H^3(0, 1)$.

We believe that it is interesting to summarize the conclusion of these papers as follows:

(1) For the P version of the FEM (or spectral method (see [13])): If $\xi \in (0, 1)$, the convergence of the best fit is of the order of $\frac{C}{P^{\alpha-\frac{1}{2}}}$ (i.e., $\frac{C}{P^r}$, where r is related to the regularity of the function). Note that, if $\xi = 0$ (or $\xi = 1$), the convergence of the best fit is of the order of $\frac{C}{P^{2\alpha-1}}$. This phenomenon is known as the doubling of convergence for singular functions (see, e.g., [4] for more results in this direction).

(2) For the $h - P$ version of the FEM (or spectral element method): The approximation is generally of the order of $h^{\min(\alpha-\frac{1}{2}, P+1)}$.

(3) For the $h - P$ version, with a graded mesh, i.e., the size of the mesh diminishes as one gets closer to the singularities and P uniformly increasing: The approximation can be of exponential order with respect to the number of degrees of freedom.

(4) For the optimal $h - P$ version of the finite element method: The approximation can be of exponential order with a better rate (with respect to the above rate) if the degree P that is used in the largest elements increases while the graded mesh is refined in the neighborhood of the singularity. Starting from a uniform mesh, the elements that contain the singularity are recursively refined; starting from the singularity, the degree of the approximation is equal to 1 and linearly increases with the distance to the singularities in the other elements; the error then scales like $\exp(-cN_h^\beta)$, where N_h is the number of degrees of freedom of the finite element approximation.

2.2 Regularity results

The natural question is then: What is the regularity of the density, the solution to the Hartree Fock or Kohn Sham problems?

It is proven (see, e.g., the careful analysis of [26–28]) that the solution to such systems is analytic (with exponential convergence to zero on unbounded domains) at least away from the position of the nuclei, where, if exact singular potential is used there, the solution is not better than $H^{\frac{5}{2}}$ around the singularities (this one being of the shape $e^{-\frac{Zr}{2}}$).

For the same reasons as the doubling of convergence, if the finite element vertices are on the nuclei positions, then there is a doubling of convergence for the P and $h - P$ version of the approximation leading to a convergence rate like P^{-3} for the solution obtained with polynomial degree 4, if the mesh is uniform. The energy is approximated with another doubling of accuracy, i.e., $P^{-6} \dots$. This analysis deals only with the polynomial approximation without taking care of any h effect and is consistent with the analysis of the paper [20]. At this level, we want to emphasize on two points for which we refer to [16]. The first one deals with a better understanding of the characteristics of the singularity of the solution of the Hartree Fock problem at the level of nuclei; indeed it appears that locally, when expressed in spherical coordinates around the nuclei, the solution is infinitely differentiable. The second is to indicate that, from this knowledge, it is actually possible to propose combined approximations that allows exponential convergence with respect to the number of degrees of freedom (see also the

recent approach in [39]).

In order to be more precise on the regularity of the solutions to such systems, we are going to place ourselves in an adapted framework. We follow [53–54] to define, over any regular bounded domain Ω that contains (far from the boundary) all nuclei R_j , $j = 1, \dots, M$, some weighted Sobolev spaces well suited for the numerical analysis of adapted finite element methods (as explained in [17], these weighted Sobolev spaces are well suited to characterize the singular behavior of solutions of general second-order elliptic boundary value problems in polyhedra). First, we define the subdomain Ω_0 which is the complementary in Ω to the union of small enough balls ω_j around each nuclei position R_j , $j = 1, \dots, M$. In addition, to each nuclei position R_j , $j = 1, \dots, M$, we associate an exponent β_j , and the following semi-norms for any $m \in \mathbb{N}$:

$$|u|_{M_{\underline{\beta}}^m(\Omega)}^2 = |u|_{H^m(\Omega_0)}^2 + \sum_{j=1}^M \sum_{|\underline{\alpha}|=m} \|r_j^{\beta_j+|\underline{\alpha}|} D^{\underline{\alpha}} u\|_{L^2(\omega_j)}, \quad (2.1)$$

where r_j denotes the distance to R_j and norm

$$\|u\|_{M_{\underline{\beta}}^m(\Omega)}^2 = \sum_{k=0}^m |u|_{M_{\underline{\beta}}^k(\Omega)}^2, \quad (2.2)$$

where $D^{\underline{\alpha}}$ denotes the derivative in the local coordinate directions corresponding to the multi-index $\underline{\alpha}$.

The space $M_{\underline{\beta}}^m(\Omega)$ is then the closure of $\mathcal{C}_0^\infty(\Omega)$ of all infinitely differentiable functions that vanish on the boundary of Ω .

From the results stated above, we deduce that the solutions of the Hartree-Fock problem ϕ_i^0 for any i ($1 \leq i \leq N$) belong to such spaces (they are said asymptotically well behaved) and moreover

$$|\phi_i^0|_{M_{\underline{\beta}}^m(\Omega)} \leq C^m m! \quad (2.3)$$

with $\beta_j > -\frac{3}{2}$. In [16], it is indicated that the same type of result can be assumed for the solution to the Kohn-Sham problem, at least for regular enough exchange correlation potential. In what follows we shall assume that the same regularity result holds for those solutions.

3 Galerkin Approximation

3.1 Generalities on the variational approximation

Let us consider a family of finite dimensional spaces X_δ , with dimension N_δ . We assume that it is defined through the data of a finite basis set $\{\chi_\mu\}_{1 \leq \mu \leq N_\delta}$. Let us assume that these are subspaces of $H_0^1(\Omega)$ (for the time being this means that the discrete functions should be continuous).

The variational approximations of the Hartree-Fock or Kohn-Sham problems are

$$\mathcal{I}_{N,\delta}^{HF}(V) = \inf \left\{ \mathcal{E}^{HF}(\Phi_\delta), \Phi_\delta = (\phi_{1,\delta}, \dots, \phi_{N,\delta})^T \in (X_\delta)^N, \int_{\mathbb{R}^3} \phi_{i,\delta} \phi_{j,\delta} dx = \delta_{ij}, 1 \leq i, j \leq N \right\} \quad (3.1)$$

and

$$\mathcal{I}_{N,\delta}^{KS}(V) = \inf \left\{ \mathcal{E}^{KS}(\Phi_\delta), \Phi_\delta = (\phi_{1,\delta}, \dots, \phi_{N,\delta})^T \in (X_\delta)^N, \int_{\mathbb{R}^3} \phi_{i,\delta} \phi_{j,\delta} dx = \delta_{ij}, 1 \leq i, j \leq N \right\}. \quad (3.2)$$

