On the asymptotic exactness of Thomas-Fermi theory in the thermodynamic limit*

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Abstract

In this paper we obtain a new version of stability of matter, which in particular shows that Thomas-Fermi theory is asymptotically correct in the limit of large nuclear charges uniformly in the number of nuclei. As a consequence we give a new lower bound on the volume of matter with an improved dependence on the nuclear charges.

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Contents:

1 Introduction.

One of the most celebrated results in mathematical physics is the Theorem on Stability of Matter. This result, which was originally proved by Dyson and Lenard [5], states that the binding energy per particle, for a a system of charged quantum particles, where either the positive or negatively charged particles are fermions, is bounded independently of the number of particles.

Another and maybe more intuitively understandable formulation of this result is that the volume occupied by the particles increases at least linearly in the number of particles.

Since the original work of Dyson and Lenard there has been numerous improvements and generalizations. In particular the work of Lieb and Thirring [21] (see also the review [14]) established the connection between stability of matter and the semi-classical Thomas-Fermi theory and greatly improved the numerical constants found by Dyson and Lenard. Among other proofs of stability of matter we can mention the work of Federbush [6] and the recent proof of Graf [10], which we shall use in the present work.

The result on stability of matter has been generalized to include relativistic effects [3, 9, 22, 20], classical magnetic fields [8, 17], and quantized fields [7].

In the present work we are concerned with another type of generalization of stability of matter. We are interested in the correct dependence in the physical parameters. One of the remarkable features of macroscopic matter is that the mean atomic spacing is nearly independent of the type of atoms that the matter consists of. Or put differently the mean atomic spacing is nearly independent of the nuclear charges.

In Thomas-Fermi theory distances scale as the $-1/3$ power of the nuclear charge, i.e., $Z^{-1/3}$. One would therefore naively expect that in macroscopic matter the volume per particle would behave as Z^{-1}. This is however in stark contrast to the near independence of Z which is found experimentally.

The Lieb-Thirring proof of stability of matter implies (see [21]) a lower bound on the volume per atom of the form Z^{-1} for large Z. Our main goal here is to show that this is indeed not optimal. We prove that there exists $\delta' > 0$ such that the volume per atom is bounded below by $Z^{-1+\delta'}$. Based on the experimental evidence one would hope to prove $\delta' = 1$, we are, however, very far from such a result (see Theorem 3).

Our proof is based on first showing that Thomas-Fermi theory not only gives a bound on the energy, but that this bound is indeed asymptotically correct in the limit of large nuclear charges. The bound of volume of matter is arrived at by a careful study of Thomas-Fermi theory.

The fact that Thomas-Fermi theory is asymptotically correct in the limit of large nuclear charge is a classical result due to Lieb and Simon [19].

The new feature is that we establish this asymptotics uniformly in the number of nuclei allowing us to use the Thomas-Fermi approximation independently of the number of nuclei.

We consider matter formed by M nuclei of charges $Z_j \geq 1$, $j = 1, \ldots, M$ located at positions $R_j \in \mathbb{R}^3$. We denote $\mathcal{R} = (R_1, \ldots, R_M)$ and $\mathcal{Z} = (Z_1, \ldots, Z_M)$. 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

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

Our improvement on stability of matter is as follows.

Theorem 1 (Stability of Matter). *Let $\overline{Z} = \frac{1}{M}\sum_{i=1}^{M} Z_i$. Assume there are $0 < a \leq A < \infty$ such that the charges satisfy $a\overline{Z} \leq Z_j \leq A\overline{Z}$ for all j and that $\overline{Z} \geq 1$. Then there is $\delta > 0$ and $C > 0$ a finite constant only depending on a, A such that*

$$\inf_{\mathcal{R}:\, \#\mathcal{R}=M} \inf_{\Psi \in \mathcal{H},\, \|\Psi\|=1} \langle \Psi, H_{\mathcal{R},\mathcal{Z},N} \Psi \rangle_{\mathcal{H}} \geq -C_{\mathrm{TF}} \sum_{j=1}^{M} Z_j^{7/3} - CM\overline{Z}^{7/3-\delta} \tag{2}$$

Here the Hilbert space where the Hamiltonian acts is $\mathcal{H} = \bigwedge^{N} L^2(\mathbb{R}^3; \mathbb{C}^2)$ (Fermion space).

In Theorem 1, the constant C_{TF} is the corresponding Thomas-Fermi constant (see Sect. 4 below for the definition) in the case $Z=1$, $M=1$. It is worth noting that the kind of estimate given in this theorem is essentially optimal. In fact, by taking the nuclei very far apart and using the Theorem of Lieb and Simon on the exactness of Thomas-Fermi theory for one nucleus we obtain

$$\inf_{\mathcal{R}:\,\#\mathcal{R}=M}\ \inf_{\Psi\in\mathcal{H},\,\|\Psi\|=1} \langle\Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi\rangle_{\mathcal{H}} \leq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + CM\overline{Z}^{7/3-\delta} \tag{3}$$

As an application of Theorem 1 we shall derive our results on the total volume and density of matter. This is the content of the next two theorems. The first is really a strengthening of Theorem 1, which requires an estimate on the "pressure" (the extra energy we have for confining particles in a bounded set). The estimate is a generalization to the case of many nuclei of a result by Brezis and Lieb [2] on the long-range potentials in Thomas-Fermi theory. The last theorem follows straightforwardly from that, and shows that for nuclear configurations giving us an energy close to the minimal possible one, almost all nuclei are very far from each other (on the natural scale of Thomas-Fermi theory, i.e., $\overline{Z}^{-1/3}$) and therefore that matter under such conditions should fill a volume in space much larger than $\mathrm{const}M\overline{Z}^{-1}$, which is the estimate that the simpler model of matter given by Thomas-Fermi theory predicts.

Theorem 2 (Pressure in macroscopic matter). *Let $\mathcal{R},\mathcal{Z}$ be a configuration of nuclei and charges fulfilling the conditions of Theorem 1 and such that*

$$\inf\operatorname{spec} H_{\mathcal{R},\mathcal{Z},N} \leq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} + C_0 M\overline{Z}^{7/3-\delta}$$

for a (fixed) constant C_0. Then there exists $C,c>0$ depending only on a, A, and C_0 such that

$$\inf\operatorname{spec} H_{\mathcal{R},\mathcal{Z},N} \geq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} - CM\overline{Z}^{7/3-\delta} + c\overline{Z}^{7/3}\sum_{j=1}^{M}\Gamma\left(\overline{Z}^{1/3}\delta(R_j)\right) \tag{4}$$

where $\Gamma(t)=\min\{t^{-1},t^{-7}\}$, $t>0$ and $\delta(R_j)=\min_{i\neq j}|R_j-R_i|$ is the distance from R_j to the nearest other nuclei.

Theorem 3 (The volume of matter). *With the conditions in Theorem 2, we have that $\mathcal{R}$ should satisfy, for $0<\delta_1<\delta/7$ and k finite*

$$\#\left\{j : \delta(R_j) \leq \overline{Z}^{-1/3+\delta_1}\right\} \leq kM\overline{Z}^{-(\delta-7\delta_1)} = o(M),\ \ \overline{Z}\mapsto\infty \tag{5}$$

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

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

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

$$\text{volume} \geq k' M \overline{Z}^{-1+3\delta_1} \tag{6}$$

where $k' > 0$ is a universal constant.

We shall prove these theorems using a tiling of space into simplices and an electrostatic inequality developed by Graf [10] and Graf-Schenker [11] which enables us to localize the electrostatic interactions into the tiles and to ignore the electrostatic interactions between these tiles up to some error which can be controlled. This reduces our problem to bounded regions, and for these we shall use Thomas-Fermi theory in order to estimate the maximal number of nuclei which is allowed in order to have non-positive energy. We ignore the tiles with positive energy, in the tiles which may have non-positive energy, we show how to reduce the asymptotic estimates to that of the whole space.

2 Graf & Schenker (GS) electrostatic inequality.

The setting we shall use for the GS inequality is as follows: Let $Q = [0,1]^3$ be the unit cube in $\mathbb{R}^3$. The cube Q can be written as a union of 24 congruent tetrahedra. (To see this first note that there are 6 pyramids with top at the center of the cube and base equal to one of the faces of the cube. Each pyramid consists of 4 congruent tetrahedra.) Denote by $\mathcal{D}_0$ the open interior of one of these tetrahedra. We then have a "tiling" $T = \{\mathcal{D}_\alpha\}_{\alpha\in\mathbb{N}}$, i.e, a collection of disjoint tetrahedra all congruent to $\mathcal{D}_0$ such that $\bigcup_{\alpha\in\mathbb{N}} \overline{\mathcal{D}_\alpha} = \mathbb{R}^3$. We shall also need to consider the tiling $T_l = \{l\mathcal{D}_\alpha\}_{\alpha\in\mathbb{N}}$ of scale $l > 0$, (which will be chosen later to be $\overline{Z}^{-1/3+\delta}$).

Given a rotation $R \in SO(3)$ and a $y \in Q$ we denote by $R(T_l + ly)$ the tiling $\{R(l\mathcal{D}_\alpha + ly)\}$.

We are now ready to state the result of Graf and Schenker. Given points $x_1, \ldots, x_K \in \mathbb{R}^3$. We then consider the function

$$\delta_{R,y}(x, x') = \begin{cases} 1 & \text{if } x, x' \text{ belong to the same tetrahedron of } R(T_l + ly) \\ 0 & \text{otherwise} \end{cases}$$

for $R \in SO(3)$ and $y \in Q$.

Theorem 4 (GS inequality). *There is a $C > 0$ such that for all $K \in \mathbb{N}$, all $(x_1, \dots, x_K) \in \mathbb{R}^{3K}$, all $(z_1, \dots, z_K) \in \mathbb{C}^K$, and any $l > 0$ we have*

$$\sum_{\substack{1 \le i,j \le K \\ i \ne j}} \frac{z_i \overline{z_j}}{|x_i - x_j|} \ge \left\langle \sum_{\substack{1 \le i,j \le K \\ i \ne j}} \frac{z_i \overline{z_j}}{|x_i - x_j|} \delta_{R,y}(x_i, x_j) \right\rangle - \frac{C}{l} \sum_{i=1}^{K} |z_i|^2 \tag{7}$$

For any function f on $SO(3) \times Q$ we have here defined its average over translations and rotations

$$\langle f \rangle := \int_{SO(3)\times Q} f(R,y) d\mu(R) dy \tag{8}$$

where $d\mu(R)$ stands for Haar measure on $SO(3)$.

