A proof of Scott's correction for Matter

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Abstract

In this paper is given a strenghtening of *Stability of Matter*, which in particular shows that Thomas-Fermi theory; which is already known to give the leading order contribution to the energy of Matter, if supplemented with the so-called *Scott correction* is correct uniformly in the number of nuclei. New more precise estimates of the volume of Matter also follows.

Contents:

1 Introduction.

Stability of Matter is one the cornerstones of our present understanding of how Quantum Mechanics (QM in what follows) describes the real world, and since the first rigurous proof of that fact by F.Dyson and E.Lénard in the late sixties much effort has been devoted to improve and to generalize their results either in the direction of getting sharper and sharper estimates and/or considering more general quantum models than that of the standard non-relativistic of Schrödinger by including relativity, arbitrary magnetic fields or quantized fields.

In this paper I am concerned in a kind of strenghtening of *Stability of Matter* which tries to obtain the right dependence of the total energy in the physical parameters. It is also related to the remarkable fact that experimentally one finds that mean nuclear spacing is nearly independent of the kind of atoms that matter is made of.

In the Thomas-Fermi theory (TF in the next), distances scale as the $-1/3$ power of the nuclear average charge Z, i.e, we would expect that volume per particle should behave like $Z^{-1/3}$. As I have pointed out, one finds experimentally that the real behaviour seems to be almost independent of Z, and is a very challenging problem to try to explain rigurously that fact.

The usual Lieb-Thirring's proof of Stability of Matter indeed imply a lower bound of the volume per particle of order Z^{-1}. By the results I am going to explain, a bound of the volume per atom of the order $Z^{-1+\delta}$ follows, for some suitable $\delta > 0$ (see Theorem 3), which is still far of the bound of order $Z^0 = 1$ one might hope, but nevertheless is the best one already given as far as the author is aware of.

We consider matter formed by M nuclei of charges $Z_j \geq 1$, $j = 1, \dots, M$ located at positions $R_j \in \mathbb{R}^3$. We denote $\mathcal{R} = \{R_1, \dots, R_M\}$ and $\mathcal{Z} = (Z_1, \dots, Z_M)$. We consider these nuclei as static and consider the non-relativistic Hamiltonian of N electrons moving in the electric potential of the nuclei. The Hamiltonian is

$$H_{\mathcal{R},\mathcal{Z},N} = \sum_{i=1}^{N} \left\{ -\Delta_i - \sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|} \right\} + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le i < j \le M} \frac{Z_i Z_j}{|R_i - R_j|} \tag{1}$$

Our improvement on stability of matter is as follows.

Theorem 1 (Stability of Matter). *Assume there is a constant $0 < A < \infty$ such that the charges satisfy $Z \le Z_j \le AZ$ for all j and that $Z \ge 1$. Then there are $C, c > 0$ finite constants only depending on A and some absolute $\delta > 0$ ($\delta = 8/51$ could do) such that*

$$E^Q_{\mathcal{R},\mathcal{Z},N} := \inf_{\Psi \in \mathcal{H},\, \|\Psi\|=1} \langle \Psi, H_{\mathcal{R},\mathcal{Z},N} \Psi \rangle_{\mathcal{H}} \ge \sum_{j=1}^{M} E^Q(Z_j) + cZ^{7/3} \sum_{j=1}^{M} \Gamma\left(Z^{1/3}\delta_j\right) - CMZ^{2-\delta} \tag{2}$$

where $E^Q(Z)$ stands for the quantum energy of an atom of charge Z, which is given by

$$E^Q(Z) := \inf_{N \ge 1} \inf \operatorname{spec} H_{\{0\},(Z),N} \tag{3}$$

Here the Hilbert space where the Hamiltonian acts is $\mathcal{H} = \bigwedge^{N} L^2(\mathbb{R}^3; \mathbb{C}^2)$ (Fermion space), $\Gamma(t) = \min\{t^{-1}, t^{-7}\}$ and $\delta_j = \min_{i \ne j} |R_i - R_j|$ is the distance of R_j to its nearest neighbor.

As the QM energy $E^Q(Z)$ is given by the three-term asymptotics

$$E^Q(Z) = -C_{\mathrm{TF}} Z^{7/3} + \frac{1}{4} Z^2 - C_{\mathrm{DS}} Z^{5/3} + o(Z^{5/3-\delta}) \tag{4}$$

where in (4) $\delta > 0$ is some absolute constant and the second term, of order Z^2 is known as the *Scott term*. In Theorem 1, the constants C_{TF}, C_{DS} are, respectively, the corresponding *Thomas-Fermi* constant (see Sect. 2 below for the definition) and the *Dirac-Schwinger* one. This work shall not address this one.

Theorem 1 in particular shows that adding up the contributions of Thomas-Fermi (the main one of order $Z^{7/3}$) and the Scott's over all atoms gives us absolute bounds for the total QM energy up to an error of smaller order uniformly in the number of nuclei. Unfortunately the method does not give the next Dirac-Schwinger term, not even a remainder of its order. This drawback might be hopefully overcome if one uses instead of the *reduced Hartree-Fock model*, which is merely a 1-particle aproximation to the full quantum problem the whole Hartree-Fock model, which even if it is also another aproximation to the quantum problem, can be shown to yield an energy much closer to the quantum one than its baby brother, which is nevertheless easier to handle because it avoids the subtle correlation effects. Despite this, the reasons I chose to use this *reduced Hartree-Fock model* are twofold: The first is because it can be shown to approximate the QM energy up to energies of order $Z^{5/3}$ (at least for isolated atoms) and the second is its simplicity, which is mainly due to the fact it is a 1-particle model (a complete treatment of the quantum Hamiltonian would require a 2-particle formulation, due to the fact the electronic interactions are of 2-particle type).

We can write down a full two-term asymptotics for the QM energy if one restricts attention to configurations of uniformly separated nuclei, which is the content of next Theorem:

Theorem 2 (Asymptotics for the QM energy of uniformly separated nuclei). *Assume the conditions of Th. 1 are fulfilled, and besides that all nuclear distances $\delta_j \geq \mu Z^{-1/3}$ for some fixed $\mu > 0$. Then the following asymptotics holds*

$$C_1 M Z^{2-\delta_1} \geq E^Q_{\mathcal{R},\mathcal{Z}} - E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} - \frac{1}{4}\sum_{j=1}^{M} Z_j^2 \geq -C_2 M Z^{2-\delta} \tag{5}$$

(where C_1, C_2 are two positive and finite constants only depend on μ above and A). $E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ stands for the Thomas-Fermi energy of the full configuration (look at section 2 for definition) with parameter $\beta = \frac{3^{5/3}\pi^{4/3}}{5}$. and the unrestricted quantum energy $E^Q_{\mathcal{R},\mathcal{Z}}$ is given by

$$E^Q_{\mathcal{R},\mathcal{Z}} := \inf_{N\geq 0} E^Q_{\mathcal{R},\mathcal{Z},N} \tag{6}$$

i.e. it is the quantum energy when one arrives at electronic saturation (and thus adding up more of them does not lower the energy). The exponent δ is the same as in Th. 1, and we can take $\delta_1 = 5/27$.

Remark: As the Thomas-Fermi energy

$$E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} \geq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + cZ^{7/3}\sum_{j=1}^{M}\Gamma(Z^{1/3}\delta_j) \quad \text{(Strong form of Teller's non-binding Theorem)}$$

the asymptotics given by (5) indeed makes more precise the energy estimate given in Thm 1.

As Corollary of our main Theorem 1, it follows that if we are given a configuration of nuclei of total energy close to the minimun possible one, nuclear distances should be bigger in average than $Z^{-1+\delta'}$; $\delta' = \frac{1+3\delta}{7}$. To be more precise we have the following result:

Theorem 3 (The volume of matter). *With the conditions in Theorem 1, assume moreover that for the configuration $\mathcal{R}$*

$$\inf_{\Psi\in\mathcal{H},\,||\Psi||=1}\langle\Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} \leq \sum_{j=1}^{M} E^{Q}(Z_j) + CMZ^{2-\delta} \tag{7}$$

(observe that because of Theorem 2) such configurations indeed exist). Then we have that $\mathcal{R}$ should satisfy,

$$\langle\delta\rangle := \frac{1}{M}\sum_{j=1}^{M}\delta_j \geq \kappa Z^{1/3(-1+\delta')};\ \delta' = \frac{1+3\delta}{7} \tag{8}$$

Another interpretation of this result is as follows: Let us call

$$\text{volume} = \sum_{j=1}^{M}\left|B_{\frac{1}{2}\delta_j}(R_j))\right|;\ B_r(\mathrm{x}) = \left\{\mathrm{y}\in\mathbb{R}^3 : |\mathrm{x}-\mathrm{y}|\leq r\right\}$$

(Above, and hereafter, $|G|$ stands for Lebesgue measure of G). Then we have the estimate

$$\text{volume} \geq \kappa' M Z^{-1+\delta'} \tag{9}$$

where $\kappa, \kappa' > 0$ are universal constants.

2 Estimates on the Thomas-Fermi potential.

In this section we are going to derive two results which will be essential to generalize the previously known results of V.Ivrii and I.M.Sigal [16] on the correctedness of Scott correction for molecules to the case of many nuclei and therefore to be able to go beyond their analysis, which was based on the assumption of having a fixed number of them.

Let us call $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ the *Thomas-Fermi* potential of a configuration $\mathcal{R},\mathcal{Z}$. Recall that the Thomas-Fermi (TF in the next) model is given by the following functional

$$\begin{aligned}\mathcal{E}^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}(\rho) &= \beta\int_{\mathbb{R}^3}\rho(x)^{5/3}dx - \int_{\mathbb{R}^3}V(x)\rho(x)dx \\ &+\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy + \sum_{l<s}^{M}\frac{Z_l Z_s}{|R_l-R_s|}\end{aligned} \tag{10}$$

where the potential is $V(x) = \sum_{i=1}^{M}\frac{Z_i}{|x-R_i|}$ and $\beta > 0$ is a parameter. In our units the physical value of this parameter is $\beta_{\mathrm{phys}} = \frac{3}{5}(3\pi^2)^{2/3}$ (taking spin into account). We shall however use also Thomas-Fermi theory for other values of this parameter and we therefore allow it to be arbitrary for the moment. The Thomas-Fermi energy is defined by

$$E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}} := \inf_{0\le\rho\in L^1(\mathbb{R}^3)\cap L^{5/3}(\mathbb{R}^3)} \mathcal{E}^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}(\rho) \tag{11}$$

When $\beta = \beta_{\mathrm{phys}}$ we shall write $E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}$ simply as $E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$. If $M = 1$ and $Z = 1$ we shall write C^{β}_{TF} instead of $|E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}|$ and if $\beta = \beta_{\mathrm{phys}}$ simply C_{TF} (see also Theorems 1–3).

The energy satisfies the scaling properties

$$E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}} = \lambda E^{\mathrm{TF},\lambda\beta}_{\lambda\mathcal{R},\mathcal{Z}} = \lambda^7 E^{\mathrm{TF},\beta}_{\lambda\mathcal{R},\lambda^{-3}\mathcal{Z}} \tag{12}$$

for any $\lambda > 0$.

It is known that there is a unique function ρ which minimizes the functional (11). This function fulfils the Thomas-Fermi equations

$$\begin{array}{rcl} \frac{5}{3}\beta\rho^{2/3}(x) & = & \phi(x) \\ \phi(x) & = & V(x) - \frac{1}{|y|} * \rho(x) \end{array} \tag{13}$$

and is moreover the unique non-negative solution ρ of (13). This $\rho := \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ is called the *TF density* and then $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} := V - |\cdot|^{-1} * \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ is the *TF potential* mentioned above.

Our aim is to derive good bounds for it and its derivatives, but as the TF potential $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ satisfies the next scaling relations:

$$\left\{ \begin{array}{rcl} \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) & = & Z^{4/3}\Phi^{\mathrm{TF}}_{Z^{1/3}\mathcal{R},Z^{-1}\mathcal{Z}}(Z^{1/3}x) \\ \Phi^{\mathrm{TF},\lambda\beta}_{\mathcal{R},\mathcal{Z}}(x) & = & \lambda^{-1}\Phi^{\mathrm{TF}}_{\lambda^{-1}\mathcal{R},\mathcal{Z}}(\lambda^{-1}x) \end{array} \right. \tag{14}$$

we are led to the case where all charges are of the same order. Moreover, using the *Thomas-Fermi equation* next given that the TF potential $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ fulfils (and which shall allow us to express any derivative of $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ in terms of some integral operators applied to itself) and *Teller's Lemma*, which says that the total TF potential increases everywhere as long as any of its charges increases we can assume in the following that all charges are equal to one.

Now we are going to introduce the fundamental estimate of this section:

Lemma 1 (The size of TF potential of uniformly separated nuclei). *Let us be given a set $\{R_j\}_{j=1}^M \subset \mathbb{R}^3$ and assume that $\delta_j \ge 1\,\forall j$ (recall that $\delta_j = \min_{i:i\ne j}|R_i - R_j|$). Then there exists two absolute positive constants $0 < c \le C < \infty$ such that the following estimate holds for any $x \in \mathbb{R}^3$ (below $\langle x\rangle := (1+|x|^2)^{1/2}$)*

$$c\,\rho(x)^{-1}\langle\rho(x)\rangle^{-3} \le \Phi_{\mathcal{R}}(x) \le C\,\rho(x)^{-1}\langle\rho(x)\rangle^{-3} \tag{15}$$

where $\Phi_{\mathcal{R}} := \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$; $Z_1 = \ldots = Z_M = 1$ and the distance function $\rho(x)$ in 15 is given by

$$\rho(x) := \min\{|x - R_j| : j = 1, \ldots, M\} \tag{16}$$

Proof. First we note that we can reformulate Lemma 1 by introducing the so-called *Voronoi cells* $\{D_j\}_{j=1}^M$ associated to the set $\mathcal{R}$ and which are given by

$$D_j = \{x : |x - R_i| \geq |x - R_j| \, \forall \, i = 1, \ldots, M\} \tag{17}$$

Then we have $x \in D_j \Leftrightarrow \rho(x) = |x - R_j|$, so the proof of Lemma 1 is reduced to prove the next estimate for any Voronoi cell:

$$c\,|x - R_j|^{-1}\langle |x - R_j|\rangle^{-3} \leq \Phi_{\mathcal{R}}(x) \leq C\,|x - R_j|^{-1}\langle |x - R_j|\rangle^{-3};\ x \in D_j \tag{18}$$

We have two cases:

a) Assume $x \in B_{1/2}(R_j)(\subset D_j)$. Then $|x - R_i| \geq 1/2|R_i - R_j|$ for any $i \neq j$. The TF potential satisfies

$$\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) \leq \sum_{j=1}^{M} \Phi^{\mathrm{TF}}_{R_j,Z_j}(x) = \sum_{j=1}^{M} \Phi^{\mathrm{TF}}_{0,Z_j}(x - R_j) \tag{19}$$

and for $\varphi = \Phi^{\mathrm{TF}}_{0,1}$ we have the 2-sided estimate

$$c|x|\langle x\rangle^{-3} \leq \varphi(x) \leq C|x|\langle x\rangle^{-3} \ \forall x \tag{20}$$

where in (20) c, C are some positive absolute constants. Therefore, if $|x - R_j| \leq 1/2$, from (19), (20) we get

$$\Phi(x) \leq \varphi(x - R_j) + C \sum_{i:i\neq j}^{M} |R_i - R_j|^{-4} \tag{21}$$

Let us call $\tilde{R}_i = R_i - R_j$ for $i \neq j$. We can assume $1 \leq |\tilde{R}_1| \leq \ldots \leq |\tilde{R}_M|$ and since $|\tilde{R}_k - \tilde{R}_l| \geq 1$ the measure of the set $\bigcup_{i:i\neq j}^{N} B_{1/2}(\tilde{R}_i)$ equals $N|B_{1/2}(0)|$ for any $1 \leq N \leq M$. But

$$\bigcup_{i:i\neq j}^{N} B_{1/2}(\tilde{R}_i) \subset B_{|\tilde{R}_N|+1/2}(0) \tag{22}$$

and therefore we get

$$|\tilde{R}_N| \geq \max\left\{1, \frac{1}{2}N^{1/3}\right\} \sim N^{1/3} \tag{23}$$

Using (20), (21), (23) we get for $|x - R_j| \leq 1/2$

$$\begin{aligned} \Phi(x) &\leq \varphi(x - R_j) + C \sum_{n=1}^{M-1} n^{-4/3} \\ &\leq \varphi(x - R_j) + C \\ &\leq C\varphi(x - R_j);\ \varphi(x - R_j) \sim |x - R_j|^{-1} \geq 1 \end{aligned} \tag{24}$$

We consider now the case $x \in D_j \setminus B_{1/2}(R_j)$ and we note that $\Psi(x) := 144|x|^{-4}$ is a solution (the *Sommerfeld solution*) of the PDE $\Delta\Psi = \Psi^{3/2}$ in $\mathbb{R}^3 \setminus \{0\}$. Next we consider

$$\begin{aligned} \Psi_\lambda(x) &:= \lambda|x - R_j|^{-4} \\ \lambda &:= \max\{144, \sup\{\Phi(x) : |x - R_j| = 1/2\}\} \end{aligned} \tag{25}$$

So we have $\Psi_\lambda \geq \Phi$ if $|x - R_j| = 1/2$ and consider $\Gamma := \Psi_\lambda - \Phi$. We want to show that $\Gamma \geq 0$ on $D_j \setminus B_{1/2}(R_j)$. Let $\Omega = \{x \in \mathrm{int}(D_j) \setminus \overline{B}_{1/2}(R_j) : \Gamma(x) < 0\}$. Since there are no singularities of the potential on the set $\mathrm{int}(D_j) \setminus \overline{B}_{1/2}(R_j)$, Γ is continuous, Ω is open and $\Gamma = 0$ on $\partial\Omega$. For $x \in \Omega$ we find

$$\begin{aligned} \Delta\Gamma(x) &= 12\lambda|x - R_j|^{-6} - \Phi(x)^{3/2} \\ &\leq \lambda^{3/2}|x - R_j|^{-6} - \Phi(x)^{3/2} \text{ (since } \lambda \geq 144) \\ &= \Phi_\lambda(x)^{3/2} - \Phi(x)^{3/2} \\ &< 0 \text{ (since } \Gamma(x) < 0) \end{aligned} \tag{26}$$

meaning that Γ is *superharmonic* in Ω, which implies that Γ takes its minimum on $\partial\Omega \cup \{\infty\}$, but as $\Gamma(x)|_{\partial\Omega\cup\{\infty\}} = 0$, $\Omega = \emptyset$ and $\Gamma \geq 0$, which proves the upper bound in (15). The lower bound is an inmediate consequence of Teller's Lemma, which in particular implies that $\Phi_{\mathcal{R}}(x) \geq \varphi(x - R_j)$. □

> **Remark:** It should be noted that the lower bound in (15) holds for *any* nuclear configuration, and this is again just a simple consequence of Teller's Lemma. So this Lemma provides a condition to ensure that we have an upper bound for the Thomas-Fermi potential of the same kind that the lower one.

Our next Lemma essentially claims that *arbitrary* nuclear configurations behave essentially as if their nuclei where uniformly separated in those points which are separated by distance one or more to the nuclear configuration:

Lemma 2 (The size of TF potential away from the nuclei). *Let us be given an* **arbitrary** *configuration $\mathcal{R} \subset \mathbb{R}^3$ and assume $\rho(x) \geq 1/2$ (ρ is as in Lemma 1). Then the estimate (15) still holds*

Proof. Let us assume $\delta = \min\{|R_i - R_j| : i, j : 1, \dots, M; i \neq j\} \leq 1$, since otherwise by Lemma 1 there would be nothing to prove. Then we have

$$\begin{aligned} \Phi_{\mathcal{R}}(x) &= \delta^{-4}\Phi^{\mathrm{TF}}_{\delta^{-1}\mathcal{R},(\delta^3,\dots,\delta^3)}(\delta^{-1}x) \text{ (by TF scaling (14))} \\ &\leq \delta^{-4}\Phi^{\mathrm{TF}}_{\delta^{-1}\mathcal{R},(1,\dots,1)}(\delta^{-1}x) \text{ (by Teller's Lemma)} \\ &= \delta^{-4}\Phi_{\delta^{-1}\mathcal{R}}(\delta^{-1}x) \end{aligned} \tag{27}$$

Note that $x \in D_R \Leftrightarrow \delta^{-1}x \in D_{\delta^{-1}R}$ and the new configuration $\delta^{-1}\mathcal{R}$ is suitable to apply Lemma 1 to it. So we get

$$\delta^{-4}\Phi_{\delta^{-1}\mathcal{R}}(\delta^{-1}x) \le C\delta^{-4}|\delta^{-1}(x-R)|^{-1}\langle\delta^{-1}(x-R)\rangle^{-3} \tag{28}$$

If $\lambda = \delta^{-1} \ge 1$ and $|x| \ge 1/2$, we have $\mu\lambda\langle x\rangle \le \langle\lambda x\rangle \le \lambda\langle x\rangle$ for some fixed $\mu > 0$, and from (28) we get then

$$\delta^{-4}\Phi_{\delta^{-1}\mathcal{R}}(\delta^{-1}x) \le C|x-R|^{-1}\langle x-R\rangle^{-3} \tag{29}$$

which concludes the proof. □

Next result is the main result of this section and explains that we can obtain bounds for the derivatives of the TF potential from the bounds for the size of the potential just derived. It shall be essential in section 4 in order to apply the methods of *Multiscale Analysis*

Theorem 4 (Size of derivatives of TF potential). *Let us be given charges $(Z_1,\dots,Z_M)$ such that $1 \le Z_i \le A$ for some fixed positive A and assume either:*

i. There is given a nuclear configuration $\mathcal{R}$ such that $\delta_i \ge 1\ \forall\, i$. Then for any multiindex $\alpha \in \mathbb{N}^3$ the next bound holds for any $x \in \mathbb{R}^3$ for some finite constant C only depending on the number of derivatives $|\alpha|$ and A:

$$|\partial^\alpha \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)| \le C\rho(x)^{-1-|\alpha|}\langle\rho(x)\rangle^{-3} \tag{30}$$

ii. There is given an **arbitrary** *nuclear configuration $\mathcal{R}$ and assume moreover $\rho(x) \ge 1/2$. Then the bound (30) still holds.*

Proof. We are going to give a proof by induction on $|\alpha|$. By lemmas 1 and 2, Theorem 4 is valid if $\alpha = 0$ and all charges are equal to one. By the scaling relation (12) and Teller's Lemma, lemmas 1 and 2 inmediately generalize to the case $Z \le Z_j \le AZ\ \forall\, j$ and the bounds provided by these lemmas are the same except the constants now depend on A.