The solution to the Galerkin approximation procedure is determined by

$$\phi_{i,\delta} = \sum_{\mu=1}^{N_\delta} C_{\mu i} \chi_\mu.$$

Hence by the determination of the rectangular matrix $C \in \mathcal{M}(N_\delta, N)$ contains the N_δ coefficients of the molecular orbital $\phi_{i,\delta}$ in the basis $\{\chi_\mu\}_{1 \leq \mu \leq N_\delta}$. It is classical in this context to introduce the so-called overlap matrix S defined as

$$S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu dx, \quad (3.3)$$

so that the constraints $\int_{\mathbb{R}^3} \phi_{i,\delta} \phi_{j,\delta} dx = \delta_{ij}$ on the discrete solutions read

$$\delta_{ij} = \sum_{\mu=1}^{N_\delta} \sum_{\nu=1}^{N_\delta} C_{\mu j} S_{\mu\nu} C_{\nu i},$$

or again in matrix form

$$C^* S C = I_N.$$

Similarly,

$$\begin{aligned} & \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_{i,\delta}|^2 dx + \int_{\mathbb{R}^3} \rho_{\Phi_\delta} V^{\text{nuc}} dx \\ &= \sum_{i=1}^N \left(\frac{1}{2} \int_{\mathbb{R}^3} \left| \nabla \sum_{\mu=1}^{N_\delta} C_{\mu i} \chi_\mu \right|^2 dx + \int_{\mathbb{R}^3} V^{\text{nuc}} \left| \sum_{\mu=1}^{N_\delta} C_{\mu i} \chi_\mu \right|^2 dx \right) \\ &= \sum_{i=1}^N \sum_{\mu=1}^{N_\delta} \sum_{\nu=1}^{N_\delta} h_{\mu\nu} C_{\nu i} C_{\mu i} = \text{Trace}(h C C^*), \end{aligned}$$

where $h \in \mathcal{M}_S(N_\delta)$ denotes the matrix of the operator $-\frac{1}{2}\Delta + V^{\text{nuc}}$ in the basis $\{\chi_k\}$:

$$h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu dx + \int_{\mathbb{R}^3} V^{\text{nuc}} \chi_\mu \chi_\nu dx. \quad (3.4)$$

Finally, we can write the Coulomb and exchange terms by introducing first the notations

$$(\mu\nu \mid \kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(x) \chi_\nu(x) \chi_\kappa(x') \chi_\lambda(x')}{|x - x'|} dx dx', \quad (3.5)$$

and, for any matrix X with size $N_\delta \times N_\delta$

$$J(X)_{\mu\nu} = \sum_{\kappa, \lambda=1}^{N_\delta} (\mu\nu \mid \kappa\lambda) X_{\kappa\lambda}, \quad K(X)_{\mu\nu} = \sum_{\kappa, \lambda=1}^{N_\delta} (\mu\lambda \mid \nu\kappa) X_{\kappa\lambda}.$$

The Coulomb and exchange terms can respectively be expressed as

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi_\delta}(x) \rho_{\Phi_\delta}(x')}{|x - x'|} dx dx' = \sum_{\mu, \nu, \kappa, \lambda=1}^{N_\delta} \sum_{i, j=1}^N (\mu\nu \mid \kappa\lambda) C_{\mu i} C_{\nu i} C_{\kappa j} C_{\lambda j} = \text{Trace}(J(C C^*) C C^*)$$

and

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\tau_{\Phi_\delta}(x, x')|^2}{|x - x'|} dx dx' = \sum_{\mu, \nu, \kappa, \lambda=1}^{N_\delta} \sum_{i, j=1}^N (\mu\lambda|\kappa\nu) C_{\mu i} C_{\nu i} C_{\kappa j} C_{\lambda j} = \text{Trace} (K(CC^*)CC^*).$$

The discrete problem, is thus written equivalently as a minimization problem over the space

$$\mathcal{W}_N = \{\mathcal{W}_{N_\delta} \in \mathcal{M}(N_\delta, N), \ C^*SC = I_N\},$$

as

$$\inf\{E^{HF}(CC^*), \ C \in \mathcal{W}_{N_\delta}\}, \quad (3.6)$$

where for any $D \in \mathcal{M}_S(N_\delta)$,

$$E^{HF}(D) = \text{Trace} (hD) + \frac{1}{2}\text{Trace} (J(D)D) - \frac{1}{2}\text{Trace} (K(D)D).$$

The energy can also be written in term of the so-called density matrix

$$D = CC^*$$

leading to the problem

$$\inf\{E^{HF}(D), \ D \in \mathcal{P}_N\} \quad (3.7)$$

with

$$\mathcal{P}_N = \{D \in \mathcal{M}_S(N), \ DSD = D, \ \text{Trace} (SD) = N\}.$$

Similarly, the Kohn-Sham problem (3.2) reads

$$\mathcal{I}_{N,\delta}^{KS}(V) = \inf\{E^{KS}(CC^*), \ C \in \mathcal{W}_{N_\delta}\} \quad (3.8)$$

with

$$E^{KS}(D) = 2\text{Trace} (hD) + 2\text{Trace} (J(D)D) + E_{xc}(D),$$

here $E_{xc}(D)$ denotes the exchange-correlation energy:

$$E_{xc}(D) = \int_{\mathbb{R}^3} \rho(x) \epsilon_{xc}^{\text{LDA}}(\rho(x)) dx \quad \text{with} \quad \rho(x) = 2 \sum_{i=1}^N D_{\mu\nu} \chi_\mu(x) \chi_\nu(x).$$

For general analysis of these discrete problems and the associated approximation results, we refer to [10–11, 18–19, 24, 36, 46, 65] and the references therein.

3.2 The adapted $h - P$ discrete spaces

Part 1 Definition of the $h - P$ discrete spaces

The purpose of this section is to introduce the class of $h - P$ finite elements spaces for the approximation of the minimization problems (1.2) and (1.5) which we want to propose and analyze in this paper. They will be used to get an exponential convergence for the finite element approximation of the solution to the Hartree-Fock and Kohn-Sham problems. We start by truncating the domain $\mathbb{R}^3$ in a regular bounded domain Ω that, for the sake of simplicity, we shall consider to be a ball large enough to contain largely each nuclei, similarly as in papers where this class of approximations was proposed (see [3, 26–27, 48–49]).

The first step of the discretization consists in defining an initial triangulation $\mathcal{T}^0$ of Ω composed of hexahedral elements K subject to the following classical assumptions:

$$(1) \overline{\Omega} = \bigcup_{K \in \mathcal{T}^0} \overline{K};$$

(2) Each element K is the image of the reference cube $(-1, 1)^3$ under a diffeomorphism, that, in most cases, is a homothetic transformation (except of course on the boundary of Ω , but we shall not carefully analyze the approximation there since the solution is very regular at this level);

(3) The initial triangulation is conforming in the sense that the intersection of two different elements K and K' is either empty, a common vertex, a common edge or a common face;

(4) The initial triangulation is regular and quasi-uniform in the sense that there exist two constants $\kappa_1, \kappa_2 > 0$ with $\kappa_2 h \leq h_K \leq \kappa_1 \rho_K$, where h_K denotes the diameter of K , ρ_K denotes the diameter of the largest circle that can be inscribed into K and $h = \max_K \{h_K\}$.

