New coherent states and a new proof of the Scott correction

Jan Philip Solovej and Wolfgang L Spitzer

Abstract. We introduce new coherent states and use them to prove semi-classical estimates for Schrödinger operators with regular potentials. This can be further applied to the Thomas-Fermi potential yielding a new proof of the Scott correction for molecules.

1. Introduction

In this paper we review a novel proof of the Scott correction for neutral molecules. So suppose, we have M nuclei of positive charges $Z = (Z_1, \dots, Z_M) \in \mathbb{R}_+^M$ located at positions $R = (R_1, \dots, R_M) \in \mathbb{R}^{3N}$. We choose the charge of an electron equal to -1, so that neutrality is expressed as $|Z| = \sum_{j=1}^M Z_j = N$, where N is the number of electrons. Further, we use atomic units where $\hbar^2 = m$.

The interaction of a single electron with all the nuclei is equal to

$$V(Z, R, x) = \sum_{j=1}^{M} \frac{Z_j}{|x - R_j|}. \tag{1.1}$$

We now write the molecular non-relativistic Schrödinger operator in the form

$$\begin{aligned} H(Z,R) &= H(Z_1, \dots, Z_M; R_1, \dots, R_M) \\ &= \sum_{i=1}^{N} \left(-\tfrac{1}{2}\Delta_i - V(Z,R,x_i)\right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}. \end{aligned}$$

The operator $H(Z,R)$ acts on the space $\bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{-1,1\})$, where ± 1 refers to the spin variables. We are interested in the ground state energy,

$$E(Z,R) = \inf \operatorname{spec} H(Z,R), \tag{1.2}$$

and in particular, in an asymptotic expansion for large charges. Let us state the main theorem in this paper.

1991 *Mathematics Subject Classification.* 81Q20, 35P20.

Key words and phrases. Scott correction, semi-classical analysis, coherent states.

Theorem 1.1 (Scott correction). *Let $Z = |Z|(z_1, \ldots, z_M)$, where $z_1, \ldots, z_M > 0$ and $R = |Z|^{-1/3}(r_1, \ldots, r_M)$, with $|r_i - r_j| > r_0 > 0$, for all $i \neq j$. Then,*

$$E(Z,R) = E^{TF}(Z,R) + \tfrac{1}{2} \sum_{1\le j\le M} Z_j^2 + \mathcal{O}(|Z|^{2-1/30}), \tag{1.3}$$

as $|Z| \to \infty$, where the error term $\mathcal{O}(|Z|^{2-1/30})$ besides $|Z|$ depends only on $z_1, \ldots, z_M$, and r_0.

The leading Thomas-Fermi (TF) term, which is of the order $|Z|^{7/3}$ was first rigorously derived in the seminal work by Lieb and Simon [**LSi**] using the Dirichlet-Neumann bracketing method.

The Scott correction, i.e., the term $\frac{1}{2}\sum_{1\le j\le M} Z_j^2$ was proven by Hughes [**H**] (a lower bound), and by Siedentop and Weikard [**SW**] (both bounds) in the case of atoms. The atomic case is simpler since in TF theory atoms are spherically symmetric. Bach [**B**] proved the Scott correction for ions. Finally, Ivrii and Sigal [**IS**] accomplished a proof of the Scott correction for molecules, which was recently extended to matter by Balodis Matesanz [**M**]. Here, we present another proof for molecules.

It was later shown by Lieb [**L1**] (and independently by Thirring [**T**]) how coherent states can be used to give a simple proof of the leading TF term with good upper and lower bounds; see also a recent improvement by Balodis Matesanz and Solovej [**MS**]. We want to stress that in order to prove an asymptotic expansion for $E(Z,R)$ capturing the Scott term one basically needs to prove a local trace formula for regular potentials (see Theorem 4.1 with $n = 3$) up to the order $h^{-2+\varepsilon}$ where ε is any positive number. We accomplish $\varepsilon = 1/5$.

A quick explanation for the Z^2-correction goes as follows. Whereas the leading TF term comes from the bulk of electrons, the correction comes *only* from electrons close to the nuclei where the Coulomb attraction is unscreened by the presence of the other electrons. From the exact solution of the hydrogen atom one may extract the Scott correction (see [**L1**]). Notice, that the Scott correction for molecules is just the sum of the corresponding atomic corrections. This is not the case for the leading term.

This review is organized as follows. In Section 2 we recall the main analytic tools and state the main properties of the TF potential. We introduce the new coherent states in Section 3. In Section 4 we sketch the proof of the semi-classical estimates on the sum of negative eigenvalues for regular and the TF potential. In the last Section we present the proof of the main Theorem 1.1. For more details we refer to our paper [**SS**].