We refer to [10] and [11] for a proof of this inequality.

3 Localizing the Hamiltonian into the tiles.

The inequality of Graf and Schenker allows us to localize the potential energy into tiles. We shall also localize the kinetic energy. Since we are asking for estimates from *below* it is natural to do this by Neumann-bracketing.

Lemma 1 (Localization estimate). *Corresponding to a tiling $R(T_l + ly)$ with $R \in SO(3)$, $y \in Q$ we define the Neumann Laplacians $-\Delta_\alpha$ for the tile $l\mathcal{D}_\alpha(R,y) := R(l\mathcal{D}_\alpha + ly)$, $\alpha \in \mathbb{N}$. and in terms of this the Hamiltonians*

$$\begin{aligned} H_{\alpha,N'} \quad := \quad & \sum_{i=1}^{N'} \left\{ -\Delta_\alpha^i - \sum_{j=1}^{M} \frac{Z_j \chi_\alpha(R_j)}{|x_i - R_j|} \right\} + \sum_{1 \le i < j \le N'} \frac{1}{|x_i - x_j|} \\ & + \sum_{1 \le i < j \le M} \frac{Z_i Z_j \chi_\alpha(R_i) \chi_\alpha(R_j)}{|R_i - R_j|} \end{aligned} \tag{9}$$

acting on $\bigwedge^{N'} L^2(l\mathcal{D}_\alpha(R,y); \mathbb{C}^2)$. Here χ_α is the characteristic function of $l\mathcal{D}_\alpha(R,y)$. Then we have the following decoupling inequality:

$$\inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N} \ge \inf_{N_\alpha : \sum_\alpha N_\alpha = N} \left\{ \sum_\alpha \left\langle \inf \mathrm{spec} H_{\alpha, N_\alpha} \right\rangle \right\} - \frac{C}{l}(N + \sum_{j=1}^{M} Z_j^2) \tag{10}$$

Proof. Given $\tilde{\alpha} = (\alpha_1, \dots, \alpha_N) \in \mathbb{N}^N$. We consider the subset $A_{\tilde{\alpha}}(R,y)$ of $\mathbb{R}^{3N}$ given by

$$A_{\tilde{\alpha}}(R,y) = \{(x_1, \dots, x_N) \in \mathbb{R}^{3N} \ : \ x_j \in l\mathcal{D}_{\alpha_j}(R,y), \ j = 1, \dots, N\}$$

We let N_α, $\alpha \in \mathbb{N}$ denote the number of j such that $\alpha_j = \alpha$. The sets $A_{\tilde\alpha}(R,y)$ corresponding to different $\tilde\alpha$ are disjoint and we can write $\mathbb{R}^{3N}$ as the union

$$\mathbb{R}^{3N} = \bigcup_{\tilde\alpha} \overline{A_{\tilde\alpha}(R,y)}$$

We denote by $\Psi_{\tilde\alpha} = \Psi\chi_{A_{\tilde\alpha}}$. We first investigate the kinetic energy

$$(\Psi, \sum_{j=1}^N -\Delta_j \Psi) = \sum_{\tilde\alpha}\sum_{j=1}^N \int_{A_{\tilde\alpha}(R,y)} |\nabla_j \Psi|^2 = \sum_{\tilde\alpha}\sum_{\alpha=1}^\infty \left\langle \sum_{j:\alpha_j=\alpha} \left(\Psi_{\tilde\alpha}, -\Delta_\alpha^j \Psi_{\tilde\alpha}\right)\right\rangle$$

The left side is independent of R and y and we may therefore average over rotated and translated tiles. From the Graf-Schenker inequality we have

$$\begin{aligned}
&\Big(\Psi, \Big[-\sum_{j=1}^M\sum_{i=1}^N \frac{Z_j}{|x_i - R_j|} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} + \sum_{1\le i<j\le M} \frac{Z_iZ_j}{|R_i - R_j|}\Big]\Psi\Big) \\
\geq\ & \Big\langle\Big(\Psi, \Big[-\sum_{j=1}^M\sum_{i=1}^N \frac{Z_j\delta_{R,y}(x_i,R_j)}{|x_i - R_j|} + \sum_{1\le i<j\le N} \frac{\delta_{R,y}(x_i,x_j)}{|x_i - x_j|} \\
&+ \sum_{1\le i<j\le M} \frac{Z_iZ_j\delta_{R,y}(R_i,R_j)}{|R_i - R_j|}\Big]\Psi\Big)\Big\rangle - \frac{C}{l}(N + \sum_{j=1}^M Z_j^2) \\
=\ & \sum_{\tilde\alpha}\sum_{\alpha=1}^\infty\Big\langle\Big(\Psi_{\tilde\alpha}, \Big[-\sum_{j=1}^M\sum_{i=1}^N \frac{Z_j\chi_\alpha(x_i)\chi_\alpha(R_j)}{|x_i - R_j|} + \sum_{1\le i<j\le N} \frac{\chi_\alpha(x_i)\chi_\alpha(x_j)}{|x_i - x_j|} \\
&+ \sum_{1\le i<j\le M} \frac{Z_iZ_j\chi_\alpha(R_i)\chi_\alpha(R_j)}{|R_i - R_j|}\Big]\Psi_{\tilde\alpha}\Big)\Big\rangle - \frac{C}{l}(N + \sum_{j=1}^M Z_j^2)
\end{aligned}$$

Note that, although $\Psi_{\tilde\alpha}$ is not antisymmetric in all variables, it is antisymmetric in the variables belonging to the same tile. Hence

$$(\Psi, H_{\mathcal{R},\mathcal{Z},N}\Psi) \geq \sum_{\tilde\alpha}\sum_{\alpha=1}^\infty \Big\langle \inf \mathrm{spec} H_{\alpha,N_\alpha}\Big\rangle \|\Psi_{\tilde\alpha}\|^2 - \frac{C}{l}(N + \sum_{j=1}^M Z_j^2)$$

Noting that $\sum_{\tilde\alpha}\|\Psi_{\tilde\alpha}\|^2 = 1$ we conclude (10). $\square$

4 Some results about Thomas-Fermi Theory

In this section we shall prove a result purely about Thomas-Fermi theory. It is closely related to the results (and ideas) of Brezis and Lieb in [2] about the asymptotic behavior of many-body potentials in Thomas-Fermi theory. In this section we shall assume that we deal with neutral systems. The effect of screening in neutral systems is that long-range interactions are much smaller than for non-neutral systems.

Suppose we have some configuration of M nuclei of charges $\mathcal{Z} = (Z_1, \ldots, Z_M)$ and positions $\mathcal{R} = (R_1, \ldots, R_M)$. The Thomas-Fermi model for this problem is defined by the following functional on positive densities $\rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3)$.

$$\begin{aligned} \mathcal{E}^{\beta}_{\mathrm{TF},\mathcal{R},\mathcal{Z}}(\rho) &= \beta \int_{\mathbb{R}^3} \rho(x)^{5/3} dx - \int_{\mathbb{R}^3} V(x)\rho(x) dx \\ &\quad + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy + \sum_{l<s}^{M} \frac{Z_l Z_s}{|R_l - R_s|} \end{aligned} \tag{11}$$

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 $\beta_{\mathrm{phys}} = \frac{3}{5}(6\pi^2)^{2/3}$. We shall however also use 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

$$E^{\beta}_{\mathrm{TF},\mathcal{R},\mathcal{Z}} := \inf_{0 \le \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3)} \mathcal{E}^{\beta}_{\mathrm{TF},\mathcal{R},\mathcal{Z}}(\rho) \tag{12}$$

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

The energy satisfies the scaling properties

$$E^{\beta}_{\mathrm{TF},\mathcal{R},\mathcal{Z}} = \lambda E^{\lambda\beta}_{\mathrm{TF},\lambda\mathcal{R},\mathcal{Z}} = \lambda^7 E^{\beta}_{\mathrm{TF},\lambda\mathcal{R},\lambda^{-3}\mathcal{Z}} \tag{13}$$

for any $\lambda > 0$.

It is known that there is a unique function ρ which minimizes the functional (12). This function fulfills the Thomas-Fermi equations

$$\begin{aligned} \tfrac{5}{3}\beta\rho^{2/3}(x) &= \phi(x) \\ \phi(x) &= V(x) - \tfrac{1}{|y|} * \rho(x) \end{aligned} \tag{14}$$

and is moreover the unique non-negative solution ρ of (14). This function has the property that $\int \rho = \sum_{j=1}^{M} Z_j$, i.e., the density minimizing the functional (11) corresponds to a neutral system. For future use we shall denote by $\phi(\mathcal{R}, \mathcal{Z}, x)$ the unique solution ϕ of (14), and $\phi^{\mathrm{at}}(R, Z, x)$ the one corresponding to a single "atom" of charge Z located at $R \in \mathbb{R}^3$. We refer to the original paper [19] or the review [15] for the proofs of these statements and for further results on Thomas-Fermi theory.

We consider the following function:

$$f^{\beta}(\mathcal{R}, \mathcal{Z}) = E^{\beta}_{\mathrm{TF},\mathcal{R},\mathcal{Z}} + C^{\beta}_{\mathrm{TF}} \sum_{J=1}^{M} Z_j^{7/3} \tag{15}$$

Using the scaling properties of Thomas-Fermi theory we have

$$f^{\beta}(\mathcal{R},\mathcal{Z})=\overline{Z}^{7/3}f^{\beta}\left(\overline{Z}^{1/3}\mathcal{R},\overline{Z}^{-1}\mathcal{Z}\right) \tag{16}$$

In [2] the asymptotics of $\lambda^7 f^{\beta}(\lambda\mathcal{R},\mathcal{Z})$ for large λ was studied in the case of a finite number of nuclei. Our goal here is to show an estimate on $f^{\beta}(\mathcal{R},\mathcal{Z})$ similar to the asymptotics of [2] which holds uniformly in the number of nuclei.