1.- Starting with $|\alpha| = 0$, fix $x_0 \in D_j \setminus B_{1/4}(R_j)$. We call $D_j = D_{R_j}$. Pick $\zeta \in C_c^\infty(\mathbb{R}^3)$ such that

$$\begin{cases} \zeta = 1, & |y| \le 1/2 \\ \zeta = 0, & |y| \ge 1/4 \end{cases} \tag{31}$$

and assume (30) is already proven for any multiindex α such that $|\alpha| \le N$. If $|\alpha'| = N+1$, $\partial^{\alpha'} = \partial^\alpha\partial^j$ for some $j = 1,2,3$ and $|\alpha| = N$ We introduce the functions

$$\begin{cases} \zeta_{x_0}(x) & = & \zeta(\frac{x-x_0}{|R_j-x_0|}) \\ & & \\ \Phi_{x_0} & = & \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\zeta_{x_0} \end{cases} \tag{32}$$

If x belongs to the support of Φ_{x_0}, a computation gives $|R_i - x| \geq 1/2|R_j - x_0| \geq 1/4 \ \forall\, i$. Therefore, the function Φ_{x_0} has no singularities. By standard elliptic estimates, we get $\Phi_{x_0} \in C_c^\infty$. Also, since $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ and Φ_{x_0} agree in a neighborhood of x_0, all their derivatives coincide at that point. A calculation, using the TF equation (13) yields

$$\Delta\Phi_{x_0} = 4\pi(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\zeta_{x_0} + 2\nabla\zeta_{x_0}\cdot\nabla\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\Delta\zeta_{x_0} \tag{33}$$

which could be written as follows:

$$\begin{aligned} \Phi_{x_0} &= |\cdot|^{-1} * ((\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\zeta_{x_0}) + \frac{1}{2\pi}|\cdot|^{-1} * (\nabla\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\cdot\nabla\zeta_{x_0}) \\ &\quad + \frac{1}{2\pi}|\cdot|^{-1} * (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\Delta\zeta_{x_0}) \\ &= |\cdot|^{-1} * ((\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\zeta_{x_0}) - \frac{1}{4\pi}|\cdot|^{-1} * (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\Delta\zeta_{x_0}) \\ &\quad - \frac{1}{2\pi}\sum_{i=1}^{3}\frac{y_i}{|y|^3} * (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\partial_i\zeta_{x_0}) \text{ (integrating by parts)} \end{aligned} \tag{34}$$

which implies

$$\partial^\alpha\Phi_{x_0} = h^i * f_1^\alpha - \frac{1}{4\pi}g_\alpha * f_2 - \frac{1}{2\pi}\sum_{i=1}^{3} h^i_\alpha * f_3^i \tag{35}$$

where

$$\left\{ \begin{array}{lcl} f_1^\alpha &=& \partial^\alpha\left[(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\zeta_{x_0}\right] \\ f_2 &=& \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\Delta\zeta_{x_0} \\ f_3^i &=& \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\partial_i\zeta_{x_0} \\ g_\alpha &=& \partial^\alpha|\cdot|^{-1} \\ h^i_\alpha &=& \partial^\alpha\partial^i|\cdot|^{-1} \\ h^i &=& h^i_0 \end{array} \right. \tag{36}$$

It is elementary to show by induction that g_α has always the form

$$g_\alpha(x) = \frac{P_\alpha(x)}{|x|^{2|\alpha|+1}};\ P_\alpha: \text{ polinomial of degree } |\alpha|$$

Recall $|R_i - x| \geq 1/4$ for x in the support of ζ_{x_0}, so the estimate of Lemma 2 applies (maybe with modified constants) and now we estimate any of pieces of (35) at x_0:

First we estimate pointwise f_i^α. Call $F := \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$. Then $F > 0$ and we can write

$$\partial^\alpha F^p = \sum_{n=1}^{|\alpha|} p(p-1)\dots(p-n+1)F^{p-N+n}\sum_{\beta:\beta\leq\alpha,\,|\beta|=n}\partial^\beta F\partial^{\alpha-\beta}F \tag{37}$$

$$f_i^\alpha = \sum_{\beta\le\alpha} C_{\alpha,\beta}\partial^\beta[(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}]\partial^{\alpha-\beta}\zeta_{x_0} \tag{38}$$

From Lemma 2 (notice that we have to use the 2-sided estimate (15) (37), (38) and recalling $|R_i - x| \ge 1/4$ for x in the support of ζ_{x_0}, it follows that $\|f_i^\alpha\|_\infty \le C_\alpha |x_0 - R_j|^{-6-|\alpha|}$. Then we apply the induction hypothesis and we get:

$$\begin{aligned}
|h^i * f_1^\alpha(x_0)| &= \left|\int d^3x \frac{f_1^\alpha(x)}{|x-x_0|^2}\right| \\
&\le C\int_{|x-x_0|\le\frac{1}{2}|x_0-R_j|} d^3x \frac{|f_1^\alpha(x)|}{|x-x_0|^2} \\
&\le C\int_{|x-x_0|\le\frac{1}{2}|x_0-R_j|} d^3x \frac{|x_0-R_j|^{-6-|\alpha|}}{|x-x_0|^2} \\
&= C|x_0-R_j|^{-4-|\alpha|}
\end{aligned} \tag{39}$$

Analogously

$$\begin{aligned}
|g_\alpha * f_2(x_0)| &\le C\frac{1}{4\pi}\int d^3x \frac{\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)|\Delta\zeta_{x_0}|}{|x-x_0|^{|\alpha|+1}} \\
&\le C\frac{1}{4\pi}|x_0-R_j|^{-6}\int_{\frac{1}{4}|x_0-R_j|\le|x-x_0|\le\frac{1}{2}|x_0-R_j|} \frac{d^3x}{|x-x_0|^{-|\alpha|-1}} \\
&\le C|x_0-R_j|^{-4-|\alpha|}
\end{aligned} \tag{40}$$

since $\|\Delta\zeta_{x_0}\|_\infty \le C|x_0-R_j|^{-2}$. Finally

$$\begin{aligned}
|h^i_\alpha * f_3^i(x_0)| &\le C\int_{\frac{1}{4}|x_0-R_j|\le|x-x_0|\le\frac{1}{2}|x_0-R_j|} d^3x \frac{\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)|\partial^i\zeta_{x_0}|}{|x-x_0|^{|\alpha|+2}} \\
&\le C|x_0-R_j|^{-5}\int_{\frac{1}{4}|x_0-R_j|\le|x-x_0|\le\frac{1}{2}|x_0-R_j|} d^3x|x-x_0|^{-|\alpha|-2} \\
&= C|x_0-R_j|^{-4-|\alpha|}
\end{aligned} \tag{41}$$

since $\|\partial^i\zeta_{x_0}\|_\infty \le C|x_0-R_j|^{-1}$.

2.- We assume now that all $\delta_i \ge 1$ and pick $x \in D_j$ with $\rho(x) \le 1/2$. We fix $\eta \in C^\infty(\mathbb{R}^3)$ with the properties

$$\begin{cases} \eta = 0, & |y| \le 1/2 \\ \eta = 1, & |y| \ge 3/4 \end{cases} \tag{42}$$

For fixed $j = 1, \dots, M$ we consider

$$\begin{cases}
\Phi_j^1(x) &= V(x) - \frac{Z_j}{|x-R_j|} - |\cdot|^{-1} * (\eta_j(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2})(x) \\
\Phi_j^2(x) &= |\cdot|^{-1} * (\psi_j(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2})(x) \\
\eta_j &= \eta(\cdot - R_j) \\
\psi_j &= 1-\eta_j
\end{cases} \tag{43}$$

so that $\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) = \Phi^1_j(x) - \Phi^2_j(x) - \frac{Z_j}{|x-R_j|}$. The functions Φ^2_j are uniformly bounded by some fixed constant, because by Lemma 1 we have

$$\Phi^2_j \leq C|\cdot|^{-1} * G_j;\ G_j(x) = G(x - R_j);\ G(x) = \frac{1}{|x|^{3/2}}\chi_{B_{3/4}(0)} \tag{44}$$

The function G is radial, therefore by Newton's Theorem, $G(x) \leq \int \frac{G(y)}{|y|}\,dy$, which is finite.

We can easily check that $\Delta\Phi^1_j = 0$ in the ball $B_{1/2}(R_j)$. As a result, we can write that function using the Poisson kernel:

$$\Phi^1_j(x) = \frac{r^2 - |x|^2}{4\pi r}\int_{|y-R_j|=r} \frac{\Phi^1_j(y)}{|x-y|^3}\,d\sigma(y);\ r = 1/2 \tag{45}$$

and since by Lemma 1 and (44), $\sup\{\Phi^1_j\big|_{|x-R_j|=1/4}\} \leq C$, we get $|\partial^\alpha\Phi^1_j(x)| \leq C$ if $|x - R_j| \leq 1/2$ for all multiindex α.

We are going now to estimate the derivatives of Φ^1_j. To do so, assume it has already been proven that $\rho(x) \leq 1/2$ implies $|\partial^\alpha\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)| \leq C\rho(x)^{-1-|\alpha|}$ for any multiindex α with $|\alpha| \leq n$. Then consider again $\partial^{\alpha'} = \partial^j\partial^\alpha$ for $j = 1, 2, 3$. We have:

$$\begin{aligned} |\partial^{\alpha'}\Phi^1_j(x)| &= |\partial^j\partial^\alpha\Phi^i_j(x)| \\ &= |h^k * (\partial^\alpha(\psi_j(x)\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2}))| \\ &\leq C\int d^3y \frac{|\partial^\alpha(\psi_j(x)\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2})|}{|x-y|^2} \end{aligned} \tag{46}$$

Reasoning as in the previous part, we get the estimate

$$|\partial^\alpha(\psi_j(x)\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2})| \leq C|x - R_j|^{-3/2-|\alpha|} \tag{47}$$

Putting together estimates (46) and (47) follows

$$\begin{aligned} |\partial^{\alpha'}\Phi^1_j(x)| &= |\partial^j\partial^\alpha\Phi^i_j(x)| \\ &\leq C\int d^3y \frac{|x-R_j|^{-3/2-|\alpha|}}{|x-y|^2} \\ &\leq C\int_{|y-R_j|\leq 3/4} d^3y|x-y|^{-2}|y-R_j|^{-3/2-|\alpha|} \\ &\leq C|x-R_j|^{-1/2-|\alpha|}\int d^3x|1-x|^{-2}|x|^{-3/2-|\alpha|} \\ &= C|x-R_j|^{-1/2-|\alpha|} \end{aligned} \tag{48}$$

Since the coulombic term $Z_j/|x - R_j|$ obviously satisfies the conclusion of Theorem 4, proof of Theorem 4 is complete. $\square$

Another result about the TF potential we shall need is to isolate near the singularities of a configuration of uniformly separated nuclei the asymptotic coulombic term and the rest. The result is as follows:

Lemma 3 (regular part of TF potential near singularities). *Assume $\delta_i \geq 1\, \forall i$, $1 \leq Z_j \leq A$*

1.- Write

$$\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) = \frac{Z_j}{|x-R_j|} + \lim_{x\to 0}\left[\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) - \frac{Z_j}{|x-R_j|}\right] + \mu_j(x);\ \ |x-R_j| \leq 1/2 \quad (49)$$

We have the estimate

$$|\partial^\alpha \mu_j(x)| \leq C_\alpha \rho(x)^{1/2-|\alpha|};\ \ |x-R_j| \leq 1/2,\ \alpha \in \mathbb{N}^3 \quad (50)$$

2.- Now write

$$\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) = Z_j^{4/3}\varphi(Z_j^{1/3}(x-R_j)) + w_j(x);\ \ |x-R_j| \leq 1/2 \quad (51)$$

Then we have the estimates

$$\|\partial^\alpha w_j\|_\infty \leq C_\alpha;\ \alpha \in \mathbb{N}^3 \ \text{ and } w_j \geq 0 \quad (52)$$

3.- Write

$$k_j = \lim_{x\to R_j}\left[\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) - \frac{Z_j}{|x-R_j|}\right] \quad (53)$$

Then we have the estimate

$$|k_j| \leq C \quad (54)$$

Proof. An easy calculation using the TF equation (13) yields the result

$$\lim_{x\to R_j}\left[\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x) - \frac{Z_j}{|x-R_j|}\right] = \sum_{i=1,i\neq j}^{M} \frac{Z_j}{|R_i-R_j|} - |\cdot|^{-1} * \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(R_j) \quad (55)$$

which is finite given that $\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ belongs to L^1 and therefore $|\cdot|^{-1} * \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ is continuous. Then, reasoning like in the second part of the proof of Theorem 4 we get (50) (see ecs. (46), (47), (48)). The second assertion can be justified as follows:

$$-\frac{1}{4\pi}\Delta w_j = \sum_{i:i\neq j}^{M} Z_i \delta_{R_i} + Z_j^2 \varphi(Z_j^{1/3}(\cdot - R_j))^{3/2} - (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} \quad (56)$$

From eq. (56) and Lemma 4) follows that

$$\|\partial^\alpha(\Psi \Delta w_j)\|_\infty \leq C_\alpha;\ \ \alpha \in \mathbb{N}^3 \quad (57)$$

where $0 \leq \Psi \in C_c^\infty(B_{3/4}(R_j))$, $\Psi = 1$ if $|x - R_j| \leq 1/2$ and following the procedure above the estimates holds:

$$\|\partial^\alpha(\Psi w_j)\|_\infty \leq C_\alpha;\ \alpha \in \mathbb{N}^3 \tag{58}$$

The fact that w_j is positive is a simple consequence of Teller's Lemma.

Finally we have, again by Teller's Lemma and (19)

$$Z^{4/3}\varphi(Z^{1/3}(x - R_j)) \leq \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}(x) \leq Z^{4/3}\varphi(Z^{1/3}(x - R_j)) + \Phi^{\rm TF}_{\mathcal{R}_j,\mathcal{Z}_j}(x);\ \mathcal{R}_j = \mathcal{R} \setminus \{R_j\} \tag{59}$$

and from (59) follows that

$$C_1 \leq Z^{4/3}k \leq k_j \leq C_1 \leq Z^{4/3}k + \Phi^{\rm TF}_{\mathcal{R}_j,\mathcal{Z}_j}(R_j) \leq C_2;\ k = \lim\left[\varphi(x) - \frac{1}{|x|}\right] \tag{60}$$

where we have applied again Theorem 1. □

Remarks:

i. Looking at the case of an isolated atom, the constant correction $k = \lim_{x\to 0}\left[Z^{4/3}\varphi(Z^{1/3}x) - \frac{Z}{|x|}\right]$ can be written as

$$k = \frac{d}{dZ}E^{\rm TF}(Z) = -\frac{7}{3}C_{\rm TF}Z^{4/3};\ C_{\rm TF} = |E^{\rm TF}(1)| > 0 \tag{61}$$

so the correction is *strictly negative* in that case.

ii. For the case of an isolated atom, the μ appearing in (55) is *negative.* This follows from the estimate $\varphi(x) \leq \frac{1}{|x|}$.

3 Reduction to the case of uniformly separated nuclei.

In this section our object of study will be the so-called *reduced Hartree-Fock model* (RHF in the next), which is one intermediate in sophistication between the purely semiclassical TF model and the fully quantum Schrödinger one. I will also ignore the spin, because its effect tourns to be just a modification of some constants (something which already happens when one compares the Schrödinger model with the TF one).

The RHF model is given by the functional

$$\begin{aligned}
\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) &:= \operatorname{Tr}\left[(-\Delta - V_{\mathcal{R},\mathcal{Z}})\gamma\right] + D(\rho_\gamma) + U_{\mathcal{R},\mathcal{Z}} \\
V_{\mathcal{R},\mathcal{Z}}(x) &:= \sum_{j=1}^{M} \frac{Z_j}{|x-R_j|} \\
D(f,g) &:= \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{f(x)\overline{g(y)}}{|x-y|}dxdy;\ f,g\in L^{6/5}(\mathbb{R}^3) \\
\rho_\gamma &:= \ \text{density of } \gamma\in Sp^1(L^2(\mathbb{R}^3));\ 0\le\gamma\le 1;\ \operatorname{Tr}[(-\Delta)\gamma]<\infty \\
U_{\mathcal{R},\mathcal{Z}} &:= \sum_{1\le l<s\le M} \frac{Z_l Z_s}{|R_l-R_s|}
\end{aligned} \tag{62}$$

Analogously, we define the *RHF energy*

$$E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} := \inf\{\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) : \gamma\in Sp^1(L^2(\mathbb{R}^3));\ 0\le\gamma\le 1;\ \operatorname{Tr}[(-\Delta)\gamma]<\infty\} \tag{63}$$

(by Sp^q; $1\le q<\infty$ is meant the *Schatten-Von Neumann class* of compact operators). Notice that the restrictions posed to the *density matrices* γ are sufficient to ensure that all the terms in (62) are finite, so this gives to us a well-defined model. Now the important thing to note is the *positive definiteness* of the *Coulomb kernel* $D(f,g)$: $D(f)\ge 0\,\forall f$. The way we are going to use this fact is as follows: We divide the configuration into two parts: $\mathcal{R}_1$ and $\mathcal{R}_2$ such that $\mathcal{R}=\mathcal{R}_1\cup\mathcal{R}_2$; $\mathcal{R}_1\cap\mathcal{R}_2=\emptyset$ and similarly with the nuclear charges. The first one shall contain those nuclei which are very close one another, and shall be thought as the "bad part". The second part shall contain nuclei which are uniformly bounded away one another by a distance of order $Z^{-1/3}$. Our aim is to get rid of the 'bad' nuclei.

We fix $\lambda=\mu Z^{-1/3}$ for some $\mu>0$ to be chosen later. We assume the nuclei are ordered in such a way that $0<\delta_1\le\delta_2\le\ldots\le\delta_M$ and define

$$\begin{aligned}
M_1 &= \begin{cases} \max\{j\in\{1,\ldots,M\}:\delta_i\le\lambda\} & \text{if } \exists i \text{ such that } \delta_i\le\lambda \\ 0 & \text{otherwise}\end{cases} \\
\tilde{\Omega}_1 &= \bigcup_{j=1}^{M_1} \overline{B}_{\frac{\lambda}{2}}(R_i)
\end{aligned}$$

In this way the set $\tilde{\Omega}_1$ contains the 'bad' set $\mathcal{R}_1=\{R_i\}_{i=1}^{M_1}$. Fix $\Psi\in C_c^\infty(\mathbb{R}^3)$ such that:

i. $\int\Psi=1$.

ii. $\Psi\ge 0$ and $\Psi=0$ if $|x|\ge\frac{\lambda}{4}$.

iii. $\|\nabla\Psi\|_\infty\le\frac{C}{\lambda}$ with C independent of λ.