2. Preliminaries

2.1. Some Inequalities. Here we collect the main inequalities which we need in this paper. Various constants are typically denoted by the same letter C, and in all cases sharp constants do not play a role.

Let $p \ge 1$, then a complex-valued function f (and only those will be considered here) is said to be in $L^p(\mathbb{R}^n)$ if the norm $\|f\|_p := \left(\int |f(x)|^p\, dx\right)^{1/p}$ is finite. For any $1 \le p \le t \le q \le \infty$ we have the inclusion $L^p \cap L^q \subset L^t$, since by Hölder's inequality $\|f\|_t \le \|f\|_p^\lambda \|f\|_q^{1-\lambda}$ with $\lambda p^{-1} + (1-\lambda)q^{-1} = t^{-1}$.

We call γ a density matrix on $L^2(\mathbb{R}^n)$ if it is a trace class operator on $L^2(\mathbb{R}^n)$ satisfying the operator inequality $\mathbf{0} \le \gamma \le \mathbf{1}$. The density of a density matrix γ is the L^1 function ρ_γ such that $\mathrm{Tr}(\gamma\theta) = \int \rho_\gamma(x)\theta(x)dx$ for all $\theta \in C_0^\infty(\mathbb{R}^n)$ considered as a multiplication operator.

If $\psi \in \bigotimes_{i=1}^N L^2(\mathbb{R}^3 \times \{-1,1\})$ is an N-body wave-function, then its one-particle density, ρ_ψ, is defined by

$$\rho_\psi(x) = \sum_{i=1}^N \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \int |\psi(x_1,s_1;\ldots;x_N,s_N)|^2\, \delta(x_i - x)\, dx_1 \cdots x_N.$$

The next inequality we recall is crucial to most of our estimates.

THEOREM 2.1 (Lieb-Thirring inequality). **One-body case:** *Let γ be a density operator on $L^2(\mathbb{R}^n)$, then we have the Lieb-Thirring (LT) inequality*

$$\mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] \geq K_n \int \rho_\gamma^{1+2/n}, \tag{2.1}$$

where K_n is some positive constant. Equivalently, let $V \in L^{1+n/2}(\mathbb{R}^n)$ and γ a density operator, then

$$\mathrm{Tr}[(-\tfrac{1}{2}\Delta + V)\gamma] \geq -L_n \int |V_-|^{1+n/2}, \tag{2.2}$$

where $x_- := \min\{x, 0\}$, and L_n some positive constant.

Many-body case: *Let $\psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{-1,1\})$. Then,*

$$\left\langle \psi, \sum_{i=1}^N -\tfrac{1}{2}\Delta_i \psi \right\rangle \geq 2^{-2/3} K_3 \int \rho_\psi^{5/3}. \tag{2.3}$$

The original proofs of these inequalities can be found in [**LT**]. From the min-max principle it is clear that the right hand side of (2.2) is in fact a lower bound on the sum of the negative eigenvalues of the operator $-\frac{1}{2}\Delta + V$.

We shall use the following standard notation for the Coulomb energy:

$$D(f) = D(f,f) = \frac{1}{2} \iint \bar{f}(x)|x-y|^{-1} f(y)\, dxdy.$$

It is not difficult to see (by Fourier transformation) that $\|f\| := D(f)^{1/2}$ is a norm.

THEOREM 2.2 (Hardy-Littlewood-Sobolev inequality). *There exists a constant C such that*

$$D(f) \leq C\, \|f\|_{6/5}^2. \tag{2.4}$$

The sharp constant C has been found by Lieb [**L4**], see also [**LL**].

Finally, we state the two inequalities which we shall need to estimate the many-body ground state energy, $E(Z,R)$, by an energy of an effective one-particle quantum system. The first one is the electrostatic inequality providing us with a lower bound. This inequality is due to Lieb [**L3**], and was improved in [**LO**].

THEOREM 2.3 (Lieb-Oxford inequality). *Let $\psi \in L^2(\mathbb{R}^{3N})$ be normalized, and ρ_ψ its one-electron density. Then,*

$$\left\langle \psi, \sum_{1 \leq i < j \leq N} |x_i - x_j|^{-1} \psi \right\rangle \geq D(\rho_\psi) - C \int \rho_\psi^{4/3}. \tag{2.5}$$

An upper bound to $E(Z,R)$ is furnished by a variational principle for fermionic systems. This is also due to Lieb [**L2**].

