Local density approximations for the energy of a periodic Coulomb model

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Abstract: We deal with local density approximations for the kinetic and exchange energy term, $\mathcal{E}_{kin}(\rho)$ and $\mathcal{E}_{ex}(\rho)$, of a periodic Coulomb model. We study asymptotic approximations of the energy when the number of particles goes to infinity and for densities close to the constant averaged density. For the kinetic energy, we recover the usual combination of the von-Weizsäcker term and the Thomas-Fermi term. Furthermore, we justify the inclusion of the Dirac term for the exchange energy and the Slater term for the local exchange potential.

1 Introduction

The aim of this work is to provide a justification of the Thomas-Fermi-von Weizsäcker and Thomas-Fermi-von Weizsäcker-Dirac models ([L1], [CBL1]) in a crystal. We use the method of deformations (local scaling transformations) [PSK], [BG1], [BG3] of wave functions of constant electron density. To this end we consider a cubic crystal with N electrons and P nuclei in the elementary cell $\Omega = [-\frac{L}{2}, \frac{L}{2}]^3$.
We regard the periodic Hamiltonian:

$$H_{per} := -\sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} V_{ext}(x_i) + \sum_{i<j} G(x_i - x_j) \tag{1}$$

where the $x_i \in \Omega$ denote the fermion positions, $V_{ext}(x) = -\sum_{l=1}^{P} Z_l G(x - R_l)$, Z_l and R_l are respectively the charges and the positions of the P nuclei. Notice that the $1/x$ function of the Coulomb interaction has been replaced by the "periodized version" $G(x)$ of e.g. [LS1], which is the periodic solution of the equation $\Delta G = -4\pi \left(\sum_{k\in L\mathbb{Z}^3} \delta(\cdot - k) - 1/L^3\right)$, satisfying $\int_\Omega G = 0$.
The choice of the periodic Hamiltonian (1) allows for a setting where the rigorous derivation can be done without heavy mathematical machinery. It is motivated by the results of [CBL1] ,

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[CBL2] where a periodic energy functional corresponding to our use of G in (1) is derived as a thermodynamic limit.

As the Hamiltonian is periodic, the N-particle wave-functions are Bloch functions, i.e. a shift for a lattice vector γ results in a mere phase factor : $\Psi(x+\gamma) = e^{i\Theta\cdot\gamma}\Psi(x)$ for all $x \in \mathbb{R}^{3N}$ and $\gamma \in (L\mathbb{Z}^3)^N$ and for some $\Theta = (\theta_1, \dots, \theta_N)$ fixed in $([0, 2\pi/L[^3)^N$. On the other hand, the N-particle wave-functions have to be antisymmetric by the Pauli principle[1] which implies $\theta_1 = \dots = \theta_N$. These conditions lead us to consider the following space of wave functions

$$\Lambda := \bigoplus_{\theta\in[0,2\pi/L[^3} \Lambda_\theta$$

where

$$\Lambda_\theta := \left\{\Psi(x_1, ..., x_N) = e^{i\theta\cdot(x_1+\dots+x_N)}\Phi(x_1, ..., x_N),\ \Phi \in H^1_a((\mathbb{R}^3/L\mathbb{Z}^3)^N)\right\} .$$

(The index ”a” means that the functions Φ are antisymmetric.)
Note that for periodic Hamiltonians, the Bloch decomposition of L^2 allows to reduce the spectral problem from the whole space to a basic cell Ω (see e.g. [GMMP], where the generalization beyond the usual scalar case of the one particle Schrödinger equation (e.g. [MMP]) is given.)
For technical reasons (cf. Lemma 3.2) we will also consider the space of continuous wave functions in Λ, i.e.

$$\Lambda^c := \Lambda \ \cap\ C^0(\mathbb{R}^{3N}) .$$

The fundamental energy per cell of this N fermion system is then given by

$$\begin{aligned} E_0 &:= \inf\{\langle H_{per}\Psi,\ \Psi\rangle \mid \ \Psi \in \Lambda,\ ||\Psi||_{L^2} = 1\} \\ &= \inf\{\langle H_{per}\Psi,\ \Psi\rangle \mid \ \Psi \in \Lambda^c,\ ||\Psi||_{L^2} = 1\} , \end{aligned} \tag{2}$$

where $\langle, \rangle$ denotes the Hermitian scalar product in $L^2(\Omega^N)$.

The aim of the density functional theory is to replace the minimization problem (2) by a minimization problem with respect to the density (per cell) ρ associated to the wave function Ψ :

$$\rho_\Psi(x) := N \int_{\Omega^{N-1}} |\Psi(x, x_2, \dots, x_N)|^2 dx_2 \dots dx_N. \tag{3}$$

This procedure reduced the number of variables from $3N$ to 3.
Using (1), we can decompose the energy per cell of a wave function Ψ as follows:

$$E(\Psi) := \langle H_{per}\Psi,\ \Psi\rangle = E_{kin}(\Psi) + \int_\Omega V_{ext}(x)\rho_\Psi(x)dx + E_{ee}(\Psi). \tag{4}$$

In formula (4) E_{kin} denotes the kinetic energy,

$$E_{kin}(\Psi) := \int_{\Omega^N} |\nabla\Psi(x)|^2 dx, \tag{5}$$

[1] In order to simplify the presentation we do not explicitly consider the spin.

while E_{ee} denotes the inter-electron energy,

$$E_{ee}(\Psi) := \int_{\Omega^2} \rho_{2,\Psi}(x,x')G(x-x')dxdx', \tag{6}$$

where

$$\rho_{2,\Psi}(x,x') := \frac{N(N-1)}{2} \int_{\Omega^{N-2}} \left|\Psi(x,x',x_3,\ldots,x_N)\right|^2 \; dx_3 \cdots dx_N \; . \tag{7}$$

Following ([L2], Theorem 1.2), it can be shown that the map $\Psi \mapsto \rho_\Psi$ maps Λ^c onto

$$D := \{\rho \in C^0(\mathbb{R}^3/L\mathbb{Z}^3),\; \rho \geq 0,\; \int_\Omega \rho = N,\; \sqrt{\rho} \in H^1_{loc}(\mathbb{R}^3)\}. \tag{8}$$

Therefore we can define the density functionals corresponding to the kinetic and the global energy term by

$$\begin{aligned} \mathcal{E}_{kin}(\rho) &:= \inf\{E_{kin}(\Psi) | \Psi \in \Lambda^c \text{ and } \rho_\Psi = \rho\} \\ \mathcal{E}(\rho) &:= \inf\{E(\Psi) | \Psi \in \Lambda^c \text{ and } \rho_\Psi = \rho\}, \end{aligned} \tag{9}$$

and we have

$$E_0 = \inf\{\mathcal{E}(\rho) \mid \rho \in D\}.$$

We shall use Schauder estimates in Hölder spaces, this leads us to consider the space of densities $D_\alpha \subset D$, with $0 < \alpha < 1$

$$D_\alpha := \{\rho \in C^{0,\alpha}(\mathbb{R}^3/L\mathbb{Z}^3),\; \rho > 0,\; \int_\Omega \rho = N,\; \sqrt{\rho} \in H^1_{loc}(\mathbb{R}^3)\}$$

where $C^{0,\alpha}(\mathbb{R}^3/L\mathbb{Z}^3)$ denotes the space of Hölderian functions of degree α on the torus $\mathbb{R}^3/L\mathbb{Z}^3$ or equivalently the space of periodic function in the Hölder space $C^{0,\alpha}(\mathbb{R}^3)$.
We introduce the semi norm $|\cdot|_{0,\alpha}$ defined by

$$|\epsilon|_{0,\alpha} := \sup_{x \neq y \in \mathbb{R}^3} \frac{|\epsilon(y) - \epsilon(x)|}{|y-x|^\alpha} \; . \tag{10}$$

Our results are based on the crucial assumption that ρ is close to the averaged constant electron density ρ_0 given by

$$\rho_0 := \frac{N}{|\Omega|} = \frac{N}{L^3} \; .$$

Precisely, we shall assume that $L^\alpha |\epsilon_\rho|_{0,\alpha}$ is small, where

$$\epsilon_\rho(x) := \frac{\rho(x) - \rho_0}{\rho_0} \; .$$

Extending [BM], [BGM1] we demonstrate how the heuristic idea of the “free electron approximation” can be used in a mathematically rigorous way by using the method of deformations (local scaling transformations) of plane waves [PSK], [KL], [BG2], [BG3].
In this article we essentially prove that (see section 2 for precise statements):

- *The exact kinetic energy, as a functional of the density ρ, is equal to the Thomas-Fermi-von Weizsäcker functional up to small remainder terms depending on $L^\alpha\epsilon_\rho$ and N.*

- *The global energy, as a functional of the density ρ, is majorized by the Thomas-Fermi-von Weizsäcker-Dirac functional up to small remainder terms depending on $L^\alpha\epsilon_\rho$ and N.*

The "high density limit" ([LS1], [GS], [BM]) is obtained by letting $N \to \infty$ for a given size of the periodicity cell (i.e $L = cst.$). In this limit and for our choice of the periodic model (with an equi-distribution of the external potential), the assumption $\epsilon_\rho \to 0$, is physically reasonable. Nevertheless this assumption is not yet mathematically proved in a general context (see [LS1] for a proof in the Thomas-Fermi context).
The "thermodynamic limit" is obtained by letting $N \to \infty$ and $L \to \infty$ in such way that ρ_0 is constant (see e.g. [LS1], [L1], [F] for a discussion on different types of limits). In this case, there is no physical reason for the ground state density to be close to the constant density ρ_0. Thus the assumption $L^\alpha\epsilon_\rho \to 0$ (i.e. $N^{\alpha/3}\epsilon_\rho \to 0$) does not seem so relevant in the thermodynamic limit.
That is why our results should be rather considered in the "high density limit" context than in the case where $L \to \infty$.

Remark on the choice of the density space: All our results are stated for density ρ in the Hölder space $C^{0,\alpha}(\mathbb{R}^3/L\mathbb{Z}^3)$ and thus depend on the choice of $\alpha \in (0,1)$ (α cannot be 0). However the choice of the Hölder space is only determined by Lemma 3.1 (where we use Schauder estimates). This deformation Lemma can be established in Sobolev spaces (essentially using reference [Y] instead of [DM]). Then all the results stated in section 2 can be established for density ρ in the Sobolev space $H^2(\mathbb{R}^3/L\mathbb{Z}^3)$ (i.e. two derivatives in $L^2(\mathbb{R}^3/L\mathbb{Z}^3)$). In this case the basic assumption would be "$\|\epsilon_\rho\|_{H^2}$ small" instead of "$L^\alpha|\epsilon_\rho|_{0,\alpha}$ small". This point of view seems, *a priori*, to be better when we consider the thermodynamic limit (since $L \to \infty$). Nevertheless, the $\|.\|_{H^2}$-norm is an integrated norm and thus when L grows the domain of integration also grows and the condition "$\|\epsilon_\rho\|_{H^2}$ small" becomes more restrictive.

The article is organized as follows:
In section 2 we precisely state our results.
In section 3 we describe the deformation method (as introduced in [PSK], [BG1] and [BG3]). We prove a deformation Lemma, based on a fundamental result of B. Dacorogna and J. Moser [DM], which is used, in section 4, to estimate the kinetic energy functional with respect to its values at $\rho = \rho_0$.
In section 4 we use precise estimates on the number of lattice points in a ball (given by number theory) to obtain a refined estimate of $\mathcal{E}_{kin}(\rho_0)$, the kinetic energy functional at $\rho = \rho_0$. Then we deduce Theorem 1 and Theorem 2.
In section 5 we justify the so called X_α method which allows us to approximate the exchange energy at the Hartree Fock level and then to obtain an upper bound for the global energy functional.

Part of the results have been announced in [BGM1], [BGM2] and [BGM3].