Lemma 2 (Pressure in Thomas-Fermi Theory). *Assume there is a constant $a>0$ such that $a\overline{Z}\le Z_j$ for all j. Then there is a universal $c>0$ (in particular independent of M) such that for each $\mathcal{R}\in\mathbb{R}^{3M}$ we have*

$$f^{\beta}\left(\mathcal{R},\mathcal{Z}\right)\ge c\beta^{-1}(a\overline{Z})^{7/3}\sum_{j=1}^{M}\Gamma\left((a\overline{Z})^{1/3}\beta^{-1}\delta(R_j)\right) \tag{17}$$

where $\Gamma(t)=\min\{t^{-1},t^{-7}\}$ and $\delta(R_j)=\min_{i\neq j}|R_i-R_j|$ is as before the nearest neighbor distance. Moreover, f^{β} is a non-decreasing function of all the Z_i variables.

Proof. By the scaling property (13) it is enough to prove the lemma for $Z_j\ge 1$ and $\beta=\beta_{\text{phys}}$ and in this case we omit the superscript. Then we have the following (a Feynman-Hellman type result)

$$\frac{\partial}{\partial Z_i}f\left(\mathcal{R},\mathcal{Z}\right)=\lim_{x\mapsto R_i}\left[\phi(\mathcal{R},\mathcal{Z},x)-\phi^{\text{at}}(R_i,Z_i,x)\right] \tag{18}$$

The right side of (18) is non-negative because of Teller's Lemma (see [15] Theorem 3.4) , which implies that $f\left(\mathcal{R},\mathcal{Z}\right)$ is non-decreasing in any of the Z_i arguments. Therefore we have that

$$f\left(\mathcal{R},\mathcal{Z}\right)\ge f\left(\mathcal{R},(1\ldots,1)\right) \tag{19}$$

Let $H(\lambda)$ be defined by

$$H(\lambda)=f\left(\mathcal{R},(\lambda,\ldots,\lambda)\right) \tag{20}$$

Applying Feynman-Hellman's formula again we obtain

$$\frac{d}{d\lambda}H(\lambda)=\sum_{i=1}^{M}\lim_{x\mapsto R_i}\left[\phi(\mathcal{R},(\lambda,\ldots,\lambda),x)-\phi^{\text{at}}(R_i,\lambda,x))\right] \tag{21}$$

For any of the points R_i we choose a *nearest neighbor*, which shall be denoted R_i', i.e., $|R_i-R_i'|=\delta(R_i)$. Then, by Teller's Lemma once again, we have that

$$\frac{d}{d\lambda}H(\lambda)\ge\sum_{i=1}^{M}\lim_{x\mapsto R_i}\left[\phi((R_i,R_i'),(\lambda,\lambda),x)-\phi^{\text{at}}(R_i,\lambda,x))\right] \tag{22}$$

Since $H(0) = 0$, the estimate (22) implies that

$$
\begin{aligned}
H(1) &\geq \int_0^1 d\lambda \sum_{i=1}^{M} \lim_{x \mapsto R_i} [\phi((R_i, R_i'), (\lambda, \lambda), x) - \phi^{\mathrm{at}}(R_i, \lambda, x))] \\
&= \frac{1}{2} \int_0^1 d\lambda \sum_{i=1}^{M} \Big[\lim_{x \mapsto R_i} [\phi((R_i, R_i'), (\lambda, \lambda), x) - \phi^{\mathrm{at}}(R_i, \lambda, x))] \\
&\quad + \lim_{x \mapsto R_i'} [\phi((R_i, R_i'), (\lambda, \lambda), x) - \phi^{\mathrm{at}}(R_i', \lambda, x))] \Big] \qquad (23) \\
&= \frac{1}{2} \sum_{i=1}^{M} f((R_i, R_i'), (1, 1)) \\
&= \frac{1}{2} \sum_{i=1}^{M} f((0, R_i - R_i'), (1, 1))
\end{aligned}
$$

In order to finish the proof, it is hence enough to show that there is a $c > 0$ such that

$$
c\Gamma(R) \leq f((0, R), (1, 1)) \qquad (24)
$$

If $|R| \geq 1$, (24) follows from the analysis in [2]. On the other hand, if $|R| \leq 1$ we will use the Thomas-Fermi equation directly to analyze the behavior. We have by the Thomas-Fermi scaling

$$
\begin{aligned}
\phi((0, R), (\lambda, \lambda), x) - \phi^{\mathrm{at}}(0, \lambda, x) &= \lambda^{4/3} \Big(\phi((0, \lambda^{1/3} R), (1, 1), \lambda^{1/3} x) \\
&\quad - \phi^{\mathrm{at}}(0, 1, \lambda^{1/3} x)) \Big)
\end{aligned}
$$

By the Thomas-Fermi (14) equation and the fact (see [15] Corollary 3.6) that $\phi((0, r), (1, 1), x) \leq \phi^{\mathrm{at}}(0, 1, x) + \phi^{\mathrm{at}}(r, 1, x)$ we have

$$
\begin{aligned}
&\lim_{|x| \to 0} \left[\phi((0, r), (1, 1), x) - \phi^{\mathrm{at}}(0, 1, x) \right] \\
&= \frac{1}{|r|} + \int \frac{(3\phi^{\mathrm{at}}(0, 1, y))^{3/2}}{(5\beta_{\mathrm{phys}})^{3/2} |y|} dy - \int \frac{(3\phi((0, r), (1, 1), y))^{3/2}}{(5\beta_{\mathrm{phys}})^{3/2} |y|} dy \\
&\geq \frac{1}{|r|} + (1 - \sqrt{2}) \int \frac{(3\phi((0, r), (1, 1), y))^{3/2}}{(5\beta_{\mathrm{phys}})^{3/2} |y|} dy - \sqrt{2} \int \frac{(3\phi(y - r))^{3/2}}{(5\beta_{\mathrm{phys}})^{3/2} |y|} dy \\
&\geq \frac{1}{|r|} - C
\end{aligned}
$$

for $r < 1$. The estimate (24) then follows from the Feynman-Hellmann identity (18). $\square$

5 Estimating the Kinetic Energy

Now, in order to compare the localized Hamiltonians with their localized Thomas-Fermi counterparts, we need to establish some inequalities like those of Lieb-Thirring. More specifically, we ask for estimates on $\mathrm{Tr}(-\Delta_0 - V)_-^\alpha$ where Δ_0 is the Neumann-Laplacian on the tile $l\mathcal{D}_0$ and V is a real-valued function. We are interested mainly in the cases $\alpha = 0, 1$. We point out that if we were dealing with Dirichlet Laplacians, the problem can be automatically reduced to that of the whole space just by extension. In the case at hand, this is not allowed, and because of that we shall formulate and prove first a version of these inequalities in the case of a cube. Finally we are dealing with tiles rather than cubes, but the problem for the tiles can be reduced to that of the cubes as explained in the appendix below.

Theorem 5 (Lieb-Thirring type estimate). *Let Q be the unit cube in $\mathbb{R}^3$ and $0 \leq \alpha$. If V is a real-valued function in $L^1_{\mathrm{loc}}(Q)$ for which $[V]_- \in L^{3/2+\alpha}(Q)$, then the following trace estimate holds:*

$$\mathrm{Tr}\,(-\Delta_Q - V)_-^\alpha \leq C_\alpha \int_Q [V]_-^{3/2+\alpha} + C_\alpha \left[\int_Q [V]_-\right]^\alpha \tag{25}$$

Here $-\Delta_Q$ is the Neumann-Laplacian in Q. The constant C_α depends only on α. The same result (possibly with a different constant C_α) holds if the cube Q is replaced by the tile $\mathcal{D}_0$.

We did not find a reference for this theorem and we therefore include a proof in the appendix. Using the theorem above we can provide an estimate for the kinetic energy of N antisymmetric particles on a tile (of any scale $l > 0$) in terms of the 1-particle density $\rho_\psi(x)$ which is defined as

$$\rho_\psi(x) := N \int_{(l\mathcal{D}_0)^{N-1}} \|\psi(x, x_2, \dots, x_N)\|^2_{\mathbb{C}^{2^N}}\, dx_2, \dots, dx_N \tag{26}$$

for $\psi \in \bigwedge^N (L^2(l\mathcal{D}_0; \mathbb{C}^2))$ normalized.

This function is an analogue of a charge distribution, and has the property $\int_{l\mathcal{D}_0} \rho_\psi = N$.

Theorem 6 (Kinetic energy estimate for fermions on a tile). *Let $\psi \in \bigwedge^N L^2(l\mathcal{D}_0; \mathbb{C}^2)$ normalized and define ρ_ψ as before. Then, if*

$$H_0 = \sum_{i=1}^N (-\Delta_0^i)$$

we have

$$\langle\psi, H_0\psi\rangle \geq K_{\mathrm{LT}} \int_{l\mathcal{D}_0} \rho_\psi(x)^{5/3}dx - K_1|l\mathcal{D}_0|^{-1}\int_{l\mathcal{D}_0} \rho_\psi(x)^{2/3}dx \tag{27}$$

where K_{LT} and K_1 are positive and finite absolute constants.

Proof. By a simple rescaling it is enough to consider the case $l = 1$. Let us define the potential $V(x) = -\rho_\psi(x)^{2/3}$ and the N-particle Hamiltonian $H_N := \sum_{i=1}^N(-\Delta_0^i + \lambda V(x_i))$ where $\lambda > 0$ is a parameter to be fixed later. This Hamiltonian acts on $\bigwedge^N(L^2(l\mathcal{D}_0;\mathbb{C}^2))$, and it can be diagonalized by the eigenfunctions of $H_V = -\Delta_0 + V$ on $L^2(l\mathcal{D}_0;\mathbb{C}^2)$. In fact, the lowest eigenvalue of H_N is just the sum of the first N negative eigenvalues of H_V so we have from Theorem 5 that

$$\inf \mathrm{spec} H_N = -\mathrm{Tr}(H_V)_- \geq -C_{\mathrm{LT}}\lambda^{5/2}\int_{\mathcal{D}_0} \rho_\psi(x)^{5/3}dx - \frac{C_1\lambda}{|\mathcal{D}_0|}\int_{\mathcal{D}_0}\rho_\psi(x)^{2/3}dx$$

From the variational principle

$$\langle\psi, H_0\psi\rangle - \frac{\lambda}{|\mathcal{D}_0|}\int_{\mathcal{D}_0}\rho_\psi(x)^{5/3}dx = \langle\psi, H_N\psi\rangle \geq \inf \mathrm{spec} H_N$$

and thus we get

$$\langle\psi, H_0\psi\rangle \geq (\lambda - C_{\mathrm{LT}}\lambda^{5/3})\int_{\mathcal{D}_0}\rho_\psi(x)^{5/3}dx - \frac{C_1\lambda}{|\mathcal{D}_0|}\int_{\mathcal{D}_0}\rho_\psi(x)^{2/3}dx \tag{28}$$

The theorem follows by choosing λ appropriately. □

Theorem 6 will be one of the main tools to provide a link between Quantum Theory and Thomas-Fermi theory. This is the subject of the next section.