We assume in addition that the positions of the nuclei $R_1, R_2, \dots, R_M$ are the vertices of some element in the initial triangulation $\mathcal{T}^0$. Starting from this initial hexahedral triangulation $\mathcal{T}^0$ of Ω , for the $h - P$ procedure, we define a family of so-called σ -geometric triangulations.

First for the triangulation, we refine recursively (by partitioning into 4 hexahedra) each hexahedron that admits a nuclei at the vertex. This partitioning is based on a ratio $(\sigma, 1 - \sigma)$ (with $0 < \sigma < 1$) of each edge starting from the vertex that coincide at the nucleus, as explained in Figure 1. Note that the refinement only deals the elements that have a nuclei as a vertex, this refinement preserves the conformity with the non-refined elements. The first refinement allows to define the triangulation denoted as $\mathcal{T}^1$. Next, the same process applied to $\mathcal{T}^i$ allows to define $\mathcal{T}^{i+1}$. For any element K of the new triangulations $\mathcal{T}^i$ (that of course are not quasi-uniform anymore), h_K still denotes the diameter of K .

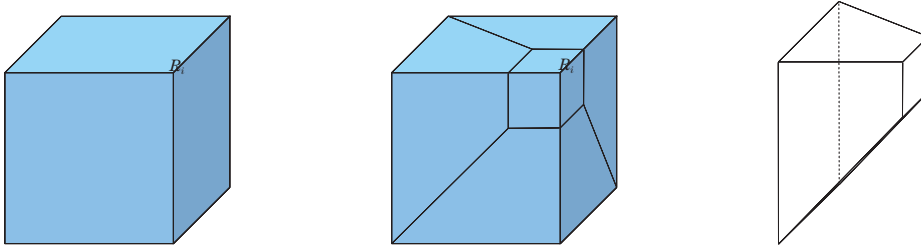


Figure 1 The partitioning of a hexahedron, that admits a nuclei at R_i as a vertex, in a $(\sigma, 1 - \sigma)$ -ratio (the left: before the refinement, the middle: after the refinement, the right: an element created in the refined hexahedron that maintains the conformity with adjacent elements).

Concerning the degree of the approximation that is used over each elements, we start at the level $\mathcal{T}^0$ by using polynomials in Q_1 , i.e., tri-affine, over each element. Then each time a triangulation refinement is performed, the new elements, created at this stage, are provided with Q_1 polynomials, while, on the other elements that did not change, the degree of the polynomial is increased by 1 unit in each variable (or by a fixed factor $\sigma > 0$ to be more general). In particular, the partial degree of the polynomial on the elements of a triangulation $\mathcal{T}^i$ that have never been cut is $\leq 1 + i\sigma$ and is uniform in all directions.

The discrete finite element space X_{h-P}^i is composed of all continuous such piecewise polynomials (associated to the triangulation $\mathcal{T}^i$) that vanish on the boundary of Ω . From the analysis in 1D explained in [26], exponential convergence for pointwise singular solutions can be obtained from the combination of the σ -geometric mesh refinement and σ -linear increase of the degree of the polynomials.

Part 2 Analysis of the $h - P$ approximation

The difficulty in this analysis lies in the conjunction of three facts:

- (1) The problem is set in three dimensions.
- (2) Neither the mesh nor the degree from one element to the other is uniform.
- (3) We are interested in approximation results for functions asymptotically well behaved.

For asymptotically well behaved functions, we modify the analysis proposed in [49] that dealt with discontinuous finite element methods. We thus start from the existence of one dimensional operators $\widehat{\pi}_{p,k}$ defined for any integer $k \geq 0$ and any integer $p \geq 2k + 1$: $H^k(-1, 1) \rightarrow \mathbb{P}^p(-1, 1)$ such that

$$(\widehat{\pi}_{p,k})^{(j)} u(\pm 1) = u^{(j)}(\pm 1), \quad j = 0, 1, \dots, k-1. \quad (3.9)$$

These operators can actually be chosen such that the following proposition holds.

Proposition 3.1 *For every $k \in \mathbb{N}$, there exists a constant $C_k > 0$ such that*

$$\|\widehat{\pi}_{p,k} u\|_{H^k(-1,1)} \leq C_k \|u\|_{H^k(-1,1)}, \quad \forall u \in H^k(-1, 1), \quad \forall p \geq 2k + 1. \quad (3.10)$$

For integers, $p, k \in \mathbb{N}$ with $p > 2k - 1$, $\kappa = p - k + 1$ and for $u \in H^{k+s}(-1, 1)$ with $k \leq s \leq \kappa$, there holds the error bound

$$\|(u - \pi_{p,k} u)^{(j)}\|_{L^2(\Omega)}^2 \leq \frac{(\kappa - s)!}{(\kappa + s)!} \|u^{(k+s)}\|_{L^2(\Omega)}^2 \quad (3.11)$$

for any $j = 0, 1, \dots, k$.

We then notice that, on the particular mesh of interest $\mathcal{T}^i$ (except for those elements of $\mathcal{T}^i$ — that are actually also in $\mathcal{T}^0$ — that are close to the boundary and for which there is no problem of regularity nor approximation), there are essentially two reference elements: A perfect cube $\widehat{K} = (-1, 1)^3$ and a truncated pyramid $\widehat{TP}$ like the one represented in Figure 2 below:

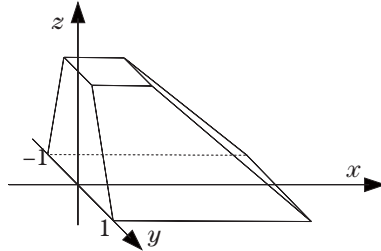


Figure 2 The reference truncated pyramidal element $\widehat{TP}$.

Over such a reference element $\widehat{TP}$, we want to propose a local reference quasi-interpolant and we follow, for this sake, the same construction as in [49] that is dedicated to the cube $\widehat{C}$.

It uses the tensorization of the one dimensional operator $\hat{\pi}_{p,2}$ that leads to the operator over $\hat{\mathcal{C}}$ defined by

$$\hat{\Pi}_{p,2}^3 = \hat{\pi}_{p,2}^{(x)} \otimes \hat{\pi}_{p,2}^{(y)} \otimes \hat{\pi}_{p,2}^{(z)}$$

for which it is proved (see [49, Proposition 5.2]).