THEOREM 2.4 (Lieb's Variational Principle). *Let γ be a density operator on $L^2(\mathbb{R}^3)$ satisfying $2\mathrm{Tr}\gamma = 2\int \rho_\gamma(x)\,dx \le Z$ (i.e., less than or equal to the number of electrons) with the kernel $\rho_\gamma(x) = \gamma(x,x)$. Then,*

$$E(Z,R) \le 2\mathrm{Tr}\Big[\big(-\tfrac{1}{2}\Delta - V(Z,R,x)\big)\,\gamma\Big] + D(2\rho_\gamma). \tag{2.6}$$

The factors 2 above are due to the spin degeneracy. The ground state wavefunction carries a spin and is really a function on $L^2(\mathbb{R}^{3Z};\mathbb{C}^{2^Z})$, but only its spatial dependency is of interest here.

2.2. Thomas-Fermi Theory. Here we quickly state the properties about TF theory which are needed for our proof. The original proofs can be found in [**LSi**] and [**L1**].

Consider $\mathbf{z} = (z_1,\dots,z_M) \in \mathbb{R}_+^M$ and $\mathbf{r} = (r_1,\dots,r_M) \in \mathbb{R}^{3M}$. Let $0 \le \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ then the TF energy functional, $\mathcal{E}^{\mathrm{TF}}$ (omitting the nuclei-nuclei interactions), is defined as

$$\mathcal{E}^{\mathrm{TF}}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}\int \rho(x)^{5/3}\,dx - \int V(\mathbf{z},\mathbf{r},x)\rho(x)\,dx + D(\rho), \tag{2.7}$$

where V is as in (1.1).

THEOREM 2.5 (Thomas-Fermi minimizer). *For all $\mathbf{z} = (z_1,\dots,z_M) \in \mathbb{R}_+^M$ and $\mathbf{r} = (r_1,\dots,r_M) \in \mathbb{R}^{3M}$ there exists a unique non-negative $\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)$ such that $\int \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)\,dx = \sum_{k=1}^M z_k$ and*

$$\mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) = \inf\Big\{\mathcal{E}^{\mathrm{TF}}(\rho) \;:\; 0 \le \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)\Big\}.$$

We shall denote by $E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) := \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}})$ the TF-energy. Moreover, let

$$V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) := V(\mathbf{z},\mathbf{r},x) - \rho^{\mathrm{TF}} * |x|^{-1}. \tag{2.8}$$

be the TF-potential, then $V^{\mathrm{TF}} > 0$ and $\rho^{\mathrm{TF}} > 0$, and ρ^{TF} is the unique solution in $L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ to the TF-equation:

$$V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) = \tfrac{1}{2}(3\pi^2)^{2/3}\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)^{2/3}. \tag{2.9}$$

Very crucial for a semi-classical approach is the *scaling* behavior of the TF-potential. It says that for any positive parameter h

$$V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) = h^{-4}V^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r},h^{-1}x), \tag{2.10}$$

$$\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) = h^{-6}\rho^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r},h^{-1}x), \tag{2.11}$$

$$E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) = h^{-7}E^{\mathrm{TF}}(h^3\mathbf{z},h^{-1}\mathbf{r}). \tag{2.12}$$

By $h^{-1}\mathbf{r}$ (and likewise for $h^3\mathbf{z}$) we mean that each coordinate is scaled by h^{-1}. Notice that the Coulomb-potential, V, has the claimed scaling behavior. The rest follows from the uniqueness of the solution of the TF-energy functional.

We shall now state the crucial estimates that we need about the TF potential. Let

$$d(x) = \min\{|x - r_k| \mid k = 1,\dots,M\}, \tag{2.13}$$

and

$$f(x) = \min\{d(x)^{-1/2}, d(x)^{-2}\}. \tag{2.14}$$

For each $k = 1, \dots, M$ we define the function

$$W_k(\mathbf{z}, \mathbf{r}, x) = V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) - z_k|x - r_k|^{-1}. \tag{2.15}$$

The function W_k can be continuously extended to $x = r_k$. We have the following estimate for the TF potential.

THEOREM 2.6 (Estimate on TF potential). *Let $\mathbf{z} = (z_1, \dots, z_M) \in \mathbb{R}_+^M$ and $\mathbf{r} = (r_1, \dots, r_M) \in \mathbb{R}^{3M}$. For all multi-indices α and all x with $d(x) \neq 0$ we have*

$$\left|\partial_x^\alpha V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x)\right| \leq C_\alpha f(x)^2 d(x)^{-|\alpha|}, \tag{2.16}$$

where $C_\alpha > 0$ is a constant which depends on α, $z_1, \dots, z_M$, and M.

Moreover, for $|x - r_k| < r_{\min}/2$, where $r_{\min} = \min_{k \neq \ell} |r_k - r_\ell|$ we have

$$0 \leq W_k(\mathbf{z}, \mathbf{r}, x) \leq C r_{\min}^{-1} + C, \tag{2.17}$$

where the constant $C > 0$ here depends on $z_1, \dots, z_M$, and M.