6 Estimating the energy of the tiles with too many nuclei.

The principal task we will pursue in this section is to prove that the energy of the localized pieces of the Hamiltonian on tiles is positive if the tile contains a large enough number of nuclei, depending only on the average charge $\overline{Z}$ of these nuclei and the scale l of the tiles. We shall use the estimate for the kinetic energy given by Theorem 6, but we also need an estimate which allow us to compare the electron-electron repulsion term of the localized quantum Hamiltonians with the corresponding term in the Thomas-Fermi functional (11). Such an estimate is provided by the Lieb-Oxford inequality (see [18]).

Lemma 3 (Lieb-Oxford inequality). *Let* $\psi \in L^2(\mathbb{R}^{3N}; \mathbb{C}^{2^N})$ *normalized and* $\rho_\psi(x)$ *the corresponding 1-particle density function. Then*

$$\left\langle \psi, \sum_{i<j}^{N} \frac{1}{|x_i - x_j|} \psi \right\rangle \geq \frac{1}{2} \iint \frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|} dxdy - 1.68 \int \rho_\psi(x)^{4/3} dx \tag{29}$$

We are now in a position to prove a lower bound on the localized Hamiltonians in terms of the *neutral* Thomas-Fermi theory.

Lemma 4 (Lower bound in terms of TF theory). *Let* $H_{\alpha,N'}$ *be the operator defined in (9) acting acting on* $\bigwedge^{N'} L^2(l\mathcal{D}_\alpha(R,y); \mathbb{C}^2)$. *We assume as before that* $a\overline{Z} \leq Z_j \leq A\overline{Z}$ *for all* $j = 1, \ldots, M$. *Then there exists a* $c > 0$ *depending only on* a, A *such that*

$$\inf \mathrm{spec} H_{\alpha,N'} \geq E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} - cN'(l^{-2} + 1) \tag{30}$$

where $\beta_0 = K_{\mathrm{LT}}/2$ *and* $\mathcal{R}_\alpha$ *and* $\mathcal{Z}_\alpha$ *are the coordinates and charges of the nuclei in the tile* $l\mathcal{D}_\alpha(R,y)$.

Proof. From the kinetic energy estimate (27) and the Lieb-Oxford inequality (29) we get, for $\psi \in \bigwedge^{N'} (L^2(l\mathcal{D}_\alpha(R,y); \mathbb{C}^2))$ normalized that

$$\begin{aligned} \langle \psi, H_{\alpha,N'} \psi \rangle \geq\ & K_{\mathrm{LT}} \int \rho_\psi^{5/3} - \int V_\alpha(x) \rho_\psi(x) dx \\ & + \frac{1}{2} \iint \frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|} dxdy + U_\alpha \\ & - C\left(\int \rho_\psi^{4/3} + l^{-3} \int \rho_\psi^{2/3} \right) \end{aligned} \tag{31}$$

where

$$V_\alpha(x) := \sum_{j=1}^{M} \frac{Z_j}{|x - R_j|} \chi_\alpha(R_j) \quad \text{and} \quad U_\alpha := \sum_{i<j}^{M} \frac{Z_i Z_j}{|R_i - R_j|} \chi_\alpha(R_i)\chi_\alpha(R_j) \tag{32}$$

Using Hölder's inequality and the fact that ρ_ψ is supported in $l\mathcal{D}_\alpha(R,y)$ we have

$$\int \rho_\psi^{4/3} \leq \left(\int \rho_\psi^{5/3} \right)^{1/2} (N')^{1/2} \quad \text{and} \quad \int \rho_\psi^{2/3} \leq c(N')^{2/3} l \leq N' l \tag{33}$$

Hence

$$\frac{K_{\mathrm{LT}}}{2} \int \rho_\psi^{5/3} - C\left(\int \rho_\psi^{4/3} + l^{-3} \int \rho_\psi^{2/3} \right) \geq -cN'(l^{-2} + 1)$$

□

We shall see now that if a tile contains too many nuclei then the Thomas-Fermi energy $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$ is positive. If on the other hand the tile contains so few nuclei that the Thomas-Fermi energy is negative we shall in the next section prove an estimate similar to (30) but with the correct physical constant β_{phys} rather than β_0.

Lemma 5. *Consider a tile $l\mathcal{D}_\alpha(R,y)$ and let $\mathcal{Z}_\alpha$ and $\mathcal{R}_\alpha$ denote the charges and positions of nuclei in this tile. Assume as before that all the nuclear charges are bounded below by $a\overline{Z}$ and above by $A\overline{Z}$. Let M_α denote the number of nuclei in the tile. There is then a constant $c>0$ depending only on a, and A such that for all $\beta>0$ $E^{\beta}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}\geq 0$ if $M_\alpha\geq\max\{2,c\beta^{-3}l^3\overline{Z}\}$.*

Proof. By the scaling property (13) of Thomas-Fermi theory we need only consider the case $\beta=\beta_{\mathrm{phys}}$ and $l=1$. From Lemma 2 we have

$$E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}\geq -C_{\mathrm{TF}}M_\alpha(A\overline{Z})^{7/3}+c(a\overline{Z})^{7/3}\lambda^{-1}M' \tag{34}$$

where M' is the number of nuclei in the tile for which the distance to the nearest other nuclei in the tile is less than or equal to $\lambda(a\overline{Z})^{-1/3}$ for some $0<\lambda<1$. We can place $M_\alpha-M'$ disjoint balls of radius $(a\overline{Z})^{-1/3}\lambda/2$ centered at all the remaining nuclei. Since $M_\alpha\geq 2$ it is clear that either $M_\alpha-M'=0$ or this radius is universally bounded. Thus we see that these balls cover a region of universally bounded volume. We conclude that $(M_\alpha-M')\leq ca\overline{Z}\lambda^{-3}$.

Hence

$$E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}\geq M_\alpha\overline{Z}^{7/3}\left(-C_{\mathrm{TF}}A^{7/3}+ca^{7/3}\lambda^{-1}\right)-c(a\overline{Z})^{10/3}\lambda^{-4}$$

and the lemma follows if we choose λ small enough. ☐

7 Proving the main result.

We shall now use a semiclassical approximation to show that if the number of nuclei in a tile is small enough then one may use the correct physical constant β_{phys} instead of β_0 in the lower bound in (30) . The semiclassical approximation will be done using the method of coherent states in a manner very similar to the argument given in [15].

Lemma 6 (Lower bound in terms of physical TF theory). *Let $H_{\alpha,N'}$ be the operator defined in (9) acting acting on $\bigwedge^{N'}L^2(l\mathcal{D}_\alpha(R,y);\mathbb{C}^2)$. We assume as before that $a\overline{Z}\leq Z_j\leq A\overline{Z}$ for all $j=1,\ldots,M$. Assume moreover that $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}\leq 0$, where $\beta_0=K_{\mathrm{LT}}/2$ and $\mathcal{R}_\alpha$ and $\mathcal{Z}_\alpha$ are the coordinates and charges of the nuclei in the tile $l\mathcal{D}_\alpha(R,y)$. Then there exist constants $c,C>0$ depending only on a,A such that if we choose $\delta=2/87$ and $l=\overline{Z}^{-\frac{1}{3}+\delta}$ then*

$$\inf\mathrm{spec}H_{\alpha,N'}\geq E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}-cN'\overline{Z}^{\frac{4}{3}-\delta}-CM_\alpha\overline{Z}^{\frac{7}{3}-\delta}, \tag{35}$$

where M_α is the number of nuclei in the tile.

Proof. Lemma 5 shows that the condition $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \leq 0$ implies that $M_\alpha \leq \max\{2, Cl^3\overline{Z}\}$. We shall choose l such that $l^3\overline{Z} \geq 1$ (see the end of the proof) we may therefore assume that $M_\alpha \leq Cl^3\overline{Z}$.

For $\psi \in \bigwedge^{N'}(L^2(\mathcal{D}_\alpha(R,y);\mathbb{C}^2))$ normalized we consider again the 1-particle density function $\rho_\psi(x)$ defined in (26). Using the Lieb-Oxford inequality (29) and the positivity of the Coulomb kernel,

$$D(f,g) := \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{f(x)\overline{g(y)}}{|x-y|}dxdy$$

we find that for any $0 \leq \tilde{\rho} \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3)$ and $0 < \epsilon < 1$ we have

$$\langle\psi, H_{\alpha,N'}\psi\rangle \geq \left\langle \psi, \sum_{i=1}^{N'} h_i\psi \right\rangle - D(\tilde{\rho},\tilde{\rho}) - (1.68)\int \rho_\psi(x)^{4/3}dx + \epsilon\langle\psi, H_0\psi\rangle + U_\alpha \tag{36}$$

where we have introduced the one-particle operator

$$h := -(1-\epsilon)\Delta_\alpha - V_\alpha(x) + |\cdot|^{-1} * \tilde{\rho}(x)$$

and used V_α and U_α defined in (32). In equation (36) we have kept part of the kinetic energy $\langle\psi, H_0\psi\rangle = \sum_{i=1}^{N'}\langle\psi, -\Delta^i_\alpha\psi\rangle$ in order to later use it to control errors.

We choose $\tilde{\rho}$ to be the density that minimizes the Thomas-Fermi problem with parameter β equal to $(1-\epsilon)\beta_{\mathrm{phys}}$, i.e., $\mathcal{E}^\beta_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}(\tilde{\rho}) = E^\beta_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$.