Theorem 3.1 *For any integer $3 \leq s \leq p$, the operator $\hat{\Pi}_{p,2}^3$ satisfies*

$$\|u - \hat{\Pi}_{p,2}^3 u\|_{H_{\text{mix}}^2(\hat{\mathcal{C}})}^2 \leq \frac{(p-s)!}{(p+s-2)!} \|u\|_{H^{s+5}(\hat{\mathcal{C}})}^2 \quad (3.12)$$

and

$$H_{\text{mix}}^2(\hat{\mathcal{C}}) = H^2(-1, 1) \otimes H^2(-1, 1) \otimes H^2(-1, 1).$$

In order to get the same type of result, over $\widehat{TP}$, we modifying the operator $\hat{\Pi}_{p',2}^3$ defined above over $\hat{\mathcal{C}}$ by using the affine transform from the cube to the truncated pyramid $\widehat{TP}$. This results in an operator with range equal to the set of all polynomials over $\widehat{TP}$ with partial degree $\leq p'$ with respect to x and y but $\leq 3p'$ with respect to the z direction. In order to be an operator of degree $\leq p$, we choose $p' = \frac{p}{3}$, and denote by $\hat{\Pi}_{p,2,TP}^3$ this operator for which the following theorem holds.

Theorem 3.2 *For any integer $3 \leq s \leq p$, the operator $\hat{\Pi}_{p,2,TP}^3$ satisfies*

$$\|u - \hat{\Pi}_{p,2,TP}^3 u\|_{H_{\text{mix}}^2(\widehat{TP})}^2 \leq (c_{\widehat{TP}})^s \frac{(p-s)!}{(p+s-2)!} \|u\|_{H^{s+5}(\widehat{TP})}^2, \quad (3.13)$$

where the constant $c_{\widehat{TP}} \geq 1$ only depends on the shape of $\widehat{TP}$.

In order to construct a quasi-interpolant in the equivalent DG space to X_{h-P}^i built over $\mathcal{T}^i$, the operator $\hat{\Pi}_{p,2}^3$ was then used in [49] by scaling it on each element of the mesh $\mathcal{T}^i$ with the appropriate degree to propose a discontinuous approximation of the solution. Here we need to be a little bit more cautious since we want the approximation to be continuous since X_{h-P}^i is a conforming approximation of $H_0^1(\Omega)$.

We nevertheless proceed as in [49]. We first notice that every element $K \in \mathcal{T}^i$, is canonically associated to a reference element $\hat{K}$ that is either $\hat{\mathcal{C}}$ or $\widehat{TP}$. The mapping that allows to go from K to $\hat{K}$ is denoted as χ_K and is composed of a rotation, i.e., a homothetic transformation that thus preserve the polynomial degree. From these transformations, we first build from the operators $\hat{\Pi}_{p,2}^3$ and $\hat{\Pi}_{p,2,TP}^3$ a totally discontinuous approximation of any $H_0^1(\Omega)$ function u with the appropriate degree as in X_{h-P}^i . We denote by $\tilde{\Pi}_i^{DG}$ this operator. From the analysis performed in [49] based on the same regularity results as in (2.3), this first nonconforming approximation satisfies (see (5.21), (5.25) and (5.35) in [49]):

$$\begin{aligned} & \sum_{K \in \mathcal{T}^i} \frac{p_K^2}{h_K^2} \|u - \tilde{\Pi}_i^{DG} u\|_{L^2(K)}^2 + \sum_{K \in \mathcal{T}^i} \|\nabla(u - \tilde{\Pi}_i^{DG} u)\|_{L^2(K)}^2 \\ & \leq C \sum_{K \in \mathcal{T}^i} h_K \|\hat{u}|_K - \hat{\pi}(\hat{u}|_K)\|_{H_{\text{mix}}^2}^2, \end{aligned} \quad (3.14)$$

where, for any $K \in \mathcal{T}^i$, we denote by $\hat{u}|_K$ the pull back function associated with $u|_K$ through χ_K . The argument of the function $\hat{u}|_K$ is thus points $\mathbf{x} \in \hat{K}$. It can thus be projected with the appropriate reference operator $\hat{\pi}$ equal to either $\hat{\Pi}_{p,2}^3$ or $\hat{\Pi}_{p,2,TP}^3$.

We have now to make the approximation conforming (continuous) between two adjacent elements. This is done by lifting the discontinuities one after the other starting from the discontinuities at the vertex, then at the sides and then, finally at the faces.

Let us start with the vertices. We consider the set of all elements of $\mathcal{T}^i$ that share a common vertex $\mathbf{a}$ and denote them as $K_{\mathbf{a}}^j$ with $j = 1, \dots, J$. The non-conforming approximation $\tilde{\Pi}_i^{DG} u$ thus proposes J distinct, but close, values. The rectification first consists in modifying this value so that the new approximation over $K_{\mathbf{a}}^j$ with $j = 2, \dots, J$ is equal to $[\tilde{\Pi}_i^{DG} u]_{|K_{\mathbf{a}}^1}(\mathbf{a})$. Assume that for a given $K_{\mathbf{a}}^j$ with $j = 2, \dots, J$, the associated $\hat{K}$ is $\hat{\mathcal{C}}$, and that the associated pull back transformation maps the vertex $\mathbf{a}$ onto $(1, 1, 1)$. The rectification of $\hat{\pi}(\hat{u}_{|K_{\mathbf{a}}^j})$ is obtained by adding a quantity

$$\widehat{\text{rect}}_{\mathbf{a},j}(\hat{x}, \hat{y}, \hat{z}) = \varepsilon_{\mathbf{a},j} \mathcal{H}_{p,1}(\hat{x}) \mathcal{H}_{p,1}(\hat{y}) \mathcal{H}_{p,1}(\hat{z}),$$

where $\mathcal{H}_{p,1}$ is the polynomial $\mathcal{H}_{p,1}(\hat{x}) = \alpha(1 - \hat{x})L'_p(\hat{x})$; here L_p stands for the Legendre polynomial with degree p , and α is such that $\mathcal{H}_{p,1}(1) = 1$.