Let $\zeta_1:=\Psi*\chi_\Omega$. As it is easy to check, this function has the following properties:

$$\begin{cases}
\operatorname{supp}\zeta_1\subset\overline{B}_{\frac{\lambda}{4}}+\Omega = \bigcup_{j=1}^{M_1}\overline{B}_{\frac{3\lambda}{4}}(R_i)=\Omega_1 \\
\zeta_1(x) = 1 \text{ if } x\in\bigcup_{j=1}^{M_1}\overline{B}_{\frac{\lambda}{4}}(R_i)=\tilde{\Omega}_2 \\
\|\nabla\zeta_1\|_\infty \le \|\nabla\Psi\|_\infty
\end{cases} \tag{64}$$

By means of function ζ_1 we define also:

$$\begin{cases} \Theta_1 & = & \frac{\zeta_1}{(\zeta_1^2+(1-\zeta_1)^2)^{1/2}} \\ \Theta_2 & = & \frac{1-\zeta_1}{(\zeta_1^2+(1-\zeta_1)^2)^{1/2}} \end{cases} \tag{65}$$

So, $\{\Theta_1^2, \Theta_2^2\}$ is a partition of unity with the properties:

$$\begin{cases} \operatorname{supp}\Theta_1 & \subset & \Omega_1 \\ \operatorname{supp}\Theta_2 & \subset & \Omega_2 := \mathbb{R}^3 \setminus \operatorname{int}\tilde{\Omega}_2 \\ \|\nabla\Theta_i\|_\infty & \leq & \frac{C}{\lambda} \text{ with } C \text{ independent of } \lambda \end{cases} \tag{66}$$

The nuclei in the first configuration $\mathcal{R}_1$ shall be treated by direct comparison to the energy of the corresponding TF model, with a suitably modified parameter β (cf. 10). Those 'good' nuclei of the second configuration shall be treated with the Multiscale methods introduced by Ivrii&Sigal. In order to get rid of the bad nuclei, we write

$$\begin{aligned} 0 &\leq D(\rho_\gamma - \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} - \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) \\ &= D(\rho_\gamma) + D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) + D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) - 2D(\rho_\gamma, \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) \\ &\quad -2D(\rho_\gamma, \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + 2D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}, \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) \end{aligned} \tag{67}$$

In (67), $\beta > 0$ is some fixed parameter to be chosen later. Then a calculation using the TF equation (13) and (67) yields

$$\begin{aligned} \mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) &\geq \operatorname{Tr}[(-\Delta - \Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} - \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\gamma] - D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) - D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) \\ &\quad +U_{\mathcal{R}_1,\mathcal{Z}_1} + U_{\mathcal{R}_2,\mathcal{Z}_2} + \Delta U_{1,2} \\ U_{\mathcal{R}_1,\mathcal{Z}_1} &:= \sum_{1\leq l<s\leq M_1} \frac{Z_l Z_s}{|R_l - R_s|} \\ U_{\mathcal{R}_2,\mathcal{Z}_2} &:= \sum_{M_1\leq l<s\leq M} \frac{Z_l Z_s}{|R_l - R_s|} \\ \Delta U_{1,2} &:= U_{\mathcal{R},\mathcal{Z}} - U_{\mathcal{R}_1,\mathcal{Z}_1} - U_{\mathcal{R}_2,\mathcal{Z}_2} - 2D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}, \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) \end{aligned} \tag{68}$$

We can estimate the $\Delta U_{1,2}$ term in the following way:

Lemma 4. *The value of $\Delta U_{1,2}$ is given by:*

$$\Delta U_{1,2} = \int \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \int \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} \Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} \tag{69}$$

In particular, $\Delta U_{1,2} \geq 0$.

Proof. We just write

$$2D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}, \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) = \int \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} |\cdot|^{-1} * \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}$$

and use the TF equations any of the terms satisfy. □

To continue our splitting procedure we use the partition of unity constructed before by means of the IMS localization identity: given a density matrix γ call $\gamma_i := \Theta_i\gamma\Theta_i$, $i = 1, 2$. Then IMS identity says

$$\mathrm{Tr}\,[(-\Delta)\gamma] = \mathrm{Tr}\,[(-\Delta)\gamma_1] + \mathrm{Tr}\,[(-\Delta)\gamma_2] - \int (|\nabla\Theta_1|^2 + |\nabla\Theta_2|^2)\rho_\gamma \tag{70}$$

From (66), (70) and the fact that we can assume our density matrices γ to have $\mathrm{Tr}\,\gamma \leq 2\sum_{j=1}^{M} Z_j + M$ by the general argument of Lieb and Benguria [20], we get the kinetic energy localization estimate

$$\mathrm{Tr}\,[(-\Delta)\gamma] \geq \mathrm{Tr}\,[(-\Delta)\gamma_1] + \mathrm{Tr}\,[(-\Delta)\gamma_2] - C\mu^{-2}Z^{5/3}M \tag{71}$$

which is acceptable for our purposes of proving the Scott's conjecture. Then, using (68) and (71) we get the following estimate for the RHF energy:

$$\begin{aligned}
\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) &\geq \mathcal{E}_1(\gamma_1) + \mathcal{E}_2(\gamma_2) + \Delta U_{1,2} - C\mu^{-2}Z^{5/3}M \\
\mathcal{E}_1(\gamma) &:= \mathrm{Tr}\,[(-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))\gamma] - D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) + U_{\mathcal{R}_1,\mathcal{Z}_1} \qquad (72)\\
\mathcal{E}_2(\gamma) &:= \mathrm{Tr}\,[(-\Delta - (\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}))\gamma] - D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + U_{\mathcal{R}_2,\mathcal{Z}_2}
\end{aligned}$$

But if the density matrix γ is diagonalizable in $H^1(\mathbb{R}^3)$, the density matrices γ_i diagonalize in $H^1_0(\Omega_i)$ for $i = 1, 2$. As a consequence, we get the trace estimates

$$\begin{cases}
\mathcal{E}_1(\gamma) \geq \mathrm{Tr}\,[-\Delta^D_1 - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))]_- - D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) + U_{\mathcal{R}_1,\mathcal{Z}_1} \\
\mathcal{E}_2(\gamma) \geq \mathrm{Tr}\,[(-\Delta^D_2 - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))\gamma] - D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + U_{\mathcal{R}_2,\mathcal{Z}_2}
\end{cases} \tag{73}$$

where in (73), Δ^D_i are the Dirichlet Laplacians in the regions Ω_i (i=1,2) and we can take trial density matrices for the functional $\mathcal{E}_2$ such that they diagonalize in $H^1_0(\Omega_2)$.

We shall defer the analysis of the functional $\mathcal{E}_2(\gamma)$ to section 4, but we are going to consider here first $\mathcal{E}_1(\gamma)$:

Lemma 5 (The bad nuclei have positive energy). *Let $\mathcal{E}_1(\gamma)$ be as in (72). Then, we can choose $\lambda = \mu Z^{1/3}$ and β in such a way that*

$$\mathcal{E}_1(\gamma) \geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) \tag{74}$$

for some $c > 0$ only depending on λ, β. The function Γ is as Theorem 1.

If $x \in \mathrm{supp}\,\Theta_1$, by Lemma 1 and the scaling relation (14), the following estimate holds: (here $\beta = \kappa\beta_f$ where β_f is some fixed parameter taken as reference and $0 < \kappa \leq 1$)

$$\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}(x) + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}(x) = \kappa^{-1}\Phi^{\mathrm{TF}}_{\kappa^{-1}\mathcal{R}_1,\mathcal{Z}_1}(\kappa^{-1}x) + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}(x) \tag{75}$$

But with $\rho(x) = \min\{|x - R_j| : j = 1, \ldots, M_1\}$ and $\rho'(x) = \min\{|x - \kappa^{-1}R_j| : j = 1, \ldots, M_1\}$, using Lemma 1 and again (14) we get

$$\begin{aligned}
\kappa^{-1}\Phi^{\mathrm{TF}}_{\kappa^{-1}\mathcal{R}_1,\mathcal{Z}_1}(\kappa^{-1}x) &\geq c\kappa^{-1}Z\rho'(\kappa^{-1}x)^{-1}\langle\rho'(\kappa^{-1}x)\rangle^{-3} \\
&= cZ\rho(x)^{-1}\langle\kappa^{-1}Z^{1/3}\rho(x)\rangle^{-3} \\
&\geq cZ\lambda^{-1}\langle\kappa^{-1}Z^{1/3}\lambda\rangle^{-3} \\
&\geq cZ\lambda^{-1}\langle\kappa^{-1}\mu\rangle^{-3}
\end{aligned} \tag{76}$$

A similar estimate gives

$$\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}(x) \leq C\mu^{-3}Z\lambda^{-1} \tag{77}$$

and therefore

$$\begin{aligned}
\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}(x) + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}(x) &\leq (1 + C\mu^{-3}\langle\kappa^{-1}\mu\rangle^3)\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}(x) \\
&\leq C\mu^{-3}\langle\kappa^{-1}\mu\rangle^3\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}(x) \\
&\leq C\mu^{-3}\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}(x) \text{ if we take } \mu \leq \kappa
\end{aligned} \tag{78}$$

Now we are in position to estimate $\mathrm{Tr}\,[(-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Theta_1^2)\gamma]$ by means of the Lieb-Thirring inequality:

$$\begin{aligned}
\mathrm{Tr}\,[(-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Theta_1^2)\gamma] &\geq -\mathrm{Tr}\,(-\Delta - C\mu^{-3}\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1})_- \\
&\geq -K\mu^{-5}\int(\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1})^{5/2}
\end{aligned} \tag{79}$$

It will be useful for us to be able to express the TF energy only using the TF potential, the Coulomb self-energy of the density and the nuclear repulsion. This is an easy calculation using the TF equation and is as follows:

Lemma 6 (Expression of the TF energy). *It is possible to express the TF energy $E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}$ in the following way, where $\beta = \kappa\beta_f$:*

$$E^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}} = -\frac{2}{5}\left(\frac{3}{5\kappa\beta_f}\right)^{3/2}\int(\Phi^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}})^{5/2} - D(\rho^{\mathrm{TF},\beta}_{\mathcal{R},\mathcal{Z}}) + U_{\mathcal{R},\mathcal{Z}} \tag{80}$$

From Lemma 6 and (79) we get the estimate

$$\mathcal{E}_1(\gamma) \geq E^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} \tag{81}$$

assuming we have chosen $\mu \leq \kappa$ in such way that

$$K\mu^{-5} = \frac{2}{5}\left(\frac{3}{5\kappa\beta_f}\right)^{3/2} \Longleftrightarrow \mu = K'\kappa^{3/10};\ K' = \left[\frac{5K}{2}\left(\frac{5\beta_f}{3}\right)^{3/2}\right]^{1/5} \tag{82}$$

As the exponent $3/10 < 1$, the choice of μ is consistent. Now we are in position to prove Lemma 5:

Proof of Lemma 5. By the scaling relation (12) of the TF energy and Lemma 2 of [2], we get

$$\begin{aligned} E^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} &\geq \kappa^{-1} E^{\mathrm{TF}}_{\kappa^{-1}\mathcal{R}_1,\mathcal{Z}_1} \\ &\geq \kappa^{-1}\left(-C_{\mathrm{TF}}\sum_{j=1}^{M_1} Z_j^{7/3} + cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(\kappa^{-1}Z^{1/3}\delta_j)\right) \end{aligned} \tag{83}$$

But $\delta_j \leq \mu Z^{-1/3}$, so that $\kappa^{-1}Z^{1/3}\delta_j \leq K'\kappa^{3/10} \downarrow 0$ $(\kappa \downarrow 0)$ so that, by taking $\kappa > 0$ small enough we get

$$\begin{aligned} E^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} &\geq \kappa^{-1}Z^{7/3}\left(-C_{\mathrm{TF}}A^{7/3} + K''\kappa^{-3/10}\right)M_1 + c\kappa^{-1}Z^{7/3}\sum_{j=1}^{M_1}\Gamma(\kappa^{-1}Z^{1/3}\delta_j) \\ &\geq c\kappa^{-1}Z^{7/3}\sum_{j=1}^{M_1}\Gamma(\kappa^{-1}Z^{1/3}\delta_j) \text{ for } \kappa > 0 \text{ small enough} \\ &\geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) \end{aligned} \tag{84}$$

which concludes the proof. □

To end this section we are going to analyze the TF energy of a configuration of uniformly separated nuclei. This is the content of next Lemma:

Lemma 7 (Bound of the energy of uniformly separated nuclei). *Let us assume we are given a nuclear configuration $\mathcal{R},\mathcal{Z}$ such that $\delta_j \geq \mu Z^{-1/3}$ and $Z \leq Z_j \leq AZ$ for all j. Then the next upper bound of the total TF energy $E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ holds:*

$$E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} \leq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + CZ^{7/3}\mu^{-3}M \tag{85}$$

Proof. To prove estimate (85) is enough to construct a trial density ρ such that $\mathcal{E}^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(\rho) \leq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + CZ^{7/3}\mu^{-4}M$. To do so, take

$$\rho = \sum_{j=1}^{M}\lambda_j\rho^{\mathrm{TF}}_{Z_j}(\cdot - R_j)\chi_{\overline{B}_{\frac{1}{2}\mu Z^{-1/3}}} = \sum_{j=1}^{M}\rho_j;\ \lambda_j = \left[\int \rho^{\mathrm{TF}}_{Z_j}\chi_{\overline{B}_{\frac{1}{2}\mu Z^{-1/3}}}\right]^{-1}$$

Since $\int\rho^{\mathrm{TF}}_{Z} = Z$ and $\rho^{\mathrm{TF}}_{Z}(x) = Z^2\rho^{\mathrm{TF}}_1(Z^{1/3}x)$, we get, using that $\rho^{\mathrm{TF}}_1(x) \sim |x|^{-6}$; $|x| \geq \mu$, $\lambda_j - 1 \sim \mu^{-3}$.

With this choice of ρ, we get:

i.-

$$\int \rho^{5/3} \leq \sum_{j=1}^{M} \lambda_j^{5/3} \int \left(\rho_{Z_j}^{\mathrm{TF}}\right)^{5/3}$$

ii.-

$$\begin{aligned}
\int V_{\mathcal{R},\mathcal{Z}}\rho &= \sum_{j=1}^{M} Z_j |\cdot|^{-1} * \rho_j(R_j) + 2U_{\mathcal{R},\mathcal{Z}} \\
&= \sum_{j=1}^{M} \lambda_j \left[\int \frac{Z_j}{|x|} \rho_{Z_j}^{\mathrm{TF}} - |\cdot|^{-1} * [\rho_j \chi_{B^c_{\frac{1}{2}\mu Z^{-1/3}}}](0) \right] + 2U_{\mathcal{R},\mathcal{Z}} \\
&\geq \sum_{j=1}^{M} \int \frac{Z_j}{|x|} \rho_{Z_j}^{\mathrm{TF}} - \sum_{j=1}^{M} Z_j^3 Z^{-2/3} \int_{|x| \geq \frac{1}{2}\mu} \rho^{\mathrm{TF}} |\cdot|^{-1} + 2U_{\mathcal{R},\mathcal{Z}} \\
&\geq \sum_{j=1}^{M} \int \frac{Z_j}{|x|} \rho_{Z_j}^{\mathrm{TF}} - C Z^{7/3} \mu^{-4} M + 2U_{\mathcal{R},\mathcal{Z}}
\end{aligned}$$

(we have used Newton's Theorem to get the first line on the expression above)

iii.-

$$\begin{aligned}
D(\rho) &= U_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^{M} D(\rho_j) \\
&\leq U_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^{M} \lambda_j^2 D(\rho_{Z_j}^{\mathrm{TF}})
\end{aligned}$$

(again, by Newton's Theorem)

Putting the estimates above together we get

$$\begin{aligned}
\mathcal{E}_{\mathcal{R},\mathcal{Z}}^{\mathrm{TF}}(\rho) &\leq -C_{\mathrm{TF}} \sum_{j=1}^{M} Z_j^{7/3} + \sum_{j=1}^{M} (\lambda_j^3 - 1) \int \left(\rho_{Z_j}^{\mathrm{TF}}\right)^{5/3} + C Z^{7/3} \mu^{-4} M \\
&\leq -C_{\mathrm{TF}} \sum_{j=1}^{M} Z_j^{7/3} + C Z^{7/3} \mu^{-3} M \qquad (86)
\end{aligned}$$

which is (85). □

4 Semiclassics in the good region: Multiscale Analysis.

In this section we are going to analize the functional $\mathcal{E}_2(\gamma)$ by semiclassical methods taking advantage of the fact we have removed all the singularities of the potential which can get almost in top of each other. Let us call

$$\mathcal{E}(\gamma) := \mathrm{Tr}\,[(-\Delta_2^D - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))\gamma] \tag{87}$$

with γ diagonalizable in $H_0^1(\Omega_1)$. The following trace estimate holds:

$$\begin{aligned}\mathrm{Tr}\,[(-\Delta_2^D - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))\gamma] &\geq \mathrm{Tr}\,[(-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\chi_{\Omega_2})\gamma] \\ &\geq -\mathrm{Tr}\,[-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi]_- \end{aligned} \tag{88}$$

where in (88) we take Ξ with the following properties:

$$\begin{cases} \Xi \in C^\infty(\mathbb{R}^3) \\ \Xi = 1 \text{ in } \Omega_2 \\ \Xi = 0 \text{ in } \Omega = \left(\bigcup_{j=1}^{M_1} \overline{B}_{\frac{\lambda}{8}}(R_j)\right)^c \\ 0 \leq \Xi \leq 1 \\ |\nabla \Xi| \leq CZ^{-1/3} \end{cases} \tag{89}$$

To do semiclassics, we are going to use the scaling properties of the TF potential which are given by (14) and rescaling everything conjugating with the unitary operator $U_l\phi(x) := l^{-3/2}\phi(lx)$. Then a computation yields

$$\begin{aligned}\mathrm{Tr}\,[-\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi]_- &= Z^{4/3}\mathrm{Tr}[-Z^{-2/3}\Delta - W]_- \\ W &:= (\Phi^{\mathrm{TF}}_{Z^{1/3}\mathcal{R}_2,Z^{-1}\mathcal{Z}_2} + \Phi^{\mathrm{TF},\beta}_{Z^{1/3}\mathcal{R}_1,Z^{-1}\mathcal{Z}_1})\Xi(Z^{1/3}\cdot)\end{aligned} \tag{90}$$

so we are led to consider the following problem of singular perturbation of the Laplacian:

$$\mathcal{M}(h, W) := \mathrm{Tr}[-h^2\Delta - W]_-;\ h = Z^{-1/3} \tag{91}$$

We now give the fundamental theorem on this section:

Theorem 5 (Good part semiclasssics). *The quantity $\mathcal{M}(h, W)$ has the following asymptotical behaviour:*

$$|\mathcal{M}(h, W) - \frac{1}{15\pi}h^{-3}\int W^{5/2} + \frac{1}{8}h^{-2}\sum_{j=M_1+1}^{M}(\frac{Z_j}{Z})^2| \leq Ch^{-1-\delta}M \tag{92}$$

where δ is some absolute positive constant ($\delta = \frac{9}{17}$ could do) and C is a finite constant only depending on A.

To prove Theorem 5 we shall distinguish between the region of the points in $\mathbb{R}^3$ which are far away from any nuclei, which, given the rescaling we just made and the fact we got rid of the 'bad' nuclei, means we are looking at points whose distance to the nuclei is bounded away zero by fixed positive number (namely, the number μ obtained in the previous section) and its complement. Also, since most of the semiclassical estimates are already avaliable in the litterature, I will repeteadly refer to the papers of A.V.Sobolev [30, 31, 32] and to the work of V.Ivrii and I.M.Sigal [16].

Proof of Theorem 5. The potential W is everywhere regular with the exception of the set $\{Z^{1/3}R_j\}_{M_1+1}^{M}$ where it has coulombic singularities of strenght $Z^{-1}Z_j$. Moreover, by the reduction made in section 3, all those singularities are separated one another by a distance μ (at least). Our first step shall be to isolate those by means of a suitable partition of unity and then to use 'local trace estimates' in the spirit of the work of V.Ivrii&I.M.Sigal [16] and A.V.Sobolev [30, 31, 32].

-. *Step 1 (Construction of a partition of unity):*

This step will be very similar to the one in section 3 of constructing another partition of unity: we fix a function $\Psi \in C_c^\infty(\mathbb{R}^3)$ such that:

i. $0 \leq \Psi \leq 1$, $\Psi = 1$ if $|x| \leq \frac{\mu}{8}$ and $\Psi = 0$ if $|x| \geq \frac{\mu}{4}$.

ii. $\|\nabla\Psi\|_\infty \leq \frac{C}{\mu}$ with C independent of μ.

Now the partition of unity we shall take is given by

$$\left\{ \begin{array}{lcl} \Upsilon_j & = & \Psi(\cdot - Z^{1/3}R_{j+M_1});\ j = 1, \ldots, M - M_1 \\ \Upsilon_0 & = & 1 - \sum_{j=1}^{M} \Upsilon_j \end{array} \right. \tag{93}$$

-. *Step 2 (Local trace estimates):*

Notice that the supports of $\Upsilon_1, \ldots, \Upsilon_{M-M_1}$ are mutually disjoint. With this partition of unity we just constructed we can split $\mathcal{M}(h, W)$:

$$\left\{ \begin{array}{rcl} \mathcal{M}(h, W) & = & \sum_{j=0}^{M-M_1} \mathcal{M}(h, W, \Upsilon_j) \\ \mathcal{M}(h, W, \Upsilon_j) & := & \mathrm{Tr}[\Upsilon_j(-h^2\Delta - W)]_- \end{array} \right. \tag{94}$$

In the support of $\Xi(Z^{1/3}\cdot)$ we have, by the results of section 2 the global estimates

$$\left\{ \begin{array}{lcl} |\partial^\alpha \Phi^{\mathrm{TF},\beta}_{Z^{1/3}\mathcal{R}_1, Z^{-1}\mathcal{Z}_1}(x)| & \leq & C_\alpha \rho_1(x)^{-1-|\alpha|}\langle\rho_1(x)\rangle^{-3} \\ |\partial^\alpha \Phi^{\mathrm{TF}}_{Z^{1/3}\mathcal{R}_2, Z^{-1}\mathcal{Z}_2}(x)| & \leq & C_\alpha \rho_2(x)^{-1-|\alpha|}\langle\rho_2(x)\rangle^{-3} \end{array} \right. \tag{95}$$

with

$$\left\{ \begin{array}{rcl} \rho_1(x) & := & \min\{|x - R_j| : j = 1, \ldots, M_1\} \\ \rho_2(x) & := & \min\{|x - R_j| : j = M_1 + 1, \ldots, M\} \\ \rho(x) & := & \min\{|x - R_j| : j = 1, \ldots, M\} \end{array} \right. \tag{96}$$

Notice that $\rho(x) = \min\{\rho_1(x), \rho_2(x)\}$ As a result we get the global estimate

$$|\partial^\alpha W(x)| \leq C_\alpha\, \Xi(Z^{1/3}x)\rho(x)^{-1-|\alpha|}\langle\rho(x)\rangle^{-3} \tag{97}$$

which means we are in position to apply the *Multiscale Method* first developed by V.Ivrii and extended in the references of A.V.Sobolev.