It is not convenient to work with Neumann Laplacians, so our next goal is to replace them by Dirichlet Laplacians. In order to do this we take a partition of unity, with the following properties, on $l\mathcal{D}_\alpha(R,y)$

$$0 \leq \Theta_t, \Xi_t \leq 1 \tag{37}$$
$$\Theta_t^2 + \Xi_t^2 = 1 \tag{38}$$
$$\Theta_t(x) = 1 \text{ if } \mathrm{dist}(x, \partial l\mathcal{D}_\alpha) \geq t \tag{39}$$
$$\Theta_t(x) = 0 \text{ if } \mathrm{dist}(x, \partial l\mathcal{D}_\alpha) \leq \frac{t}{2} \tag{40}$$
$$|\nabla\Theta_t|_\infty + |\nabla\Xi_t|_\infty \leq \frac{C}{t} \tag{41}$$
$$|\Delta\Theta_t|_\infty + |\Delta\Xi_t|_\infty \leq \frac{C}{t^2} \tag{42}$$

For any $\phi \in L^2(l\mathcal{D}_\alpha(R,y);\mathbb{C}^2)$ we then have (omitting the parameters R, y)

$$\begin{aligned}\int_{l\mathcal{D}_\alpha} |\nabla\phi|^2 &= \int_{l\mathcal{D}_\alpha} \Theta_t^2 |\nabla\phi|^2 + \int_{l\mathcal{D}_\alpha} \Xi_t^2 |\nabla\phi|^2 \\ &= \int_{l\mathcal{D}_\alpha} |\nabla(\phi\Theta_t)|^2 + \int_{l\mathcal{D}_\alpha} |\phi|^2 \Theta_t \Delta\Theta_t + \int_{l\mathcal{D}_\alpha} |\nabla(\phi\Xi_t)|^2 + \int_{l\mathcal{D}_\alpha} |\phi|^2 \Xi_t \Delta \Xi_t \\ &\geq \int_{l\mathcal{D}_\alpha} |\nabla(\phi\Theta_t)|^2 + \int_{l\mathcal{D}_\alpha} |\nabla(\phi\Xi_t)|^2 - \frac{C}{t^2}\int_{l\mathcal{D}_\alpha} |\phi|^2 \qquad (43)\end{aligned}$$

Let γ be the one-particle density matrix on $L^2(l\mathcal{D}_\alpha;\mathbb{C}^2)$ defined as the operator with integral kernel

$$\gamma(x,y) := N' \int_{(l\mathcal{D}_\alpha(R,y))^{N'-1}} \langle \psi(y,x_2,\ldots,x_{N'}), \psi(x,x_2,\ldots,x_{N'})\rangle dx_2 \ldots dx_{N'} \qquad (44)$$

where $\langle\ ,\ \rangle$ here denotes the inner product (antilinear in the first variable) in $\mathbb{C}^{2^{N'}}$. Because of the antisymmetry of ψ, the one-particle density matrix γ satisfies the fundamental operator inequalities

$$0 \leq \gamma \leq \mathbf{1};\ \ 0 \leq \mathrm{Tr}\,\gamma \leq N' \qquad (45)$$

To any positive definite trace class operator γ' on $L^2(\mathbb{R}^3;\mathbb{C}^2)$ we have a non-negative density $\rho_{\gamma'} \in L^1(\mathbb{R}^3)$, defined by $\mathrm{Tr}(\gamma' f) = \int \rho_{\gamma'}(x) f(x) dx$ for any $f \in L^\infty(\mathbb{R}^3)$ identified as a multiplication operator on $L^2(\mathbb{R}^3;\mathbb{C}^2)$ (it is a simple exercise in measure theory to see that this defines an L^1 function). In the special case (44) we have $\rho_\gamma(x) = \gamma(x,x) = \rho_\psi(x)$. Moreover (assuming that ψ is in the operator domain of H_0) we have that $\left\langle \psi, \sum_{i=1}^{N'} h_i \psi \right\rangle = \mathrm{Tr}(h\gamma)$ so in terms of γ we can rewrite (36) as

$$\langle \psi, H_{\alpha,N'}\psi\rangle \geq \mathrm{Tr}\,(h\gamma) - D(\tilde\rho,\tilde\rho) - (1.68)\int_{\mathbb{R}^3} \rho_\psi(x)^{4/3} dx + \epsilon\langle\psi, H_0\psi\rangle + U_\alpha \quad (46)$$

By (45) γ can be written as

$$\gamma = \sum_i \lambda_i \langle u_i, \cdot\rangle u_i;\ \ 0 \leq \lambda_i \leq 1;\ \ \{u_i\} \text{ orthonormal set} \qquad (47)$$

where the functions u_i belong to the Sobolev space $H^2(l\mathcal{D}_\alpha(R,y);\mathbb{C}^2)$. using this spectral representation together with (43) yields

$$\mathrm{Tr}(h\gamma) \geq \mathrm{Tr}\,(h\Theta_t\gamma\Theta_t) + \mathrm{Tr}\,(h\Xi_t\gamma\Xi_t) - \frac{C}{t^2}N' \qquad (48)$$

where in (48) both Θ_t and Ξ_t are regarded as multiplication operators.

Let $\gamma_t^{(1)} = \Theta_t \gamma \Theta_t$ and $\gamma_t^{(2)} = \Xi_t \gamma \Xi_t$. Then $\gamma_t^{(1)}$ and $\gamma_t^{(2)}$ fulfill the bounds (45) if γ does. We now notice that

$$\operatorname{Tr}\left(h\gamma_t^{(1)}\right) = \operatorname{Tr}\left(h\Theta_t\gamma\Theta_t\right) = \operatorname{Tr}\left(\tilde{h}\Theta_t\gamma\Theta_t\right) \tag{49}$$

where $\tilde{h}$ is defined as h but with Dirichlet boundary conditions instead of Neumann boundary conditions.

Now (46), (48) and (49) imply that

$$\begin{aligned}\langle\psi, H_{\alpha,N'}\psi\rangle \;\geq\; & \operatorname{Tr}\left(\tilde{h}\gamma_t^{(1)}\right) - D(\tilde{\rho},\tilde{\rho}) + U_\alpha - (1.68)\int_{\mathbb{R}^3}\rho_\psi(x)^{4/3}dx \\ & +\epsilon\langle\psi, H_0\psi\rangle + \operatorname{Tr}\left(h\gamma_t^{(2)}\right) - \frac{C}{t^2}N' \end{aligned}\tag{50}$$

Now we shall use coherent states given as follows: pick some function $g \in H^1(\mathbb{R}^3)$ which is spherically symmetric and with $\int_{\mathbb{R}^3}|g|^2 = 1$. Introduce a parameter $r > 0$ and the family of functions $g_r := r^{-3/2}g(r^{-1}\cdot)$. The coherent states we shall use are then given by

$$f_{p,s;r}(x) = g_r(x-s)\mathrm{e}^{ip\cdot x};\; p, s \in \mathbb{R}^3 \tag{51}$$

and let us introduce the projections

$$\pi_{p,s;r} = \langle f_{p,s;r}, \cdot\rangle f_{p,s;r}\otimes I;\; I = \begin{pmatrix} 1 & 0 \\ 0 & 1\end{pmatrix} \tag{52}$$

Then, for any $m \in L^2(\mathbb{R}^3;\mathbb{C}^2)$ a computation gives

$$\begin{aligned} \|m\|^2 &= (2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\langle m, \pi_{p,s;r}m\rangle dp\, ds \\ \int_{\mathbb{R}^3}|\nabla m(x)|^2 dx &= (2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}|p|^2\langle m, \pi_{p,s;r}m\rangle dp\, ds \\ &\quad -\|m\|^2\int_{\mathbb{R}^3}|\nabla g_r(x)|^2 dx \\ \int_{\mathbb{R}^3}|m(x)|^2\tilde{\phi}_r(x)dx &= (2\pi)^{-3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\tilde{\phi}(s)\langle m, \pi_{p,s;r}m\rangle dp\, ds \end{aligned}\tag{53}$$

where $\tilde{\phi}_r(x) = |g_r|^2 * \tilde{\phi}(x)$ and $\tilde{\phi}$ is any function on $\mathbb{R}^3$. We shall now use this for the specific choice $\tilde{\phi}(x) = V_\alpha(x) - |\cdot|^{-1} * \tilde{\rho}(x)$, i.e., the potential appearing in the operators h and $\tilde{h}$. Introducing the operator $\tilde{h}_r = -(1-\epsilon)\Delta_i - \tilde{\phi}_r$ we split the first term in (50) as follows

$$\operatorname{Tr}\left(\tilde{h}\gamma_t^{(1)}\right) = \operatorname{Tr}\left(\tilde{h}_r\gamma_t^{(1)}\right) + a_r\left(\gamma_t^{(1)}\right) \tag{54}$$

Here

$$a_r(\gamma_t^{(1)}) = -\int_{\mathbb{R}^3} \left[V_\alpha(x) - |g_r|^2 * V_\alpha(x) - (\Psi(x) - |g_r|^2 * \Psi(x))\right] \rho_{\gamma_t^{(1)}}(x) dx$$

where $\Psi = |\cdot|^{-1} * \tilde{\rho}$ and $\rho_{\gamma_t^{(1)}}(x)$ is the density corresponding to the operator $\gamma_t^{(1)}$.