This modification, $\varepsilon_{\mathbf{a},j}$, is upper bounded by the L^∞ bound between $[\tilde{\Pi}_i^{DG} u]_{|K_{\mathbf{a}}^1}(\mathbf{a})$ and $[\tilde{\Pi}_i^{DG} u]_{|K_{\mathbf{a}}^j}(\mathbf{a})$, hence bounded by

$$|\varepsilon_{\mathbf{a},j}| \leq c \|\hat{u}_{|K_{\mathbf{a}}^1} - \hat{\pi}(\hat{u}_{|K_{\mathbf{a}}^1})\|_{H_{mix}^2} + \|\hat{u}_{|K_{\mathbf{a}}^j} - \hat{\pi}(\hat{u}_{|K_{\mathbf{a}}^j})\|_{H_{mix}^2}. \quad (3.15)$$

From classical considerations we know that

$$\|\mathcal{H}_{p,1}\|_{L^2(-1,1)} \leq C \frac{1}{p}, \quad \|\nabla \mathcal{H}_{p,1}\|_{L^2(-1,1)} \leq Cp.$$

Hence

$$\|\nabla[\varepsilon_{\mathbf{a},j} \mathcal{H}_{p,1}(\hat{x}) \mathcal{H}_{p,1}(\hat{y}) \mathcal{H}_{p,1}(\hat{z})]\|_{L^2(\hat{K})} \leq C \frac{1}{p}.$$

The associated modification of the approximation $\tilde{\Pi}_i^{DG} u$ of u , that we denote by $\text{rect}_{\mathbf{a},j}$ over $K_{\mathbf{a}}^j$ is thus upper bounded with an additional factor ch_K :

$$\|\nabla[\text{rect}_{\mathbf{a},j}]\|_{L^2(K_{\mathbf{a}}^j)} \leq c \frac{h_K}{p_K} \varepsilon_{\mathbf{a},j}.$$

Let us continue on the rectification. We proceed similarly with the edge values, and then the faces values. Let us present the face rectification. We only have two elements K and K' , that share a whole common face which we denote by $\mathcal{F}_{K,K'}$. The two approximations (already rectified at each vertex and edge) only differ from the internal values on this face. The difference is thus a function $\varepsilon(x, y)$ (say) that vanishes on the boundary of the face, and that we are going to lift on the element that has the largest degree (say K'). This lifting is again performed thanks to a function $\mathcal{H}_{p,1}(\hat{z})$:

$$\text{rect}_{\mathcal{F}_{K,K'}}(\hat{x}, \hat{y}, \hat{z}) = \varepsilon(\hat{x}, \hat{y}) \mathcal{H}_{p,1}(\hat{z}),$$

the norm of which satisfies

$$\|\nabla[\text{rect}_{\mathcal{F}_{K,K'}}]\|_{L^2(K')} \leq c \left[\frac{h_{K'}}{p_{K'}} \|\nabla \varepsilon_{\mathbf{a},j}\|_{L^2(\mathcal{F}_{K,K'})} + \frac{p_{K'}}{h_{K'}} \|\varepsilon_{\mathbf{a},j}\|_{L^2(\mathcal{F}_{K,K'})} \right]. \quad (3.16)$$

By summing up these three type of corrections, we deduce that the new conforming approximation still satisfies

$$\sum_{K \in \mathcal{T}^i} \|\nabla(u - \Pi_i^{\text{conf}} u)\|_{L^2(K)}^2 \leq C \sum_{K \in \mathcal{T}^i} h_K \|\widehat{u}_{|K} - \hat{\pi}(\widehat{u}_{|K})\|_{H_{mix}^2}^2. \quad (3.17)$$

We finish up as in [49] where the term on the right-hand side above is bounded, with the regularity (2.3) by upper bounding this contribution by $\exp(-ci)$, where i is the index of the triangulation $\mathcal{T}^i$, hence by $\exp(-c\sqrt[4]{N_i})$ where N_i is the total number of degrees of freedom of X_{h-P}^i .

Let us now introduce the $H_0^1(\Omega)$ orthogonal projection operator $\Pi_{H^1, h-P}^i$ over X_{h-P}^i thus defined as follows:

$$\Pi_{H^1, h-P}^i(\varphi) \in X_{h-P}^i, \quad \forall \varphi \in H_0^1(\Omega) \quad \text{and} \quad \int_{\Omega} \nabla(\varphi - [\Pi_{H^1, h-P}^i(\varphi)]) \nabla \psi \, dx = 0, \quad \forall \psi \in X_{h-P}^i. \quad (3.18)$$

We can state as follows.

Theorem 3.3 *There exists a constant $C_0 > 0$, such that, for all u that satisfies the regularity assumption (2.3),*

$$\|u - [\Pi_{H^1, h-P}^i(u)]\|_{H^1} \leq C_0 \exp(-c \sqrt[4]{N_i}). \quad (3.19)$$

4 A Priori Analysis

4.1 The Hartree-Fock problem

Part 1 Preliminary analysis

Let us first start with the discretization of the Hartree-Fock problem.

Following (3.1), the $h - P$ approximation of the Hartree-Fock problem is

$$\begin{aligned} \mathcal{I}_{N, h-P}^{HF, i}(V) = \inf \Big\{ \mathcal{E}^{HF}(\Phi_{h-P}), \quad \Phi_{h-P} = (\phi_{1, h-P}, \dots, \phi_{N, h-P})^T \in (X_{h-P}^i)^N, \\ \int_{\Omega} \phi_{i, h-P} \phi_{j, h-P} \, dx = \delta_{ij}, \quad 1 \leq i, j \leq N \Big\}. \end{aligned} \quad (4.1)$$

Remark 4.1 The various integrals appearing in this energy should be — and are — generally computed through numerical quadrature. These affect (sometimes dramatically) the convergence of the discrete ground state to the exact one. We shall not investigate here this effect that is well described in e.g. [7] in more simple settings.

The lack of uniqueness for the minimization problem, as recalled in (1.13) is a difficulty for the error analysis that requires the understanding of the the geometry of the Grassmann manifold $\mathcal{M}$, this was first addressed in [41]. For each $\Phi = (\phi_1, \dots, \phi_N)^T \in \mathcal{M}$, we denote by

$$T_{\Phi} \mathcal{M} = \left\{ (\psi_1, \dots, \psi_N)^T \in (H_0^1(\Omega))^N \mid \forall 1 \leq i, j \leq N, \int_{\Omega} (\phi_i \psi_j + \psi_i \phi_j) \, dx = 0 \right\}$$

the tangent space to $\mathcal{M}$ at Φ , and we also define

$$\Phi^{\perp} = \left\{ \Psi = (\psi_1, \dots, \psi_N)^T \in (H_0^1(\Omega))^N \mid \forall 1 \leq i, j \leq N, \int_{\Omega} \phi_i \psi_j \, dx = 0 \right\}.$$

Let us recall (see, e.g., [41, Lemma 4]) that

$$T_{\Phi} \mathcal{M} = \mathcal{A} \Phi \oplus \Phi^{\perp},$$

where $\mathcal{A} = \{A \in \mathbb{R}^{N \times N} \mid A^T = -A\}$ is the space of the $N \times N$ antisymmetric real matrices.