Step 3: Estimating the regular part of W:

The zeroth term in (94) is the easiest to handle, because it has no singularities of the potential. Therefore the results (Theorem 5.2 of [31]) can be directly applied to it: Call

$$\left\{ \begin{array}{rcl} f(x) & := & (\rho(x)^{-2}\langle\rho(x)\rangle^{-6} + h^2)^{1/4} \\ l(x) & := & (\sigma^2\rho(x)^2 + h)^{1/2};\ 0<\sigma<1/2 \end{array} \right. \tag{98}$$

to be chosen later. We have to break up again this piece as $\mathcal{M}(h,W,\Upsilon_0) = \mathcal{M}(h,W,\Upsilon_{0,h}) + \mathcal{M}(h,W,\upsilon_0)$ where $\Upsilon_{0,h}$ is supported in $\cap_{j=1}^M\{x:\mu\le|x-R_j|\le h^{-1}: j=1,\dots,M\}$, equals one in $\cap_{j=1}^M\{x:\mu\le|x-R_j|\le\frac{1}{2}h^{-1}:j=1,\dots,M\}$ and is bounded along together with all its derivatives uniformly in M (this will be justified later on). As $\rho(x)$ is given as the minimun of the Lipschitz functions $x\mapsto|x-Z^{1/3}R_j|$ all having the same Lipschitz constant (namely, 1), the same property holds for ρ and an easy calculation yields the bounds for any $x\in\operatorname{supp}\Upsilon_{0,h}$ and $0<h\le h_0$ for $h_0>0$ small enough (but independent of M, so this only amounts to take the parameter Z big enough)

$$\left\{ \begin{array}{c} (1-2\sigma)\rho(y)\le\rho(x)\le(1+2\sigma)\rho(y);\quad x\in B_{l(y)}(y) \\ (1+2\sigma)^{-2}f(y)\le f(x)\le(1-2\sigma)^{-2}f(y);\quad x\in B_{l(y)}(y) \end{array} \right. \tag{99}$$

(where in (99) we have taken into account that $\frac{h}{\rho(y)}\le\frac{8h}{\mu}$ for $y\in\operatorname{supp}\Upsilon_0$ and $h\mapsto 0+$) meaning that ρ, f are functions of *slow variation*. Moreover, for any $|\alpha|\ge 1$, the derivatives $\partial^\alpha\Upsilon_{0,h}$ are in $L^\infty(\mathbb{R}^3)$ uniformly in the number of nuclei M and are supported in

$$\bigcup_{j=1}^M\left\{x:\frac{\mu}{8}\le|x-Z^{1/3}R_j|\le\frac{\mu}{4}\text{ or }\frac{h^{-1}}{2}\le|x-Z^{1/3}R_j|\le h^{-1};j=1,\dots,M\right\}$$

Therefore, the bounds

$$|\partial^\alpha\Upsilon_0(x)|\le C_\alpha l(x)^{-|\alpha|} \tag{100}$$

trivially holds. Now, we have to take γ sufficiently small such that if we take

$$\mathcal{D}=\bigcup_{j=1}^M\{x:\gamma\mu\le|x-R_j|\le\gamma^{-1}h^{-1}\} \tag{101}$$

the following inclusion holds:

$$\bigcup_{x\in\mathcal{D}:B_{l(x)}(x)\cap\operatorname{supp}\Upsilon_0\neq\emptyset} B_{8l(x)}(x)\subset\mathcal{D} \tag{102}$$

The choices $\sigma = \frac{7}{56}\,(< \frac{1}{8})$ and $\gamma = 1 - 8\sigma$ are fine, since

i. If $x \in \mathcal{D} : B_{l(x)}(x) \cap \operatorname{supp} \Upsilon_0 \neq \emptyset$, $x \in \operatorname{supp} \Upsilon_0$, $|x' - x| \leq 8l(x)$ and $x \in D_i$ (Voronoi cell of the point $Z^{1/3}Z_i$, we have, for $j = 1, \ldots, M$

$$\begin{aligned} |x' - Z^{1/3}R_j| &\geq |x - Z^{1/3}R_j| - |x - x'| \\ &\geq |x - Z^{1/3}R_i| - 8\sigma|x - Z^{1/3}R_i| \text{ since } |x - x'| \leq 8l(x) = 8\sigma|x - Z^{1/3}R_i| \\ &\geq (1 - 8\sigma)\,|x - R_i| \qquad (103) \\ &\geq (1 - 8\sigma)\,\frac{\mu}{8} = \gamma\mu \end{aligned}$$

Similarly

$$\begin{aligned} |x' - Z^{1/3}R_j| &\leq |x - Z^{1/3}R_j| + |x - x'| \\ &\leq (1 + 8\sigma\gamma^{-1})h^{-1} \qquad (104) \\ &= \frac{1 + 56\sigma}{1 - 8\sigma}h^{-1} < \gamma^{-1}h^{-1} \end{aligned}$$

ii. If $x \in \mathcal{D} : B_{l(x)}(x) \cap \operatorname{supp} \Upsilon_0 \neq \emptyset$, $x \notin \operatorname{supp} \Upsilon_0$, $|x' - x| \leq 8l(x)$ and $x \in D_i$, we have, for $|x' - x| \leq 8l(x)$ and $j = 1, \ldots, M$ and taking $y \in B_{l(x)}(x) \cap \operatorname{supp} \Upsilon_0$

$$\begin{aligned} |x' - R_j| &\geq |x - R_j| - |y - x| - |x - x'| \\ &\geq \frac{\mu}{8} - 2l(x) \\ &\geq \frac{\mu}{8} - \frac{\sigma}{4}\mu \text{ since } l(x) \leq \sigma|x - R_i| < \frac{\sigma}{8}\mu \qquad (105) \\ &> \frac{3}{4}\mu > \gamma\mu \end{aligned}$$

iii. Let $F : \mathbb{R} \times \mathbb{R}^3 \mapsto \mathbb{R}_+;\ (t, x) \mapsto t + |x|^2$. There is a 'non-critical' condition that looks as follows: For some $\omega > 0$ the next condition is satisfied:

$$F\left(|W(x)| + h\frac{f(x)}{l(x)}, \frac{l(x)}{f(x)}\nabla W(x)\right) \geq \omega f(x)^2 \qquad (106)$$

Condition (106) is fulfilled because of the estimate from below provided by Theorem 4. Finally the supplementary condition on the scale functions $f(x)l(x) \geq h$ is also trivially satisfied.

As a consequence, all the hypothesis of Theorem 5.2 of [31] are satisfied and applying that Theorem we get

$$
\begin{aligned}
|\mathcal{M}(h,W,\Upsilon_{0,h}) \;\; &- \;\; \frac{1}{15\pi^2}h^{-3}\int \Upsilon_{0,h}W^{5/2}| \\
&\le \; C\int_{\mathcal{D}} f(x)^2\frac{f(x)l(x)}{h}l(x)^{-3}\,dx \\
&\le \; C\,h^{-1}\int_{\mathcal{D}}(\rho(x)^{-2}\langle\rho(x)\rangle^{-6}+h^2)^{3/4}((\rho(x)^2+h^2)^{-1}\,dx \\
&\le \; C\,h^{-1}\sum_{j=1}^{M}\int_{D_j\cap\mathcal{D}}(\rho(x)^{-3/2}\langle\rho(x)\rangle^{-9/2}+h)\rho(x)^{-2}\,dx \quad (107) \\
&\le \; C\,h^{-1}\sum_{j=1}^{M}\int_{\gamma\mu\le|x|}|x|^{-7/2}\,dx+\sum_{j=1}^{M}\int_{|x|\le\gamma^{-1}h^{-1}}|x|^{-2}\,dx \\
&\le \; Ch^{-1}M+Ch^{-1}M \\
&\le \; Ch^{-1}M;\;\; 0<h\le 1
\end{aligned}
$$

for some finite absolute C independent of $h>0$ and. To control the other piece of $\mathcal{M}(h,W,\Upsilon_0)$, namely, $\mathcal{M}(h,W,v_0)$, we shall just use the Lieb-Thirring inequality and we get

$$
\begin{aligned}
\mathcal{M}(h,W,v_0) \;\; &\le \;\; \mathrm{Tr}\,[v_0(-h^2\Delta-W)]_- \\
&\le \;\; h^2\mathrm{Tr}\,(-\Delta-h^{-2}\chi_{\mathrm{supp}\,v_0}W)_- \\
&\le \;\; Kh^{-3}\int_{x:\rho(x)\ge\frac{1}{2h}}\rho(x)^{5/2}\,dx \qquad (108) \\
&\le \;\; Ch^{-3}\sum_{j=1}^{M}\int_{x:|x-Z^{1/3}R_j|\ge\frac{1}{2h}}|x-Z^{1/3}R_j|^{-6}\,dx \\
&\le \;\; CM
\end{aligned}
$$

and therefore it is very small compared to the error coming from the term $\mathcal{M}(h,W,\Upsilon_{0,h})$, and so, putting together estimates (107) and (108) we get

$$
|\mathcal{M}(h,W,\Upsilon_0)-\frac{1}{15\pi^2}h^{-3}\int\Upsilon_0W^{5/2}|\le Ch^{-1}M \tag{109}
$$

It remains to consider the other terms of the sum in (94). The Scott terms shall come entirely from them. In order to study those terms, we note that for $x\in\mathrm{supp}\,\Upsilon_i;\;\; M_1\le i\le M$ we can write

$$
W(x)=\varphi(\lambda_i(x-Z^{1/3}R_i))+w_i(x);\;\; \lambda_i:=\frac{Z_i}{Z} \tag{110}
$$

where $\varphi=\Phi^{\mathrm{TF}}_{0,1}$ and $w_i\in C^\infty(B_{\frac{\mu}{4}}(Z^{1/3}R_i))$ is bounded along together with any of its derivatives uniformly in M. We can use this information to get estimates on local traces firstly for a purely coulombic potential near its singularity

Step 4: Estimating the singularities of W:

Here we shall consider first spectral characteristics of coulombic potentials and the analysis of this problem, suitably modified, would yield the result for the full TF potential of a configuration of uniformly separated nuclei. So, to begin with, we consider the following result:

Lemma 8 (Semiclassics for the Coulomb potential). *Consider we are given $\psi \in C_c^\infty(B_r(0))$ ($0 < r \leq 1$) and $s > 0$ such that $\psi = 1$ if $|x| \leq r/2$ and ψ satisfies estimates of the kind $\|\partial^\alpha \psi\|_\infty \leq C_\alpha r^{-|\alpha|}, \forall \alpha \in \mathbb{N}^3$. Then we have*

$$\begin{aligned} |\mathcal{M}(h,\psi) &- \frac{1}{15\pi^2} h^{-3} \int \psi(x) \left(\frac{1}{|x|} - s\right)_+^{5/2} dx + \frac{1}{8} h^{-2}| \leq \\ & C(s^{-1/2} + r^{-1/2}) h^{-1};\ 0 < h \leq 1 \end{aligned} \tag{111}$$

where $\mathcal{M}(h,\psi) := \mathrm{Tr}\,[\psi(-h^2\Delta - \frac{1}{|x|} + s)_-]$ and the remainder estimate is uniform in ψ in the sense that only depends on the constants C_α above.

Proof. Call $\mathcal{M}(h) := \mathcal{M}(h,1)$. Then,

$$\mathcal{M}(h,\psi) = \mathcal{M}(h) - \mathcal{M}(h, 1-\psi) \tag{112}$$

Using Multiscale Analysis like in Step 2 above, we get

$$\begin{aligned} |\mathcal{M}(h,1-\psi) &- \frac{1}{15\pi^2} h^{-3} \int (1-\psi(x)) \left(\frac{1}{|x|} - s\right)_+^{5/2} dx| \leq CI \\ I &= \int_{\gamma r \leq |x| \leq \gamma^{-1}} |x|^{-7/2}\, dx \\ &\leq Cr^{-1/2} h^{-1};\ 0 < h \leq 1 \end{aligned} \tag{113}$$

The point now is that the quantity $\mathcal{M}(h)$ (i.e, the sum of eigenvalues less than $-s$ of a hydrogenic atom) can be exactly computed:

Consider the Hamiltonian $H := -h^2\Delta - \left(\frac{1}{|x|} - s\right)$. Its eigenvalues are

$$\lambda_n = -\frac{1}{4h^2n^2} + s;\ n = 1, 2, \ldots;\ \text{multiplicity} = n^2 \tag{114}$$

We have the formula

$$S_m := \sum_{n=1}^{m} n^2 = \frac{1}{3}m^3 + \frac{1}{2}m^2 + \frac{1}{6}m \tag{115}$$

and from (114) follows

$$\lambda_n \leq 0 \Leftrightarrow n \leq m = \left[\frac{1}{2hs^{1/2}}\right] \tag{116}$$

Write $\alpha = (2hs^{1/2})^{-1} - m \in [0,1)$. Then

$$\begin{aligned}
\operatorname{Tr}\left[-h^2\Delta - \left(\frac{1}{|x|} - s\right)\right]_- &= \sum_{n=1}^{m}\left(\frac{1}{4h^2n^2} - s\right)n^2 \\
&= \frac{1}{4h^2}m - sS_m \\
&= \frac{1}{4h^2}((2hs^{1/2})^{-1} - \alpha) - \frac{1}{24s^{1/2}}h^{-3} \qquad (117)\\
&\quad - \left(\frac{1}{8} - \frac{\alpha}{4}\right)h^{-2} + \mathcal{O}(s^{-1/2}h^{-1}) \\
&= -\frac{1}{12s^{1/2}}h^{-3} + \frac{1}{8}h^{-2} + \mathcal{O}(s^{-1/2}h^{-1})
\end{aligned}$$

On the other hand, we can compute

$$\begin{aligned}
\int \left(\frac{1}{|x|} - s\right)_+^{5/2} dx &= 4\pi s^{-1/2}\int_0^1 t^{-1/2}(1-t)^{5/2}\,dt \\
&= 4\pi s^{-1/2} B\left(\frac{1}{2}, \frac{7}{2}\right) \qquad (118)\\
&= 4\pi s^{-1/2}\frac{\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{7}{2}\right)}{\Gamma(4)} \\
&= \frac{15\pi^2}{12s^{1/2}}
\end{aligned}$$

so we can write

$$\begin{aligned}
\operatorname{Tr}\left[-h^2\Delta - \left(\frac{1}{|x|} - s\right)\right]_- &= -\frac{1}{15\pi^2}h^{-3}\int\left(\frac{1}{|x|} - s\right)_+^{5/2} dx \\
&\quad + \frac{1}{8}h^{-2} + \mathcal{O}(s^{-1/2}h^{-1}) \qquad (119)
\end{aligned}$$

Substracting (119) from (113) we get (111). □

Lemma 9 (Semiclassics for a regular perturbation of TF potential). *Consider we are given $\psi \in C_c^\infty(B_1(0))$ such that $\psi = 1$ if $|x| \le 1/2$ and $w \in C_c^\infty(B_1(0))$ such that $\forall \alpha \in \mathbb{N}^3$, $\|\partial^\alpha\psi\|_\infty$, $\|\partial^\alpha w\|_\infty \le C_\alpha$. Then we have, for $\delta = 9/17$*

$$|\mathcal{M}(h, w, \psi) - \frac{1}{15\pi^2}h^{-3}\int \psi(\varphi + w)^{5/2} + \frac{1}{8}h^{-2}| \le Ch^{-2+\delta}; 0 < h \le 1 \qquad (120)$$

where the remainder estimate is uniform in w in the sense that only depends on the constants C_α above.

We shall defer for a moment the proof of Lemma 9, but note that Theorem 5 inmediately follows from it and the estimate (109), since by a shift and a rescaling (which does not affect the uniformity of the estimates, given that $1 \leq \lambda_i = \frac{Z_i}{Z} \leq A$) we get

$$\begin{aligned} |\mathcal{M}(h, W, \Upsilon_i) &- \frac{1}{15\pi^2} h^{-3} \int \Upsilon_i(x)(\varphi(\lambda_i(x - Z^{1/3}R_i)) + w(x))^{5/2}\,dx + \frac{1}{8}h^{-2}| \\ &\leq Ch^{-2+\delta};\ 0 < h \leq 1 \end{aligned} \tag{121}$$

and putting together estimate (121), the decomposition of W given in (110) and the decomposition in local traces (94) we get the global trace estimate (92) by collecting estimates. □

Proof of Lemma 9. Given $0 \leq \psi \in C_c^\infty(B_1(0))$ such that $\psi = 1$ if $|x| \leq 1/2$ and call $\psi_r := \psi(r^{-1}\cdot)$, so that ψ_r satisfies estimates of the kind $\|\partial^\alpha \psi_r\|_\infty \leq C_\alpha r^{-|\alpha|}$ and $h^2 \leq r \leq 1$ is to be chosen later.

First we write $\psi = \psi_r + \psi(1 - \psi_r)$ and split the local trace $\mathcal{M}(h, w, \psi)$ as

$$\mathcal{M}(h, w, \psi) = \mathcal{M}(h, w, \psi(1 - \psi_r)) + \mathcal{M}(h, w, \psi_r) = I + II \tag{122}$$

The estimate for the first piece follows directly from the Multiscale Analysis machinery and yields

$$|I - \frac{1}{15\pi^2} h^{-3} \int \psi(1 - \psi_r)(\varphi + w)^{5/2}| \leq Cr^{-1/2}h^{-1};\ h^2 \leq r \leq 1 \tag{123}$$

To estimate the second piece we use the fact that for $|x| \leq r \ll 1$ the total TF potential is well aproximated by the Coulomb one. Recall that from Lemma 3 we can write, recalling the remark after the proof of Lemma 3, for $|x| \leq \frac{1}{2}$

$$\begin{aligned} \varphi(x) + w(x) &= \left(\frac{1}{|x|} - k\right) + \mu(x) + w(x) \\ |\partial^\alpha \mu(x)| &\leq C_\alpha |x|^{1/2 - |\alpha|} \\ \mu(x) &\leq 0 \\ \|\partial^\alpha w\|_\infty &\leq C_\alpha \\ 0 &\leq w \leq c < \infty;\ c \text{ absolute} \end{aligned} \tag{124}$$

Let us define

$$\left\{ \begin{aligned} w_r &:= \operatorname{sup\,ess}_{|x| \leq r} w(x) \\ \nu_r &:= \operatorname{sup\,ess}_{|x| \leq r} |\nu(x)| \end{aligned} \right. \tag{125}$$

For $0 < r \leq 1$, we have $0 \leq w_r, \nu_r \leq C$ for some absolute C. We have the operator inequalities

$$\psi_r^{1/2}(-h^2\Delta - V - w_r)\psi_r^{1/2} \leq \psi_r^{1/2}(-h^2\Delta - \varphi - w)\psi_r^{1/2} \leq \psi_r^{1/2}(-h^2\Delta - V + \nu_r)\psi_r^{1/2} \tag{126}$$

Since $A \leq B$ implies $[A]_- \geq [B]_-$ and the trace is a functional operator monotone, we get

$$M(h, -w_r, \psi_r) \geq \mathcal{M}(h, w, \psi_r) \geq M(h, \nu_r, \psi_r) \tag{127}$$

where

$$M(h, \nu, \psi) := \mathrm{Tr}\,[\psi(-h^2\Delta - V + \nu)_-];\;\; V(x) = \frac{1}{|x|} - k \tag{128}$$

We want to compute $M(h, \nu, \psi_r)$ for $|\nu| \leq C$. By the Lieb-Thirring inequality

$$\begin{aligned} M(h, \nu, \psi_r) &\leq M(h, \nu_-, \psi_r) \\ &\leq \mathrm{Tr}\,[\psi_r(-h^2(1-\epsilon)\Delta - V)_-] + \mathrm{Tr}\,[\psi_r(-h^2\epsilon\Delta - \nu_-)_-];\;\; 0 < \epsilon < 1 \\ &= M(h(1-\epsilon)^{1/2}, 0, \psi_r) + \mathrm{Tr}\,[\psi(-h^2\epsilon\Delta - \nu_-\psi_r)_-] \qquad (129) \\ &\leq M(h(1-\epsilon)^{1/2}, 0, \psi_r) + Kh^{-3}\epsilon^{-3/2}r^3\nu_-^{5/2} \end{aligned}$$

We have, by Lemma 8

$$M(h, \nu_r, \psi_r) = \frac{1}{15\pi^2}h^{-3}\int \psi_r(x)\left(\frac{1}{|x|} - k - \nu_r\right)_+^{5/2} dx - \frac{1}{8}h^{-2} + \mathcal{O}(r^{-1/2}h^{-1}) \tag{130}$$

Also we can estimate

$$\begin{aligned} 0 &\leq \int \psi_r(x)\left(\frac{1}{|x|} - k\right)_+^{5/2} dx - \int \psi_r(x)\left(\frac{1}{|x|} - k - \nu_r\right)_+^{5/2} dx \\ &\leq \int_{|x|\leq r}\left(\frac{1}{|x|} - k - \nu_r\right)_+^{5/2}\left[\left(1 + \frac{\nu_r}{\frac{1}{|x|} - k - \nu_r}\right)^{5/2} - 1\right] dx \qquad (131) \\ &\leq K\nu_r\int_{|x|\leq r}|x|^{-3/2}\,dx \\ &\leq Cr^{3/2} \end{aligned}$$

From (130) and (131) we get

$$M(h, \nu_r, \psi_r) = \frac{1}{15\pi^2}h^{-3}\int \psi_r(x)\left(\frac{1}{|x|} - k\right)_+^{5/2} dx - \frac{1}{8}h^{-2} + \mathcal{O}(r^{-1/2}h^{-1} + r^{3/2}h^{-3}) \tag{132}$$

Analogously, by (129) we can write the estimate

$$\begin{aligned} M(h, w_r, \psi_r) &= \frac{1}{15\pi^2}h^{-3}\int \psi_r(x)\left(\frac{1}{|x|} - k\right)_+^{5/2} dx - \frac{1}{8}h^{-2} \\ &\quad + \mathcal{O}(r^{-1/2}h^{-1} + \epsilon^{-3/2}r^3h^{-3} + \epsilon h^{-3}) \qquad (133) \end{aligned}$$

we can estimate the difference of weylian terms of $M(h,0,\psi_r)$ and $\mathcal{M}(h,w,\psi_r)$ as in (131):

$$\begin{aligned}|\int \psi_r(x)(\varphi+w)^{5/2}\,dx \quad &- \quad \int \psi_r(x)\left(\frac{1}{|x|}-k-\nu_r\right)_+^{5/2} dx| \\ &\leq \quad Kr^{3/2} \qquad (134)\end{aligned}$$

Putting together the decomposition (122) and estimates (123); (127), (132), (133), (134) we get

$$\begin{aligned}\mathcal{M}(h,w,\psi) \quad &= \quad \frac{1}{15\pi^2}h^{-3}\int \psi(x)(\varphi+w)^{5/2}\,dx - \frac{1}{8}h^{-2} \\ &\quad +\mathcal{O}(r^{-1/2}h^{-1}+\epsilon^{-3/2}r^3h^{-3}+\epsilon h^{-3}+r^{3/2}h^{-3}) \qquad (135)\end{aligned}$$

Taking $\epsilon = h^\alpha$, $r = h^\beta$ and $\epsilon^{-3/2}r^3h^{-3} = r^{-1/2}h^{-1} = \epsilon h^{-3}$ we get $\epsilon = h^{24/17} \ll r = h^{20/17}$ and the final estimate

$$\mathcal{M}(h,w,\psi) \quad = \quad \frac{1}{15\pi^2}h^{-3}\int \psi(x)(\varphi+w)^{5/2}\,dx - \frac{1}{8}h^{-2} + \mathcal{O}(h^{-1-9/17}) \qquad (136)$$

which concludes the proof. $\square$

As a Corollary of Theorem 5 we can write the next lower bound for the RHF energy:

Corollary 1 (RHF energy of a good configuration: lower bound). *Assume that $\mathcal{R}$, $\mathcal{Z}$ is a configuration of nuclear charges fulfilling the hypothesis of Th. 2. Then the following lower bound for the RHF energy holds:*

$$\begin{aligned}E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \quad &\geq \quad -\mathrm{Tr}\,[-\Delta-\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}]_- - D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) + U_{\mathcal{R},\mathcal{Z}} \qquad (137) \\ &\geq \quad -\frac{1}{15\pi^2}\int (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2} - D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) + U_{\mathcal{R},\mathcal{Z}} - CMZ^{2-\delta}\end{aligned}$$

($\delta = \frac{9}{51}$ could do).