2 Results

Our first result states that the exact kinetic energy, as a functional of the density, is equal to the Thomas-Fermi-von Weizsäcker functional [L1] up to small remainder terms depending on ϵ_ρ and N.

Theorem 1 *Let $0 < \alpha < 1$. For densities $\rho \in D_\alpha$, the functional $\mathcal{E}_{kin}(\rho)$ defined in (9) has the following behaviour in a neighborhood of $\rho = \rho_0$ and $N = +\infty$:*

$$\mathcal{E}_{kin}(\rho) = \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3} dx \{1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha}) + O(\frac{1}{N^{1/2}})\} \tag{11}$$

where $C_F := \frac{3}{5}(6\pi^2)^{2/3}$ is the Fermi constant (in our context)[2].
Furthermore there exists $\eta(\alpha) > 0$ such that the error terms are uniform with respect to (N, L, ρ) satisfying $L^\alpha |\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$.

Note that this Theorem remains true if we make another choice of a periodic Hamiltonian (and thus of the periodic model). Actually Theorem 1 depends only on the choice of the space Λ of wave functions. However, this result becomes physically relevant only if, for the chosen model, we are able to prove that the density of the ground state is close to the constant density.

Remark 2.1 *In the "high density limit", estimate (11) becomes*

$$\mathcal{E}_{kin}(\rho) = \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3} dx \{1 + O(|\epsilon_\rho|_{0,\alpha}) + O(\frac{1}{N^{1/2}})\}$$

while in the thermodynamic limit, estimate (11) becomes

$$\mathcal{E}_{kin}(\rho) = \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3} dx \{1 + O(N^{\alpha/3} |\epsilon_\rho|_{0,\alpha}) + O(\frac{1}{N^{1/2}})\}.$$

Remark 2.2 *The $O(1/N^{1/2})$ term in (11) can be slightly improved to $O((logN)^6/N^{5/9})$ (see Remark 4.2). The same remark holds for the estimates in Theorem 2 and Theorem 4.*

The estimate (11) is also valid locally: denoting

$$\mathcal{E}_{kin}^{loc}(\Psi)(x) \quad := \quad N \int_{\Omega^{N-1}} |\nabla_x \Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N \tag{12}$$

we have, for any wave function $\Psi \in \Lambda^c$ minimizing $\mathcal{E}_{kin}(\rho)$,

$$\mathcal{E}_{kin}(\rho) = \int_\Omega \mathcal{E}_{kin}^{loc}(\Psi)(x)\, dx$$

and

$$\mathcal{E}_{kin}^{loc}(\Psi)(x) \quad = \quad |\nabla\sqrt{\rho}(x)|^2 + C_F \rho^{5/3}(x) \{1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha}) + O(\frac{1}{N^{1/2}})\}\,. \tag{13}$$

[2]In general, $C_F := \frac{3}{5}(\frac{6\pi^2}{s})^{2/3}$, where s is the spin number. In our context, $s = 1$.

Furthermore, if we consider only wave functions which are Slater determinants, i.e. $\Psi(x_1, ..., x_N) = \frac{1}{\sqrt{N!}}\det(\phi_j(x_i))$, with $\int_\Omega \phi_i\bar{\phi}_j = \delta_{ij}$, we obtain with the same assumption as in Theorem 1 an upper bound of order 2 in ϵ_ρ:

Theorem 2 *Let $0 < \alpha < 1$. For densities $\rho \in D_\alpha$, we have:*

$$\mathcal{E}_{kin}(\rho) \leq \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3} dx \big\{1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}})\big\} \tag{14}$$

where $C_F := \frac{3}{5}(6\pi^2)^{2/3}$ is the Fermi constant (in our context).
Furthermore there exists $\eta(\alpha) > 0$ such that the error terms are uniform with respect to (N, L, ρ) satisfying $L^\alpha|\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$.

Again, the upper bound (14) is valid locally, cf. Remark 4.3 for a precise statement.

On the other hand, the estimate (11) allows us to prove, in our specific context, a well known conjecture of March and Young (cf. [MY] and also [L1]). Namely we have the following Corollary:

Corollary 1 *Let $0 < \alpha < 1$. There exists $C(\alpha) > 0$ and $\eta(\alpha) > 0$ such that for any $\rho \in D_\alpha$ and for any $N > 0$, $L \geq 1$ satisfying $L^\alpha|\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$ we have*

$$\mathcal{E}_{kin}(\rho) \leq \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C(\alpha)\int_\Omega \rho^{5/3} dx.$$

Remark 2.3 *An application of these techniques in the case of a system of N fermions in $\mathbb{R}^3$ faces the problem to find an equivalent of ρ_0 in the non periodic case. Note that in [BG1] we have proved the estimate*

$$\mathcal{E}_{kin}(\rho) \leq CN^{2/3}\int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 dx$$

by deforming $\mathbb{R}^3$ onto the unit cube.

Remark 2.4 *We recently learned about a similar approach in [DR], based, however, on more formal estimations.*

Our second result concerns the local exchange potential occurring in the $X\alpha$ method as an approximation of the exchange potential V_{ex} for the Hartree-Fock model. We define the Hartree Fock energy as follows:

$$E^{HF} := \inf\{\langle H_{per}\Psi,\ \Psi\rangle \mid\ \Psi \in \Lambda^c,\ \Psi = [\psi_j],\ \langle\psi_i, \psi_j\rangle = \delta_{ij}\} \tag{15}$$

where for a given family of N functions (orbitals) $\psi_1, \ldots, \psi_N$ in $L^2(\Omega)$, $[\psi_j]$ denotes the following N-particle wave function called Slater determinant

$$[\psi_j](x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} det(\psi_j(x_i))_{1\leq i,j\leq N}. \tag{16}$$

Since the constraints $\langle\psi_i,\psi_j\rangle = \delta_{ij}$, $1 \leq i,j \leq N$ implies that $||\Psi||_{L^2} = 1$, we have $E_0 \leq E^{HF}$. In this Hartree-Fock context of such Slater determinants the electron density writes $\rho_\Psi(x) := \sum_{j=1}^N |\psi_j(x)|^2$. The inter-electron energy (6) can be decomposed into two terms (see [PY]):

$$E_{ee}(\Psi) = J(\rho_\Psi) + E_{ex}([\psi_j]) \tag{17}$$

with

$$J(\rho) := \frac{1}{2}\int_{\Omega^2} \rho(x)\rho(x')G(x-x')dxdx', \tag{18}$$

$$E_{ex}([\psi_j]) := -\frac{1}{2}\int_{\Omega\times\Omega} |D(x,y,[\psi_j])|^2 G(x-y)\,dx\,dy\ , \tag{19}$$

and where

$$D(x,y,[\psi_j]) := \sum_{j=1}^N \psi_j(x)\overline{\psi_j}(y) \tag{20}$$

denotes the density matrix. Note that we stress explicitly the dependence on the orbitals entering via a Slater determinant by the notation $D(x,y,[\psi_j])$.
In (17), J corresponds to the usual electrostatic self-repulsion energy, and only depends on the density ρ. The second term, the so-called exchange energy E_{ex}, takes into account the Pauli principle (a purely quantum effect) but *a priori* does not depend only on the density.

The existence of a minimum for (15), which is a difficult problem when posed on $\mathbb{R}^3$ [LS2], [PLL], can be more easily proved here since Ω is compact. This minimization gives (after a unitary transformation on the orbitals) an equation of Hartree-Fock's type

$$-\Delta\psi_i + V_{ext}(x)\psi_i + (\int_\Omega G(x-y)\rho(y)dy)\,\psi_i + (V_{ex}\psi_i)(x) = \epsilon_i\psi_i \tag{21}$$

where (ϵ_i) are the eigenvalues and where V_{ex} is a non-local operator, defined by:

$$(V_{ex}\psi_j)(x) := -\int_\Omega D(x,y,[\psi_j])G(x-y)\psi_j(y)\,dy. \tag{22}$$

There is no exact local expression for the complicated *exchange potential* V_{ex}. However, V_{ex} can be astonishingly well approximated by $-C_S\rho^{1/3}(x)$ (for some constant C_S) as proposed by Slater [Sl] and widely used under the name "$X\alpha$ method". We refer to [PY] for a review of such approximations. A first mathematical approach to this Slater approximation based on deformations of plane waves has been given in [BM]. Following [Sl] we first approximate the exact exchange potential V_{ex} by the *average exchange potential* V_{av}:

$$V_{av}(x,[\psi_j]) := -\int_\Omega \frac{|D(x,y,[\psi_j])|^2}{\rho(x)}G(x-y)\,dy. \tag{23}$$

This formula comes from the "Slater averaging" of the HF exchange potential $(V_{ex}\psi_i)(x)$ by the weighted densities of the i-th wave function : $\sum_{j=1}^N (V_{ex}\psi_i)(x)\frac{|\psi_i|^2}{\rho(x)}$. The advantage of V_{av} is that it can be used as a "local" approximation of (21) : $(V_{ex}.\psi_k)(x) \sim V_{av}(x,[\psi_j])\psi_k(x)$. Furthermore, we can recover the exact exchange energy from V_{av}, even if V_{av} is an approximation, since we have from (19), (23) :

$$E_{ex}([\psi_j]) = \frac{1}{2}\int_\Omega \rho(x)V_{av}(x,[\psi_j])\,dx\;. \tag{24}$$

The following asymptotic results is proved in section 5:

Theorem 3 (Averaged exchange potential estimate) *Let $0<\alpha<1$. For each $\rho \in D_\alpha$ sufficiently close to ρ_0, and for a particular choice [3] of orthonormals orbitals $(\psi_j)_{j=1,\dots,N}$ with $\rho = \sum_{j=1}^N |\psi_j|^2$, we have uniformly for $x\in\Omega$,*

$$V_{av}(x,[\psi_j]) = -C_S\;\rho(x)^{1/3}\left\{1+O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta)+O(\frac{1}{N^{1/3}})\right\} \tag{25}$$

where $\beta = \min(2,\frac{1}{1-\alpha})$ and $C_S = \frac{3}{2}(\frac{6}{\pi})^{1/3}$ is the "Slater constant" [Sl] (in our context).[4]

As a consequence of Theorem 3 and of (24), we obtain immediately:

Corollary 2 (Exchange energy estimate) *Under the same assumptions as in Theorem 3:*

$$E_{ex}([\psi_j]) = -\frac{C_S}{2}\int_\Omega \rho^{4/3}(x)\,dx\left\{1+O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta)+O(\frac{1}{N^{1/3}})\right\}$$

Remark 2.5 *Since $1/(1-\alpha) > 1+\alpha$, Theorem 3 and Corollary 2 still hold with $\beta = 1+\alpha$.*

This is a refined version of a result in [BM]. We use the work of Friesecke [F] in order to deal with planes waves whose wave numbers are in the Fermi sphere (instead of the cube used for simplicity in [MY], [BM]).
Note also that Corollary 2 gives a justification of the Dirac approximation $\int_\Omega \rho^{4/3}dx$ (see [D]) of the exchange energy. In an other context, justification of the Dirac term (and also the Thomas-Fermi term) have also been obtained, see V. Bach [B], C. Fefferman and L.A. Seco [FS], G.M. Graf and J.P. Solovej [GS]. In [B] and [FS] the authors consider a model in $\mathbb{R}^3$ and the Thomas-Fermi density ρ_{TF} plays the role of ρ_0.

Finally our method of deformation gives an approximation of the energy $\mathcal{E}(\rho)$. Nevertheless, we have to restrict ourself to wave functions of Slater determinant type which are deformation of plane waves . This is why we only obtain an upper bound for the global energy. Combining the kinetic energy and exchange potential estimations, we obtain in section 5:

[3] This choice is explicit, cf. Section 5.1.
[4] In general, $C_S := \frac{3}{2}(\frac{6}{s\pi})^{1/3}$, where s is the spin number (for $s=1$ or $s=2$); in our context, $s=1$.