The second order condition associated to the minimization problem (1.2) reads

$$a_{\Phi^0}(W, W) \geq 0, \quad \forall W \in T_{\Phi^0}\mathcal{M},$$

where for all $\Psi = (\psi_1, \dots, \psi_N)^T$ and $\Upsilon = (v_1, \dots, v_N)^T$ in $(H_0^1(\Omega))^N$,

$$\begin{aligned} a_{\Phi^0}(\Psi, \Upsilon) &= \frac{1}{4} \mathcal{E}^{\text{HF}''}(\Phi^0)(\Psi, \Upsilon) - \sum_{i=1}^N \epsilon_i^0 \int_{\Omega} \psi_i v_i dx \\ &= \sum_{i=1}^N \langle (\mathcal{H}_{\rho^0}^{\text{KS}} - \epsilon_i^0) \psi_i, v_i \rangle_{H^{-1}, H_0^1} + 4 \sum_{i,j=1}^N \int_{\Omega} \int_{\Omega} \frac{\phi_i^0(x) \psi_i(x) \phi_j^0(y) v_j(y)}{|x-y|} dx dy \\ &\quad - 2 \sum_{i,j=1}^N \int_{\Omega} \int_{\Omega} \frac{v_i(x) \phi_i^0(y) \phi_j^0(x) \psi_j(y)}{|x-y|} dx dy \\ &\quad - 2 \sum_{i,j=1}^N \int_{\Omega} \int_{\Omega} \frac{\phi_i^0(x) v_i(y) \phi_j^0(x) \psi_j(y)}{|x-y|} dx dy. \end{aligned} \quad (4.2)$$

It follows from the invariance property (1.13) that

$$a_{\Phi^0}(\Psi, \Psi) = 0 \quad \text{for all } \Psi \in \mathcal{A}\Phi^0.$$

This leads us, as in [41], to make the assumption that a_{Φ^0} is positive definite on $\Phi^{0,\perp}$, so that, as in [41, Proposition 1], it follows that a_{Φ^0} is actually coercive on $\Phi^{0,\perp}$ (for the H_0^1 norm). In all what follows, we thus assume that there exists a positive constant c_{Φ^0} such that

$$a_{\Phi^0}(\Psi, \Psi) \geq c_{\Phi^0} \|\Psi\|_{H_0^1}^2, \quad \forall \Psi \in \Phi^{0,\perp}. \quad (4.3)$$

Remark 4.2 As noticed in [8], in the linear framework, the coercivity condition (4.3) is satisfied if and only if

- (i) $\epsilon_1^0, \dots, \epsilon_N^0$ are the lowest N eigenvalues (including multiplicities) of the linear self-adjoint operator $h = -\frac{1}{2}\Delta + V^{\text{nuc}}$;
- (ii) There is a gap $c_{\Phi^0} > 0$ between the lowest N^{th} and $(N+1)^{\text{st}}$ eigenvalues of h .

The topology of the Grassmann manifold $\mathcal{M}$ quotiented by the equivalence relation through unitary transformations (see e.g. [19]) was analyzed in this context in [41] and in [8]. In particular,

- (1) Let $\Phi \in \mathcal{M}$ and $\Psi \in \mathcal{M}$. If $M_{\Psi, \Phi}$ is invertible, then $U_{\Psi, \Phi} = M_{\Psi, \Phi}^T (M_{\Psi, \Phi} M_{\Psi, \Phi}^T)^{-\frac{1}{2}}$ is the unique minimizer to the problem $\min_{U \in \mathcal{U}(N)} \|U\Psi - \Phi\|_{(L^2(\Omega))^N}$.

- (2) The set

$$\mathcal{M}^{\Phi} := \left\{ \Psi \in \mathcal{M} \mid \|\Psi - \Phi\|_{L^2} = \min_{U \in \mathcal{U}(N)} \|U\Psi - \Phi\|_{L^2} \right\}$$

verifies

$$\mathcal{M}^{\Phi} = \{(1_N - M_{W, W})^{\frac{1}{2}} \Phi + W \mid W \in \Phi^{\perp}, 0 \leq M_{W, W} \leq 1_N\}.$$

Hence, for any $\Phi \in \mathcal{M}$ and any $\Psi \in \mathcal{M}^{\Phi}$ there exists $W \in \Phi^{\perp}$ such that

$$\Psi = \Phi + \mathcal{S}(W)\Phi + W, \quad (4.4)$$

where $\mathcal{S}(W) = (1_N - M_{W,W})^{\frac{1}{2}} - 1_N$ is an $N \times N$ symmetric matrix, and the converse also holds. Similarly, at the discrete level, for any $\Phi_{h-P} \in [X_{h-P}^i]^N \cap \mathcal{M}$ and any $\Psi_{h-P} \in V_{h-P}^N \cap \mathcal{M}^{\Phi_{h-P}}$ there exists $W_{h-P} \in [X_{h-P}^i]^N \cap \Phi_{h-P}^\perp$ such that

$$\Psi_{h-P} = \Phi_{h-P} + \mathcal{S}(W_{h-P})\Phi_{h-P} + W_{h-P}, \quad (4.5)$$

where $\mathcal{S}(W_{h-P}) = (1_N - M_{W_{h-P}, W_{h-P}})^{\frac{1}{2}} - 1_N$ is an $N \times N$ symmetric matrix, and the converse also holds.

In what follows, we shall compare, as in [8], the error between the solution to (4.1) and Φ^0 , the solution to (1.2), with its best approximation in $(X_{h-P}^i)^N \cap \mathcal{M}$ (see [8, Lemma 4.3]).

Lemma 4.1 (1) Let $\Phi = (\phi_1, \dots, \phi_N)^T \in \mathcal{M}$. If $i \in \mathbb{N}$ is such that

$$\dim(\text{span}(\Pi_{L^2, h-P}^i(\phi_1), \dots, \Pi_{L^2, h-P}^i(\phi_N))) = N,$$

then the unique minimizer of the problem $\min_{\Phi_{i, h-P} \in (X_{h-P}^i)^N \cap \mathcal{M}} \|\Phi_{i, h-P} - \Phi\|_{[L^2(\Omega)]^N}$ is

$$\pi_{i, h-P}^{\mathcal{M}} \Phi = (M_{\Pi_{L^2, h-P}^i \Phi, \Pi_{L^2, h-P}^i \Phi})^{-\frac{1}{2}} \Pi_{L^2, h-P}^i \Phi. \quad (4.6)$$