We may then write

$$\begin{aligned} \operatorname{Tr}\left(\tilde{h}_r \gamma_t^{(1)}\right) &= (2\pi)^{-3} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \left[(1-\epsilon)|p|^2 - \tilde{\phi}(s)\right] M(p,s) dp\, ds \\ &\quad - \operatorname{Tr} \gamma_t^{(1)} \int_{\mathbb{R}^3} |\nabla g_r(x)|^2 dx \end{aligned} \tag{55}$$

where $M(p,s) = \operatorname{Tr}\left(\gamma_t^{(1)} \pi_{p,s;r}\right)$. We have here considered $\gamma_t^{(1)}$ as an operator on all of $L^2(\mathbb{R}^3; \mathbb{C}^2)$. The function $M(p,s)$ satisfies

$$0 \leq M(p,s) \leq 2 \tag{56}$$

If we minimize (55) over the functions with the property (56) we find that the minimum is given by the "bath-tub" principle, which tell us that the minimizer actually is the function $M(p,s) = 2\chi_{\{(p,s):\tilde{\phi}(s)-(1-\epsilon)|p|^2 \geq 0\}}$. A straightforward calculation then shows that

$$\operatorname{Tr}\left(\tilde{h}_r \gamma_t^{(1)}\right) - D(\tilde{\rho}, \tilde{\rho}) + U_\alpha \geq E^{\beta}_{\mathrm{TF}, \mathcal{R}_\alpha, \mathcal{Z}_\alpha} - CN' r^{-2} \tag{57}$$

Returning to the estimate of the error term a_r we note that $\Psi - |g_r|^2 * \Psi \geq 0$ since (being the convolution of $|\cdot|^{-1}$ against some integrable function) ψ is *superharmonic* and $|g_r|^2$ is spherically symmetric and of integral one. Therefore

$$\begin{aligned} a_r(\gamma_t^{(1)}) &\geq -\int_{\mathbb{R}^3} \left(V_\alpha - |g_r|^2 * V_\alpha\right) \rho_{\gamma_t^{(1)}} \\ &\geq -\left\|V_\alpha - |g_r|^2 * V_\alpha\right\|_{5/2} \left\|\rho_{\gamma_t^{(1)}}\right\|_{5/3} \end{aligned} \tag{58}$$

by Hölder's inequality. We will use the term $\epsilon\langle\psi, H_0\psi\rangle$ in (50) to control the errors $a_r(\gamma_t^{(1)})$ and $-C\int \rho_\psi^{4/3}$ through the use of the Lieb-Thirring estimate Theorem 6. If we write

$$b_r := \epsilon\langle\psi, H_0\psi\rangle - (1.68)\int \rho_\psi(x)^{4/3} dx - a_r(\gamma_t^{(1)}) \tag{59}$$

we find from Theorem 6 and Hölder's inequality (see also (33))that

$$b_r \geq -C\epsilon^{-3/2} \left\|V_\alpha - |g_r|^2 * V_\alpha\right\|_{5/2}^{5/2} - C(\epsilon^{-1} + l^{-2})N' \tag{60}$$

where we have used the obvious fact that $\rho_{\gamma_t^{(1)}} \leq \rho_\psi$. From Minkowski's inequality we have that

$$\begin{aligned} \left\| V_\alpha - |g_r|^2 * V_\alpha \right\|_{5/2} &\leq \sum_{j=1}^{M_\alpha} Z_j \left\| |\cdot - R_j|^{-1} - |g_r|^2 * |\cdot - R_j|^{-1} \right\|_{5/2} \\ &\leq A\overline{Z} \sum_{j=1}^{M_\alpha} \left\| |\cdot - R_j|^{-1} - |g_r|^2 * |\cdot - R_j|^{-1} \right\|_{5/2} \end{aligned}$$

but a computation gives

$$\left\| |\cdot - R_j|^{-1} - |g_r|^2 * |\cdot - R_j|^{-1} \right\|_{5/2} = Cr^{1/5} \tag{61}$$

so we get

$$\left\| V_\alpha - |g_r|^2 * V_\alpha \right\|_{5/2}^{5/2} \leq Cr^{1/2} (\overline{Z} M_\alpha)^{5/2} \leq CM_\alpha r^{1/2} l^{9/2} \overline{Z}^4 \tag{62}$$

It remains to estimate the term $\mathrm{Tr}\left(h\gamma_t^{(2)}\right)$ in (50). First we note that

$$\mathrm{Tr}\left(h\gamma_t^{(2)}\right) = \mathrm{Tr}\left(h_t\gamma_t^{(2)}\right) \quad \text{with} \quad h_t = -(1-\epsilon)\Delta_\alpha - V_\alpha(x)\chi_{\{x:\mathrm{dist}(x,\partial(l\mathcal{D}_\alpha))\leq t\}} \tag{63}$$

Now we will apply the Lieb-Thirring inequality from Theorem 5

$$\begin{aligned} \mathrm{Tr}\left(h_t\gamma_t^{(2)}\right) &\geq -\mathrm{Tr}\left(h_t\gamma_t^{(2)}\right)_- \geq -\mathrm{Tr}\,(h_t)_- \\ &\geq -C_{\mathrm{LT}} \int_{l\mathcal{D}_\alpha} V_\alpha(x)^{5/2} \chi_{\{x:\mathrm{dist}(x,\partial(l\mathcal{D}_\alpha))\leq t\}} dx \\ &\quad -C_1 l^{-3} \int_{l\mathcal{D}_\alpha} V_\alpha(x) \chi_{\{x:\mathrm{dist}(x,\partial(l\mathcal{D}_\alpha))\leq t\}} dx \end{aligned} \tag{64}$$

where in (64) we have used that $0 \leq \gamma_t^{(2)} \leq \mathbf{1}$. Again using Minkowski's inequality we conclude that

$$\int_{l\mathcal{D}_\alpha} V_\alpha(x)^{5/2} \chi_{\{x:\mathrm{dist}(x,\partial(l\mathcal{D}_\alpha))\leq t\}} dx \leq C\left(M_\alpha \overline{Z}\right)^{5/2} t^{1/2} \leq CM_\alpha t^{1/2} l^{9/2} \overline{Z}^4 \tag{65}$$

$$l^{-3} \int_{l\mathcal{D}_\alpha} V_\alpha(x) \chi_{\{x:\mathrm{dist}(x,\partial(l\mathcal{D}_\alpha))\leq t\}} dx \leq CM_\alpha l^{-2} t \overline{Z} \tag{66}$$

Finally we must deal with the fact that it is $\beta = (1-\epsilon)\beta_{\mathrm{phys}}$ and not β_{phys} that appears in (57). We first note that it follows from the assumption that $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \leq 0$ that $E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \leq CM_\alpha \overline{Z}^{7/3}$. To see this note first that if we use the minimizer ρ_{β_0} for the functional $\mathcal{E}^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$ as a trial density in the functional $\mathcal{E}^{\beta_0/2}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$ we conclude that

$$0 \geq E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq \frac{\beta_0}{2}\int \rho_{\beta_0}^{5/3} + E^{\beta_0/2}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq \frac{\beta_0}{2}\int \rho_{\beta_0}^{5/3} - CM_\alpha \overline{Z}^{7/3}$$

where the last estimate follows from the no-binding Theorem of Thomas-Fermi theory, i.e., the positivity of the function $f^{\beta_0/2}$ (see Lemma 2). Now using ρ_{β_0} as a trial density in the physical Thomas-Fermi functional $\mathcal{E}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$ gives

$$\begin{aligned} E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} &\leq \mathcal{E}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}(\rho_{\beta_0}) = (\beta_{\mathrm{phys}} - \beta_0)\int \rho_{\beta_0}^{5/3} + E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \\ &\leq (\beta_{\mathrm{phys}} - \beta_0)\int \rho_{\beta_0}^{5/3} \leq 2(\beta_{\mathrm{phys}} - \beta_0)\beta_0^{-1} CM_\alpha \overline{Z}^{7/3} \end{aligned}$$

We are now in a position to estimate $E^{\beta}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$ in terms of the physical Thomas-Fermi energy $E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha}$. Indeed using the scaling (13) we see that

$$\begin{aligned} E^{\beta}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} &= (1-\epsilon)^6\, E_{\mathrm{TF},\mathcal{R}_\alpha,(1-\epsilon)^{-3}\mathcal{Z}_\alpha} \\ &= (1-\epsilon)^6 \left\{ f(\mathcal{R}_\alpha, (1-\epsilon)^{-3}\mathcal{Z}_\alpha) - C_{\mathrm{TF}}\,(1-\epsilon)^{-7} \sum_{j=1}^M Z_j^{7/3}\chi_\alpha(R_j) \right\} \\ &\geq (1-\epsilon)^6 \left\{ f(\mathcal{R}_\alpha, \mathcal{Z}_\alpha) - C_{\mathrm{TF}}\,(1-\epsilon)^{-7} \sum_{j=1}^M Z_j^{7/3}\chi_\alpha(R_j) \right\} \\ &= (1-\epsilon)^6 \left\{ E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} - C_{\mathrm{TF}}\left[(1-\epsilon)^{-7} - 1\right] \sum_{j=1}^M Z_j^{7/3}\chi_\alpha(R_j) \right\} \\ &\geq E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} - CM_\alpha \overline{Z}^{7/3}[2 - (1-\epsilon)^6 - (1-\epsilon)^{-7}] \end{aligned} \tag{67}$$

where in the third line of (67) we have used that f is a nondecreasing function of the nuclear charges. together with the observation that $(1-\epsilon)^{-3} > 1$ and in the bottom line the fact that $E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \leq CM_\alpha \overline{Z}^{7/3}$ and $(1-\epsilon)^6 < 1$.

The lemma now follows if we combine all the estimates (50), (54), (57), (59), (60), (62), (64), (65), (66), and (67) and choose $\epsilon = \overline{Z}^{-\delta}$, $r = \overline{Z}^{-57\delta/2}$, $l = \overline{Z}^{-1/3+\delta}$, $t = \overline{Z}^{-51\delta/2}$, where $\delta = 2/87$. $\square$

We are now ready to prove the main result Theorem 1.

Proof of Theorem 1. We use a tiling as before with $l = \overline{Z}^{-1/3+\delta}$. For this tiling we apply (10) together with the estimates (30) and (35). If for a tile $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq 0$ we use (30) and simply use the trivial estimate

$$E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq 0 \geq -C_{\mathrm{TF}} \sum_{j=1}^M Z_j^{7/3}\chi_\alpha(R_j)$$

If $E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \leq 0$ we apply (35) together with the no-binding Theorem (the positivity of f in Lemma 2), i.e., $E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq -C_{\mathrm{TF}} \sum_j^M Z_j^{7/3} \chi_\alpha(R_j)$. We then find from (10) that

$$\inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N} \geq -C_{\mathrm{TF}} \sum_{j=1}^M Z_j^{7/3} - C\overline{Z}^{4/3-\delta} N - CM\overline{Z}^{\frac{7}{3}-\delta} - \frac{C}{l}(N + \sum_{j=1}^M Z_j^2)$$

It is a result of Lieb [16] that if $N > N_0$ where N_0 is the greatest integer smaller than or equal to $2\sum_{j=1}^M Z_j + M$ then $\inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N} \geq \inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N_0}$. We may therefore without loss of generality assume that $N \leq c(\overline{Z}+1)M$. We hence conclude that

$$\inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N} \geq -C_{\mathrm{TF}} \sum_{j=1}^M Z_j^{7/3} - CM\overline{Z}^{7/3-\delta}.$$

□

8 Estimating the density.

So far, we were concerned with estimating from *below* the quantum-mechanical energy uniformly with respect to the nuclear configurations. Now, it turns out that this can be applied to give a new bound on the density of macroscopic objects. The observation is that in Theorem 1 we disregard an important effect in Thomas-Fermi theory, namely, the positivity of the pressure. This gives us a *positive* correction to the previous estimate.