Theorem 4 *Let $0 < \alpha < 1$. For densities $\rho \in D_\alpha$, the functional $\mathcal{E}(\rho)$ admits the following upper bound in a neighborhood of $\rho = \rho_0$ and $N = +\infty$:*

$$\begin{aligned}\mathcal{E}(\rho) \;\; &\leq \;\; \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3}(x)dx \Big\{ 1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}}) \Big\} \\ &+ \int_\Omega V_{ext}(x)\rho(x)dx + J(\rho) - \frac{C_S}{2}\int_\Omega \rho^{4/3}(x)dx \Big\{ 1 + O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{N^{1/3}}) \Big\}\end{aligned} \tag{26}$$

where $J(\rho) = \frac{1}{2}\int_{\Omega^2} \rho(x)\rho(y)G(x-y)\; dxdy$ is the Coulomb energy, *$C_F := \frac{3}{5}(6\pi^2)^{2/3}$ is the Fermi constant and $C_S := \frac{3}{2}(\frac{6}{\pi})^{1/3}$ is the "Slater" constant (in our context).*
Furthermore there exists $\eta(\alpha) > 0$ such that the error terms are uniforms with respect to (L, N, ρ) satisfying $L^\alpha|\epsilon_\rho|_{0,\alpha}\epsilon_\rho < \eta(\alpha)$ and $L \geq 1$.

Remark 2.6 *In the "high density limit" (L fixed), estimate (26) becomes (cf. Section 5.2):*

$$\begin{aligned}\mathcal{E}(\rho) \;\; &\leq \;\; \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3}(x)dx \Big\{ 1 + O(|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}}) \Big\} \\ &+ \int_\Omega V_{ext}(x)\rho(x)dx + J(\rho) - \frac{C_S}{2}\int_\Omega \rho^{4/3}(x)dx\end{aligned}$$

while in the thermodynamic limit (ρ_0 fixed), estimate (26) becomes

$$\begin{aligned}\mathcal{E}(\rho) \;\; &\leq \;\; \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3}(x)dx + \int_\Omega V_{ext}(x)\rho(x)dx \\ &+ J(\rho) - \frac{C_S}{2}\int_\Omega \rho^{4/3}(x)dx \Big\{ 1 + O((N^{\alpha/3}|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{N^{1/3}}) \Big\}\end{aligned}$$

Remark 2.7 *The error terms in Theorem 4 can also be bounded as follows:*

$$\int_\Omega \rho^{5/3} \Big\{ O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}}) \Big\} \leq cst.\, \frac{N^{5/3}}{L^2} \left\{ L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha} + \frac{1}{N^{1/2}} \right\}$$

When compared with our result announced in [BGM1], the leading error term in the TFvW approximation of the kinetic energy is improved (we obtain $O(\frac{1}{N^{1/2}})$ instead of $O(\frac{1}{N^{1/3}})$ in [BGM1]). This is technically more complicated but essential for combining it with the Dirac term, $\int \rho^{4/3} \sim cst.\,\frac{N^{4/3}}{L}$ which is now asymptotically larger than the improved error term, $O(\frac{N^{5/3}}{L^2}\frac{1}{N^{1/2}}) = O(\frac{N^{7/6}}{L^2})$ (independently of $L \geq 1$).

3 Deformations

Our crucial assumption is that ρ is close to the averaged constant electron density ρ_0.
Indeed, we shall start from wave functions of constant density ρ_0, and then use a deformation of the space close to identity in order to obtain wave functions of density ρ (close to ρ_0).
This idea has already been used in Density Functional Theory, see [PSK, KL] or [BG3, BG1, BG2], or [DR].

Definition 3.1 *We say that f is a periodic deformation on the cube Ω with sidelenght L if f is a C^1 diffeomorphism on $\mathbb{R}^3$ satisfying $f(x+L\,m) = f(x) + L\,m$ for any $m \in \mathbb{Z}^3$ and $x \in \mathbb{R}^3$. This means that f is a C^1 diffeomorphism of the torus $\mathbb{R}^3/L\mathbb{Z}^3$.*
Further we denote $J_f(x) := \det(Df(x))$ the Jacobian of f.

We use the following Hölder semi norm on $C^{0,\alpha}(\mathbb{R}^3)$

$$|a|_{0,\alpha} := \sup\{\frac{|a(x)-a(y)|}{|x-y|^\alpha} \ | \ x \neq y \in \mathbb{R}^3\}$$

Based on a fundamental result of B. Dacorogna and J. Moser [DM] we prove

Lemma 3.1 *Let $0 < \alpha < 1$ and $L \geq 1$. There exist $\eta(\alpha) > 0$ and $K(\alpha) > 0$ such that, for any $\rho \in D_\alpha$ satisfying $L^\alpha |\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$, there exists a periodic deformation of the cube $[-L/2, L/2]^3$, f, solution of the Jacobian equation $J_f(x) = \frac{\rho(x)}{\rho_0}$.*
Furthermore $f \in C^{1,\alpha}(\mathbb{R}^3)$ and f satisfies

$$|D(f-Id)|_{0,\alpha} \leq K(\alpha)\ |\epsilon_\rho|_{0,\alpha}, \tag{27}$$

$$\|D(f-Id)\|_\infty \leq (\sqrt{3}L)^\alpha K(\alpha)\ |\epsilon_\rho|_{0,\alpha}. \tag{28}$$

Remark 3.1 *At this point we need to assume that ρ is Hölder continuous since we want to use Schauder estimates (see below).*

Remark 3.2 *Following [DM], we can prove the existence (but not estimate (27)) of the periodic deformation in Lemma 3.1 without assuming $|\epsilon_\rho|_{0,\alpha}$ small.*

Before proving Lemma 3.1 we explain how we use it in order to deform a wave function of density ρ_0 into a wave function of density $\rho \in D_\alpha$.
Let ρ be a density in D_α, f be the periodic deformation associated to ρ given by Lemma 3.1 and Ψ be a (N-particle) wave function in Λ^c. Then $(J_f)^{1/2}$ and $\Psi(f(x_1), \ldots, f(x_N))$ are both in $H^1 \cap C^0$ and we define the deformed wave function $T_f(\Psi)$ by

$$T_f\Psi(x_1, \ldots, x_N) := \prod_{j=1}^{N} (J_f(x_j))^{1/2}\Psi(f(x_1), \ldots, f(x_N)), \tag{29}$$

which is again in Λ^c. By a straightforward change of variables one gets

$$\rho_{T_f\Psi}(x) = \frac{\rho(x)}{\rho_0}\rho_\Psi(f(x)).$$

As in [BG1], one easily deduces

Lemma 3.2 *For $\rho \in D_\alpha$, the operator T_f induces an isometry (for the L_2 norm) from $\{\Psi \in \Lambda^c \ | \ \rho_\Psi = \rho_0\}$ onto $\{\Psi \in \Lambda^c \ | \ \rho_\Psi = \rho\}$.*

Proof of Lemma 3.1. We follow closely the lines of the proof of [DM] Lemma 4.
Let $\mathbb{T}_L$ be the torus $\mathbb{T}_L := \mathbb{R}^3/L\mathbb{Z}^3$. We define

$$\mathcal{X} := \{b \in C^{0,\alpha}(\mathbb{T}_L, \mathbb{R}) \mid \int_\Omega b = 0\}$$

and

$$\mathcal{Y} := \{v \in C^{1,\alpha}(\mathbb{T}_L, \mathbb{R}^3) \mid \int_\Omega v = 0\}.$$

Note that a function in $\mathcal{X}$ has to vanish somewhere in Ω and therefore the $|\cdot|_{0,\alpha}$ semi norm is a norm on $\mathcal{X}$. In the same way, if $v \in \mathcal{Y}$ then v and any of its partial derivatives have to vanish somewhere in Ω (use the periodicity). Thus the semi norm $|Dv|_{0,\alpha}$ is a norm on $\mathcal{Y}$ that we will denote $\|v\|_{\mathcal{Y}}$:

$$\|v\|_{\mathcal{Y}} := |Dv|_{0,\alpha} .$$

We note for the sequel that if $u \in C^{0,\alpha}$ with $\int_\Omega u = 0$, then

$$\|u\|_\infty \leq (\sqrt{3}L)^\alpha |u|_{0,\alpha} \tag{30}$$

and in particular if $v \in \mathcal{Y}$

$$\|Dv\|_\infty \leq (\sqrt{3}L)^\alpha \|v\|_{\mathcal{Y}} \tag{31}$$

For $b \in \mathcal{X}$, let $a \in C^{2,\alpha}(\mathbb{T})$ be the unique solution of the Laplace equation

$$\Delta a = b$$

satisfying $\int_\Omega a = 0$. By Schauder estimates (see for instance [LU]), there exists a constant $C = C(\alpha, L)$ such that

$$|D^2 a|_{0,\alpha} \leq C\,(|b|_{0,\alpha} + \|b\|_\infty + \|a\|_\infty) .$$

Considering the Fourier series representation of a and b ($a(x) = \sum_{k\in\frac{2\pi}{L}\mathbb{Z}^3} \hat{a}(k)e^{ikx}$ and $b(x) = \sum_{k\in\frac{2\pi}{L}\mathbb{Z}^3} \hat{b}(k)e^{ikx}$) the relation $\Delta a = b$ with $\int_\Omega a = 0$ writes

$$\hat{a}(k) = \frac{1}{k^2}\hat{b}(k) \ \text{ for } k \neq 0 \text{ and } \hat{a}(0) = 0 .$$

Therefore, with $C' = C'(L) = \left(\sum_{k\in\frac{2\pi}{L}\mathbb{Z}^3} \frac{1}{k^4}\right)^{1/2}$

$$\|a\|_\infty \leq \sum_{k\in\frac{2\pi}{L}\mathbb{Z}^3} \frac{|\hat{b}(k)|}{k^2} \leq C' \left(\sum_{k\in\frac{2\pi}{L}\mathbb{Z}^3} |\hat{b}(k)|^2\right)^{1/2} = C' L^{-3/2}\|b\|_{L^2} \leq C'\|b\|_\infty .$$

Thus using (30) one concludes that there exists a constant $K = K(\alpha, L)$ such that

$$|D^2 a|_{0,\alpha} \leq K\,|b|_{0,\alpha} . \tag{32}$$

Note that K does in fact not depend on L as can be verified by a scaling argument:
Let $\tilde{a}(x) := \left(\frac{1}{L}\right)^2 a\left(\frac{1}{L}x\right)$ and $\tilde{b}(x) := b\left(\frac{1}{L}x\right)$. Then $\Delta\tilde{a} = \tilde{b}$ on $\Omega_1 = [-1/2, 1/2]^3$ and $\int_{\Omega_1} \tilde{a} = 0$. Thus $|D^2\tilde{a}|_{0,\alpha} \leq K(\alpha, 1)\, |\tilde{b}|_{0,\alpha}$ and as $|D^2 a|_{0,\alpha} = \left(\frac{1}{L}\right)^\alpha |D^2\tilde{a}|_{0,\alpha}$ and $|b|_{0,\alpha} = \left(\frac{1}{L}\right)^\alpha |\tilde{b}|_{0,\alpha}$, one obtains (32) with $K(\alpha) = K(\alpha, 1)$.