The relation of TF theory to semi-classical analysis is that the semi-classical density of a gas of non-interacting electrons moving in the TF potential is simply the TF density. More precisely, the semi-classical approximation to the density of the projection onto the eigenspace corresponding to negative eigenvalues of the Hamiltonian $-\frac{1}{2}\Delta - V^{\mathrm{TF}}$ is

$$2\int_{\frac{1}{2}p^2 - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) \leq 0} 1 \frac{dp}{(2\pi)^3} = 2^{3/2}(3\pi^2)^{-1}(V^{\mathrm{TF}})^{3/2}(\mathbf{z}, \mathbf{r}, x) = \rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x).$$

Here, the factor two on the very left is due to the spin degeneracy. Similarly, the semi-classical approximation to the energy of the gas, i.e., to the sum of the negative eigenvalues of $-\frac{1}{2}\Delta - V^{\mathrm{TF}}$ is

$$\begin{aligned} 2\int \left(\frac{1}{2}p^2 - V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x)\right)_- \frac{dpdx}{(2\pi)^3} &= -\frac{4\sqrt{2}}{15\pi^2}\int V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x)^{5/2} dx \\ &= E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}) + D(\rho^{\mathrm{TF}}). \end{aligned} \tag{2.18}$$

In Section 4 we shall make the semi-classical approximation more precise.

3. New coherent states

Coherent states provide a natural semi-classical description of quantum mechanics. We shall denote these states by $|u, q\rangle$, where $(u, q) \in \mathbb{R}^{2n}$ is a point in phase-space. Their wave-function is given by

$$\langle x|u, q\rangle = (\pi h)^{-n/4} e^{-(x-u)^2/2h} e^{iqx/h}. \tag{3.1}$$

Let $\Pi_{u,q} = |u, q\rangle\langle u, q|$ be the projection onto the coherent state $|u, q\rangle$, then they satisfy the completeness condition (in the sense of quadratic forms)

$$\int \Pi_{u,q} \frac{dudq}{(2\pi h)^n} = \mathbf{1}. \tag{3.2}$$

As functions on phase-space the coherent states are localized on a scale of the order of h. We want to broaden this by defining the operator

$$\mathcal{G}_{u,q} := \int w(u - u', q - q')\, \Pi_{u',q'}\, du'dq' \tag{3.3}$$

with

$$w(u,q) = \left(\frac{2ha}{1-ha}\right)^n e^{-a/(1-ha)\,(u^2+q^2)}.$$

The new scale is $1/a > h$, which becomes clearer when we look at its kernel,

$$\mathcal{G}_{u,q}(x,y) = (\pi h)^{-n/2} e^{-a\left(\frac{x+y}{2}-u\right)^2 + iq(x-y)/h - \frac{1}{4h^2a}(x-y)^2}. \tag{3.4}$$

For simplicity, we have chosen a Gaussian weight, w, in the definition of $\mathcal{G}_{u,q}$. We shall use the operators $\mathcal{G}_{u,q}$ as our new coherent states. [1] Note that if we let $a \to 1/h$ then $\mathcal{G}_{u,q}$ converges to $\Pi_{u,q}$. A straightforward calculation gives the following result.

Lemma 3.1 (Completeness of new coherent states). *These new coherent operators satisfy*

$$\int \mathcal{G}_{u,q}^2 \frac{dudq}{(2\pi h)^n} = \mathbf{1}. \tag{3.5}$$

This resolution of the identity provides us with a representation of Schrödinger operators as phase-space integrals. This will be useful when we prove a lower bound on the sum of the negative eigenvalues of Schrödinger operators.

Theorem 3.2 (Coherent states representation). *Consider functions F and V in $C^3(\mathbb{R}^n)$, for which all second and third derivatives are bounded. Let $\sigma(u,q) = F(q) + V(u)$, then we have for $a < 1/h$ and $b = 2a/(1+h^2a^2)$ the representation*

$$F(-ih\nabla) + V(\hat{x}) = \int \mathcal{G}_{u,q}\widehat{H}_{u,q}\mathcal{G}_{u,q}\frac{dudq}{(2\pi h)^n} + \mathbf{E} \tag{3.6}$$

as quadratic forms on $C_0^\infty(\mathbb{R}^n)$ with the operator-valued symbol

$$\widehat{H}_{u,q} = \sigma(u,q) + \frac{1}{4b}\Delta\sigma(u,q) + \partial_u\sigma(u,q)(\hat{x}-u) + \partial_q\sigma(u,q)(-ih\nabla - q). \tag{3.7}$$