In addition, $\pi_{i, h-P}^{\mathcal{M}} \Phi \in (X_{h-P}^i)^N \cap \mathcal{M}^\Phi$,

$$\|\pi_{i, h-P}^{\mathcal{M}} \Phi - \Phi\|_{[L^2(\Omega)]^N} \leq \sqrt{2} \|\Pi_{L^2, h-P}^i \Phi - \Phi\|_{[L^2(\Omega)]^N}, \quad (4.7)$$

and for all i large enough,

$$\|\pi_{i, h-P}^{\mathcal{M}} \Phi - \Phi\|_{[H^1(\Omega)]^N} \leq \|\Phi\|_{[H^1(\Omega)]^N} \|\Pi_{L^2, h-P}^i \Phi - \Phi\|_{[L^2(\Omega)]^N}^2 + \|\Pi_{L^2, h-P}^i \Phi - \Phi\|_{[H^1(\Omega)]^N}. \quad (4.8)$$

(2) Let $i \in \mathbb{N}$ such that $\dim(X_{h-P}^i) \geq N$ and $\Phi_{i, h-P} \in (X_{h-P}^i)^N \cap \mathcal{M}$. Then

$$(X_{h-P}^i)^N \cap \mathcal{M}^{\Phi_{i, h-P}} = \{(1_N - M_{W_{i, h-P}, W_{i, h-P}})^{\frac{1}{2}} \Phi_{i, h-P} + W_{i, h-P} \mid W_{i, h-P} \in (X_{h-P}^i)^N \cap \Phi_{i, h-P}^\perp, 0 \leq M_{W_{i, h-P}, W_{i, h-P}} \leq 1_N\}. \quad (4.9)$$

The following Lemma 4.2 (see [8]) collects some properties of the function $W \mapsto \mathcal{S}(W)$.

Lemma 4.2 Let

$$K = \{W \in (L^2(\Omega))^N \mid 0 \leq M_{W,W} \leq 1_N\},$$

and $\mathcal{S} : K \rightarrow \mathbb{R}_S^{N \times N}$ (the space of the symmetric $N \times N$ real matrices) defined by

$$\mathcal{S}(W) = (1_N - M_{W,W})^{\frac{1}{2}} - 1_N.$$

The function $\mathcal{S}$ is continuous on K and differentiable on the interior $\overset{\circ}{K}$ of K . In addition,

$$\|\mathcal{S}(W)\|_F \leq \|W\|_{L^2}^2, \quad \forall W \in K, \quad (4.10)$$

where $\|\cdot\|_F$ denotes the Frobenius norm. For all $(W_1, W_2, Z) \in K \times K \times (L^2(\Omega))^N$ such that $\|W_1\|_{L^2} \leq \frac{1}{2}$ and $\|W_2\|_{L^2} \leq \frac{1}{2}$,

$$\|\mathcal{S}(W_1) - \mathcal{S}(W_2)\|_F \leq 2(\|W_1\|_{L^2} + \|W_2\|_{L^2})\|W_1 - W_2\|_{L^2}, \quad (4.11)$$

$$\|(\mathcal{S}'(W_1) - \mathcal{S}'(W_2)) \cdot Z\|_F \leq 4\|W_1 - W_2\|_{L^2}\|Z\|_{L^2}, \quad (4.12)$$

$$\|(\mathcal{S}''(W_1)(Z, Z))\|_F \leq 4\|Z\|_{L^2}^2. \quad (4.13)$$

Now, we recall the following stability results that can be proved following the same lines as in [8].

Lemma 4.3 *There exists $C \geq 0$ such that*

(1) *for all $(\Upsilon_1, \Upsilon_2, \Upsilon_3) \in ((H_0^1(\Omega))^N)^3$,*

$$|(\mathcal{E}^{\text{HF}''}(\Phi^0 + \Upsilon_1) - \mathcal{E}^{\text{HF}''}(\Phi^0))(\Upsilon_2, \Upsilon_3)| \leq C(\|\Upsilon_1\|_{L^2}^2 + \|\Upsilon_1\|_{H_0^1}^2) \|\Upsilon_2\|_{H_0^1} \|\Upsilon_3\|_{H_0^1};$$

(2) *for all $(\Upsilon_1, \Upsilon_2, \Upsilon_3) \in ((H^2(\Omega))^N)^3$,*

$$|(\mathcal{E}^{\text{HF}''}(\Phi^0 + \Upsilon_1) - \mathcal{E}^{\text{HF}''}(\Phi^0))(\Upsilon_2, \Upsilon_3)| \leq C(\|\Upsilon_1\|_{L^2}^2 + \|\Upsilon_1\|_{L^2}^2) \|\Upsilon_2\|_{L^2} \|\Upsilon_3\|_{H^2}.$$

In addition, for all $(q, r, s) \in \mathbb{R}_+^3$ such that $\frac{3}{2} < q$, $s > \frac{3}{2}$ and $r \leq \min(q, s)$, and all $0 < M < \infty$, there exists a constant $C \geq 0$ such that

(1) *for all $(\Upsilon_1, \Upsilon_2, \Upsilon_3) \in (H^q(\Omega))^N \times (H_0^{-r}(\Omega))^N \times (H_0^s(\Omega))^N$ such that $\|\Upsilon_1\|_{H^q} \leq M$,*

$$|(\mathcal{E}^{\text{HF}''}(\Phi^0 + \Upsilon_1) - \mathcal{E}^{\text{HF}''}(\Phi^0))(\Upsilon_2, \Upsilon_3)| \leq C \|\Upsilon_1\|_{H^q} \|\Upsilon_2\|_{H^{-r}} \|\Upsilon_3\|_{H^s}.$$

Following the same lines as in [8, Lemma 4.7], we deduce from Lemma 4.3 that there exists $C \geq 0$ such that for all $\Psi \in \mathcal{M}$,

$$\mathcal{E}^{\text{HF}}(\Psi) = \mathcal{E}^{\text{HF}}(\Phi^0) + 2a_{\Phi^0}(\Psi - \Phi^0, \Psi - \Phi^0) + R(\Psi - \Phi^0) \quad (4.14)$$

with

$$|R(\Psi - \Phi^0)| \leq C(\|\Psi - \Phi^0\|_{H_0^1}^3 + \|\Psi - \Phi^0\|_{H_0^1}^4). \quad (4.15)$$

Part 2 Existence of a discrete solution

We now use the parametrization of the manifold $X_{h-P}^i \cap \mathcal{M}^{\Phi_{i,h-P}}$ explained in (4.9) to express a given minimizer of the problem (4.1) close to Φ^0 in terms of an element $W_{i,h-P}$ in a neighborhood of 0 expressed as $W_{i,h-P} \in \mathcal{B}_{i,h-P}$, where

$$\mathcal{B}_{i,h-P} := \{W^{i,h-P} \in [X_{h-P}^i]^N \cap [\pi_{i,h-P}^{\mathcal{M}} \Phi^0]^\perp \mid 0 \leq M_{W^{i,h-P}, W^{i,h-P}} \leq 1\}.$$

Indeed, we can define

$$\mathbf{E}_{i,h-P}(W^{i,h-P}) = \mathcal{E}^{\text{HF}}(\pi_{i,h-P}^{\mathcal{M}} \Phi^0 + \mathcal{S}(W^{i,h-P}) \pi_{i,h-P}^{\mathcal{M}} \Phi^0 + W^{i,h-P}), \quad (4.16)$$

the minimizers of which are in one-to-one correspondence with those of (4.1). Then the same line as in the proof of Lemma 4.8 in [8] leads to the following lemma.