Note that $v = \nabla a$ is in $\mathcal{Y}$ and satisfies $\operatorname{div} v = b$. We can then define a bounded linear operator $\mathcal{L} : \mathcal{X} \to \mathcal{Y}$ which associates to every element b in $\mathcal{X}$ an element $v = \mathcal{L}(b)$ in $\mathcal{Y}$ satisfying

$$\operatorname{div} v = b$$

and

$$\|\mathcal{L}(b)\|_{\mathcal{Y}} = |Dv|_{0,\alpha} \leq K(\alpha)\, |b|_{0,\alpha} \ . \tag{33}$$

In order to solve $J_f = \rho/\rho_0 = 1 + \epsilon_\rho$, we look for $f(x)$ in the form

$$f(x) = x + v(x) \ .$$

Hence the Jacobian equation on f is equivalent to the problem of finding a vector field $v(x)$ such that

$$\operatorname{div}(v) + Q(Dv) = \epsilon_\rho$$

where for any 3×3 matrix A,

$$Q(A) := \det(Id + A) - 1 - \operatorname{tr}(A). \tag{34}$$

Now we define

$$\mathcal{N}(v) := \epsilon_\rho - Q(Dv) \tag{35}$$

and we remark that a solution of the Jacobian problem, $\operatorname{div}(v) = \mathcal{N}(v)$, is obtained from the following fixed-point equation

$$v = \mathcal{L}\mathcal{N}(v). \tag{36}$$

Note that denoting $v = (v_1, v_2, v_3)$,

$$Q(Dv) = \det(Dv) + \sum_{1 \leq i < j \leq 3} \det \begin{pmatrix} \partial_i v_i & \partial_j v_i \\ \partial_i v_j & \partial_j v_j \end{pmatrix}. \tag{37}$$

By integration by part (assuming v has C^2 regularity) and using the periodicity of v we have

$$\int_\Omega \det \begin{pmatrix} \partial_i v_i & \partial_j v_i \\ \partial_i v_j & \partial_j v_j \end{pmatrix} = -\int_\Omega \det \begin{pmatrix} v_i & \partial_i \partial_j v_i \\ v_j & \partial_i \partial_j v_j \end{pmatrix} = \int_\Omega \det \begin{pmatrix} \partial_j v_i & \partial_i v_i \\ \partial_j v_j & \partial_i v_j \end{pmatrix}.$$

Thus

$$\int_\Omega \det \begin{pmatrix} \partial_i v_i & \partial_j v_i \\ \partial_i v_j & \partial_j v_j \end{pmatrix} = 0$$

and similarly,

$$\int_\Omega \det(Dv) = 0 \, .$$

Hence by density of C^2-functions in $\mathcal{Y}$, we get

$$\int_\Omega Q(Dv) = 0 \, , \text{ for any } v \in \mathcal{Y}.$$

Since $\int_\Omega \epsilon_\rho = 0$, one deduces that $\mathcal{N}$ maps $\mathcal{Y}$ into $\mathcal{X}$ and thus $\mathcal{L}\mathcal{N}$ maps $\mathcal{Y}$ into $\mathcal{Y}$.
Now we want to solve Equation (36) by the contraction principle. Let

$$\mathcal{B} := \left\{ u \in \mathcal{Y} \,\middle|\, |Du|_{0,\alpha} \leq 2K \, |\epsilon_\rho|_{0,\alpha} \right\} ,$$

and let C be a positive constant independent of L and α such that for any w_1 and w_2 in $C^{0,\alpha}$ with $\|w_1\|_\infty, \|w_2\|_\infty \leq 1$,

$$|Q(w_1) - Q(w_2)|_{0,\alpha} \leq C(\|w_1\|_\infty + \|w_2\|_\infty)|w_1 - w_2|_{0,\alpha} \tag{38}$$

(C exists since $Q(w)$ is a sum of terms which are quadratic and cubic with respect to the components of w).

We claim that for

$$L^\alpha |\epsilon_\rho|_{0,\alpha} < \eta_\alpha := \min\{\frac{1}{2(\sqrt{3})^\alpha K(\alpha)}, \frac{1}{4(\sqrt{3})^\alpha C K(\alpha)}, \frac{1}{4(\sqrt{3})^\alpha C K(\alpha)^2}\},$$

$\mathcal{L}\mathcal{N}$ is a contraction mapping on $\mathcal{B}$ with respect to the norm $\|.\|_\mathcal{Y}$.
Indeed, if $v \in \mathcal{B}$ then using (33),

$$\begin{aligned} \|\mathcal{L}\mathcal{N}v\|_\mathcal{Y} &= |D(\mathcal{L}\mathcal{N}v)|_{0,\alpha} \leq K|\mathcal{N}v|_{0,\alpha} \\ &\leq K(|\epsilon_\rho|_{0,\alpha} + |Q(Dv)|_{0,\alpha}). \end{aligned}$$

As $L^\alpha |\epsilon_\rho|_{0,\alpha} < \eta_\alpha$ and in view of (31) one has for $v \in \mathcal{B}$,

$$\|Dv\|_\infty \leq 2(\sqrt{3}L)^\alpha K |\epsilon_\rho|_{0,\alpha} < 1.$$

Thus, using (38) with $w_1 = v$ and $w_2 = 0$,

$$\begin{aligned} \|\mathcal{L}\mathcal{N}v\|_\mathcal{Y} &\leq K(|\epsilon_\rho|_{0,\alpha} + C\|Dv\|_\infty |Dv|_{0,\alpha}) \\ &\leq K(1 + 4(\sqrt{3}L)^\alpha K C |\epsilon_\rho|_{0,\alpha}) |\epsilon_\rho|_{0,\alpha} \\ &\leq 2K|\epsilon_\rho|_{0,\alpha} \end{aligned}$$

where we used in the last inequality that $L^\alpha |\epsilon_\rho|_{0,\alpha} \le \eta_\alpha \le \frac{1}{4(\sqrt{3})^\alpha C K}$.
Analogously, if u and v are in $\mathcal{B}$, we have similarly

$$\begin{aligned}
\|\mathcal{L}\mathcal{N}v - \mathcal{L}\mathcal{N}u\|_{\mathcal{Y}} &\le K|\mathcal{N}v - \mathcal{N}u|_{0,\alpha} \\
&\le K|Q(Dv) - Q(Du)|_{0,\alpha} \\
&\le KC(\|Dv\|_\infty + \|Du\|_\infty)\|v-u\|_{\mathcal{Y}} \\
&\le 2(\sqrt{3}L)^\alpha K^2 C|\epsilon_\rho|_{0,\alpha}\|v-u\|_{\mathcal{Y}} \\
&\le \frac{1}{2}\|v-u\|_{\mathcal{Y}}
\end{aligned}$$

where we used $L^\alpha |\epsilon_\rho|_{0,\alpha} \le \eta_\alpha \le \frac{1}{4(\sqrt{3})^\alpha C K^2}$.

Therefore by the contraction principle, equation (36) has a unique solution v in $\mathcal{Y}$. Hence $f := Id + v$ is a $C^{1,\alpha}$ function which solves the Jacobian equation $J_f(x) = \frac{\rho(x)}{\rho_0}$ and satisfies

$$|D(f - Id)|_{0,\alpha} \le 2K|\epsilon_\rho|_{0,\alpha}.$$

Furthermore as v is periodic, $f(x) = x + v(x)$ satisfies $f(x + L\,m) = f(x) + L\,m$ for any $m \in \mathbb{Z}^3$ and $x \in \mathbb{R}^3$.
That f is a diffeomorphism is a consequence of $\|D(f - I)\|_\infty < 1$.
Finally, in view of (31), we deduce (27) from (28). ■

We will need later the following technical estimate.

Corollary 3.1 *Let ρ and f be as in Lemma 3.1. Then*

$$\operatorname{div}(f - Id) = \epsilon_\rho + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\ .$$

Proof. We use $\operatorname{div}(f - Id) = \epsilon_\rho + Q(Dv)$, the fact that Q has quadratic and cubic terms (see formula (37)), and the estimates (31), (27). ■

Notice that, with our definition, the image of the basic cell Ω by a periodic deformation is not necessarily equal to Ω. However, a periodic deformation is a diffeomorphism of the torus $\mathbb{T}_L$, hence $f(\mathbb{T}_L) = \mathbb{T}_L$ and we have

Lemma 3.3 *Let f be a periodic deformation of the cube Ω and g be an integrable periodic function. Then*

$$\int_{f(\Omega)} g(x)dx = \int_\Omega g(x)dx.$$

4 Kinetic energy estimates

4.1 Rewriting the kinetic energy using deformations

Using the deformation f of Lemma 3.1, we replace the minimization problem (9), for a given density ρ by the same minimization problem for the constant density ρ_0 and we control the error. Let $0 < \alpha < 1$ and $\eta(\alpha)$ as in Lemma 3.1.

Lemma 4.1 *For any $\rho \in D_\alpha$, one has uniformly for $L^\alpha |\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$:*

$$\mathcal{E}_{kin}(\rho) = \int_\Omega |\nabla \sqrt{\rho}|^2 dx \, + \, \mathcal{E}_{kin}(\rho_0)(1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha})). \tag{39}$$

Proof. Let ρ be a density in D_α such that $|\epsilon_\rho|_{0,\alpha} < \eta(\alpha)$. By Lemma 3.1 there exists a periodic deformation, f , satisfying $J_f = \frac{\rho}{\rho_0}$. Using Lemma 3.2 and (5),

$$\mathcal{E}_{kin}(\rho) = \inf \left\{ \int_{\Omega^N} |\nabla (T_f \Psi)(x)|^2 dx, | \;\; \Psi \in \Lambda^c \text{ and } \rho_\Psi(x) = \rho_0 \right\}. \tag{40}$$

It remains to compute the kinetic energy of the deformed wave function given by (29):

$$\begin{aligned}
\int_{\Omega^N} |\nabla (T_f \Psi)(x)|^2 dx &= N \int_{\Omega^N} |\nabla_1 (T_f \Psi)(x)|^2 dx \\
&= N \int_{\Omega^N} \Big| \nabla (J_f(x_1))^{1/2} \prod_{j=2}^N (J_f(x_j))^{1/2} \Psi(f(x_1), \ldots, f(x_N)) \\
&\quad + \prod_{j=1}^N (J_f(x_j))^{1/2} [Df(x_1)]^T \nabla_1 \Psi(f(x_1), \ldots, f(x_N)) \Big|^2 dx
\end{aligned}$$

where ∇_1 denotes the gradient with respect to the first variable. By the change of variable $y_j = f(x_j)$ for $j = 2, \ldots, N$, we get using Lemma 3.3,

$$\int_{\Omega^N} |\nabla (T_f \Psi)(x)|^2 dx = A + B + C \tag{41}$$

where, denoting $y' = (y_2, \ldots, y_N)$,

$$A := N \int_{\Omega^N} \left| \nabla (J_f(x_1))^{1/2} \Psi(f(x_1), y') \right|^2 dx_1 dy', \tag{42}$$

$$B := N \int_{\Omega^N} \left| (J_f(x_1))^{1/2} [Df(x_1)]^T \nabla_1 \Psi(f(x_1), y') \right|^2 dx_1 dy' \tag{43}$$

and

$$C := N \int_{\Omega^N} (J_f(x_1))^{1/2} \nabla (J_f(x_1))^{1/2} \cdot \nabla_1 |\Psi(f(x_1), y')|^2 dx_1 dy'. \tag{44}$$

By the change of variable $y_1 = f(x_1)$ in (43) we obtain denoting $y = (y_1, \ldots, y_N)$

$$B = N \int_{\Omega^N} \left| [Df(f^{-1}(y_1))]^T \nabla_1 \Psi(y_1, y') \right|^2 dy. \tag{45}$$

Integrating with respect to y' and using $\rho_\Psi = \rho_0$, (42) leads to

$$A = \int_\Omega \left| \nabla (J_f(x_1))^{1/2} \right|^2 \rho_0(f(x_1)) dx_1 = \int_\Omega |\nabla \sqrt{\rho(x_1)}|^2 dx_1 \tag{46}$$

while (44) leads to

$$C = \int_{\Omega} (J_f(x_1))^{1/2} \nabla (J_f(x_1))^{1/2} \cdot \nabla \rho_0(f(x_1)) dx_1 = 0 \tag{47}$$

since ρ_0 is a constant function. Thus combining (41), (45), (46) and (47) we conclude

$$\int_{\Omega^N} |\nabla (T_f \Psi)(x)|^2 dx = \int_{\Omega} |\nabla \sqrt{\rho}|^2 dx \, + \, S(f, \Psi), \tag{48}$$

where

$$S(f, \Psi) := N \int_{\Omega^N} \left| [Df(f^{-1}(x_1))]^T \nabla_1 \Psi(x) \right|^2 dx. \tag{49}$$

Finally using estimate (28) of Lemma 3.1 we deduce

$$\begin{aligned} S(f, \Psi) &= N \textstyle\int_{\Omega^N} |\nabla_1 \Psi(x)|^2 dx \, (1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha})) \\ &= \textstyle\int_{\Omega^N} |\nabla \Psi(x)|^2 dx \, (1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha})). \end{aligned} \tag{50}$$

Combining (40), (48) and (50), Lemma 4.1 is proved. ■

Remark 4.1 *In the same way it can be proved that for any Ψ minimizing $\mathcal{E}_{kin}(\rho)$*

$$\mathcal{E}_{kin}^{loc}(\Psi)(x) = |\nabla \sqrt{\rho}(x)|^2 + \frac{1}{L^3} E_{kin}(\Psi) \, (1 + O(L^\alpha |\epsilon_\rho|_{0,\alpha})) \, .$$

This estimate leads to the local estimate (13).