Proof. Proof of Corollary 1 follows inmediately from Theorem 2 by taking in it $\mathcal{R}_1 = \emptyset$, $h = Z^{-1/3}$, $W = \Phi^{\mathrm{TF}}_{Z^{1/3}\mathcal{R},Z^{-1}\mathcal{Z}}$ and applying the scaling properties of TF potential and density as given by eq. (12) to the final result. $\square$

I am going to conclude this section with an upper bound for the RHF energy of uniformly separated nuclei which taken together with Theorem 5 yields a complete two-term asymptotics for the RHF energy in such a case.

Theorem 6 (RHF energy of a good configuration: upper bound). *Assume that $\mathcal{R}$, $\mathcal{Z}$ is a configuration of nuclear charges fulfilling the hypothesis of Th. 2. Then the following upper and lower bounds for the RHF energy holds:*

$$0 \leq E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} + \mathrm{Tr}\,[-\Delta-\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}]_- + D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) - U_{\mathcal{R},\mathcal{Z}} \leq CMZ^{2-5/27} \qquad (138)$$

where C is a finite positive constant only depending on μ and A.

Proof. The lower bound (137) is trivial and holds for any configuration. To prove the upper bound. we write down the identity, for any density matrix γ

$$\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) = \mathrm{Tr}\,[(-\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\gamma]_{-} - D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) + U_{\mathcal{R},\mathcal{Z}} + D(\rho_\gamma - \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) \tag{139}$$

Our aim would be to show it is possible to choose γ properly in such a way that

$$D(\rho_\gamma - \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) \leq CMZ^{2-5/27} \tag{140}$$

Since $\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) \geq E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}$, assuming (140) is right the estimate (138) will follow from Lemmas 3, 11, 13 and 14 below, together with the pletora of auxiliary results hanging around them which are presented into the next sections.

The major difficulty in proving (138) is to control the Coulomb norm squared of $\rho_\gamma - \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$, since it is not in principle linear in the number of nuclei M. To overcome this problem we must use cancellation properties of $\rho_\gamma - \rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$, since just by using size estimates of it would not be sufficient to obtain our result (by-the-way, this is the main reason I am not just following here the procedure of [16]). To produce a trial density matrix γ which approximates well enough the energy and besides makes the Coulomb norm of the error term small we shall take one made up of several pieces. This will be done in several steps: (here we assume again we have made a rescaling of our configuration to one such that $\delta_i \geq \mu$ and $1 \leq Z_i \leq A$, all i.)

i. Construction of a partition of unity:

Pick $0 \leq \eta \in C_c^\infty(\overline{B}_1(0))$ with $\int \eta = 1$. Now make out of it an approximation of identity $(\eta_r)_{r>0}$ by the recipe $\eta_r := r^{-3}\eta(r^{-1}\cdot)$ (r shall be some small parameter we shall choose later, depending on h). Take $\zeta_j := \eta_r * \chi_{D_j}$ so that $\sum_{j=1}^M \eta_j = 1$. Moreover the functions η_j have the properties:

$$\begin{cases} \zeta_j(x) = 1 \text{ if } x \in D_j \text{ and } \mathrm{dist}(x, \partial D_j) \geq r \\ \zeta_j(x) = 0 \text{ if } x \notin D_j \text{ and } \mathrm{dist}(x, \partial D_j) \geq r \end{cases} \tag{141}$$

Once we have constructed the partition $\{\eta_j\}_{1\leq j\leq M}$ we shall refine it as follows: fix some radial function $0 \leq \Upsilon \in C_c^\infty(\overline{B}_1(0))$ with the properties

$$\begin{cases} \Upsilon = 1 & \text{if } |x| \leq 1/2 \\ \Upsilon = 0 & \text{if } |x| \geq 3/4 \end{cases}$$

More importantly, we shall impose the following sort of orthogonality conditions on Υ:

$$\int \Delta\Upsilon|\cdot|^{-5/2} = \int \Delta\Upsilon|\cdot|^{-3/2} = \int \Delta\Upsilon|\cdot|^{-1/2} = 0 \tag{142}$$

Consider then $\overline{\Upsilon}_j := \Upsilon(r(\cdot - R_j))$; $j = 1\ldots, M$ (r is the same as above). Now take, for $M+1 \leq j \leq 2M$, $\Upsilon_j = \zeta_j - \overline{\Upsilon}_{j-M}$. Next, following an standard procedure, we make out the partition of unity $\{\overline{\Upsilon}_j\}_{1\leq j\leq 2M}$ another one, denoted as

$\{\Upsilon_j\}_{1\le j\le 2M}$ that *squares*, such that $\operatorname{supp}\Upsilon_j = \operatorname{supp}\overline{\Upsilon}_j$ and $\|\nabla\Upsilon_j\| \le C\|\nabla\overline{\Upsilon}_j\|$. In addition, for sufficiently small $r>0$, $\Upsilon_j = \overline{\Upsilon}_j^{1/2}$; $j=1,\ldots,M$, so the partition of unity $\{\Upsilon_j\}_{1\le j\le 2M}$ is such that

$$\int \Delta\Upsilon_j^2|\cdot|^{-5/2} = \int \Delta\Upsilon_j^2|\cdot|^{-3/2} = \int \Delta\Upsilon_j^2|\cdot|^{-1/2} = 0 \tag{143}$$

Moreorer, with $\xi_j := (\Upsilon_j^2 + \Upsilon_{j+M}^2)^{1/2}$; $j=1,\ldots,M$, $\{\xi_j^2\}_{j=1}^M$ is also another partition of unity. This latter one is such that

$$\begin{cases} \xi_j(x) = 1 \text{ if } x\in D_j \text{ and } \operatorname{dist}(x,\partial D_j)\ge r \\ \xi_j(x) = 0 \text{ if } x\notin D_j \text{ and } \operatorname{dist}(x,\partial D_j)\ge r \end{cases}$$

Only some words about the conditions (142). We shall only convince ourselves that those orthogonality conditions leaves us a lot of freedom. I am not going to present here an explicit example of such a function, but leave instead this as an instructive exercise for the interested reader.

ii. Coherent states:

We shall construct our trial density matrix by patching together the projection into the negative part of the spectrum of $-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$ with another pieces made up of coherent states, These coherent states are given as follows:

Pick some function $g\in H^1(\mathbb{R}^d)$ which is spherically symmetric and with $\int_{\mathbb{R}^d}|g|^2 = 1$. Introduce a parameter $r>0$ and the family of functions $g_r := r^{-d/2}g(r^{-1}\cdot)$. The coherent states we shall use are then given by

$$f_{p,s;r}(x) = g_r(x-s)\mathrm{e}^{ip\cdot x};\ p,s\in\mathbb{R}^d \tag{144}$$

and let us introduce the projections

$$\pi_{p,s;r} = \langle f_{p,s;r},\cdot\rangle f_{p,s;r} \tag{145}$$

Then, for any $m\in L^2(\mathbb{R}^d)$ a computation gives

$$\begin{aligned} \|m\|^2 &= (2\pi)^{-d}\iint_{\mathbb{R}^d\times\mathbb{R}^d}\langle m,\pi_{p,s;r}m\rangle dp\,ds \\ \int_{\mathbb{R}^3}|\nabla m(x)|^2dx &= (2\pi)^{-d}\iint_{\mathbb{R}^d\times\mathbb{R}^d}|p|^2\langle m,\pi_{p,s;r}m\rangle dp\,ds - s^{-2}\|m\|^2\|g^2\|^2 \\ \int_{\mathbb{R}^3}|m(x)|^2\phi_r(x)dx &= (2\pi)^{-d}\iint_{\mathbb{R}^d\times\mathbb{R}^d}\phi(s)\langle m,\pi_{p,s;r}m\rangle dp\,ds \qquad (146) \\ (2\pi)^{-d}\iint_{\mathbb{R}^d\times\mathbb{R}^d}\pi_{p,s;r}dp\,ds &= \mathbf{I} \text{ on } L^2(\mathbb{R}^d) \text{ (closure relation)} \end{aligned}$$

where

$$\begin{cases} \phi_r &= h_r * \phi \\ h_r &:= |g_r|^2 \end{cases}$$

($(h_r)_{r>0}$ is an standard approximation of identity). For all density matrices γ we have the following formulas generalizing (146):

$$\begin{aligned}
\mathrm{Tr}\,[(-\Delta)\gamma] &= (2\pi)^{-d} \iint_{\mathbb{R}^d\times\mathbb{R}^d} \mathrm{Tr}\,[\pi_{p,s;r}\gamma]|p|^2\,dp\,ds - s^{-2}\|g^2\|^2 \mathrm{Tr}\,\gamma \\
\mathrm{Tr}\,[(h_s * V)\gamma] &= (2\pi)^{-d} \iint_{\mathbb{R}^d\times\mathbb{R}^d} \mathrm{Tr}\,[\pi_{p,s;r}\gamma] V(s)\,dp\,ds \qquad (147)
\end{aligned}$$

iii. Construction of a trial density matrix

Consider, for $d = 3$,

$$\gamma := (2\pi)^{-3} \iint_{h^2|p|^2 - V(s)\le 0} \pi_{p,s;r}\,dp\,ds$$

By the closure relation given in eq. (146), we see that γ is a density matrix. Its density is obtained by restricting its Schwarz kernel to the diagonal:

$$\begin{aligned}
\rho_\gamma(x) &= (2\pi)^{-d} \iint_{h^2|p|^2 - V(s)\le 0} \pi_{p,s;r}(x,x)\,dp\,ds \\
&= (2\pi)^{-d} \iint_{h^2|p|^2 - V(s)\le 0} h_r(x-s)\,dp\,ds \\
&= \frac{|S^{d-1}|}{d(2\pi h)^d} h_r * V_+(x)^{d/2} \qquad (148) \\
&= \frac{1}{6\pi^2 h^3} h_r * V_+(x)^{3/2} \text{ (for } d=3)
\end{aligned}$$

We can compute also

$$\begin{aligned}
\mathrm{Tr}\,[(-\Delta)\pi_{p,s;r}] &= \int_{\mathbb{R}^d} |\nabla f_{p,s;r}(x)|^2\,dx \\
&= |p|^2 + r^{-2}\|\nabla g\|^2 \qquad (149)
\end{aligned}$$

Using (149) we can compute (in the next, $d = 3$)

$$\mathrm{Tr}\,[(-h^2\Delta)\gamma] = \frac{1}{10\pi^2 h^3} \int_{\mathbb{R}^3} V_+(x)^{5/2}\,dx + \frac{\|\nabla g\|^2}{6\pi^2 r^2 h} \int_{\mathbb{R}^3} V_+(x)^{3/2}\,dx \qquad (150)$$

Given a function θ such that $0 \le \theta \le 1$, consider $\gamma_\theta := \theta\gamma\theta$. Then γ_θ is a density matrix if γ is. Its density is $\rho_{\gamma_\theta} = \theta^2 \rho_\gamma$. Then we easily compute, with γ as above,

$$\mathrm{Tr}\,[V\gamma_\theta] = \frac{1}{6\pi^2 h^3} \int_{\mathbb{R}^3} \theta^2 V(x) h_r * V_+(x)^{3/2}\,dx \qquad (151)$$

Similarly,

$$\operatorname{Tr}\left[(-\Delta)\gamma_\theta\right] = (2\pi)^{-3} \iint_{h^2|p|^2-V(s)\le 0} \operatorname{Tr}\left[(-\Delta)\theta\pi_{p,s;r}\theta\right] dp\, ds$$

But a calculation yields

$$\begin{aligned} \operatorname{Tr}\left[(-\Delta)\theta\pi_{p,s;r}\theta\right] &= |p|^2 h_r * \theta^2(s) + h_r * [\theta(-\Delta\theta)](s) + r^{-2}\mu_r * \theta^2(s) \\ \mu_r &:= |(\nabla g)_r|^2 \le C h_r \end{aligned} \tag{152}$$

so we obtain

$$\begin{aligned} \operatorname{Tr}\left[(-h^2\Delta)\gamma_\theta\right] &= \frac{1}{10\pi^2 h^3}\int_{\mathbb{R}^3} h_r * \theta^2(x) V_+(x)^{5/2}\, dx \\ &\quad + \frac{1}{6\pi^2 h}\int_{\mathbb{R}^3 h} h_r * [\theta(-\Delta\theta)](x) V_+(x)^{3/2}\, dx \\ &\quad + \frac{1}{6\pi^2 r^2 h}\int_{\mathbb{R}^3} \mu_r * \theta^2(x) V_+(x)^{3/2}\, dx \end{aligned} \tag{153}$$

Equations (151) and (153) have both semiclassical character, since the main terms on the r.h.s of both identities converges to weylian expressions as $r \to 0$. Now we make this more explicit when $V = \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}$. Next Lemma is a convenient tool for that business:

Lemma 10. *[Regularization of a C^{3+1} function] Consider an approximation of identity $(h_r)_{r>0}$; $h_r = r^{-d}h(r^{-1}\cdot)$ with the properties:*
i. $h \ge 0$ is radial.
ii. h is supported in $\overline{B}_1(0)$.
iii. $\int h = 1$.
Now, given a function $V \in C^{3+1}(\mathbb{R}^d)$. Then, with $K := K(h) = \frac{1}{2}\int h(x)|x|^2\, dx$, the next approximation hols:

$$\|V - h_r * V - K r^2 \Delta V\|_\infty \le C r^4 \max_{|\alpha|=4}\{\|\partial^\alpha V\|_\infty\} \tag{154}$$

Proof. Since $\int h_s = 1$, we can write

$$h_r * V(x) - V(x) = \int h_r(x-y)\left(V(y) - V(x)\right)\, dy \tag{155}$$

We can write down also Taylor's formula in the following way:

$$V(y)-V(x) = \sum_{j=1}^{3}\sum_{|\alpha|=j}\frac{\partial^\alpha V(x)}{j!}(y-x)^\alpha + \frac{1}{3!}\sum_{|\alpha|=4}(y-x)^\alpha \int_0^1 \partial^\alpha V((1-t)x+ty)(1-t)^3\, dt$$

Because of the radial symmetry, $\int h_r(x)x^\alpha\, dx = 0$ if either $|\alpha| = 1,\ 3$ or $\partial^\alpha = \partial^i\partial^j$ with $i \neq j$. Therefore, plugging the Taylor expansion into (155) and taking into account the cancellations just mentioned we get

$$\begin{aligned} h_r * V(x) &= V(x) + Kr^2\Delta V(x) \qquad (156)\\ &+\frac{1}{3!}\sum_{|\alpha|=4}\int_0^1 (1-t)^3\, dt \int dy\, h_r(x-y)(y-x)^\alpha\partial^\alpha V((1-t)x+ty)) \end{aligned}$$

The next estimate holds:

$$\begin{aligned} &\left|\int_0^1 (1-t)^3\, dt \int dy\, h_r(x-y)(y-x)^\alpha\partial^\alpha V((1-t)x+ty))\right| \\ &\qquad\leq \|\partial^\alpha V\|_\infty \left|\int dy\, h_r(x-y)(y-x)^\alpha\right| \\ &\qquad= Cr^4\int h(x)|x^\alpha|\, dx\|\partial^\alpha V\|_\infty \\ &\qquad\leq Cr^4\|\partial^\alpha V\|_\infty \end{aligned}$$

and plugging it into (156) we get (154) $\square$

We can also localize the conclusion of Lemma 10. This is given in next Corollary:

Corollary 2 (Local regularization of a C^{3+1} function). *Assume the conditions of Lemma 10. Then, at a given $x \in \mathbb{R}^d$ the next approximation holds:*

$$|h_r * V(x) - V(x) - Kr^2\Delta V(x)| \leq Cr^4(1+s^{-4})\max_{|\alpha|\leq 4}\left\{\|\partial^\alpha V|_{B_s(x)}\|_\infty\right\} \qquad (157)$$

Proof. Fix some function $\theta \in C_c^\infty(\overline{B}_1(0))$ such that $\theta = 1$ if $|x| \leq 1/2$. With $\theta_{s,x} := \theta(s^{-1}(y-x))$, $h_r * V(x) = h_r * (f\theta_{s,x})(x)$ as long as $r \leq 2s$. Also all the derivatives of $V\theta_{r,x}$ coincide with those of V at x. Writing down Leibnitz's formula

$$\partial^\alpha\left(V\theta_{s,x}\right) = \sum_{\beta\leq\alpha} C_{\alpha,\beta}\left(\partial^\beta\theta_{s,x}\right)\partial^{\alpha-\beta}V$$

so, if $\alpha = 4$ we can estimate

$$|\partial^\alpha\left(V\theta_{s,x}\right)(x)| \leq C(1+s^{-4})\sum_{|\alpha|\leq 4}\|\partial^\alpha V|_{B_s(x)}\|_\infty$$

and the result follows by Lemma 10. $\square$

Now consider the following problem:

We are given a potential W and a function $\theta \in C_c^\infty(\overline{B}_r(0))$, $\theta = 1$ on $\overline{B}_{r/2}(0)$ such that $\theta = 1$ on $\overline{B}_{r/2}(0)$ and $\|\partial^\alpha\theta\|_\infty \leq C_\alpha r^{-|\alpha|}$. Now consider the functional

$$\mathcal{E}_{h,W,\theta}(\gamma) := \mathrm{Tr}\left[(-h^2\Delta - W)\gamma_\theta\right];\ \gamma\ \text{ density matrix} \qquad (158)$$

Define

$$E_{h,W,\theta} := \inf\{\mathcal{E}_{h,W,\theta}(\gamma) : 0 \leq \gamma \leq \mathbf{1}\} \tag{159}$$

Now the following result holds:

Lemma 11 (A localization estimate). *Let $E_{W,\theta}$, W, θ be as above with $W = \varphi_1^{\mathrm{TF}} + w$, where $w \in C^\infty(\overline{B}_\mu(0))$ (μ is some fixed number, i.e, independent of $h > 0$) and $\|\partial^\alpha w\|_\infty \leq C_\alpha$. Fix some $\xi \in C_c^\infty(B_\mu(0))$ such that $0 \leq \xi \leq 1$ and $\xi = 1$ if $|x| \leq \mu/2$ also fulfilling the same kind of estimates as w does. Finally assume $\psi = (1-\theta^2)^{1/2}$ fulfils the same kind of estimates as θ does. Then the next estimate holds for $0 < r \leq \mu/2$:*

$$E_{h,W,\theta} = -\frac{1}{15\pi^2} h^{-3} \int \theta^2 W^{5/2} + \frac{1}{8} h^{-2} + \mathcal{O}(r^{-2}h^{-1}) \tag{160}$$

where C only depens on the constants C_α above. Moreover, we can achieve the estimate (160) by choosing

$$\gamma = \Gamma_\theta;\ \Gamma := \chi_{(-\infty,0]}(-h^2\Delta - \xi^2 W) \tag{161}$$

Remarks:

i.- The final asymptotics in Lemma 11 does not depend at all on the choice of the auxiliar function ξ

ii.- The presence of function ξ estress the fact that in the asymptotics given by eq. (160) only depends on the behaviour of W on a ball around the origin of radius $r' = \mathrm{const}\, r$. The only global information we need is semiboundedness from below of our functional.