Using our estimate on the energy and the already mentioned result about the positivity of the pressure, we shall now prove that if we look at nuclear configurations which are close to those which give the minimal possible energy, then the number of nuclei per unit volume is bounded above by $\mathrm{const}\overline{Z}^{1-\delta'}$. This is the content of Theorem 2.

We shall prove Theorem 2 by applying Lemma 2. Lemma 2 is, however, purely a result about Thomas-Fermi theory. We can therefore not use it directly since we need to know beforehand that given a particular nuclear configuration the quantum energy can be well approximated from below by the physical Thomas-Fermi model. We have proved this only for the tiles where the number of nuclei and their configuration is such that the unphysical Thomas-Fermi energy is non-positive (see Lemma 6). This is where the assumption that we look only at configuration with nearly minimizing energy plays its rôle. Since it allows us to show that the number of "bad" tiles (with positive energy) should be very small. This is the content of the next lemma.

Lemma 7 (Controlling the number of nuclei in bad tiles). *Consider again the tiling of scale $l = \overline{Z}^{-1/3+\delta}$ of $\mathbb{R}^3$ and assume $\mathcal{R} \in \mathbb{R}^{3M}$ is a nuclear configuration of M nuclei of charges Z_j, $j = 1, \dots, M$ for which the assumptions of Theorem 2 hold. Let $\mathcal{A} = \{\alpha \ : \ E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \geq 0\}$, where $\mathcal{R}_\alpha$ and $\mathcal{Z}_\alpha$ are the positions and charges of the nuclei in tile $l\mathcal{D}_\alpha(R, y)$. Denote by M_α the number of nuclei in the tile. Then there exists $k > 0$ depending only on a, A, and the constant C_0 from Theorem 2 such that*

$$\left\langle \sum_{\alpha\in\mathcal{A}} M_\alpha \right\rangle \leq kM\overline{Z}^{-\delta} \tag{68}$$

Proof. As in the proof of Theorem 1 we use (10) together with the estimates (30) and (35) and the result of [16] to conclude that

$$\inf \mathrm{spec} H_{\mathcal{R},\mathcal{Z},N} \geq -C_{\mathrm{TF}} \left\langle \sum_{\alpha\notin\mathcal{A}} \sum_{j=1}^{M} Z_j^{7/3} \chi_\alpha(R_j) \right\rangle - CM\overline{Z}^{7/3-\delta} \tag{69}$$

Thus if the nuclei fulfill the assumption of Theorem 2 we immediately conclude (68). □

The following Lemma is of purely geometrical content, and. It claims that if two nuclei are nearest neighbors and are close enough, then the set of $(R, y) \in SO(3)\times Q$ for which the two nuclei belong to the same tile of the tiling $\{l\mathcal{D}_\alpha(R, y)\}$ has positive measure.

Lemma 8. *Let $B(x_0, r_0) \subset \mathcal{D}_0$ be the maximal ball contained in $\mathcal{D}_0$ and assume that $x, x' \in \mathbb{R}^3$ satisfy $|x - x'| \leq lr_0/2$. Then, if we call*

$$A_{x,x'} = \{(R, y) \in SO(3) \times Q : x, x' \text{ belong to the same tile of } \{l\mathcal{D}_\alpha(R, y)\}\}$$

we have the estimate

$$\mu(A_{x,x'}) \geq \frac{\pi}{6} r_0^3, \quad \mu = \text{ measure on } SO(3) \times Q \tag{70}$$

Proof. It is fairly easy to see that the claim is translationally invariant. We may therefore assume that $x = x_0 = 0$. Then $x, x' \in B(0, lr_0/2)$. For $|y| \leq r_0/2$ and all $R \in SO(3)$ we have

$$R^{-1}(B(0, r_0/2)) - y = B(0, r_0/2) - y \subset \mathcal{D}_0$$

Hence $x, x' \in B(0, lr_0/2) \subset lR(\mathcal{D}_0 + y) = l\mathcal{D}_\alpha(R, y)$ and the result follows. □

We are now prepared to give the proof of Theorem 2.

Proof of Theorem 2. We make the tiling localization as before with a tiling of scale $l = \overline{Z}^{-1/3+\delta}$. Let $\mathcal{A}$ be defined as in Lemma 7. We then find from (10) together with(30) and (35) and the result of [16] that

$$\inf \operatorname{spec} H_{\mathcal{R},\mathcal{Z},N} \geq \left\langle \sum_{\alpha\in\mathcal{A}} E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \right\rangle + \left\langle \sum_{\alpha\notin\mathcal{A}} E_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \right\rangle - CM\overline{Z}^{7/3-\delta} \tag{71}$$

Denote the ratio $\beta_0/\beta_{\mathrm{phys}} = t \in (0,1]$ we then have by (13) and Lemma 2

$$\begin{aligned} E^{\beta_0}_{\mathrm{TF},\mathcal{R}_\alpha,\mathcal{Z}_\alpha} &= t^{-1}E_{\mathrm{TF},t^{-1}\mathcal{R}_\alpha,\mathcal{Z}_\alpha} \\ &\geq -At^{-1}C_{\mathrm{TF}}M_\alpha\overline{Z}^{7/3} + c\overline{Z}^{7/3}\sum_{j=1}^{M}\Gamma\left(t^{-1}\overline{Z}^{1/3}\delta_\alpha(R_j)\right)\chi_\alpha(R_j) \\ &\geq -At^{-1}C_{\mathrm{TF}}M_\alpha\overline{Z}^{7/3} + c'\overline{Z}^{7/3}\sum_{j=1}^{M}\Gamma\left(\overline{Z}^{1/3}\delta_\alpha(R_j)\right)\chi_\alpha(R_j) \end{aligned} \tag{72}$$

where $c' > 0$ and $\delta_\alpha(R_j)$ denotes the nearest neighbor distance among nuclei in the tile $l\mathcal{D}_\alpha(R,y)$. We have used the scaling properties of Thomas-Fermi theory together with the fact $\Gamma(tx) \geq C(t)\Gamma(x)$ for $0 < t \leq 1$ and $C(t) > 0$ (which is easily verified).

If we insert (72) into (71) and apply Lemma 7 and Lemma 2 we arrive at

$$\begin{aligned} \inf \operatorname{spec} H_{\mathcal{R},\mathcal{Z},N} &\geq -C_{\mathrm{TF}}\sum_{j=1}^{M} Z_j^{7/3} - CM\overline{Z}^{7/3-\delta} \\ &\quad + c'\overline{Z}^{7/3}\sum_{j=1}^{M}\left\langle \sum_\alpha \Gamma\left(\overline{Z}^{1/3}\delta_\alpha(R_j)\right)\chi_\alpha(R_j)\right\rangle \end{aligned} \tag{73}$$

If $\delta(R_j) \leq lr_0/2$ we use Lemma 8 to conclude that

$$\left\langle \sum_\alpha \overline{Z}^{7/3}\Gamma\left(\overline{Z}^{1/3}\delta_\alpha(R_j)\right)\chi_\alpha(R_j)\right\rangle \geq c''\overline{Z}^{7/3}\Gamma\left(\overline{Z}^{1/3}\delta(R_j)\right)$$

For a nucleus R_j such that $\delta(R_j) \geq lr_0/2$ we cannot argue as above, but in this case we have that $\overline{Z}^{7/3}\Gamma(\overline{Z}^{1/3}\delta(R_j)) \leq \overline{Z}^{7/3-7\delta} \ll \overline{Z}^{7/3-\delta}$ and this contribution can therefore be included at the expense of increasing the constant in front of the error term. This concludes the proof of Theorem 2. □

Proof of Theorem 3. Follows immediately from Theorem 2 noticing that

$$\sum_{j=1}^{M}\Gamma\left(\overline{Z}^{1/3}\delta(R_j)\right) \geq \overline{Z}^{-7\delta_1}\#\left\{R_j \in \mathcal{R} : \delta(R_j) \leq \overline{Z}^{-1/3+\delta_1}\right\}$$

□

A Appendix: The Lieb-Thirring inequality (Th. 5):

Proof of Theorem 5. We shall look first at the case $\alpha = 0$. In the case of the Laplacian on the whole space the corresponding inequality, which holds without the last term, is the celebrated CLR estimate, proved independently by Cwickel [4], Lieb [13], and Rozenblum [23]. We are however not aware of a reference in the Neumann case. For completeness we therefore include a proof. The method of Lieb uses the Feynman-Kac formula and gives by far the best constant. In order not to introduce the Feynman-Kac formula on the cube we here appeal to Rozenblum's method.

The appearance of the constant term is due to the fact that even if $V = 0$, 0 is an eigenvalue corresponding to a constant eigenfunction.

On the orthogonal complement of the constants the Neumann Laplacian satisfies a Sobolev inequality similar to the Dirichlet Laplacian (see e.g. [1]). More precisely, there exists $C_S > 0$ such that for all rectangular boxes $\tilde{Q} \subset \mathbb{R}^3$ with eccentricity (the ratio between the longest and the shortest side) bounded by 2 we have for all $\phi \in L^2(\tilde{Q})$ with $\int_{\tilde{Q}} \phi = 0$ that

$$\int_{\tilde{Q}} |\nabla\phi|^2 \geq C_S \left\{ \int_{\tilde{Q}} |\phi|^6 \right\}^{1/3}$$

Thus if

$$\int_{\tilde{Q}} [V]_-^{3/2} \leq (C_S)^{3/2} \equiv A \tag{74}$$

we have for all ϕ with $\int_{\tilde{Q}} \phi = 0$ that

$$\begin{aligned} \int_{\tilde{Q}} |\nabla\phi|^2 + \int_{\tilde{Q}} V|\phi|^2 &\geq \int_{\tilde{Q}} |\nabla\phi|^2 - \int_{\tilde{Q}} [V]_-|\phi|^2 \\ &\geq C_S \left\{ \int_{\tilde{Q}} |\phi|^6 \right\}^{1/3} - \left\{ \int_{\tilde{Q}} [V]_-^{3/2} \right\}^{2/3} \left\{ \int_{\tilde{Q}} |\phi|^6 \right\}^{1/3} \geq 0 \end{aligned}$$

Hence $-\Delta_{\tilde{Q}} + V \geq 0$ in $\{\chi_{\tilde{Q}}\}^\perp$ if $\int_{\tilde{Q}} [V]_-^{3/2} \leq (C_S)^{3/2} \equiv A$.