When restricting our analysis to wave functions that are deformations of plane waves we can improve the error term in Lemma 4.1 This will be used to prove Theorem 2.
Let $K := \{k_1, \ldots, k_N\}$ be a subset of $\mathbb{Z}^3$, and let $\psi_j(x)$ be the "free electron plane waves" defined by

$$\psi_j(x) := \frac{1}{\sqrt{L^3}} \exp(\frac{2i\pi}{L} \, k_j \cdot x) \quad , \, j = 1, \ldots, N. \tag{51}$$

For this set of orbitals the following Slater determinant (cf (16))

$$\Psi_K := [\psi_j] \tag{52}$$

is a plane wave of density ρ_0. The corresponding deformed orbitals are

$$\psi_j^f(x) := (J_f(x))^{1/2} \psi_j(f(x)). \tag{53}$$

The corresponding deformed N-wave-function is given by

$$\Psi_K^f := T_f \Psi_K = [\psi_j^f] \tag{54}$$

and has density ρ in the case where f is solution of the Jacobian equation $J_f = \rho/\rho_0$.

Definition 4.1 *We say that a set $K \subset \mathbb{Z}^3$ is symmetric if there exists $r \in \mathbb{R}$ such that K is equal to the intersection of $\mathbb{Z}^3$ with the ball in $\mathbb{R}^3$ of center 0 and radius r.*

For symmetric K we have:

- For any $k = (k^1, k^2, k^3) \in K$ and for any $\epsilon_1 = \pm 1$, $\epsilon_2 = \pm 1$ and $\epsilon_3 = \pm 1$ we have that $(\epsilon_1 k^1, \epsilon_2 k^2, \epsilon_3 k^3)$ is again in K.
- For any $k = (k^1, k^2, k^3) \in K$ and for any permutation σ we have that $(k^{\sigma(1)}, k^{\sigma(2)}, k^{\sigma(3)})$ is again in K.

The following Lemma gives a second order (in ϵ_ρ) approximation of $E_{kin}(\Psi_K^f)$ in term of $E_{kin}(\Psi_K)$ and $\int_\Omega |\nabla\sqrt{\rho}|^2 dx$ when K is symmetric:

Lemma 4.2 *Let K be a symmetric subset of $\mathbb{Z}^3$ whose cardinality is N. Let $0 < \alpha < 1$ and for any $\rho \in D_\alpha$ let f be the deformation defined in Lemma 3.1. Then we have for the kinetic energy of the deformed plane waves :*

$$E_{kin}(\Psi_K^f) = \int_\Omega |\nabla\sqrt{\rho}|^2 dx \, + \, E_{kin}(\Psi_K)(1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})).$$

Proof. As $(\psi_j^f)_{j=1,\ldots,N}$ is a set of orthonormal functions in $L^2(\Omega)$, we have

$$E_{kin}(\Psi_K^f) = \int_{\Omega^N} |\nabla\Psi_K^f|^2 = \sum_{j=1}^N \int_\Omega |\nabla\psi_j^f|^2.$$

Using (48) for $N = 1$ we obtain for each $j = 1, \ldots, N$:

$$\int_\Omega |\nabla\psi_j^f|^2 = \frac{1}{N}\int_\Omega |\nabla\sqrt{\rho}|^2 + \int_\Omega \left|[Df(f^{-1}(x))]^T \nabla\psi_j(x)\right|^2 dx.$$

Therefore we obtain

$$\int_{\Omega^N} |\nabla(T\Psi_K^f)(x)|^2 dx = \int_\Omega |\nabla\sqrt{\rho}|^2 dx \, + \, S(f, \Psi_K) \tag{55}$$

and

$$\begin{aligned} S(f, \Psi_K) &= \frac{1}{L^3}\sum_{j=1}^N \int_\Omega |Df(f^{-1}(x))^T \, \frac{2\pi}{L} k_j|^2 dx \\ &= \frac{1}{L^3}\int_\Omega J_f(x) \sum_{k\in K} |Df(x)^T \, \frac{2\pi}{L} k|^2 dx. \end{aligned} \tag{56}$$

Let $M(x) := Df(x)\ Df(x)^T = (M_{\alpha,\beta})_{\alpha,\beta=1,2,3}$ and $k = (k^1, k^2, k^3)$. Using the symmetries of K we obtain

$$\begin{aligned}\sum_{k\in K} |Df(x)^T \cdot k|^2 &= \sum_{\alpha,\beta=1}^{3} M_{\alpha,\beta}\big(\sum_{k\in K} k^\alpha k^\beta\big) \\ &= \sum_{\alpha,\beta=1}^{3} M_{\alpha,\beta}\delta_{\alpha,\beta}\big(\sum_{k\in K}(k^\alpha)^2\big) \\ &= \frac{1}{3}\sum_{\alpha=1}^{3} M_{\alpha,\alpha}\big(\sum_{k\in K}|k|^2\big)\ . \end{aligned} \tag{57}$$

Therefore, using (56), (57), and

$$E_{kin}(\Psi_K) = \sum_{k\in K} |\frac{2\pi}{L}k|^2,$$

we obtain

$$S(f, \Psi_K) = \frac{1}{3\,|\Omega|} E_{kin}(\Psi_K) \int_\Omega J_f(x)\ Tr(Df(x)\ Df(x)^T)\ dx\ . \tag{58}$$

Denoting $f = Id + v$ we get

$$\int_\Omega J_f(x)\ Tr(Df(x)\ Df(x)^T)\ dx = \int_\Omega (1+\epsilon_\rho(x))(3 + 2\text{div}(v)(x) + Tr(Dv(x)\ Dv(x)^T))\ dx\ .$$

By Corollary 3.1, we have $\text{div}(v) = \epsilon_\rho + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})$. Furthermore by Lemma 3.1, we have $\|Dv\|_\infty = O(L^\alpha|\epsilon_\rho|_{0,\alpha})$ and thus $\|Tr(Dv\ Dv^T)\|_\infty = O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})$. Hence we get

$$\begin{aligned}\int_\Omega J_f(x)\ Tr(Df(x)\ Df(x)^T)\ dx &= \int_\Omega (1+\epsilon_\rho(x))(3 + 2\epsilon_\rho(x) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\ dx \\ &= \int_\Omega 3\left(1 + \frac{5}{3}\,\epsilon_\rho(x) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\right) dx \\ &= 3L^3(1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}))\end{aligned} \tag{59}$$

where we used in the last equality, $\int_\Omega \epsilon_\rho(x)dx = 0$.
Thus Lemma 4.2 follows by combining (55), (58) and (59). ■

4.2 Proof of Theorem 1

In view of Lemma 4.1, to obtain Theorem 1 it suffices to prove the following statement:

Proposition 4.3

$$\mathcal{E}_{kin}(\rho_0) = C_F(1 + O(\frac{1}{N^{1/2}})) \int_\Omega {\rho_0}^{5/3} dx\ .$$

Notice that $e_0 := \inf\{E_{kin}(\Psi), \Psi \in \Lambda, \|\Psi\|_{L^2} = 1\}$ is reached by plane waves and that the density of a plane wave (c.f (52)) of L^2-norm 1 is equal to ρ_0. Hence $e_0 = \mathcal{E}_{kin}(\rho_0)$ and the minimum $\mathcal{E}_{kin}(\rho_0)$ is also reached by plane waves.
Therefore, we have

$$\mathcal{E}_{kin}(\rho_0) = \big(\frac{2\pi}{L}\big)^2\, T(N), \tag{60}$$

where

$$T(N) := \min\{\sum_{k\in K} |k+\theta|^2 \mid \ \theta \in \mathbb{R}^3 \text{ and } K \subset \mathbb{Z}^3,\ \#K = N\}. \tag{61}$$

Note also that

$$\sum_{k\in K} |k+\theta|^2 = \sum_{k\in K} |k|^2 + 2(\sum_{k\in K} k,\ \theta) + N|\theta|^2.$$

Thus for each K, the optimal choice for θ is given by $\theta_K := -\frac{1}{N}(\sum_{k\in K} k)$ and the corresponding energy is

$$\sum_{k\in K} |k+\theta_K|^2 = \sum_{k\in K} |k|^2 - \frac{1}{N}(\sum_{k\in K} k)^2. \tag{62}$$

By a translation argument on K and θ, we can restrict the minimization (61) over sets K for which $\theta_K \in [-\frac{1}{2}, \frac{1}{2})^3$. Therefore $|\sum_{k\in K} k| \le \frac{\sqrt{3}}{2}N$ and (62) leads to

$$\sum_{k\in K} |k+\theta_K|^2 \ge \sum_{k\in K} |k|^2 - \frac{3}{4}N\ .$$

Hence we have proved

$$T(N) = T_0(N) + O(N) \tag{63}$$

where

$$T_0(N) := \min\{\sum_{k\in K} |k|^2 \mid \ K \subset \mathbb{Z}^3, \#K = N\}\ . \tag{64}$$

Since $\int_\Omega \rho_0^{5/3} = N^{5/3}/L^2$, Proposition 4.3 is then a consequence of (60), (63) and of the following Lemma:

Lemma 4.4 *For any* $N \in \mathbb{N}$*,*

$$T_0(N) = \frac{1}{(2\pi)^2} C_F\ N^{5/3}\big(1 + O\big(\frac{1}{N^{1/2}}\big)\big)\ .$$

where C_F *is the Fermi constant (i.e* $\frac{1}{(2\pi)^2}C_F = \frac{3}{5}\big(\frac{3}{4\pi}\big)^{2/3}$*).*

Note that Lemma 4.4 is an improvement of the more classical estimate (see for instance [FS])

$$T_0(N) = \frac{1}{(2\pi)^2} C_F \; N^{5/3}\big(1 + O\big(\frac{1}{N^{1/3}}\big)\big) \; .$$

This improvement is essential for our purpose as explained in Remark 2.7.