The error term, $\mathbf{E}$, is a bounded operator with operator norm

$$\|\mathbf{E}\| \le Cb^{-3/2}\sum_{|\alpha|=3}\|\partial^\alpha\sigma\|_\infty + Ch^2 b\sum_{|\alpha|=2}\|\partial^\alpha\sigma\|_\infty. \tag{3.8}$$

Starting with the identity (3.5), the representation of Schrödinger operators as in (3.6) arises by splitting the product $\mathcal{G}_{u,q}^2$ apart while sandwiching the symbol $\hat{H}_{u,q}$. This operator-valued symbol can be thought of as the first order Taylor expansion of the classical symbol $\sigma(u,q)$ at $(\hat{x}, -ih\nabla)$. Clearly, one could consider higher order expansions but this in not needed here. Also notice that as $a \downarrow 1/h$ the linear term in (3.7) does not contribute in (3.6) and one gets the familiar classical approximation $\sigma(u,q) + \frac{h}{4}\Delta\sigma(u,q)$. The representation (3.6) is symmetric in space and momentum due to the symmetric Gaussian weights in the definition of $\mathcal{G}_{u,q}$.

---

[1] Sometimes (e.g. see [**L1**]) it is useful to consider other coherent states where the Gaussian function in (3.1) is replaced by a general L^2 function. Similarly, one could use them to define corresponding generalized coherent states but from a computational point of view the above choice is the simplest.

These new coherent states should not be confused with the quantum coherent operators introduced by Lieb and Solovej in [**LSo**] in order to compare two quantum systems.

One major advantage of coherent states is that a positive (upper) symbol leads to a positive operator. This is important when writing down explicit variational states and brings us to consider more generally operators of the form

$$\int \mathcal{G}_{u,q}\, f(\widehat{A}_{u,q})\, \mathcal{G}_{u,q}\, du dq. \tag{3.9}$$

Here, $\widehat{A}_{u,q} = B_0(u,q) + B_1(u,q)\cdot\hat{x} - ihB_2(u,q)\cdot\nabla$ is a Hermitian operator which is linear in $\hat{x}$ and $-ih\nabla$, and $f:\mathbb{R}\to\mathbb{R}$ is any polynomially bounded real function. We shall denote by $A_{u,q}$ the linear function $A_{u,q}(v,p) = B_0(u,q) + B_1(u,q)\cdot v + B_2(u,q)\cdot p$. When $A_{u,q}(v,p)$ is independent of (v,p), i.e., if $B_1 = B_2 = 0$ and if $a \to h^{-1}$ we recover the usual coherent states representation of an operator. Thus on the one hand, we do not use as sharp a phase-space localization as the one-dimensional coherent state projection since $a < 1/h$, but on the other hand, we use a better approximation than if $A_{u,q}$ were just a constant.

4. Proof of semi-classical estimates

4.1. Regular potentials. The key application of coherent states will be a proof of a semi-classical expansion of the sum of negative eigenvalues of (localized) Schrödinger operators. We shall restrict ourselves to localization functions supported in balls. Recall that we use the convention, $x_- = (x)_- = \min\{x, 0\}$.

THEOREM 4.1 (Local semi-classics). *Let $n \geq 3$, $\phi \in C_0^{n+4}(\mathbb{R}^n)$ be supported in a ball B_ℓ of radius $\ell > 0$. Let $V \in C^3(\bar{B}_\ell)$ be a real potential. Let $H = -h^2\Delta + V$, $h > 0$ and $\sigma(u,q) = q^2 + V(u)$. Then for all $h > 0$ and $f > 0$ we have*

$$\left|\mathrm{Tr}[\phi H \phi]_- - (2\pi h)^{-n}\int \phi(u)^2\sigma(u,q)_-\, du dq\right| \leq C h^{-n+6/5} f^{n+4/5}\ell^{n-6/5}, \tag{4.1}$$

where the constant C depends only on the dimension n,

$$\sup_{|\alpha|\leq n+4} \|\ell^{|\alpha|}\partial^\alpha\phi\|_\infty, \qquad \textit{and} \qquad \sup_{|\alpha|\leq 3}\|f^{-2}\ell^{|\alpha|}\partial^\alpha V\|_\infty. \tag{4.2}$$

Moreover, there exists a density matrix γ such that

$$\mathrm{Tr}[\phi H \phi\gamma] \leq (2\pi h)^{-n}\int \phi(u)^2\sigma(u,q)_-\, du dq + C h^{-n+6/5} f^{n+4/5}\ell^{n-6/5}, \tag{4.3}$$

and such that its density $\rho_\gamma(x)$ satisfies

$$\left|\rho_\gamma(x) - (2\pi h)^{-n}\omega_n\, |V(x)_-|^{n/2}\right| \leq C h^{-n+9/10} f^{n-9/10}\ell^{-9/10}, \tag{4.4}$$

for (almost) all $x \in B_\ell$, and

$$\left|\int \phi(x)^2\rho_\gamma(x)dx - (2\pi h)^{-n}\omega_n \int \phi(x)^2\, |V(x)_-|^{n/2}\, dx\right| \leq C h^{-n+6/5} f^{n-6/5}\ell^{n-6/5}. \tag{4.5}$$

The constants $C > 0$ in the above estimates again depend only on the dimension n, the parameters in (4.2), and the volume of the unit ball in $\mathbb{R}^n$, ω_n.