Proof. As $0 < r \leq \mu/2$, $\xi = 1$ on the support of θ, $\xi\theta = \theta$ and so we can write, for any density matrix γ,

$$\mathcal{E}_{h,W,\theta}(\gamma) = \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\gamma_\theta].$$

By the cyclicity of the trace we can therefore write

$$\begin{aligned} \mathcal{E}_{h,W,\theta}(\gamma) &= \mathrm{Tr}\,[\theta(-h^2\Delta - \xi^2 W)\theta\gamma] \\ &\geq -\mathrm{Tr}\,[\theta(-h^2\Delta - \xi^2 W)\theta]_- \\ &= -\mathrm{Tr}\,[\theta^2(-h^2\Delta - \xi^2 W)]_- \end{aligned} \tag{162}$$

Also we can decompose, with $A := -h^2\Delta - \xi^2 W$,

$$\theta A \theta = \theta A_+ \theta - \theta A_- \theta \geq -\theta A_- \theta$$

since is easily verified that $\theta A_{+/-}\theta \geq 0$. As a consequence, $(\theta A\theta)_- \leq \theta A_-\theta$ and then

$$-\mathrm{Tr}\,[\theta A \theta]_- \geq -\mathrm{Tr}\,[\theta A_- \theta] = -\mathrm{Tr}\,[\theta^2 A_-] \tag{163}$$

Putting together (162) and (163) we finally obtain the lower bound

$$E_{h,W,\theta} \geq -\mathrm{Tr}\,[\theta^2(-h^2\Delta - \xi^2 W)_-]. \tag{164}$$

In order to obtain a similar upper bound we proceed as follows:

We write down $-\mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)_-] = \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma]$. Then by the IMS formula and taking into account that $\mathrm{Tr}\,\Gamma = N_-(-h^2\Delta - \xi^2 W)$ (the number of negative eigenvalues), we can write

$$\begin{aligned}
-\mathrm{Tr}\,[(-h^2\Delta &- \xi^2 W)_-] = \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma] \\
&= \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\theta] + \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\psi] \\
&\quad -h^2 \int \left(|\nabla\theta|^2 + |\nabla\psi|^2\right)\rho_\Gamma \\
&\geq \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\theta] + \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\psi] \\
&\quad -Cr^{-2}h^2 N_-(-h^2\Delta - \xi^2 W) \\
&\geq \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\theta] + \mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)\Gamma_\psi] \qquad (165)\\
&\quad -Cr^{-2}h^{-1} \int \xi^3 W^{3/2} \text{ (by the CLR estimate)} \\
&\geq E_{h,W,\theta} + E_{h,W,\psi} - Cr^{-2}h^{-1} \int \xi^3 W^{3/2} \\
&\geq E_{h,W,\theta} - \mathrm{Tr}\,[\psi^2(-h^2\Delta - \xi^2 W)_-] - Cr^{-2}h^{-1} \text{ (by (164))}
\end{aligned}$$

From estimate (165) we obtain the upper bound

$$E_{h,W,\theta} \leq -\mathrm{Tr}\,[(-h^2\Delta - \xi^2 W)_-] + \mathrm{Tr}\,[\psi^2(-h^2\Delta - \xi^2 W)_-] + Cr^{-2}h^{-1}. \tag{166}$$

Now we are in position to use the semiclassical asymptotics estimates provided by local trace estimates similar to those of eq. (94) and Lemma 9. Using these results we get

$$\left\{ \begin{array}{lcl} E_{h,W,\theta} & \geq & -\frac{1}{15\pi^2}h^{-3}\int \theta^2 W^{5/2} + \frac{1}{8}h^{-2} + \mathcal{O}(r^{-1/2}h^{-1}) \\ E_{h,W,\theta} & \leq & -\frac{1}{15\pi^2}h^{-3}\int \theta^2 W^{5/2} + \frac{1}{8}h^{-2} + \mathcal{O}(r^{-2}h^{-1}) \end{array} \right. \tag{167}$$

which concludes the proof. □

Lemma 12 (Semiclassics of the projection into the negative estates). *Assume, for a configuration of nuclear charges $\mathcal{R}$, $\mathcal{Z}$ such that $\delta_i \geq \mu$, $1 \leq Z_i \leq Z$ for all i*

$$\gamma := \chi_{(-\infty,0]}\,[-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}]_- \tag{168}$$

Then, with $R(h,x) := \rho_\gamma(x) - \frac{1}{6\pi^2 h^3}\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2}$, the estimate holds:

$$|R(h,x)| \leq \left\{ \begin{array}{rl} Ch^{-3}l(x)^{-3/2}; & l(x) \leq h^{-2} \\ Ch^{-2}l(x)^{-2}\langle l(x)\rangle^{-3}; & h^2 \leq l(x) \leq h^{-1} \\ Cl(x)^{-3}; & l(x) \geq h^{-1} \end{array} \right. \tag{169}$$

where we take

$$\begin{cases} l(x) &= \kappa\rho(x);\ 0<\kappa \text{ small enough} \\ \rho(x) &= \min\{|x-Z^{1/3}R_j| : j=1,\dots,M\}\end{cases}$$

and with the constant C uniform in all the parameters involved

Proof. Lemma 12 is proven also by the Multiscale Analysis machinery of Ivrii&Sigal. More specifically, we use Theorem 10.4 of [16] which in our case at hand yields the result (nevertheless notice that what is stated in Lemma 12 is what really follows from their proof, since their result was stated mistakenly). □

From Lemma 12 we can obtain the following Corollary:

Corollary 3 (Local trace near singularities). *Take $\psi \in C_c^\infty(\overline{B}_r(R_j))$ such that $0\le\psi\le 1$ and $\|\partial^\alpha\psi\|_\infty \le C_\alpha r^{-|\alpha|}$ and $h^2\le r\le\mu$. With γ as in Lemma 12 the following asymptotics holds with some absolute $0\le\delta<1$:*

a.-

$$\mathrm{Tr}\,[(-h^2\Delta-\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\gamma_\psi] = \frac{1}{15\pi^2}h^{-3}\int\psi^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2} - \frac{1}{8}h^{-2}Z_j^2 + \mathcal{O}(h^{-1-\delta}) \quad (170)$$

b.-

$$\mathrm{Tr}\,[\gamma_\psi] = \frac{1}{6\pi^2}h^{-3}\int\psi^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} + \mathcal{O}(h^{-2}r) \quad (171)$$

Proof. Part a.- follows inmediately from Lemma 11. To prove b.- we use Lemma 12 as follows: (recall that $\rho_{\gamma_\psi}=\psi^2\rho_\gamma$)

$$\begin{aligned}\mathrm{Tr}\,[\gamma_\psi] &= \int\psi^2\rho_\gamma \\ &= \int\psi^2\left\{\frac{1}{6\pi^2}h^{-3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} + \left(\rho_\gamma - \frac{1}{6\pi^2h^3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\right)\right\}\end{aligned}$$

and therefore, by Lemma 12

$$\begin{aligned}\left|\mathrm{Tr}\,[\gamma_\psi] - \frac{1}{6\pi^2}h^{-3}\int\psi^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\right| &\le Ch^{-3}\int_{|x|\le h^2}|x|^{-3/2}\,dx + Ch^{-2}\int_{|x|\le r}|x|^{-2}\,dx \\ &\le Ch^{-2}r\end{aligned}$$

□

Now we proceed to construct effectively a good trial density matrix we shall call Γ. This is the content of our next Lemma:

Lemma 13 (Choice of a good trial density matrix). *Given a nuclear configuration $\mathcal{R}, \mathcal{Z}$ such that $1 \le Z_j \le A$ and $\delta_j \ge \mu$ for all j, it is possible to construct a density matrix Γ with the following properties:*

-.*i*

$$\left|\rho_\Gamma(x) - \frac{1}{6\pi^2 h^3}\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2}\right| \le \begin{cases} Ch^{-3}l(x)^{-3/2}; & l(x) \le h^{-2} \\ Ch^{-2}l(x)^{-2}; & h^2 \le l(x) \le \mu \\ Ch^{-2}l(x)^{-6}; & \mu \le l(x) \le h^{-1} \end{cases} \tag{172}$$

-.*ii*

We can write $\rho_\Gamma = \sum_{j=1}^M G_j$, *where* $\operatorname{supp} G_j \subset \operatorname{supp} \xi_j$ *and*

$$\begin{cases} \int G_j &= \frac{1}{6\pi^2 h^3}\int \xi_j^2 (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} \\ & \quad + \frac{Ks^2}{6\pi^2 h^3}\int (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\Delta\xi_j^2 \\ & \\ \int G_j(x_k - (R_j)_k) &= \frac{1}{6\pi^2 h^3}\int \xi_j^2 (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}(x_k - (R_j)_k) \\ & \quad + \frac{Ks^2}{6\pi^2 h^3}\int (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\Delta\xi_j^2(x_k - (R_j)_k) \end{cases} \tag{173}$$

$\forall j = 1, \dots, M \, \forall k = 1, 2, 3$

($\{\xi_j^2\}_{j=1}^M$ is the partition of unity constructed at our first step of the proof of Theorem 6 and K is the constant appearing in Lemma 10).

-.*iii*

$$\operatorname{Tr}\left[(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\Gamma\right] \le -\frac{1}{15\pi^2 h^3}\int (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2} + \frac{1}{8}h^{-2}\sum_{j=1}^M Z_j^2 + Ch^{-1-4/9} \tag{174}$$

Proof. We shall assume from the outset that s and r are chosen in such a way that

$$\begin{cases} s = & o(h^{1/2+\epsilon}) \, \forall \epsilon > 0 \\ r \le & Ch^{\mu}; \ \mu > 0 \end{cases}$$

Then, assuming this is satisfied, we shall first construct Γ satisfying ii. The condition i. would then be fulfilled more or less automatically, and finally we shall make concrete choices of these parameters trying to satisfy condition iii.

We first observe the following fact: assume we are given a collection $\{\gamma_1, \gamma_2\}$ of density matrices and $\{\theta_j^2\}_{j=1}^N$ a partition of unity. Then we can make another density matrix out of them by the recipe $\Gamma = \sum_{j=1}^{N_1}(\gamma_1)_{\theta_j} + \sum_{j=N_1+1}^{M}(\gamma_2)_{\theta_j}$. Now we use this with

$$\begin{cases} \gamma_1 & := \ \chi_{(-\infty,0]}(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) \\ & \\ \gamma_2 & := \ (2\pi)^{-3}\int_{h^2p^2 - W(q) \le 0} \pi_{p,q;s}\, dp\, dp; \quad W = \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^M w_j \end{cases} \tag{175}$$

where in (175) the functions w_j; $j = 1, \dots, M$ are chosen subject to the conditions:

$$\begin{cases} \operatorname{supp} w_j & \subset \ A + R_j; \quad A = \left\{x : \frac{\mu}{9} \le |x| \le \frac{2\mu}{9}\right\} \\ & \\ \|w_j\|_\infty & \le \ Ch^{1+\sigma}; \quad \sigma > 0 \text{ absolute constant} \end{cases}$$

The partition of unity we shall use is $\{\Upsilon_j^2\}_{j=1}^{2M}$, so that we take

$$\Gamma := \sum_{j=1}^{M} (\gamma_1)_{\Upsilon_j} + \sum_{j=M+1}^{2M} (\gamma_2)_{\Upsilon_j} \tag{176}$$

and then

$$\rho_\Gamma = \sum_{j=1}^{M} \Upsilon_j^2 \rho_{\gamma_1} + \sum_{j=M+1}^{2M} \Upsilon_j^2 \rho_{\gamma_2} = \sum_{j=1}^{M} \left(\Upsilon_j^2 \rho_{\gamma_1} + (\xi_j^2 - \Upsilon_j^2)\rho_{\gamma_2}\right) := \sum_{j=1}^{M} G_j \tag{177}$$

Then we have:

$$\begin{aligned}
&\int G_j = \\
&= \int \Upsilon_j^2 \left(\frac{1}{6\pi^2 h^3} (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} + R(h,\cdot) \right) + \frac{1}{6\pi^2 h^3} \int (\xi_j^2 - \Upsilon_j^2) h_s * \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{k=1}^{M} w_k \right)^{3/2} \\
&= \frac{1}{6\pi^2 h^3} \int \Upsilon_j^2 (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} + \frac{1}{6\pi^2 h^3} \int h_s * \left[(\xi_j^2 - \Upsilon_j^2)\right] \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{k=1}^{M} w_k \right)^{3/2} \qquad (178) \\
&+ \frac{1}{6\pi^2 h^3} \int \Upsilon_j^2 (\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} + \frac{1}{6\pi^2 h^3} \int h_s * \left[(\xi_j^2 - \Upsilon_j^2)\right] \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + w_j \right)^{3/2} + \mathcal{O}(h^{-2} r)
\end{aligned}$$

(we have used that supp $h_s * [(\xi_j^2 - \Upsilon_j^2)]$ is only slighty bigger than that of $\xi_j^2 - \Upsilon_j^2$, and therefore only w_j contributes in the sum appearing in (178). Now we use the estimate on the regularization of a function given by Lemma 10 and then we can write, for any $s \leq r/6$, and with $B_j = \{x : r/3 \leq |x - R_j| \leq 2r\}$, $C_j = \{x : d(x, \partial D_j) \leq 2r\}$,

$$\begin{aligned}
h_s * [(\xi_j^2 - \Upsilon_j^2)] &= \xi_j^2 - \Upsilon_j^2 + K s^2 (\Delta \xi_j^2 - \Delta \Upsilon_j^2) + \kappa_j(s,\cdot) \\
|\kappa_j(s,\cdot)| &\leq C s^4 r^{-4} \left(\chi_{B_j} + \chi_{C_j} \right)
\end{aligned} \tag{179}$$

We can estimate

$$\begin{aligned}
&\left| \frac{1}{6\pi^2 h^3} \int \kappa_j(s,\cdot) \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + w_j \right)^{3/2} \right| \leq \\
&\leq C h^{-3} s^4 r^{-4} \int_{B_j} |x|^{-3/2}\, dx + C h^{-3} s^4 r^{-4} \int_{C_j - R_j} |x|^{-6}\, dx \\
&\leq C h^{-3} s^4 r^{-5/2} + C h^{-3} s^4 r^{-4} \int_{C_j - R_j} |x|^{-6}\, dx
\end{aligned}$$

To estimate the second integral above, we write $F(r) := \int_{C_j - R_j} |x|^{-6}\, dx$. Its derivative is $F'(r) = \int_{\{x : d(x, \partial(D_j - R_j) = 2r)\}} |x|^{-6}\, d\sigma_r$, where $d\sigma_r$ is the 2-dimensional measure induced by Lebesgue's measure into $\{x : d(x, \partial(D_j - R_j) = 2r)\}$. Then, $F'(r) = \mathcal{O}(1)$ if $r \geq 1/2$. Since $F(r) = \int_0^{2r} F'(r)\,dr$, we obtain $F(r) = \mathcal{O}(r)$ and the estimate

$$\left|\frac{1}{6\pi^2 h^3}\int \kappa_j(s,\cdot)\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + w_j\right)^{3/2}\right| \leq C h^{-3} s^4 r^{-3} \tag{180}$$

and therefore the estimate (178) can also be written as

$$\begin{aligned}\int G_j &= \frac{1}{6\pi^2 h^3}\int \xi_j^2\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + w_j\right)^{3/2} + \frac{Ks^2}{6\pi^2 h^3}\int \Delta\xi_j^2\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2} \\ &\quad - \frac{Ks^2}{6\pi^2 h^3}\int \Delta\Upsilon_j^2\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2} + \mathcal{O}(h^{-2} r + h^{-3} s^4 r^{-3})\end{aligned} \tag{181}$$

Since Υ_j are chosen such that $\int \Delta\Upsilon_j^2|\cdot|^{-3/2} = \int \Delta\Upsilon_j^2|\cdot|^{-1/2} = 0$ and by Lemma 3 we can write

$$\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}(x)^{3/2} = Z_j^{3/2}|x - R_j|^{-3/2} - \frac{3}{2}k_j|x - R_j|^{-1/2} + \mathcal{O}(1)$$

we obtain the estimate

$$\left|\frac{Ks^2}{6\pi^2 h^3}\int \Delta\Upsilon_j^2\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\right| \leq C\|\Delta\Upsilon_j^2\|_\infty s^2 h^{-3}\int_{|x|\leq 2r} dx \leq C r s^2 h^{-3}$$

Let us define

$$W_j := \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\left[\left(1 + \frac{w_j}{\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}}\right)^{3/2} - 1\right] \tag{182}$$

Then is easy to see that

$$\frac{1}{6\pi^2 h^3}\int \xi_j^2\left[\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + w_j\right)^{3/2} - \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\right] = \frac{1}{6\pi^2 h^3}\int W_j$$

By the conditions imposed on w_j we have that $W_j \sim w_j$. Moreover, eq. (182) defines implicitly w_j once W_j are given. So, in terms of the functions W_j, the first condition on ii. of Lemma 13 is

$$\frac{1}{6\pi^2 h^3}\int W_j = \mathcal{O}(h^{-2} r + h^{-3} s^4 r^{-3} + r s^2 h^{-3}) \tag{183}$$

Now we proceed to compute $\int G_j(x_k-(R_j)_k)$:

$$\begin{aligned}
&\int G_j(x_k-(R_j)_k) = \\
= \ & \int \Upsilon_j^2\left(\frac{1}{6\pi^2h^3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}+R(h,\cdot)\right)(x_k-(R_j)_k) \\
&+\frac{1}{6\pi^2h^3}\int(\xi_j^2-\Upsilon_j^2)h_s*\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}+\sum_{k=1}^M w_k\right)^{3/2}(x_k-(R_j)_k) \\
= \ & \frac{1}{6\pi^2h^3}\int\Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}(x_k-(R_j)_k)+\mathcal{O}(h^{-2}r^2) \qquad (184)\\
&+\frac{1}{6\pi^2h^3}\int h_s*\left[(\xi_j^2-\Upsilon_j^2)(x_k-(R_j)_k)\right]\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}+\sum_{k=1}^M w_k\right)^{3/2} \\
= \ & \frac{1}{6\pi^2h^3}\int\Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}(x_k-(R_j)_k) \\
&+\frac{1}{6\pi^2h^3}\int h_s*\left[(\xi_j^2-\Upsilon_j^2)(x_k-(R_j)_k)\right]\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}+w_j\right)^{3/2}+\mathcal{O}(h^{-2}r^2)
\end{aligned}$$

Now we can write a formula similar to (179):

$$\begin{aligned}
h_s*[(\xi_j^2-\Upsilon_j^2)(x_k-(R_j)_k)] &= (\xi_j^2-\Upsilon_j^2)(x_k-(R_j)_k)+Ks^2\Delta\xi_j^2(x_k-(R_j)_k) \\
&\quad -Ks^2\Delta\Upsilon_j^2(x_k-(R_j)_k)+Ks^2(\partial_k\xi_j^2-\partial_k\Upsilon_j^2) \\
&\quad +\nu_j(s,\cdot) \qquad (185)\\
|\nu_j(s,\cdot)| &\le Cs^4r^{-4}\left(\chi_{B_j}+\chi_{C_j}\right)
\end{aligned}$$

As before, we can estimate

$$\left|\frac{1}{6\pi^2h^3}\int\nu_j(s,\cdot)\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}+w_j\right)^{3/2}\right|\le Ch^{-3}s^4r^{-3}$$

and

$$\left|\frac{Ks^2}{6\pi^2h^3}\int\partial_k\xi_j^2\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\right|\le Ch^{-3}s^2r$$

Also, since ξ_j^2 is radial around R_j, $\int\Delta\Upsilon_j^2(x_k-(R_j)_k)|\cdot-R_j|^{-3/2}=0$ and $\int\Delta\Upsilon_j^2(x_k-(R_j)_k)|\cdot-R_j|^{-3/2}=0$, so we obtain the estimates

$$\left|\frac{Ks^2}{6\pi^2h^3}\int\Delta\Upsilon_j^2(x_k-(R_j)_k)\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\right|\le C\|\Delta\Upsilon_j^2\|_\infty s^2h^{-3}\int_{|x|\le 2r}dx\le Cr^2s^2h^{-3}$$

and similarly

$$\left|\frac{Ks^2}{6\pi^2h^3}\int\partial_k\Upsilon_j^2(x_k-(R_j)_k)\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\right|\le C\|\partial\Upsilon_j^2\|_\infty s^2h^{-3}\int_{|x|\le 2r}dx\le Cr^2s^2h^{-3}$$

and therefore we get

$$\begin{aligned}
&\int G_j(x_k-(R_j)_k) = \\
= \;& \frac{1}{6\pi^2h^3}\int \xi_j^2\left(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}+w_j\right)^{3/2}(x_k-(R_j)_k)+\frac{Ks^2}{6\pi^2h^3}\int \Delta\xi_j^2\left(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}(x_k-(R_j)_k) \\
&+\mathcal{O}(h^{-2}r^2+h^{-3}s^4r^{-3}+r^2s^2h^{-3}) \qquad (186)
\end{aligned}$$

So, the second condition on ii. of Lemma 13 is

$$\frac{1}{6\pi^2h^3}\int W_j(x_k-(R_j)_k)=\mathcal{O}(h^{-2}r^2+h^{-3}s^4r^{-3}+r^2s^2h^{-3}) \qquad (187)$$

Now, if the conditions assumed on s,r are satisfied, is easy to see that $\frac{1}{6\pi^2h^3}\int W_j$ and $\frac{1}{6\pi^2h^3}\int W_j(x_k-(R_j)_k)$ are both $o(h^{-2+\sigma})$ for sufficiently small $\sigma>0$. As a result, the restrictions posed on the functions w_j can also be fulfilled. This proves i. and ii.