Lemma 4.4 *There exist $r > 0$ and i^0 such that for all $i \geq i^0$, the functional $\mathbf{E}_{i,h-P}$ has a unique critical point $W_0^{i,h-P}$ in the ball*

$$\{W^{i,h-P} \in [X_{h-P}^i]^N \cap [\pi_{i,h-P}^{\mathcal{M}} \Phi^0]^\perp \mid \|W^{i,h-P}\|_{H_0^1} \leq r\}.$$

Besides, $W_0^{i,h-P}$ is a local minimizer of $\mathbf{E}_{i,h-P}$ over the above ball and we have the estimate

$$\|W_0^{i,h-P}\|_{H_0^1} \leq C \|\pi_{i,h-P}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H_0^1}. \quad (4.17)$$

Since the solution Φ^0 is asymptotically well behaved, i.e., satisfies (2.3), we obtain from the accuracy offered by the $h - P$ finite elements spaces X_{h-P}^i stated in Theorem 3.3 that there exists a constant C such that

$$\|W_0^{i,h-P}\|_{H_0^1} \leq C \exp(-c \sqrt[4]{N_i}).$$

Then we deduce the existence and uniqueness of a local minimizer to the problem (4.1) close to Φ^0 which satisfies that (see [8, (4.71)–(4.72)]) for i large enough,

$$\frac{1}{2} \|W_{i,h-P}^0\|_{L^2} \leq \|\Phi_{i,h-P}^0 - \Phi^0\|_{L^2} \leq 2 \|W_{i,h-P}^0\|_{L^2}, \quad (4.18)$$

$$\frac{1}{2} \|W_{i,h-P}^0\|_{H_0^1} \leq \|\Phi_{i,h-P}^0 - \Phi^0\|_{H_0^1} \leq 2 \|W_{i,h-P}^0\|_{H_0^1}. \quad (4.19)$$

Hence we have proven the following theorem.

Theorem 4.1 *Let Φ^0 be a local minimizer of the Hartree-Fock problem (1.2), and assume that it is asymptotically well behaved, i.e., satisfies (2.3). Then there exist $r^0 > 0$ and i^0 such that, for any $i \geq i^0$, the discrete problem (4.1) has a unique local minimizer $\Phi_{i,h-P}^0$ in the set*

$$\{\Psi_{i,h-P} \in (X_{h-P}^i)^N \cap \mathcal{M}^{\Phi^0} \mid \|\Psi_{i,h-P} - \Phi^0\|_{H_0^1(\Omega)} \leq r^0\},$$

and there exist constants $C > 0$ and $c > 0$, independent of i such that

$$\|\Phi_{i,h-P}^0 - \Phi^0\|_{H_0^1} \leq C \exp(-c \sqrt[4]{N_i}).$$

Finally, the discrete solution $\Phi_{i,h-P}^0$ satisfies the Euler equations

$$\langle \mathcal{H}_{\rho_{i,h-P}^0}^{\text{HF}} \phi_{j,i,h-P}^0, \psi_{j,i,h-P} \rangle_{H^{-1}, H_0^1} = \sum_{\nu=1}^N [\lambda_{i,h-P}^0]_{j\nu} (\phi_{\nu,i,h-P}^0, \psi_{\nu,i,h-P})_{L^2}, \quad \forall \Psi_{i,h-P} \in [X_{h-P}^i]^N,$$

where $\rho_{i,h-P}^0 = \rho_{\Phi_{i,h-P}^0}$ and the $N \times N$ matrix $\Lambda_{i,h-P}^0$ is symmetric (but generally not diagonal). Of course, it follows from the invariance property (1.13) that (4.1) has a local minimizer of the form $U \Phi_{i,h-P}^0$ with $U \in \mathcal{U}(N)$ for which the Lagrange multiplier of the orthonormality constraints is a diagonal matrix.

In order to get more precise results on the convergence rate of the eigenvalues, further analysis needs to be performed on the approximation properties in standard Sobolev spaces of the discrete space X_{h-P}^i . As far as we know, these results concerning

- (1) inverse inequalities,
- (2) convergence properties of the $L^2(\Omega)$ orthogonal projection operator $\Pi_{L^2,h-P}^i$ over X_{h-P}^i for e.g. H^1 functions,
- (3) convergence properties of the $H_0^1(\Omega)$ orthogonal projection operator $\Pi_{H^1,h-P}^i$ over X_{h-P}^i for e.g. H^2 functions,

do not exist in optimal form, which is what is required to get the doubling of convergence for the approximation of the eigenvalues with respect to the convergence of $\|\Phi_{i,h-P}^0 - \Phi^0\|_{H_0^1}$. These results will be proven in a paper in preparation.

4.2 The Kohn-Sham problem

Following (3.2), the $h - P$ approximation of the Kohn-Sham problem is

$$\begin{aligned} \mathcal{I}_{N,h-P}^{KS,i}(V) = \inf \left\{ \mathcal{E}^{KS}(\Phi_{h-P}), \Phi_{h-P} = (\phi_{1,h-P}, \dots, \phi_{N,h-P})^T \in (X_{h-P}^i)^N, \right. \\ \left. \int_{\Omega} \phi_{i,h-P} \phi_{j,h-P} dx = \delta_{ij}, 1 \leq i, j \leq N \right\}. \end{aligned} \quad (4.20)$$

Following the same lines as in the proof of the previous result, and the analysis of the plane wave approximation of the Kohn-Sham problem presented in [8], we can prove the following theorem.

Theorem 4.2 *Let Φ^0 be a local minimizer of the Kohn-Sham problem (1.5), and assume that it is asymptotically well behaved, i.e. satisfies (2.3), Then there exist $r^0 > 0$ and i^0 such that, for any $i \geq i^0$, the discrete problem (4.20) has a unique local minimizer $\Phi_{i,h-P}^0$ in the set*

$$\{\Psi_{i,h-P} \in (X_{h-P}^i)^N \cap \mathcal{M}^{\Phi^0} \mid \|\Psi_{i,h-P} - \Phi^0\|_{H_0^1(\Omega)} \leq r^0\},$$

and there exist constants $C > 0$ and $c > 0$, independent of i such that

$$\|\Phi_{i,h-P}^0 - \Phi^0\|_{H_0^1} \leq C \exp(-c \sqrt[4]{N_i}).$$

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