As mentioned in the Introduction, any power $\mathcal{O}(h^{-n+1+\varepsilon})$ with $\varepsilon > 0$ is sufficient to prove the Scott correction in the main theorem (1.1). The power $\frac{6}{5}$ comes from optimizing the error bound in (3.8) by choosing $b = h^{-\frac{4}{5}}$.

Sketch of proof. By a simple scaling argument we may restrict ourselves to the unit ball setting $\ell = 1$ and the case $f = 1$. We start with a sketch of the lower bound. We may assume that h is sufficiently small. Using the representation (3.6) we have that

$$\begin{aligned}\mathrm{Tr}[\phi H\phi]_- \quad &\geq \quad \mathrm{Tr}\left[\int \phi\, \mathcal{G}_{u,q}\widehat{H}_{u,q}\mathcal{G}_{u,q}\phi \frac{dudq}{(2\pi h)^n}\right]_- \\ &\quad +\mathrm{Tr}\left[\phi\left(-\epsilon h^2\Delta - C(b^{-3/2}+h^2 b)\right)\phi\right]_- . \end{aligned} \tag{4.6}$$

Here, $0<\epsilon<1/2$, and

$$\widehat{H}_{u,q} = \widetilde{\sigma}(u,q) + \frac{1}{4b}\Delta\widetilde{\sigma}(u,q) + \partial_u\widetilde{\sigma}(u,q)(\hat{x}-u) + \partial_q\widetilde{\sigma}(u,q)(-ih\nabla - q)$$

with $\widetilde{\sigma}(u,q) = (1-\epsilon)q^2 + V(u)$. Utilizing the variational principle for the first trace and the LT inequality for the second one we obtain the bound

$$(2\pi h)^n \mathrm{Tr}[\phi H\phi]_- \geq \int \mathrm{Tr}\left[\phi\, \mathcal{G}_{u,q}\left[\widehat{H}_{u,q}\right]_- \mathcal{G}_{u,q}\phi\right] dudq - C\varepsilon^{-n/2}(b^{-3/2}+h^2 b)^{1+n/2}.$$

We shall eventually choose $\varepsilon = \frac{1}{4}(b^{-3/2}+h^2 b)$. Since $\widehat{H}_{u,q}$ is a linear combination of $\hat{x}$ and ∇ this operator can be easily rotated into the momentum operator alone (up to some constant term). Then, we conveniently have an expression for the negative part of $\widehat{H}_{u,q}$, and a fortiori, the trace becomes a Gaussian-like integral which we have to estimate. In this integral, the linear function

$$H_{u,q}(v,p) = \widetilde{\sigma}(u,q) + \frac{1}{4b}\Delta\widetilde{\sigma}(u,q) + \partial_u\widetilde{\sigma}(u,q)(v-u) + \partial_q\widetilde{\sigma}(u,q)(p-q)$$

replaces the operator kernel of $\widehat{H}_{u,q}$; notice that $(\hat{x}, -ih\nabla)$ is simply substituted by (v,p).

We can show that if we consider the u-integration over u outside the ball B_2 of radius 2 then this is bounded below by $-Cb^{-3/2}$. On the other hand, the integration over B_2 can be estimated from below by

$$\int_{u\in B_2} \phi^2\left(v + h^2 ab(u-v)\right) G_b(u-v)G_b(q-p)\left[H_{u,q}(v,p)\right]_-\, dudqdpdv,$$

with $G_b(v) = (b/\pi)^{n/2}\exp(-bv^2)$. Since we are looking for a lower bound we may as well extend the last integral to $\mathbb{R}^n$. Notice that we may now perform the p-integration and obtain

$$\begin{aligned}(2\pi h)^n\mathrm{Tr}[\phi H\phi]_- \quad &\geq \quad -\frac{2\omega_n}{n+2}(1-\varepsilon)^{-\frac{n}{2}}\int \phi^2\left(v+h^2 abu\right)G_b(u)G_b(q) \\ &\qquad \times\left|\left[V(v) + \widetilde{\xi}_v(u,q) - C|u|(b^{-1}+|u|^2)\right]_-\right|^{\frac{n}{2}+1} dudqdv \\ &\quad -C(b^{-3/2}+h^2 b),\end{aligned} \tag{4.7}$$

where we have introduced the function

$$\widetilde{\xi}_v(u,q) = \frac{1}{4b}\Delta\widetilde{\sigma}(v,0) - (1-\epsilon)q^2 - \frac{1}{2}\sum_{ij}\partial_i\partial_j V(v)u_i u_j.$$