To prove iii., we proceed similarly computing the energy:

$$\begin{aligned}
&{\rm Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})\Gamma] \qquad (188)\\
= \;& \sum_{j=1}^{M}{\rm Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})(\gamma_1)_{\Upsilon_j}]+\sum_{j=M+1}^{2M}{\rm Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})(\gamma_2)_{\Upsilon_j}]
\end{aligned}$$

Now we analyze any of the terms on (188):

i.-

By Lemma 11 we have

$${\rm Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})(\gamma_1)_{\Upsilon_j}]=-\frac{1}{15\pi^2h^3}\int \Upsilon_j^2(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2}+\frac{1}{8h^2}Z_j^2+\mathcal{O}(r^{-2}h^{-1});\; j=1,\ldots,M \qquad (189)$$

ii.-

Using eqs. (151) and (153) we can write, for $j=M+1,\ldots,2M$,

$$\begin{aligned}
&{\rm Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})(\gamma_2)_{\Upsilon_j}] \\
= \;& \frac{1}{10\pi^2h^3}\int h_s*(\Upsilon_j^2)(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2}+\frac{1}{6\pi^2h}\int h_s*(\Upsilon_j(-\Delta\Upsilon_j))(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} \\
&+\frac{1}{6\pi^2hs^2}\int \mu_s*(\Upsilon_j^2)(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2}-\frac{1}{6\pi^2h^3}\int \Upsilon_j^2\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}h_s*(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} \qquad (190)
\end{aligned}$$

Now we analyze the terms of (190) (we assume now $j=M+1,\ldots,2M$ without further notice; $i=j-M$):

ii.1.-

Using (179) we can write

$$\begin{aligned}
&\frac{1}{10\pi^2h^3}\int h_s*(\Upsilon_j^2)(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}\\
=\;&\frac{1}{10\pi^2h^3}\int \Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}+\frac{Ks^2}{10\pi^2h^3}\int \Delta\xi_i^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}-\frac{Ks^2}{10\pi^2h^3}\int \Delta\Upsilon_i^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}\\
&+\frac{1}{10\pi^2h^3}\int \kappa_j(s,\cdot)(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}
\end{aligned}$$

Since $\int \Delta\Upsilon_i^2|\cdot-R_j|^{-5/2}=\int \Delta\Upsilon_i^2|\cdot-R_j|^{-3/2}=0$ we obtain

$$\left|\frac{Ks^2}{10\pi^2h^3}\int \Delta\Upsilon_i^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}\right|\leq Cs^2h^{-3}r$$

and using that $|\kappa_j(s,\cdot)|\leq Cs^4r^{-4}\left(\chi_{B_j}+\chi_{C_j}\right)$ we get

$$\left|\frac{1}{10\pi^2h^3}\int \kappa_j(s,\cdot)(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}\right|\leq Ch^{-3}s^4r^{-7/2}$$

and then

$$\begin{aligned}
\frac{1}{10\pi^2h^3}\int h_s*(\Upsilon_j^2)(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2} \;=\;& \frac{1}{10\pi^2h^3}\int \Upsilon_i^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}+\frac{Ks^2}{10\pi^2h^3}\int \Delta\xi_i^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2}\\
&+\mathcal{O}(s^2h^{-3}r+h^{-3}s^4r^{-7/2})
\end{aligned}$$

ii.2.-

Using that $h_s*[\Upsilon_j(-\Delta\Upsilon_j)]\leq C[\Upsilon_j(-\Delta\Upsilon_j)]$ is easy to see that

$$\left|\frac{1}{6\pi^2h}\int h_s*(\Upsilon_j(-\Delta\Upsilon_j))(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\right|\leq Ch^{-1}r^{-1}$$

ii.3.-

We can write $\mu_s*\Upsilon_j^2=k\Upsilon_j^2+\epsilon_j(s,\cdot)$, where $k>0$ is some constant and $|\epsilon_j(s,\cdot)|\leq Cs^2r^{-2}\left(\chi_{B_j}+\chi_{C_j}\right)$. As a result we can write

$$\frac{1}{6\pi^2hs^2}\int \mu_s*(\Upsilon_j^2)(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}=\frac{k}{6\pi^2hs^2}\int \Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}+\mathcal{O}(h^{-1}r^{-1})$$

Moreover, is easy to see that

$$\frac{k}{6\pi^2hs^2}\int \Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\sim h^{-1}s^{-2} \tag{191}$$

uniformly in j.

ii.4.-

Finally we analyze the term $\frac{1}{6\pi^2 h^3}\int \Upsilon_j^2 \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}} h_s * (\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2}$. To do so, we write

$h_s * (\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} = (\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} + Ks^2\Delta(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} + \lambda(s,\cdot)$; $|\lambda(s,\cdot)| \le Cs^4 l(x)^{-11/2}\langle l(x)\rangle^{-9/2}$ Also, outside the set $\mathcal{R}$ we can write, using that for $f>0$ and $p>0$,

$$\Delta f^p = p(p-1)f^{p-2}|\nabla f|^2 + pf^{p-1}\Delta f$$

and the TF equation (13) the expression

$$\Delta(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} = \frac{1}{4}(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{-1/2}|\nabla \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}|^2 + \tau(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^2 \tag{192}$$

where $\tau > 0$ is some constant. Now we estimate

$$\begin{aligned}\left|\frac{1}{6\pi^2 h^3}\int \Upsilon_j^2 \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}\lambda(s,\cdot)\right| &\le Ch^{-3}s^4\int_{x\in D_i: l(x)\ge r/3} l(x)^{-11/2}\langle l(x)\rangle^{-9/2}\,dx \\ &\le Ch^{-3}s^4 r^{-5/2}\end{aligned}$$

So we can write, with

$$R_j(s,h) = \frac{Ks^2}{6\pi^2 h^3}\int \Upsilon_j^2\left[\frac{1}{4}(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{1/2}|\nabla \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}|^2 + \tau(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^3\right]$$

$$\begin{aligned}\frac{1}{6\pi^2 h^3}\int \Upsilon_j^2 \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}} h_s * (\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} &= \frac{1}{6\pi^2 h^3}\int \Upsilon_j^2(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} + R_j(s,h) \\ &\quad +\mathcal{O}(h^{-3}s^4 r^{-5/2})\end{aligned}$$

Using the expression (192) we get

$$R_j(s,h) \sim s^2 h^{-3} r^{-3/2} \tag{193}$$

uniformly in j (since $\Delta\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}(x)^{-3/2} \sim |x-R_j|^{-7/2}$; $|x-R_j| \le \mu/2$) Putting together the results of ii.1,...,ii.4 we obtain

$$\begin{aligned}&{\rm Tr}\,[(-h^2\Delta - \Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})(\gamma_2)_{\Upsilon_j}] \\ &= -\frac{1}{15\pi^2 h^3}\int(\xi_i^2 - \Upsilon_i^2)(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} + \frac{Ks^2}{10\pi^2 h^3}\int \Delta\xi_i^2(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} \\ &+\frac{k}{6\pi^2 h s^2}\int \Upsilon_j^2(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{3/2} - R_j(s,h) + \mathcal{O}(s^2h^{-3}r + h^{-3}s^4r^{-5/2})\end{aligned} \tag{194}$$

Using eqs. (189), (190), (194), the estimates (191), (193) and noting that

$$\sum_{j=1}^M \frac{Ks^2}{10\pi^2 h^3}\int \Delta\xi_j^2(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} = \frac{Ks^2}{10\pi^2 h^3}\int \Delta\left[\sum_{j=1}^M \xi_j^2\right](\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} = 0$$

(since $\sum_{j=1}^M \xi_j^2 = 1$) we obtain

$$\begin{aligned}\mathrm{Tr}\,[(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\Gamma] &= -\frac{1}{15\pi^2 h^3}\int \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^M w_j\right)^{5/2} + \frac{1}{8h^2}\sum_{j=1}^M Z_j^2 \\ &\quad + \sum_{j=1}^M \frac{k}{6\pi^2 h s^2}\int \Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} - \sum_{j=1}^M R_j(s,h) \\ &\quad + \mathcal{O}((s^2h^{-3}r + h^{-3}s^4r^{-5/2})M) \qquad (195)\end{aligned}$$

Now we have $\sum_{j=1}^M R_j(s,h) \sim s^2h^{-3}r^{-3/2}M$ and $\sum_{j=1}^M \frac{k}{6\pi^2hs^2}\int \Upsilon_j^2(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2} \sim h^{-1}s^{-2}M$, so, these terms cancel out by taking $s \sim h^{1/2}r^{3/8}$ and then obtain the next estimate for the energy

$$\begin{aligned}\mathrm{Tr}\,[(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\Gamma] &= -\frac{1}{15\pi^2 h^3}\int \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^M w_j\right)^{5/2} + \frac{1}{8h^2}\sum_{j=1}^M Z_j^2 \\ &\quad + \mathcal{O}((s^2h^{-3}r + h^{-3}s^4r^{-5/2})M) \qquad (196)\end{aligned}$$

We conclude our optimization by imposing $h^{-3}s^4r^{-3} = rs^2h^{-3}$. This yields $r \sim h^{4/9}$ and $s \sim h^{2/3}$. Plugging this into the energy estimate (196) we obtain

$$\begin{aligned}\mathrm{Tr}\,[(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\Gamma] &= -\frac{1}{15\pi^2 h^3}\int \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \sum_{j=1}^M w_j\right)^{5/2} + \frac{1}{8h^2}\sum_{j=1}^M Z_j^2 \\ &\quad + \mathcal{O}(h^{-11/9}M) \qquad (197)\end{aligned}$$

and the estimates

$$\frac{1}{6\pi^2 h^3}\int W_j = \mathcal{O}(h^{-14/9}) \qquad (198)$$

and

$$\frac{1}{6\pi^2 h^3}\int W_j(x_k - (R_j)_k) = \mathcal{O}(h^{-11/9}) \qquad (199)$$

Since the functions W_j now can be taken in such a way that $\|W_j\|_\infty \leq Ch^{1+4/9}$, we also obtain the final estimate for the energy

$$\begin{aligned}\mathrm{Tr}\,[(-h^2\Delta - \Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})\Gamma] &= -\frac{1}{15\pi^2 h^3}\int \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{5/2} + \frac{1}{8h^2}\sum_{j=1}^M Z_j^2 \\ &\quad + \mathcal{O}(h^{-14/9}M) \qquad (200)\end{aligned}$$

□

iv. Estimating the Coulomb norm of $\rho_\Gamma - \frac{1}{6\pi^2 h^3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}$.

Lemma 14 (Estimate on Coulomb interaction). *A.- Let f, g be supported in $\overline{B}_1(0)$ and integrable; $|R| \geq 1$. Call*

$$\left\{ \begin{array}{rcl} \langle f \rangle & := & \int f(x)\, dx \\ F_i & := & \int f(x) x_i \, dx;\ i = 1, \ldots, 3 \\ F_{ij} & := & \int f(x) x_i x_j \, dx;\ i, j = 1, \ldots, 3 \end{array} \right. \tag{201}$$

Then the following estimates holds, with $u_i = |R|^{-1} R_i$:

i.-

$$\begin{aligned} D\left(f, g(\cdot + R)\right) &= \frac{\langle f \rangle \langle g \rangle}{2|R|} + \frac{u_i}{|R|^2}\left(\langle f \rangle G_i + \langle g \rangle F_i\right) \\ &\quad + \frac{3u_i u_j - \delta_{ij}}{|R|^3}\left(F_{ij}\langle g \rangle - 2F_i G_j + G_{ij}\langle f \rangle\right) \\ &\quad + \mathcal{O}\left(\frac{\|f\|_1 \|g\|_1}{|R|^4}\right) \end{aligned} \tag{202}$$

ii.-

$$|\cdot|^{-1} * f(x) = \frac{\langle f \rangle}{|x|} + \frac{x_i F_i}{|x|^3} + \frac{3x_i x_j - \delta_{ij}|x|^2}{|x|^5} F_{ij} + \mathcal{O}\left(\frac{\|f\|_1}{|x|^4}\right) \tag{203}$$

B.- Assume now that f, g are integrable, that $|f(x)|, |g(x)| \leq C_0 |x|^{-3}\langle x \rangle^{-3}$ and finally the cancellation conditions $\langle f \rangle = \langle g \rangle = 0$ and $f_i = g_i = 0$; $i = 1, 2, 3$. Then, with $\varphi(x) := (1 + \log_+ |x|)|x|^{-1}\langle x \rangle^{-3}$, the next estimate holds:

iv.-

$$|D\left(f, g(\cdot + R)\right)| \leq C \max\{\|f\|_1 \|g\|_1, C_0^2\} \varphi(R) \tag{204}$$

(Here we are using Einstein's convention of summation over repeated indices).

Proof. A.-

i.- For $|x| \leq 1$ and $|z = y - R| \leq 1$ we write down Taylor's expansion of $|x - y|^{-1}$ up to order three:

$$\begin{aligned} \frac{1}{|x-y|} &= \frac{1}{|R|} + \frac{u_i}{|R|^2}(x_i - z_i) + \frac{3u_i u_j - \delta_{ij}}{|R|^3}(x_i - z_i)(x_j - z_j) \\ &\quad + \mathcal{O}\left(\frac{1}{|R|^4}\right) \end{aligned} \tag{205}$$

Plugging formula (205) into the definition of $D(f, g)$ given by eq. (62) we arrive at (202).

The proof of ii.- is completely analogous.

B.-

We first estimate $|\cdot|^{-1} * f(x)$:

$$|\cdot|^{-1} * f(x) = \int \frac{f(y)}{|x-y|}\, dy = \int_{|y|\leq \frac{1}{2}|x|} + \int_{\frac{1}{2}|x|\leq|y|\leq 2|x|} + \int_{|y|\geq 2|x|} = I_1 + I_2 + I_3 \tag{206}$$

Is inmediate to estimate for f fulfilling the hypothesis B.- and for any $x \in \mathbb{R}^3$:

$$\begin{cases} |I_1| & \leq & \frac{2}{|x|}\|f\|_1 \\ |I_3| & \leq & 2\int_{|y|\geq 2|x|} |y|^{-4}\langle y\rangle^{-3}\, dy \leq C\, C_0 |x|^{-1}\langle x\rangle^{-3} \end{cases}$$

Similarly,

$$\begin{aligned} |I_2| &\leq C_0|x/2|^{-3}\langle x/2\rangle^{-3} \int_{\frac{1}{2}|x|\leq|y|\leq 2|x|} |x-y|^{-1}\, dy \\ &\leq C\, C_0|x|^{-1}\langle x\rangle^{-3} \int_{\frac{1}{2}\leq|y|\leq 2} \left|\frac{x}{|x|} - y\right|^{-1} dy \\ &= C\, C_0|x|^{-1}\langle x\rangle^{-3} \end{aligned}$$

Now we estimate more carefully the term I_1 for $|x| \geq 1$, using that for $|y| \leq 1/2|x|$ we can write

$$\frac{1}{|x-y|} = \frac{1}{|x|} + \frac{x_i y_i}{|x|^3} + \frac{3x_i x_j - \delta_{ij}|x|^2}{|x|^5} y_i y_j + \mathcal{O}\left(\frac{|y|^3}{|x|^4}\right)$$

Then we get $I_1 = a + b + c + d$ where

$$\begin{cases} a & = & \frac{1}{|x|}\int_{|y|\leq 1/2|x|} f(y)\, dy \\ b & = & \frac{x_i}{|x|^3}\int_{|y|\leq 1/2|x|} y_i f(y)\, dy \\ c & = & \frac{3x_i x_j - \delta_{ij}|x|^2}{|x|^5}\int_{|y|\leq 1/2|x|} y_i y_j f(y)\, dy \\ |d| & \leq & C\frac{1}{|x|^4}\int_{|y|\leq 1/2|x|} |y|^3 f(y)\, dy \end{cases}$$

Now we use the cancellation conditions satisfied by f to get:

a.-

$$|a| = \frac{1}{|x|}\left|\int_{|y|\geq 1/2|x|} f(y)\, dy\right| \leq C\, C_0|x|^{-4}$$

b.-

$$|b| = \left|\frac{x_i}{|x|^3}\int_{|y|\geq 1/2|x|} y_i f(y)\, dy\right| \leq C\, C_0|x|^{-4}$$

c.-

$$c = \frac{3x_ix_j - \delta_{ij}|x|^2}{|x|^5}F_{ij} + c_1;\ c_1 = \frac{3x_ix_j - \delta_{ij}|x|^2}{|x|^5}\int_{|y|\geq 1/2|x|} y_iy_jf(y)\,dy$$

and similarly

$$|c_1| \leq \left|\frac{3x_ix_j - \delta_{ij}|x|^2}{|x|^5}\int_{|y|\geq 1/2|x|} y_iy_jf(y)\,dy\right| \leq C\,C_0|x|^{-4}$$

d.-

$$|d| \leq C\,C_0|x|^{-4}\left|\int_{|y|\leq 1/2|x|}\langle y\rangle^{-3}\,dy\right| \leq C\,C_0|x|^{-4}(1+\log_+|x|)$$

and therefore we obtain the estimate

$$\left\{\begin{array}{rcl} \left|\,|\cdot|^{-1} * f(x)\right| & \leq & C\max\{\|f\|_1, C_0\}|x|^{-1} \\ \left|\,|\cdot|^{-1} * f(x) - \frac{3x_ix_j-\delta_{ij}|x|^2}{|x|^5}F_{ij}\right| & \leq & C\,C_0|x|^{-4}(1+\log_+|x|) \end{array}\right. \tag{207}$$

Now we write

$$\begin{aligned} 2D(f, g(\cdot+R)) &= \int f(x)|\cdot|^{-1} * g(x+R)\,dx \qquad (208) \\ &= \int_{|x|\leq 1/2|R|} + \int_{1/2|R|\leq|x|\leq 2|R|} + \int_{|x|\leq 1/2|R|} = A_1 + A_2 + A_3 \end{aligned}$$

and we estimate any of the terms of (208) using the estimate (207) (applied to g):

A_1.-

If $|x| \leq 1/2|R|$, $\left|\,|\cdot|^{-1} * g(x)\right| \leq C\max\{\|g\|_1, C_0\}|R|^{-1}$ and therefore $|A_1| \leq C\max\{\|g\|_1, C_0\}|R|^{-1}\|f\|_1$. If besides $|R| \geq 1$, we can write

$$|\cdot|^{-1} * g(x) = \frac{6x_iR_j - 2x_iR_i\delta_{ij}}{|R|^5}G_{ij} + \frac{G_{ii}}{|R|^3} + r(x,R) \tag{209}$$

where in (209), $|r(x,R)| \leq C\max\{\|g\|_1, C_0\}(|R|^{-4}|x| + |R|^{-4}\log_+|R|)$. Using the cancellation conditions f satisfy, we get, reasoning as above,

$$|A_1| \leq C\max\{\|f\|_1\|g\|_1, C_0^2\}\varphi(R)$$

The other two terms are estimated similarly:

A_2:-

$$\begin{aligned} |A_2| &\leq C\,C_0|R|^{-3}\langle R\rangle^{-3}\int_{1/2|R|\leq|y-R|\leq 2|R|}\left|\,|\cdot|^{-1} * g(x)\right|\,dx \\ &\leq C\max\{\|f\|_1\|g\|_1, C_0^2\}|R|^{-3}\langle R\rangle^{-3}\int_{1/2|R|\leq|y-R|\leq 2|R|}\min\{|x|^{-1}, |x|^{-3}\}\,dx \\ &\leq C\max\{\|f\|_1\|g\|_1, C_0^2\}|R|^{-1}\langle R\rangle^{-3} \end{aligned}$$

A_3:-

$$\begin{aligned}|A_3| &\le C\max\{\|g\|_1, C_0\}\int_{|x|\ge 2|R|}\min\{|x|^{-1}, |x|^{-3}\}|x|^{-3}\langle x\rangle^{-3}\,dx\\ &\le C\max\{\|f\|_1\|g\|_1, C_0^2\}|R|^{-1}\langle R\rangle^{-3}\end{aligned}$$

so we obtain (204) by collecting estimates. □

We claim that under the conditions given by eqs. (172) and (173), we can estimate

$$D\left(\rho_\Gamma - \frac{1}{6\pi^2h^3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}\right) \le Ch^{-4-2/9}M \tag{210}$$

To prove this fact, we write, with $F := \rho_\Gamma - \frac{1}{6\pi h^3}(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{3/2}$ and $F_j := G_j - \frac{Ks^2}{6\pi^2h^3}\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\Delta\Upsilon_j^2 - \left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{3/2}\Upsilon_j^2$; $j = 1, \dots, M$ (so, $F = \sum_{j=1}^M F_j$).

$$D(F) = \sum_{i,j:|R_i-R_j|\le\mu} D(F_i, F_j) + 2\sum_{i,j:|R_i-R_j|>\mu} D(F_i, F_j) = S_1 + S_2 \tag{211}$$

The terms F_j satisfy the cancellation conditions needed to apply Lemma 14. Also, given the choices of the parameters r, s obtained in the proof of Lemma 13 (namely, $r \sim h^{4/9}$ and $s \sim h^{2/3}$), $s^2r^{-2}h^{-3} \ne \mathcal{O}(h^{-2})$ meaning that the subterms $\frac{Ks^2}{6\pi^2h^3}\Delta\xi_j^2$ appearing in the $F_j's$ cannot be absorbed into the main terms, so Lemma 14 is not directly applicable. Nevertheless, this trouble is easy to overcome if we notice that the bad subterms $\frac{Ks^2}{6\pi^2h^3}\Delta\xi_j^2$ are supported into a thin neighborhood of ∂D_j of thickness $r \sim h^{4/9}$. This gives us

$$\left.\begin{array}{r}\frac{Ks^2}{6\pi^2h^3}\int\Delta\xi_j^2\\ \frac{Ks^2}{6\pi^2h^3}\int\Delta\xi_j^2(x_k-(R_j)_k)\end{array}\right\} = \mathcal{O}(h^{-2-1/9})$$

Moreover, by mimicking the proof of Lemma 14 we can obtain that $|D(F_i, F_j)| \le Ch^{-2-1/9}\varphi(R_i - R_j)$. I shall omit to check this since only repeats the arguments leading to Lemma 14 with some minor modifications.