Proof of Lemma 4.4 For $r > 0$ we define $\mathcal{N}(r)$ as the number of discrete points in a ball as follows

$$\mathcal{N}(r) = \# \left[\mathbb{Z}^3 \cap B(0,r)\right]$$

where $B(0,r)$ denotes the Euclidean ball with center 0 and radius r. The function $r \to \mathcal{N}(r)$ is increasing with values in $\mathbb{N}$. Let $(N_j)_{j\in\mathbb{N}}$ be the increasing sequence of values of $\mathcal{N}(r)$ and r_j ($j \in \mathbb{N}$) be the minimal value of r such that $\mathcal{N}(r) = N_j$.
From [Sk], we learn the following two non-trivial estimates (cf. [Hl] and [He] for the first estimate):

$$N_j = \frac{4}{3}\pi r_j^3 + O(r_j^{3/2}) \tag{65}$$

and

$$N_{j+1} - N_j = O(r_j^{3/2}) \; . \tag{66}$$

(Note that $N_{j+1} - N_j$ is equal to the number of points of $\mathbb{Z}^3$ on the sphere $S(0, r_{j+1})$.)
Let $N \in \mathbb{N}$ given. There exists $j \in \mathbb{N}$ such that $N_j \le N < N_{j+1}$ and thus by (65) and (66),

$$N_j = N + O(\sqrt{N}) \; . \tag{67}$$

Using (66) and (64) we have,

$$T_0(N_{j+1}) - T_0(N_j) \le r_{j+1}^2 \, O(r_j^{3/2}) \; .$$

Thus, as $T_0(N_j) \le T_0(N) \le T_0(N_{j+1})$, we conclude

$$T_0(N) = T_0(N_j) + O(r_j^{7/2}) \; . \tag{68}$$

It remains to calculate $T_0(N_j)$. We define

$$K_{N_j} := B(0, r_j) \cap \mathbb{Z}^3 \; . \tag{69}$$

Denote $Q := [-1/2, 1/2]^3$, $Q_k = Q + k$ ($k \in \mathbb{Z}^3$) and $D_j := \cup_{k\in K_{N_j}} Q_k$. By a direct calculation we have,

$$\begin{aligned} T_0(N_j) &= \sum_{k\in K_{N_j}} |k|^2 = \sum_{k\in K_{N_j}} \Big(\int_{Q_k} |u|^2 du - \frac{1}{4}\Big) \\ &= \int_{D_j} |u|^2 du - \frac{1}{4} N_j \; . \end{aligned} \tag{70}$$

On the other hand denoting by B_r the ball in $\mathbb{R}^3$ of center 0 and radius r, we have

$$B_{r_j-\sqrt{3}/2} \subset D_j \subset B_{r_j+\sqrt{3}/2} \, .$$

Therefore

$$\begin{aligned}
\Big| \int_{D_j} |u|^2 du - \int_{B_{r_j}} |u|^2 du \Big| &= \Big| \int_{D_j \backslash B_{r_j-\sqrt{3}/2}} |u|^2 du - \int_{B_{r_j} \backslash B_{r_j-\sqrt{3}/2}} |u|^2 du \Big| \\
&\leq \max_{\pm} \Big| (r_j \pm \sqrt{3}/2)^2 \mathrm{Vol}(D_j \backslash B_{r_j-\sqrt{3}/2}) - (r_j \mp \sqrt{3}/2)^2 \mathrm{Vol}(B_{r_j} \backslash B_{r_j-\sqrt{3}/2}) \Big| \\
&\leq r_j^2 \Big| \mathrm{Vol}(D_j \backslash B_{r_j-\sqrt{3}/2}) - \mathrm{Vol}(B_{r_j} \backslash B_{r_j-\sqrt{3}/2}) \Big| \\
&\quad + O(r_j) \, \Big(\mathrm{Vol}(D_j \backslash B_{r_j-\sqrt{3}/2}) + \mathrm{Vol}(B_{r_j} \backslash B_{r_j-\sqrt{3}/2}) \Big) \\
&\leq r_j^2 \big| \mathrm{Vol}(D_j) - \mathrm{Vol}(B_{r_j}) \big| + O(r_j^3) \, .
\end{aligned}$$

As $\mathrm{Vol}(D_j) = N_j$, we conclude, using (65), that

$$\big| \int_{D_j} |u|^2 du - \int_{B_{r_j}} |u|^2 du \big| = O(r_j^{7/2}) \, . \tag{71}$$

Furthermore, a simple calculation gives,

$$\int_{B(o,r_j)} |u|^2 du = \frac{4\pi}{5} r_j^5 \, . \tag{72}$$

Combining (70), (71) and (72), we obtain,

$$T_0(N_j) = \frac{4\pi}{5} r_j^5 + O(r_j^{7/2}) \, . \tag{73}$$

Then using successively (68), (73), (65) and (67) we get,

$$\begin{aligned}
T_0(N) &= T_0(N_j) + O(r_j^{7/2}) \\
&= \frac{4\pi}{5} r_j^5 + O(r_j^{7/2}) \\
&= \frac{4\pi}{5} (\frac{3}{4\pi})^{5/3} N_j^{5/3} + O(N_j^{7/6}) \\
&= \frac{3}{5} (\frac{3}{4\pi})^{2/3} N^{5/3} + O(N^{7/6}) \, .
\end{aligned}$$

■

Remark 4.2 *Using [V], the error term $O(r^{3/2})$ in (65) can be improved to $O(r^{4/3}(\log r)^6)$. Also using [Sk], the error term $O(r^{3/2})$ in (66) can be improved to $O(r^{1+\eta})$ (for any given $\eta > 0$). These improvements lead to the following estimate for $T_0(N)$:*

$$T_0(N) = \frac{1}{(2\pi)^2} C_F \, N^{5/3} \big(1 + O\big(\frac{(\log N)^6}{N^{5/9}} \big) \big) \, .$$

4.3 Proof of Theorem 2

To prove Theorem 2 we would like to use Lemma 4.2 and thus we first need to "symmetrize" K. Notice that by definition, for each N_j the set K_{N_j} is symmetric (cf. Definition 4.1). In particular, we can summarize formulas (63), (67) and (68) as follows:

Lemma 4.5 *For any $N \in \mathbb{N}^*$ there exists $n \in \mathbb{N}^*$ and a symmetric subset of $\mathbb{Z}^3$, K_n, of cardinal n, such that*

$$T(N) = (1 + O(\frac{1}{\sqrt{N}})) \sum_{k \in K_n} |k|^2$$

and

$$n \leq N \leq n + O(\sqrt{N}) \,.$$

Proof. It suffices to use $n = N_j$ where N_j is defined by as in the proof of Lemma 4.4 (i.e. such that $N_j \leq N < N_{j+1}$) and $K_n = K_{N_j}$ as defined in (69). ■

This Lemma allows us to prove Theorem 2.

Proof of Theorem 2. Let $\rho \in D_\alpha$ be the density of an N-wave function with $N \in \mathbb{N}$ fixed. Let $K \subset \mathbb{Z}^3$ be a minimizer for $T_0(N)$. Let $K_n \subset \mathbb{Z}^3$ as in Lemma 4.5. In particular $K_n \subset K$ and $Card(K \backslash K_n) = O(\sqrt{N})$. Let f be the periodic deformation constructed in Lemma 3.1. As Ψ_K^f has density ρ, we have

$$\mathcal{E}_{kin}(\rho) \leq E_{kin}(\Psi_K^f).$$

In the case $K = K_n$ (i.e. if K is symmetric), we obtain, using Lemma 4.2, that

$$E_{kin}(\Psi_K^f) \;\;=\;\; \int_\Omega |\nabla \sqrt{\rho}|^2 dx + E_{kin}(\Psi_K)(1 + O(L^{2\alpha} |\epsilon_\rho|^2_{0,\alpha})) \,.$$

Then using Proposition 4.3 we conclude (with $C_F := \frac{3}{5}(6\pi^2)^{2/3}$),

$$\begin{aligned} E_{kin}(\Psi_K^f) &= \int_\Omega |\nabla \sqrt{\rho}|^2 dx + C_F \int_\Omega \rho_0^{5/3} \, (1 + O(\frac{1}{\sqrt{N}}) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})) \\ &= \int_\Omega |\nabla \sqrt{\rho}|^2 dx + C_F \int_\Omega \rho^{5/3} \, (1 + O(\frac{1}{\sqrt{N}}) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})) \end{aligned}$$

where we used that $\int_\Omega \epsilon_\rho = 0$ which implies

$$\int_\Omega \rho^{5/3} = \int_\Omega \rho_0^{5/3} \, (1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})) \,. \tag{74}$$

Hence inequality (14) follows.

In the general case $K \neq K_n$, we cannot use Lemma 4.2 but we still have,

$$\mathcal{E}_{kin}(\rho) \;\;\leq\;\; E_{kin}(\Psi_K^f) = \int_\Omega |\nabla \sqrt{\rho}|^2 dx \, + \, S(f, \Psi_K) \tag{75}$$

where following (56),

$$S(f,\Psi_K) = \int_\Omega J_f(x) \sum_{k\in K} |Df(x)^T \frac{2\pi}{L} k|^2 \, dx \ .$$

We can decompose $S(f,\Psi_K)$ as follows:

$$S(f,\Psi_K) = S_1(f,\Psi_K) + S_2(f,\Psi_K) \tag{76}$$

with

$$S_1(f,\Psi_K) := \frac{1}{|\Omega|} \int_\Omega J_f(x) \sum_{k\in K_n} |Df(x)^T \frac{2\pi}{L} k|^2 \, dx \ .$$

and

$$S_2(f,\Psi_K) := \frac{1}{|\Omega|} \int_\Omega J_f(x) \sum_{k\in K\setminus K_n} |Df(x)^T \frac{2\pi}{L} k|^2 \, dx \ .$$

Notice that $S_1(f,\Psi_K) = S(f,\Psi_{K_n})$. Therefore, as K_n is symmetric, using Lemma 4.2,

$$S_1(f,\Psi_K) = E_{kin}(\Psi_{K_n})(1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})).$$

Using $E_{kin}(\Psi_{K_n}) = (\frac{2\pi}{L})^2 \ \sum_{K_n} |k|^2$ and Lemma 4.5, we have:

$$S_1(f,\Psi_K) = (\frac{2\pi}{L})^2 \ T(N) \left(1 + O(\frac{1}{\sqrt{N}}) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\right) \ .$$

Using (60) and Proposition 4.3, we obtain

$$S_1(f,\Psi_K) \ = \ C_F \int_\Omega \rho^{5/3} \ \left(1 + O(\frac{1}{\sqrt{N}}) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\right) \tag{77}$$

where we have used again (74).
On the other hand, there exists a constant C independent of N such that,

$$|S_2(f,\Psi_K)| \ \le \ C \sum_{k\in K\setminus K_n} |k|^2.$$

Using the fact that $\# K\setminus K_n = O(\sqrt{N})$ and $K_n = \mathbb{Z}^3 \cap B(0,r)$ with $r = O(N^{1/3})$ we get,

$$S_2(f,\Psi_K) = O(N^{7/6}) = O(\frac{1}{N^{1/2}}) \int_\Omega \rho^{5/3} \ . \tag{78}$$

Finally, combining (75), (76), (77) and (78) we obtain

$$E_{kin}(\Psi_K^f) \ = \ \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F \int_\Omega \rho(x)^{5/3} \, dx \ \left(1 + O(\frac{1}{\sqrt{N}}) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})\right) \tag{79}$$

which in particular, gives (14). ■

Remark 4.3 *As in Remark 4.1, using* $\rho^{5/3} = \rho_0^{5/3}\left(1 + \frac{5}{3}\epsilon_\rho + O(|\epsilon_\rho|^2_{0,\alpha})\right)$ *instead of (74), we can prove the following local estimate (where* K *and* f *are defined as above):*

$$\begin{aligned}\mathcal{E}^{loc}_{kin}(\Psi^f_K)(x) &= \sum_{j=1}^{N} |\nabla \psi^f_j(x)|^2 \\ &= |\nabla\sqrt{\rho}(x)|^2 + C_F \rho^{5/3}(x)\big\{1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}})\big\}\,.\end{aligned}$$

5 Justification of the TFvWD model and of the X_α method

In this section we prove Theorem 3 and Theorem 4.