By expanding we find that

$$
\begin{aligned}
&\left|\Big[V(v)+\widetilde{\xi}_v(u,q)-C|u|(b^{-1}+|u|^2)\Big]_-\right|^{\frac{n}{2}+1}\\
&\quad\le\ |V(v)|_-^{\frac{n}{2}+1}+\Big(\frac{n}{2}+1\Big)|V(v)_-|^{\frac{n}{2}}\widetilde{\xi}_v(u,q)\\
&\qquad+C\left(\Big|\widetilde{\xi}_v(u,q)\Big|+C|u|(b^{-1}+|u|^2)\right)^2\\
&\qquad+C|u|(b^{-1}+|u|^2).
\end{aligned}
$$

We have used that since $n\ge 3$, the function $x\mapsto |x_-|^{\frac{n}{2}+1}$ is $C^2(\mathbb{R}^n)$. Hence,

$$
\begin{aligned}
(2\pi h)^n\mathrm{Tr}[\phi H\phi]_-\ \ge\ & -\frac{2\omega_n}{n+2}(1-\varepsilon)^{-\frac{n}{2}}\int\phi^2\left(v+h^2abu\right)G_b(u)G_b(q)\\
&\times\left(|V(v)_-|^{\frac{n}{2}+1}+\Big(\frac{n}{2}+1\Big)|V(v)_-|^{\frac{n}{2}}\widetilde{\xi}_v(u,q)\right)dudqdv\\
&-C(b^{-3/2}+h^2b).
\end{aligned}
$$

We now expand ϕ^2 and use the crucial identities for Gaussian integrals,

$$
\int\widetilde{\xi}_v(u,q)G_b(u)G_b(q)dudq=0\quad\text{ and }\quad\int u\,G_b(u)du=0.
$$

We arrive at the lower bound,

$$
\begin{aligned}
(2\pi h)^n\mathrm{Tr}[\phi H\phi]_-\ \ge\ & -\frac{2\omega_n}{n+2}(1-\varepsilon)^{-\frac{n}{2}}\int\phi(v)^2|V(v)|_-^{\frac{n}{2}+1}dv-C(b^{-3/2}+h^2b)\\
=\ & (1-\varepsilon)^{-\frac{n}{2}}\int\phi(v)^2\sigma(v,p)_-dvdp-C(b^{-3/2}+h^2b).
\end{aligned}
$$

Finally, we choose $a=h^{-4/5}$ and $\epsilon=b^{-3/2}$.

Now we come to the upper bound. We shall show here only the construction of the density matrix γ. Let $\chi=\chi_{(-\infty,0]}$ be the characteristic function of $(-\infty,0]$ and

$$
\hat{h}_{u,q}=\begin{cases}\sigma(u,q)+\frac{1}{4b}\Delta\sigma(u,q)+\partial_u\sigma(u,q)(\hat{x}-u)+\partial_q\sigma(u,q)(-ih\nabla-q) & \text{if } u\in B_2\\ 0 & \text{if } u\notin B_2\end{cases}
$$

We then define

$$
\gamma=\int\mathcal{G}_{u,q}\,\chi\big[\hat{h}_{u,q}\big]\,\mathcal{G}_{u,q}\,\frac{dudq}{(2\pi h)^n}. \tag{4.8}
$$

Since $\mathbf{0}\le\chi\big[\hat{h}_{u,q}\big]\le\mathbf{1}$ it is obvious that $\mathbf{0}\le\gamma\le\mathbf{1}$. The arguments showing that

$$
\mathrm{Tr}[\gamma\phi H\phi]\le(2\pi h)^{-n}\int\phi^2(u)\sigma(u,q)_-dudq+Ch^{-n+6/5}
$$

are then very similar to the above calculations for the lower bound, see [**SS**]. ☐