Now the idea, which goes back to Rozenblum [23], is to try to cover the whole original unit cube by cubes of eccentricity bounded by 2 (which from now on will be called *bricks*) such that in each of them the condition (74) is satisfied. In order to do this we shall employ the following special case of a general covering lemma given by M. de Guzmán [12].

Lemma 9 (Covering Lemma). *Let $J(G)$ be a real-valued function defined over the class of Borel subsets of a d-dimensional cube Q which is lower-semiadditive (i.e $J(G_1 \cup G_2) \geq J(G_1) + J(G_2)$ if $G_1 \cap G_2 = \emptyset$) and continuous in measure (i.e if G_t is a nested family of sets continuous in measure, $t \to J(G_t)$ is continuous).*

Then, for every integer $n \geq 1$, there is a covering Ξ of Q by bricks $\tilde{Q} \subset Q$ such that the number of bricks $\#\Xi \leq n$, each point of the cube belongs to at most d bricks and for any $\tilde{Q} \in \Xi$

$$J(\tilde{Q}) \leq \frac{2^{d+1}}{n} J(Q) \tag{75}$$

We will use this Lemma 9 for the function

$$J(G) = \int_G [V]_-^{3/2} \tag{76}$$

together with the following, which is a consequence of the min-max principle for the eigenvalues of self-adjoint operators:

$$n_-(-\Delta_Q + V) = \min\{\operatorname{codim} \mathcal{V};\ \mathcal{V} \subset L^2(Q) : -\Delta_Q + V > 0 \text{ on } \mathcal{V}\} \tag{77}$$

where $n_-(-\Delta_Q + V)$ is the number of non-positive eigenvalues of $-\Delta_Q + V$. Now there are two cases: if $\int_{\tilde{Q}} [V]_-^{3/2} \leq A$, then we have exactly one non-positive eigenvalue. If, on the other hand, this is not satisfied, we choose n such that $\frac{16}{n} \int_Q [3V]_-^{3/2} \leq A$ and also being the smallest integer with this property. Moreover, let $\tilde{Q}_1, \ldots, \tilde{Q}_n$ be the covering given by the Guzmán Lemma and let $\mathcal{V}$ be $\operatorname{sp}\{\chi_{\tilde{Q}_1}, \ldots, \chi_{\tilde{Q}_n}\}^\perp$. Since $1 \leq \sum_{j=1}^n \chi_{\tilde{Q}_j} \leq 3$ we have, for $\phi \in \mathcal{V}$

$$\begin{aligned}
\int_Q |\nabla\phi|^2 + \int_Q V|\phi|^2 &\geq \int_Q |\nabla\phi|^2 \frac{1}{3} \sum_{j=1}^n \chi_{\tilde{Q}_j} - \int [V]_- |\phi|^2 \sum_{j=1}^n \chi_{\tilde{Q}_j} \\
&\geq \frac{1}{3} \sum_{j=1}^n \left\{ \int_{\tilde{Q}_j} |\nabla\phi|^2 - \int_{\tilde{Q}_j} [3V]_- |\phi|^2 \right\} \\
&\geq 0
\end{aligned}$$

which follows since

$$\int_{\tilde{Q}} [3V]_-^{3/2} = 3^{3/2} J(\tilde{Q}) \leq \frac{16}{n} 3^{3/2} J(Q) \leq A$$

by our choice of n and this proves the $\alpha = 0$ case. Hence

$$n_-(-\Delta_Q + V) \leq \operatorname{codim} \mathcal{V} = n \leq \frac{3^{3/2} 16}{A} \int_Q [V]_-^{3/2} + 1 \tag{78}$$

In order to deal with other α values, we need a bound on the bottom of the spectrum. This is provided by the following: write $\phi \in H^1(Q)$ as $\phi = \phi_1 + \phi_2$

where $\phi_1 = (\int_Q \phi)\chi_Q$. We have $|\phi|^2 \leq 2|\phi_1|^2 + 2|\phi_2|^2$ and then, assuming also ϕ normalized we get since $|\phi_1|^2 \leq \|\phi\|^2\chi_Q$ (recall that Q is a unit cube)

$$\begin{aligned}
\int_Q |\nabla\phi|^2 + \int_Q V|\phi|^2 &\geq C_S \left\{\int_Q |\phi_2|^6\right\}^{1/3} \\
&\quad -2\left\{\int_Q [V]_-^{\frac{3}{2-2s}}\right\}^{\frac{2-2s}{3}} \left\{\int_Q |\phi_2|^6\right\}^{\frac{1-s}{3}} - 2\int_Q [V]_- \\
&\geq \inf_{t>0}\left\{C_S t - 2\left\{\int_Q [V]_-^{\frac{3}{2-2s}}\right\}^{\frac{2-2s}{3}} t^{1-s}\right\} - 2\int_Q [V]_- \\
&\geq -C(s)\left\{\int_Q [V]_-^{\frac{3}{2-2s}}\right\}^{\frac{2(1-s)}{3s}} - 2\int_Q [V]_- \qquad (79)
\end{aligned}$$

where we have picked some $0 < s < 1$ in (79). Now we can end the proof noticing that

$$\mathrm{Tr}\,(-\Delta_Q + V)_-^\alpha = \alpha\int_0^\infty n_{-\lambda}(-\Delta_Q + V)\lambda^{\alpha-1}d\lambda \qquad (80)$$

(here $n_{-\lambda}(-\Delta_Q + V)$ is the number of eigenvalues less than or equal to λ) and moreover

$$n_{-\lambda}(-\Delta_Q + V) \leq n_-(-\Delta_Q - [V+\lambda]_-) \qquad (81)$$

which is an easy consequence of the minimax principle. Now (80), (81) together imply

$$\mathrm{Tr}\,(-\Delta_Q + V)_-^\alpha \leq \alpha\int_0^{|\inf \mathrm{spec}(-\Delta_Q+V)|} n_-(-\Delta_Q - [V+\lambda]_-)\lambda^{\alpha-1}d\lambda \qquad (82)$$

Now we choose $s = \frac{2\alpha}{3+2\alpha}$ and from (79), (80), (81) we get

$$\begin{aligned}
\mathrm{Tr}\,(-\Delta_Q + V)_-^\alpha &\leq \alpha\int_0^{|\inf \mathrm{spec}(-\Delta_Q+V)|} \lambda^{\alpha-1}d\lambda\left\{C_0\int_Q [V+\lambda]_-^{3/2}dx + 1\right\} \\
&\leq C_0\alpha\int_Q dx\int_0^{[V]_-} [V+\lambda]_-^{3/2}\lambda^{\alpha-1}d\lambda + |\inf \mathrm{spec}(-\Delta_Q+V)|^\alpha \\
&= C_0\alpha\int_Q dx[V]_-^{\frac{3}{2}+\alpha}\int_0^1 (1-\lambda)^{3/2}\lambda^{\alpha-1}d\lambda + |\inf \mathrm{spec}(-\Delta_Q+V)|^\alpha \\
&\leq C_\alpha\int_Q [V]_-^{3/2+\alpha} + 2^\alpha\left\{\int_Q [V]_-\right\}^\alpha \qquad (83)
\end{aligned}$$

where in the last inequality we have used the elementary inequalities

$$(x+y)^\alpha \leq x^\alpha + y^\alpha;\ x, y \geq 0,\ 0 < \alpha \leq 1$$

or

$$(x+y)^\alpha \leq 2^{\alpha-1}(x^\alpha + y^\alpha);\ x, y \geq 0,\ 1 < \alpha$$

and this completes the proof for the unit cube.

In order to prove the Theorem in the case of the tetrahedra described in the beginning of Sect. 2 we shall show that the Neumann eigenfunctions in a tetrahedra can be extended to Neumann eigenfunctions in the unit cube. Note that we can get all 24 tetrahedra making up the unit cube by repeated reflections (through faces) of one of the tetrahedra, say, $\mathcal{D}_0$. Moreover, it can be easily seen that it always takes an even number of reflections to return to a given tetrahedron. Since an even number of reflections leaving $\mathcal{D}_0$ invariant is the identity we see that any function on $\mathcal{D}_0$ can be extended consistently to the whole unit cube by reflections.

If ϕ is an eigenfunction of $-\Delta_{\mathcal{D}_0} - V$, then $\phi \in H^2(\mathcal{D}_0)$ (the Sobolev space of order 2) with $\partial_N \phi|_{\partial\mathcal{D}_0} = 0$. If we therefore define $\tilde{\phi}$ as the extension by reflection of ϕ to the whole unit cube Q then $\phi \in H^2(Q)$ with $\partial_N \phi|_{\partial Q} = 0$. Moreover, if $\tilde{V}$ is the reflected extension of V, then $\tilde{\phi}$ is a Neumann eigenfunction of $-\Delta_Q - \tilde{V}$ with the same eigenvalue. Thus

$$\begin{aligned}
\mathrm{Tr}\,(-\Delta_{\mathcal{D}_0} - V)_-^\alpha &\leq \mathrm{Tr}\,(-\Delta_Q - \tilde{V})_-^\alpha \\
&\leq C_\alpha \int_Q [\tilde{V}]_-^{3/2+\alpha} + C_\alpha \left(\int_Q [\tilde{V}]_-\right)^\alpha \\
&= 24 C_\alpha \int_{\mathcal{D}_0} [V]_-^{3/2+\alpha} + C_\alpha \left(24 \int_{\mathcal{D}_0} [V]_-\right)^\alpha
\end{aligned}$$

□

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