5.1 Proof of Theorem 3

Let $K = K_N$ be a set of N wave vectors $k_j \in \mathbb{Z}^3$ minimizing $T_0(N)$ (see (64)) and $\Psi_K := [\psi_j]$ be the associated Slater determinant (see (52)). Let ρ be in D_α with $L^\alpha|\epsilon_\rho|_{0,\alpha} < \eta_\alpha$ and f be the deformation defined in Lemma 3.1. Let $\Psi^f_K = [\psi^f_j]$ be the Slater determinant associated to the deformed plane waves (cf (51) - (54)).
We now prove that

$$V_{av}(x, [\psi^f_j]) = -C_S\ \rho(x)^{1/3}\left\{1 + O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{N^{1/3}})\right\}. \tag{80}$$

Recall that (cf. (23))

$$V_{av}(x_0, [\psi^f_j]) = -\int_\Omega \frac{|D(x_0, x, [\psi^f_j])|^2}{\rho(x_0)} G(x_0 - x)\, dx$$

where in view of (54) and (20),

$$D(x, y, [\psi^f_j]) = J_f(x)^{1/2}\ J_f(y)^{1/2}\ D_K(f(x) - f(y))$$

with the notation

$$D_K(h) := \frac{1}{|\Omega|}\sum_{k\in K} e^{i\frac{2\pi}{L}\,k\cdot h}\,.$$

Thus by the change of variables $y = f(x)$ one obtains with $y_0 = f(x_0)$:

$$V_{av}(x_0, [\psi^f_j]) = -\rho_0^{-1}\int_\Omega |D_K(y_0 - y)|^2 G(f^{-1}(y_0) - f^{-1}(y))\, dy$$

where we have used that f satisfies the Jacobian equation $J_f(x) = \rho(x)/\rho_0$. Finally denoting $y = y_0 + h$, and using the periodicity of G and D_K, one has

$$V_{av}(x_0, [\psi^f_j]) = -\rho_0^{-1}\int_\Omega |D_K(h)|^2 A_f(x_0; h)\ dh$$

where

$$A_f(x_0;h) := G(f^{-1}(y_0) - f^{-1}(y_0+h)).$$

In order to prove (80), it remains to find an asymptotic for $A_f(h)$ (this is done in Lemma 5.1) and to find an approximation for D_K (this is done in Lemma 5.2).

Let X denote the vector field in $\mathcal{Y}$ such that (cf. proof of Lemma 3.1)

$$f(x) = x + X(x).$$

Lemma 5.1 *Uniformly with respect to $h \in \Omega$ and $x \in \Omega$ we have:*

$$A_f(x;h) = \frac{1}{|h|}\left\{1 + \frac{\langle h,\, DX(x)h\rangle}{|h|^2} + O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{|h|}{L})\right\}.$$

where $\beta = \min(2, \frac{1}{1-\alpha})$.

Proof of Lemma 5.1. From [LS1] we learn that $G(x) - \frac{1}{|x|}$ is Lipschitz on Ω and thus $G(x) = \frac{1}{|x|} + O(\frac{1}{L})$ uniformly on Ω (the $O(\frac{1}{L})$ factor can be obtained by a scaling argument, as in the proof of Lemma 3.1). Therefore we have, with $g := f^{-1}$ and $y = f(x)$

$$A_f(x;h) = |g(y+h) - g(y)|^{-1} + O(\frac{1}{L}). \tag{81}$$

Recall that by Lemma 3.1 and (31)

$$\|DX\|_\infty \leq (\sqrt{3}L)^\alpha |DX|_{0,\alpha} = O(L^\alpha|\epsilon_\rho|_{0,\alpha}). \tag{82}$$

Let Y be a vector field such that $g(y) = y + Y(y)$.
We differentiate $g(f(x)) = x$ and obtain, with $y = f(x)$,

$$DY(y) + DX(x) + DY(y)DX(x) = 0.$$

This leads to the following estimate, for the L^∞-norm,

$$Dg(y) = I - DX(x) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}). \tag{83}$$

We claim that, uniformly in $h, y \in \Omega$,

$$g(y+h) - g(y) = (I - DX(x))\,h + |h|\left\{O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha)\right\}. \tag{84}$$

Indeed, let $y_t = y + th$, and let x_t be such that $y_t = f(x_t)$. We have $|x_t - x| \leq \|Dg\|_\infty |y_t - y| \leq C|h|$, and thus $|DX(x_t) - DX(x)| \leq |DX|_{0,\alpha}|x_t - x|^\alpha \leq O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha)$. In particular, $DX(x_t) = DX(x) + O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha)$. Then, using (83), we have $g(y+h) - g(y) = \int_0^1 Dg(y_t).hdt = (I - DX(x)).h + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}|h|) + O(|\epsilon_\rho|_{0,\alpha}|h|^{1+\alpha})$, which proves (84).
Using (84) and (82) we obtain

$$g(y+h) - g(y) = h - DX(x).h + |h|.\left\{O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha)\right\}.$$

Since $DX(x) = O(L^\alpha |\epsilon_\rho|_{0,\alpha})$, we have (with $|\cdot|$ denoting the Euclidean norm in $\mathbb{R}^3$)

$$|g(y+h) - g(y)|^2 = |h|^2 \left\{ 1 - 2\frac{\langle h,\ DX(x).h\rangle}{\langle h,\ h\rangle} + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha) \right\}.$$

Then from (81) we conclude

$$A_f(x;h) = \frac{1}{|h|}\left\{ 1 + \frac{\langle h,\ DX(x).h\rangle}{\langle h,\ h\rangle} + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha) \right\} + O(\frac{1}{L}).$$

By Young's inequality $|\epsilon_\rho|_{0,\alpha}\,|h|^\alpha = (L^\alpha|\epsilon_\rho|_{0,\alpha})(\frac{|h|}{L})^\alpha \leq (1-\alpha)\ (L^\alpha|\epsilon_\rho|_{0,\alpha})^{1/(1-\alpha)} + \alpha\ \frac{|h|}{L}$ and thus the estimate of Lemma 5.1 is proved. ■

It remains to estimate $D_K(h)$ for which we do not have a simple formula. Recall the following approximation which can be found in Friesecke [F]: there exists a constant $c_0 > 0$ such that, for any $r > 0$ and for any $x \in \mathbb{R}^3$ with $\|x\|_\infty \leq \pi$,

$$\left| \sum_{k\in\mathbb{Z}^3\cap B_r} e^{i\,k.x} - \int_{B_r} e^{i\,k.x}\,dk \right| \leq c_0\,(1 + r^{3/2}). \tag{85}$$

To make use of (85), we define $R_N > 0$ such that the volume of the Euclidean ball of center 0 and radius R_N equals N :

$$N = \frac{4}{3}\pi R_N^3 \tag{86}$$

and we define a continuous analogue of D_K, for $R > 0$,

$$\begin{aligned}\widetilde{D}_R(h) \quad &:= \quad \frac{1}{|\Omega|}\int_{B_R} e^{i\,\frac{2\pi}{L}k\cdot h} d^3k \\ &= \quad 4\pi(\frac{R}{L})^3\ \frac{\sin(t) - t\cos(t)}{t^3}, \qquad t = \frac{2\pi}{L}\ R|h|\ .\end{aligned}$$

Lemma 5.2 *Let $K = K_N$ and R_N as above. When $N \to \infty$, we have*

$$\int_\Omega \frac{|D_{K_N}(h)|^2}{\rho_0}\frac{dh}{|h|} \quad = \quad \int_\Omega \frac{|\widetilde{D}_{R_N}(h)|^2}{\rho_0}\frac{dh}{|h|} + O(\frac{1}{L}) \tag{87}$$

Proof of Lemma 5.2 in the symmetric case.
For the moment, we assume that $K = K_N$ is *symmetric*, (i.e. a *closed-shell* situation (cf e.g. [F]). We define the "Fermi radius" k_F by:

$$k_F = k_F(K) := \max\{|k|,\ k \in K\} \tag{88}$$

Since K is symmetric, we have $K = \mathbb{Z}^3 \cap B_{k_F}$.
Note that, with the notations of section 4, there exists $j \geq 1$ such that $N = N_j$ and $k_F = r_j$. In particular (65) leads to

$$k_F = R_N\ (1 + O(\frac{1}{R_N^{3/2}}))\ . \tag{89}$$

By (85) (with $x = \frac{2\pi}{L}h$) we deduce that uniformly with respect to $h \in \Omega = [-\frac{L}{2}, \frac{L}{2}]^3$ and for N large

$$|D_{K_N}(h) - \widetilde{D}_{k_F}(h)| \leq C\, L^{-3} {k_F}^{3/2} \tag{90}$$

where C is a constant.
Note also that

$$\begin{aligned} |\widetilde{D}_{k_F}(h) - \widetilde{D}_{R_N}(h)| &\leq L^{-3}\mathrm{Vol}\,(B_{R_N} \nabla B_{k_F}) \\ &\leq \frac{4}{3} L^{-3} \max(k_F, R_N)^2 |k_F - R_N| \end{aligned}$$

(where $B_{R_N} \nabla B_{k_F}$ denotes the symmetric difference $B_{R_N} \backslash B_{k_F} \cup B_{k_F} \backslash B_{R_N}$). Using (89), we deduce $|\widetilde{D}_{R_N}(h) - \widetilde{D}_{k_F}(h)| \leq C\, L^{-3} R_N^{3/2}$, and together with (90) we conclude

$$|D_{K_N}(h) - \widetilde{D}_{R_N}(h)| \leq C\, L^{-3} {R_N}^{3/2}\ . \tag{91}$$

Therefore, $|D_{K_N}(h)|^2 = |\widetilde{D}_{R_N}(h)|^2 + O(L^{-3} R_N^{3/2}) |\widetilde{D}_{R_N}(h)| + O(L^{-6} R_N^3)$, and we have

$$\int_\Omega \frac{\Big| |D_{K_N}(h)|^2 - |\widetilde{D}_{R_N}(h)|^2 \Big|}{\rho_0} \frac{dh}{|h|} \ \leq\ O(L^{-3} R_N^{3/2}) I_{N,L} + O(L^{-6} R_N^3) J_{N,L} \tag{92}$$

where $I_{N,L} := \int_\Omega \frac{|\widetilde{D}_{R_N}(h)|}{\rho_0} \frac{dh}{|h|}$ and $J_{N,L} := \int_\Omega \frac{1}{\rho_0} \frac{dh}{|h|}$. We easily obtain $I_{N,L} = O(L^2 R_N^{-2} log(R_N))$ and $J_{N,L} = O(L^5 R_N^{-3})$ (using the analytical expression of $\widetilde{D}_{R_N}$ in (87), and a change of variables $t = \frac{2\pi}{L} R_N\, h$). Thus the right side of inequality (92) is $O(L^{-1})$, as desired. ■

Proof of Lemma 5.2 in the general case.
Recall that K_N is a minimizer for $T_0(N)$ (note that now K_N is not unique in general).
We consider as in the proof of Lemma 4.4 an index $j \in \mathbb{N}$ such that $N_j \leq N < N_{j+1}$ where the integers N_j and N_{j+1} correspond to symmetric sets K_{N_j} and $K_{N_{j+1}}$ (that are minimizers for $T_0(N_j)$ and $T_0(N_{j+1})$ respectively).
As in the symmetric case, we define R_{N_k} by $N_k = \frac{4}{3}\pi R_{N_k}^3$ for $k = j$ and $k = j+1$. By (65) and (66) we deduce $N_{j+1} - N_j = O(\sqrt{N_j})$, $R_{N_j} \overset{N\to\infty}{\sim} R_N$, and

$$N_{j+1} - N_j = O\left(R_N^{3/2}\right). \tag{93}$$

We thus have

$$\begin{aligned} D_{K_N}(h) - D_{K_{N_j}}(h) &= \frac{1}{|\Omega|} \sum_{k \in K_N \backslash K_{N_j}} e^{i\frac{2\pi}{L}k.h} \\ &= L^{-3} O\left(\#(K_N \backslash K_{N_j})\right) \\ &= L^{-3} O(N - N_j) \\ &= O(L^{-3} R_N^{3/2}) \end{aligned}$$

(for the fourth equality we use (93) and $N - N_j \leq N_{j+1} - N_j$). Using the fact that in the symmetric case we have, as in (91), the estimate $D_{K_{N_j}}(h) = \widetilde{D}_{R_{N_j}}(h) + O(L^{-3} R_{N_j}^{3/2})$, we deduce

$$D_{K_N}(h) = \widetilde{D}_{R_{N_j}}(h) + O(L^{-3} R_N^{3/2}).$$

Similarly, we can prove that

$$\widetilde{D}_{R_{N_j}}(h) = \widetilde{D}_{R_N}(h) + O(L^{-3} R_N^{3/2})$$

(using $\mathrm{Vol}(B_{R_N} \backslash B_{R_{N_j}}) = N - N_j = O(R_N^{3/2})$), and we obtain

$$D_{K_N}(h) = \widetilde{D}_{R_N}(h) + O(L^{-3} R_N^{3/2}).$$

Proceeding as in the proof of Lemma 5.2 in the symmetric case, we obtain finally the estimate (87) in all cases. ■

We can now end the proof of Theorem 3.