The first sum in (211) contains no more than $2^{3/2}M$ summands (given that it is not possible to fit more than $2^{3/2}$ disjoint balls of radius 1 inside a ball of radius 2). Since $|D(F_i, F_j)| \le 2(D(F_i) + D(F_j))$, we can estimate, using the inequality

$$D(f) \le K\|f\|_{6/5}^2$$

which follows from the Hardy-Littlewood-Sobolev inequality

$$\begin{aligned}|S_1| &\le 2^{5/2}\sum_{j=1}^M D(F_j)\\ &\le C\sum_{j=1}^M \|F_j\|_{6/5}^2 \\ &\le Ch^{-4-2/9}M\end{aligned} \tag{212}$$

since it is easily verified that the $F_j's$ satify $\|F_j\|_{6/5} \leq Ch^{-2-1/9}$ uniformly in $h>0$. To estimate the second sum in (211), we use Part B. of Lemma 14 which yields, with $\varphi(x) := |x|^{-4}(1+\log_+|x|)$

$$|S_2| \leq Ch^{-4-2/9} \sum_{i,j:|R_i-R_j|>\mu} \varphi\left(|R_i-R_j|\right) \tag{213}$$

To estimate the sum in the r.h.s of (213) we proceed in a very similar way to what we have done to prove the main estimate about the size of the TF potential (Theorem 1). We shall not repeat the details here, but we point out that what we obtain is the bound

$$\begin{aligned} |S_2| &\leq Ch^{-4-2/9} \sum_{j=1}^{M} \sum_{n\geq 1} \varphi\left(cn^{1/3}\mu\right) \\ &\leq Ch^{-4-2/9}\varphi\left(\mu\right) M \sum_{n\geq 1} \varphi\left(cn^{1/3}\right) \\ &\leq C_\mu h^{-4-2/9} M \end{aligned} \tag{214}$$

which, together with estimate (212) establishes eq. (210). To finish the argument, assume now that we have a nuclear configuration $\mathcal{R},\mathcal{Z}$ which falls into the hypothesis of Thm. 2. We rescal it to the new configuration $Z^{1/3}\mathcal{Z}, Z^{-1}\mathcal{Z}$. Taking the parameter $h=Z^{-1/3}$, the Hamiltonian H appearing at the RHF model is $H=-\Delta-\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}}$ which is unitarily equivalent, via conjugation with $U_h:\psi\to h^{-3/2}\psi(h^{-1}\cdot)$ to $h^{-4}(-h^2\Delta-\Phi^{\rm TF}_{Z^{1/3}\mathcal{Z},Z^{-1}\mathcal{Z}})$ (in that case, $H=h^{-4}U_h(-h^2\Delta-\Phi^{\rm TF}_{Z^{1/3}\mathcal{Z},Z^{-1}\mathcal{Z}})U_h^*$). By cyclity of the trace, $\mathrm{Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{Z^{1/3}\mathcal{Z},Z^{-1}\mathcal{Z}})\Gamma] = \mathrm{Tr}\,[H\overline{\Gamma}]$ with $\overline{\Gamma} := U_h\Gamma U_h^*$. But is easily verified that if $K_\gamma(x,y)$ is the Schwarz kernel of a density matrix γ, with $\overline{\gamma}$ as above we have the formulas

$$\left\{ \begin{aligned} K_{\overline{\gamma}}(x,y) &= h^{-3}K_\gamma(h^{-1}x,h^{-1}y) \\ \rho_{\overline{\gamma}}(x) &= h^{-3}\rho_\gamma(h^{-1}x) \end{aligned} \right. \tag{215}$$

Now, what we do obtain are the following estimates with Γ being the density matrix constructed above:

$$\mathrm{Tr}\,[(\Delta-(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2})\overline{\Gamma}] \leq -\frac{1}{15\pi^2h^7}\int(\varphi^{\rm TF}_{Z^{1/3}\mathcal{R},Z^{-1}\mathcal{Z}})^{5/2} + \frac{1}{8h^6}\sum_{j=1}^{M}\frac{Z_j^2}{Z^2} - CMh^{-5-4/9} \tag{216}$$

By the TF scaling (14) and the relation $\mathrm{Tr}\,[(-h^2\Delta-\Phi^{\rm TF}_{Z^{1/3}\mathcal{Z},Z^{-1}\mathcal{Z}})\Gamma] = \mathrm{Tr}\,[H\overline{\Gamma}]$ we obtain

$$\mathrm{Tr}\,[(\Delta-(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2}\overline{\Gamma}] \leq -\frac{1}{15\pi^2}\int(\Phi^{\rm TF}_{\mathcal{R},\mathcal{Z}})^{5/2} + \frac{1}{8}\sum_{j=1}^{M}Z_j^2 - CMZ^{2-\delta};\ \delta=\frac{5}{27} \tag{217}$$

and using the estimate (210) we get

$$
\begin{aligned}
D\left(\rho_{\overline{\Gamma}}-\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right) &= Z^{1/3} D\left(\rho_\Gamma - \frac{Z}{6\pi^2}(\Phi^{\mathrm{TF}}_{Z^{1/3}\mathcal{Z},Z^{-1}\mathcal{Z}})^{3/2}\right) \\
&\leq CMZ^{5/3+2/27}
\end{aligned} \tag{218}
$$

Evaluating the *RHF* functional at the densiy matrix $\overline{\Gamma}$ we finally obtain

$$
\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\overline{\Gamma}) \leq -\frac{1}{15\pi^2}\int(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}})^{5/2} + \frac{1}{8}\sum_{j=1}^{M} Z_j^2 - D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) + U_{\mathcal{R},\mathcal{Z}} + CMZ^{2-5/27} \tag{219}
$$

which concludes the proof of Theorem 6 □

5 Reconstruction of the whole system and proof of the main results.

Putting together the estimates of sections 3 and 4 we have proven the following:

Claim: Let us look at the RHF energy $E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}$. Then, decomposing our system in its 'good' and 'bad' parts we have the estimates

$$
\begin{aligned}
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} &\geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) - \frac{1}{15\pi^2}\int\left(\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}+\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}\right)^{5/2}dx \\
&\quad -D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + \frac{1}{8}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) + \Delta U_{12}
\end{aligned} \tag{220}
$$

$$
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \geq -\frac{1}{15\pi^2}\int\left(\Phi^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}\right)^{5/2}dx - D(\rho^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}}) + \frac{1}{8}\sum_{j=1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \tag{221}
$$

The estimate (220) holds without any restriction on the positions $\mathcal{R}$. The more precise estimate (221) holds if $\mathcal{R}_1 = \emptyset$. Using the expression for the TF energy given by Lemma 6 we obtain

$$
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \geq E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \frac{1}{8}\sum_{j=1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \tag{222}
$$

under the hypothesis $\mathcal{R}_1 = \emptyset$. The other situation could be taken care of using next Lemma, whose easy proof I will omit:

Lemma 15 (p norm estimate of a sum). *For $1 \leq p < \infty$ and $x, y \geq 0$ the following estimate holds:*

$$
x^p + y^p \leq (x+y)^p \leq x^p + y^p + 2^{p-1}(x^{p-1}y + xy^{p-1}) \tag{223}
$$

Using Lemma 15 and estimate (220) we obtain

$$
\begin{aligned}
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \;\geq\; & cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) - \frac{1}{15\pi^2}\int\left(\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}\right)^{5/2}dx \\
& -D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + \frac{1}{8}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \qquad (224)\\
& +\Delta U_{12} - \frac{2^{5/2}}{15\pi^2}\left\{\int \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \int \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}\right\}
\end{aligned}
$$

But since $\Delta U_{1,2} = \int \rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \int \rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} \geq 0$ and $\frac{2^{5/2}}{15\pi^2} < 1$, we get

$$
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) + E^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \frac{1}{8}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \qquad (225)
$$

Inclusion of spin: The full quantum system described by the Hamiltonian (1) acts in the Fermion space $\mathcal{H} = \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$. The analogous of this for the RHF model is to look at the RHF functional, but now the Schrödinger operator $-\Delta - V_{\mathcal{R},\mathcal{Z}}$ acts on $L^2(\mathbb{R}^3;\mathbb{C}^2)$ instead of $L^2(\mathbb{R}^3)$. But by the elementary formula $\mathrm{Tr}\,(A\otimes\mathbb{C}^q) = q\mathrm{Tr}\,A$, the effect of considering spin in the semiclassics of the RHF model only amounts to get constants twice bigger, so, including spin, the estimate (225) takes the form

$$
E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) + E^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \frac{1}{4}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \qquad (226)
$$

for the concrete choice of parameter $\frac{3}{5}\left(\frac{2}{5}\right)^{2/3}q^{-2/3}\left(\frac{1}{15\pi^2}\right)^{-2/3} = \frac{3^{5/3}\pi^{4/3}}{5}$ ($q = 2$ in our case) , which follows from matching the asymptotic expression of the TF energy we obtained and the expression of it as given by Lemma 6.

Now we are in position to prove our main result:

Proof of Theorem 1. Pick $\psi \in \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$ normalized and consider the density matrix γ_ψ on $L^2(\mathbb{R}^3,\mathbb{C}^2)$ whose integral kernel is given by (notice that $\bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2) \subseteq \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^{2^N}))$

$$
\gamma_\psi(x,y) := N\int_{\mathbb{R}^{3(N-1)}}\langle\psi(y,x_2,\ldots,x_N),\psi(x,x_2,\ldots,x_N)\rangle_{\mathbb{C}^{2^N}}\,dx_2\ldots dx_N \qquad (227)
$$

(That this indeed defines a well-normalized density matrix is an instructive calculation that uses strongly the antisymmetry of γ_ψ. Without it one would simply obtain the operator inequalities $0 \leq \gamma_\psi \leq N$). Now we can compute

$$
\langle\psi,(-\Delta - V_{\mathcal{R},\mathcal{Z}})\psi\rangle = \mathrm{Tr}\,(H\gamma_\psi);\;\; H = -\Delta - V_{\mathcal{R},\mathcal{Z}} \qquad (228)
$$

By the Lieb-Oxford inequality we have the Coulomb estimate

$$\left\langle \psi, \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\psi \right\rangle \ge D(\rho_\gamma) - C\int \rho_\gamma^{4/3};\ \gamma = \gamma_\psi \tag{229}$$

(That we can take in (229) $C = 1,68$ was proven by Lieb&Oxford [23]. A simpler proof (with a much worse constant) that uses the Hardy-Littlewood Maximal Function can be found in reference [1]). So, putting together (228) and (229) we obtain

$$\langle \psi, H_{\mathcal{R},\mathcal{Z},N}\psi\rangle \ge \mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma_\psi) - C\int \rho_{\gamma_\psi}^{4/3} \tag{230}$$

We can control the $-C\int \rho_\gamma^{4/3}$ term borrowing an small part of the kinetic energy:

$$\begin{aligned}\mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma) - C\int \rho_\gamma^{4/3} &= [\mathrm{Tr}\,[(-(1-\epsilon)\Delta - V_{\mathcal{R},\mathcal{Z}})\gamma] + D(\rho_\gamma) + U_{\mathcal{R},\mathcal{Z}}] \\ &\quad \left[\mathrm{Tr}\,[(-\epsilon\Delta)\gamma] - C\int \rho_\gamma^{4/3}\right] \\ &= I + II;\ 0 < \epsilon \ll 1\end{aligned} \tag{231}$$

Then, by Schwarz's and Lieb-Thirring's inequalities we get

$$\begin{aligned} II &\ge K\epsilon\int \rho_\gamma^{5/3} - \left\{\int \rho_\gamma^{5/3}\right\}^{1/2}\left\{\int \rho_\gamma\right\}^{1/2} \\ &\ge K\epsilon\int \rho_\gamma^{5/3} - N^{1/2}\left\{\int \rho_\gamma^{5/3}\right\}^{1/2} \\ &\ge -C\epsilon^{-1}N \\ &\ge -C\epsilon^{-1}MZ \end{aligned} \tag{232}$$

where we have used the Lieb&Benguria's estimate [20] for the maximal negative charge N_c: $N \le N_c \le 2\sum_{j=1}^M Z_j + M$. Now we proceed like in section 3: Recall the estimate (68). By the same kind of reasoning the following holds:

$$\begin{aligned} I &\ge \mathrm{Tr}\,[(-(1-\epsilon)\Delta - \Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} - \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\gamma] \\ &\quad -D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) - D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + U_{\mathcal{R}_1,\mathcal{Z}_1} + U_{\mathcal{R}_2,\mathcal{Z}_2} + \Delta U_{1,2} \\ &\ge \mathcal{E}_1(\gamma) + \mathcal{E}_2(\gamma) + \Delta U_{1,2} \\ \mathcal{E}_1(\gamma) &:= \mathrm{Tr}\,[(-(1-\epsilon)\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}))\gamma] - D(\rho^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}) + U_{\mathcal{R}_1,\mathcal{Z}_1} \\ \mathcal{E}_2(\gamma) &:= \mathrm{Tr}\,[(-(1-\epsilon)\Delta - (\Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1}))\gamma] - D(\rho^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2}) + U_{\mathcal{R}_2,\mathcal{Z}_2} \end{aligned} \tag{233}$$

Write

$$\begin{aligned} -(1-\epsilon)\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi(Z^{1/3}\cdot) &= (1-2\epsilon)[\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi(Z^{1/3}\cdot)] \\ &\quad +\epsilon[-\Delta - 2(\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi(Z^{1/3}\cdot)] \\ &= A + B \end{aligned} \tag{234}$$

($\Xi(Z^{1/3}\cdot)$ is the same as in (89) of section 4). So we get

$$\mathrm{Tr}\,[-(1-\epsilon)\Delta - (\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi(Z^{1/3}\cdot)]_- \leq \mathrm{Tr}\,[A]_- + \mathrm{Tr}\,[B]_- \tag{235}$$

Applying the results of sections 3 and 4 we obtain

$$\begin{aligned} I &\geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) + E^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \frac{1}{4}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \\ &\quad -K\epsilon\int\left[(\Phi^{\mathrm{TF},\beta}_{\mathcal{R}_1,\mathcal{Z}_1} + \Phi^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2})\Xi(Z^{1/3}\cdot)\right]^{5/2} \\ &\geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) + E^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \frac{1}{4}\sum_{j=M_1+1}^{M} Z_j^2 \\ &\quad +\mathcal{O}(MZ^{2-\delta} + \epsilon MZ^{7/3}) \end{aligned} \tag{236}$$

Comparing eqs.(232) and (236) we obtain, by choosing $\epsilon = Z^{-2/3}$

$$\langle\psi, H_{\mathcal{R},\mathcal{Z},N}\psi\rangle \geq cZ^{7/3}\sum_{j=1}^{M_1}\Gamma(Z^{1/3}\delta_j) + E^{\mathrm{TF}}_{\mathcal{R}_2,\mathcal{Z}_2} + \frac{1}{4}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \tag{237}$$

Finally, we use Lemma 2 of [2] to obtain

$$\langle\psi, H_{\mathcal{R},\mathcal{Z},N}\psi\rangle \geq cZ^{7/3}\sum_{j=1}^{M}\Gamma(Z^{1/3}\delta_j) - C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + \frac{1}{4}\sum_{j=M_1+1}^{M} Z_j^2 + \mathcal{O}(MZ^{2-\delta}) \tag{238}$$

which concludes the proof. □

We continue proving Theorem 2:

Proof of Theorem 2. Our aim here is to obtain an upper bound for the QM energy of the same kind as the lower bound we have given. A way to do that is to use the full Hartree-Fock model to obtain an upper bound for the quantum energy and later on compare the Hartree-Fock with the restricted Hartree-Fock. The upper bound for the HF model is inmediate, since the HF model merely consists to restrict attention to states ψ called *Slater determinants* having the form

$$\psi = \psi_1 \wedge \ldots \wedge \psi_N;\ \{\psi_i\}_{i=1}^N \text{ orthonormal set} \Leftrightarrow \psi \in S_N \tag{239}$$

Hence the following bound inmediately holds:

$$\begin{aligned} \inf_{\Psi\in\mathcal{H},\,\|\Psi\|=1}\langle\Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} &\leq \inf_{\Psi\in S_N,\,\|\Psi\|=1}\langle\Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} \\ &:= E^{\mathrm{HF}}_{\mathcal{R},\mathcal{Z}} \end{aligned} \tag{240}$$

We can write for $\psi \in S_N$

$$\begin{aligned}
\langle \Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} &= \mathcal{E}^{\mathrm{HF}}_{\mathcal{R},\mathcal{Z}}(\psi) \\
\mathcal{E}^{\mathrm{HF}}_{\mathcal{R},\mathcal{Z}}(\psi) &:= \mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma_\psi) - \mathrm{Ex}\,(\gamma_\psi) \\
\mathrm{Ex}\,(\gamma) &:= \frac{1}{2}\iint \frac{\mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma(x,y)|^2\right]}{|x-y|}\,dx\,dy;\; 0 \le \gamma \le \mathbf{1} \text{ on } L^2(\mathbb{R}^3;\mathbb{C}^2)
\end{aligned} \tag{241}$$

The *exchange* term $\mathrm{Ex}\,(\gamma)$ is non-negative, and hence we obtain

$$E^{\mathrm{HF}}_{\mathcal{R},\mathcal{Z}} = \inf_{\psi\in S_N} \mathcal{E}^{\mathrm{HF}}_{\mathcal{R},\mathcal{Z}}(\psi) \le \inf_{\psi\in S_N} \mathcal{E}^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}}(\gamma_\psi) \le E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \tag{242}$$

Now we apply the Lieb's minimization principle for the HF model, which says that minimizing the functional in (241) over Slater determinants (we observe that the density matrices γ_ψ we obtain from a $\psi \in S_N$ are exactly all the N-dimensional proyection operators) gives the same result as to minimize over all density matrices (a proof of this fact can be found in [1]) and we have obtained

$$\inf_{\Psi\in\mathcal{H},\,\|\Psi\|=1} \langle \Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} \le E^{\mathrm{RHF}}_{\mathcal{R},\mathcal{Z}} \tag{243}$$

Hence it is enough to show that for a configuration of uniformly separated nuclei, the RHF energy could be bounded from above by the sum of the weylian term and the sum of Scott's corrections over the nuclei, but by Theorem 6 we get

$$\inf_{\Psi\in\mathcal{H},\,\|\Psi\|=1} \langle \Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} \le E^{\mathrm{TF}}_{\mathcal{R},\mathcal{Z}} + \frac{1}{4}\sum_{j=1}^{M} Z_j^2 + CMZ^{2-5/27} \tag{244}$$

Now, eq. (243) together with Corollary 1 (modifying properly the constants to take spin into account) yields Theorem 2. □

We end proving Theorem 3:

Proof of Theorem 3. Since by Lemma 7 the TF energy of a configuration of uniformly separarated nuclei tends to the sum of energies of totally separated nuclei uniformly in the number of the latter (only depending on the minimal nuclear distance), and using the asymptotic estimates provided by Theorem 2, indeed there are plenty of nuclear configurations such that the conditions of Theorem 3 are satisfied.

Now assume we have a nuclear configuration $\mathcal{R}, \mathcal{Z}$ such that

$$E^{Q}_{\mathcal{R},\mathcal{Z}} \le \sum_{j=1}^{M} E^{Q}(Z_j) + CMZ^{2-\delta};\; \delta > 0$$

By Theorem 1 the following lower bound holds:

$$E^{Q}_{\mathcal{R},\mathcal{Z}} \ge \sum_{j=1}^{M} E^{Q}(Z_j) + cZ^{7/3}\sum_{j=1}^{M} \Gamma(Z^{1/3}\delta_j) - CMZ^{2-\delta}$$

with $\Gamma(t) := \min\{t^{-1}, t^{-7}\}$ so we get

$$Z^{7/3} \sum_{j=1}^{M} \Gamma(Z^{1/3}\delta_j) \leq CMZ^{2-\delta} \tag{245}$$

Assume $\delta_1 \geq \ldots \geq \delta_M > 0$. Since Γ is decreasing and its inverse function $\gamma := \Gamma^{(-1)} : s \to \min\{s^{-1/7}, s^{-1}\}$, from (245) we get

$$\delta_j \geq Z^{-1/3}\gamma\left(CZ^{1/3}\frac{M}{M-j+1}\right) \tag{246}$$

Now, if $1 \leq j \leq \left[\frac{M}{2}\right]$, eq. (246) yields

$$\delta_j \geq cZ^{-1/3+1/7(1/3+\delta)};\ j = 1, \ldots, \left[\frac{M}{2}\right]$$

and this clearly implies the average estimate given by eq. (8). $\square$

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