Proof of Theorem 3.
Using successively Lemma 5.1 and then Lemma 5.2 we obtain the estimate

$$\begin{aligned} V_{av}(x_0, [\psi_j^f]) &= -\int_\Omega \frac{|D_K(h)|^2}{\rho_0} \frac{1}{|h|} \left\{ 1 + \frac{\langle h,\, DX(x_0) h\rangle}{|h|^2} + O((L^\alpha |\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{|h|}{L}) \right\} dh \\ &= -\int_\Omega \frac{|\widetilde{D}_{R_N}(h)|^2}{\rho_0} \frac{1}{|h|} \left\{ 1 + \frac{\langle h,\, DX(x_0) h\rangle}{|h|^2} + O((L^\alpha |\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{|h|}{L}) \right\} dh \\ &\quad + O(\frac{1}{L}) \ . \end{aligned} \tag{94}$$

Let us show that the zero-order term,

$$V_{av,0} := -\int_\Omega \frac{|\widetilde{D}_{R_N}(h)|^2}{\rho_0} \frac{1}{|h|} dh$$

and the first order term,

$$V_{av,1} := -\int_\Omega \frac{|\widetilde{D}_{R_N}(h)|^2}{\rho_0} \frac{1}{|h|} \frac{\langle h,\, DX(x_0) h\rangle}{|h|^2} dh$$

satisfy the following asymptotics:

$$V_{av,0} = -C_S\, \rho_0^{1/3} + O(\frac{1}{R_N^2}), \tag{95}$$

$$V_{av,1} = -C_S\, \rho_0^{1/3} \left(\frac{1}{3} \epsilon_\rho(x_0) + O(L^{2\alpha} |\epsilon_\rho|_{0,\alpha}^2) \right) + o(\frac{1}{R_N^2}) \tag{96}$$

where C_S is the Slater constant (cf (25)).
To prove (95) we replace $\widetilde{D}_{R_N}(h)$ by its analytical expression (87). Using a change of variables $t = \frac{2\pi}{L}R_N h$ and the identity $\rho_0 = N/L^3 = \frac{4\pi}{3}(R_N/L)^3$, we obtain

$$\begin{aligned} V_{av,0} &= -\int_{\frac{2\pi}{L}R_N\Omega} \frac{\left(4\pi(R_N/L)^3\, q(t)\right)^2}{\frac{4\pi}{3}(R_N/L)^3} \frac{1}{(\frac{2\pi}{L}R_N)^2} \frac{d^3t}{|t|} \\ &= -\frac{3}{\pi}\frac{R_N}{L} \int_{\frac{2\pi}{L}R_N\Omega} \frac{q(t)^2}{|t|} d^3t, \end{aligned}$$

where we have denoted $q(t) := \dfrac{\sin(|t|) - |t|\cos(|t|)}{|t|^3}$ and $\frac{2\pi}{L}R_N\Omega = [-\pi R_N, \pi R_N]^3$. A direct calculation gives

$$\int_{\mathbb{R}^3} \frac{q(t)^2}{|t|} d^3t = \pi \tag{97}$$

(see for instance Parr and Yang [PY], Sec. 6.1, p. 108). Furthermore, we have $\int_{\mathbb{R}^3\setminus(\frac{2\pi}{L}R_N\Omega)} \frac{q(t)^2}{|t|} d^3t = O(\frac{1}{R_N^2})$. Hence $V_{av,0} = -3\,\frac{R_N}{L} + O(\frac{1}{R_N^2}) = -C_S\rho_0^{1/3} + O(\frac{1}{R_N^2})$.
To prove (96), we proceed in the same way and obtain $V_{av,1} = \mathcal{I}_{N,L} + O(\frac{L^\alpha|\epsilon_\rho|_{0,\alpha}}{R_N^2}) = \mathcal{I}_{N,L} + o(\frac{1}{R_N^2})$, where

$$\mathcal{I}_{N,L} := -3\frac{R_N}{L}\left[\frac{1}{\pi}\int_{\mathbb{R}^3} \frac{q(t)^2}{|t|}\frac{\langle t, DX(x_0)t\rangle}{\langle t,t\rangle} d^3t\right] .$$

Then, we remark the following identity when we integrate on the unit sphere S^2 (dw denotes the measure on the sphere):

$$\int_{S^2} \frac{\langle t, DX(x_0)t\rangle}{\langle t,t\rangle} dw(t) = \frac{1}{3} div(X)(x_0) \int_{S^2} dw(t). \tag{98}$$

To see this, we develop $\langle t, DX\, t\rangle = \sum_{i,j} t_i t_j \frac{\partial_i X}{\partial x_j}$. We note that for $i \neq j$ the integral $\int_{S^2} \frac{t_i t_j}{|t|^2} dw(t)$ vanishes by symmetry and for $1 \leq i \leq 3$, the integrals $\mathcal{J}_i = \int_{S^2} \frac{t_i^2}{|t|^2} dw(t)$ are equal to the same value $\mathcal{J}$; in particular $\mathcal{J} = \frac{1}{3}(\mathcal{J}_1 + \mathcal{J}_2 + \mathcal{J}_3) = \frac{1}{3}\int_{S^2} dw(t)$. Then, using that q is radial, and formula (98), we obtain

$$\begin{aligned} \mathcal{I}_{N,L} &= -3\frac{R_N}{L}\left[\frac{Tr(DX(x_0))}{3}\frac{1}{\pi}\int_{\mathbb{R}^3} \frac{q(t)^2}{|t|} d^3t\right] \\ &= -3\frac{R_N}{L}\frac{div(X)(x_0)}{3} \\ &= -C_S\rho_0^{1/3}\,\frac{div(X)(x_0)}{3} \end{aligned} \tag{99}$$

where we have used again (97) for the second equality. Recall also that $\mathrm{div}(X)(x_0) = \epsilon_\rho(x_0) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})$ by Corollary 3.1; combined with (99) and the previous bounds, we obtain finally (96).

Now we insert the estimates (95) and (96) in (94), and since $\rho_0^{1/3} = (\frac{4}{3}\pi)^{1/3}\, R_N/L$, we obtain

$$V_{av}(x_0, [\psi_j^f]) \;=\; -C_S\rho_0^{1/3}\left(1 + \frac{1}{3}\epsilon_\rho(x_0) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}), +O(\frac{1}{R_N})\right) + O(\delta_N),$$

where $\delta_N := \delta_{1,N} + (L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta\delta_{2,N}$ and

$$\delta_{1,N} := L^{-1}\int_\Omega \frac{|\widetilde{D}_{R_N}(h)|^2}{\rho_0}\,dh, \qquad \delta_{2,N} := \int_\Omega \frac{|D_R(h)|^2}{\rho_0}\frac{dh}{|h|}.$$

As shown above, we have the bounds $\delta_{1,N} = O(L^{-1}) = O(\rho_0^{1/3}/R_N)$, and $\delta_{2,N} = O(R_N/L) = O(\rho_0^{1/3})$. Hence

$$V_{av}(x_0, [\psi_j^f]) \;=\; -C_S\,\rho_0^{1/3}\left(1 + \frac{1}{3}\epsilon_\rho(x_0) + O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{R_N})\right) \tag{100}$$

Finally, we note that $\rho(x)^{1/3} = (1+\epsilon_\rho(x))^{1/3}\ \rho_0^{1/3} = (1 + \frac{1}{3}\epsilon_\rho(x) + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}))\ \rho_0^{1/3}$ and thus

$$\rho_0^{1/3}(1 + \frac{1}{3}\epsilon_\rho(x)) = \rho(x)^{1/3}(1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha})). \tag{101}$$

Also, the errors terms in (100) satisfy:

$$\rho_0^{1/3}(O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{R_N})) = O\left(\rho(x)^{1/3}((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta + \frac{1}{R_N})\right). \tag{102}$$

Combining (101) and (102) we obtain

$$V_{av}(x_0) = -C_S\,\rho(x_0)^{1/3}\left(1 + O((L^\alpha|\epsilon_\rho|_{0,\alpha})^\beta) + O(\frac{1}{R_N})\right)\ .$$

Since $R_N = (\frac{3}{4\pi})^{1/3}N^{1/3}$ this concludes the proof of Theorem 3. ■

5.2 Proof of Theorem 4

We deduce Theorem 4 from Corollary 2 and Theorem 2 as follows:
We use that $\mathcal{E}(\rho) \le E([\psi_j^f])$ where $\Psi = [\psi_j^f]$ are the deformed plane waves (54). The deformation f is chosen as in Lemma 3.1, and $K = (k_1, \ldots, k_N) := K_N$ is chosen as in Lemma 4.5 (i.e., it is a minimizer of $T_0(N)$). In order to bound the kinetic energy, we recall the bound (79) used in the proof of Theorem 2:

$$E_{kin}([\psi_j^f]) = \int_\Omega |\nabla\sqrt{\rho}|^2 dx + C_F\int_\Omega \rho^{5/3}\left\{1 + O(L^{2\alpha}|\epsilon_\rho|^2_{0,\alpha}) + O(\frac{1}{N^{1/2}})\right\}. \tag{103}$$

Thus in view of (4), (17) and Corollary 2, Theorem 4 is proved. ■

It remains to justify Remark 2.6. The upper bound for the thermodynamic limit is a direct consequence of Theorem 4 (since ρ_0 is constant). For the "high density" limit we have to prove that the error terms in $E_{ex}([\psi_j])$ can be absorbed by the error terms of the kinetic energy bound (103). So, as $\rho = O(L^{-3}N)$ and $\beta = 1/(1-\alpha) > 1$, it is enough to prove that

$$N^{4/3}\left\{|\epsilon_\rho|_{0,\alpha} + \frac{1}{N^{1/3}}\right\} = O(N^{5/3})\ \left\{|\epsilon_\rho|^2_{0,\alpha} + \frac{1}{N^{1/2}}\right\}.$$

This relation holds since, using that $ab \leq a^2 + b^2$, we have

$$\begin{aligned} N^{4/3}|\epsilon_\rho|_{0,\alpha} &= N^{4/3}\ N^{1/6}|\epsilon_\rho|_{0,\alpha}\frac{1}{N^{1/6}} \\ &\leq N^{4/3}\left\{N^{1/3}|\epsilon_\rho|^2_{0,\alpha} + \frac{1}{N^{1/3}}\right\} \\ &\leq N^{5/3}\left\{|\epsilon_\rho|^2_{0,\alpha} + \frac{1}{N^{2/3}}\right\}. \end{aligned}$$

and Remark 2.6 follows.

■

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