4.2. Thomas-Fermi potential. In this Section we shall sketch the proof of the Scott correction for the TF potential.

THEOREM 4.2 (Scott corrected semi-classics). *For all $h > 0$ and all $r_1, \dots, r_M \in \mathbb{R}^3$ with $\min_{k\neq m}|r_m - r_k| > r_0 > 0$ we have*

$$\left|\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- - (2\pi h)^{-3}\int (p^2 - V^{\mathrm{TF}}(u))_-\, dudp - \frac{1}{8h^2}\sum_{k=1}^{M} z_k^2\right| \le Ch^{-2+\frac{1}{10}}, \tag{4.9}$$

where $C > 0$ depends only on $z_1, \dots, z_M$, M, and r_0. Moreover, we can find a density matrix γ such that

$$\mathrm{Tr}\left[(-h^2\Delta - V^{\mathrm{TF}})\gamma\right] \le \mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}\right]_- + Ch^{-2+1/10}, \tag{4.10}$$

and such that

$$D\left(\rho_\gamma - \frac{1}{6\pi^2 h^3}(V^{\mathrm{TF}})^{3/2}\right) \le Ch^{-5+4/5}, \tag{4.11}$$

and

$$\int \rho_\gamma \le \frac{1}{6\pi^2 h^3}\int V^{\mathrm{TF}}(x)^{3/2}dx + Ch^{-2+1/5}, \tag{4.12}$$

with C depending on the same parameters as before.

SKETCH OF PROOF. From Theorem 2.6 we know that the TF potential has an inverse fourth power law decay far from the nuclei. Thus, a region outside some ball of radius R (which scales with h) should contribute little to the sum of negative energies. For this purpose we introduce a first partition of unity. So let us choose

$$R = h^{-1/2}, \tag{4.13}$$

and consider functions $\Phi_\pm \in C^\infty(\mathbb{R}^n)$ such that

1. $\Phi_-^2 + \Phi_+^2 = 1$,
2. $\Phi_-(x) = 1$ if $d(x) < R$ and $\Phi_-(x) = 0$ if $d(x) > 2R$.

Denote $\mathcal{I} = (\nabla\Phi_-)^2 + (\nabla\Phi_+)^2$. Then $\mathcal{I}$ is supported on a set whose volume is bounded by CR^3 (where as before C depends on M) and $\|\mathcal{I}\|_\infty \le CR^{-2}$. Using the standard IMS localization formula and then the LT inequality we find that

$$\begin{aligned}
&\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- \\
&\quad\ge \mathrm{Tr}[\Phi_-(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_-]_- + \mathrm{Tr}[\Phi_+(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_+]_- \\
&\quad\ge \mathrm{Tr}[\Phi_-(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_-]_- - C(h^2R^{-2} + h^{-3}R^{-7}).
\end{aligned}$$

With the chosen R the last term is of the order $h^{-1/2}$.

On the support of Φ_- we want to use the hydrogenic approximation of the TF potential close (of the order of h) to the nuclei, and on the rest the semi-classical estimates from the previous Section. Let us introduce the function

$$\ell(x) = \tfrac{1}{2}\Big(1 + \sum_{k=1}^{M}(|x - r_k|^2 + h^2)^{-1/2}\Big)^{-1}. \tag{4.14}$$

Note that ℓ is a smooth function with

$$0 < \ell(x) < 1, \quad \text{and} \quad \|\nabla\ell(x)\|_\infty < 1.$$

Now, we fix some localization function $\phi \in C_0^\infty(\mathbb{R}^3)$ with support in the unit ball $\{|x| < 1\}$ and such that $\int \phi(x)^2 dx = 1$. It is not difficult (cf Theorem 22, [**SS**]) to find a corresponding family of functions $\phi_u \in C_0^\infty(\mathbb{R}^3)$, $u \in \mathbb{R}^3$, where ϕ_u is supported in the ball $\{|x-u| < \ell(u)\}$, with the properties that

$$\int \phi_u(x)^2 \ell(u)^{-3} du = 1 \quad \text{and} \quad \|\partial^\alpha \phi_u\|_\infty \leq C\ell(u)^{-|\alpha|}, \tag{4.15}$$

for all multi-indices α, where $C > 0$ depends only on α and ϕ.

One can show from (2.16) in Theorem 2.6 that for all $u \in \mathbb{R}^n$ with $d(u) > 2h$,

$$\sup_{|x-u|<\ell(u)} |\partial^\alpha V^{\mathrm{TF}}(x)| \leq Cf(u)^2 \ell(u)^{-|\alpha|}, \tag{4.16}$$

where $C > 0$ depends only on α, $z_1, \ldots, z_M$, and M. This is the requirement for the semi-classical estimates from Theorem 4.1 to apply with $\ell(u) \to \ell, f(u) \to f$.

Another application of the IMS formula shows that

$$\begin{aligned} &\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- \\ &\geq \int_{d(u)<2R+1} \mathrm{Tr}[\phi_u \left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_- \ell(u)^{-3} du - Ch^{-1/2}. \end{aligned} \tag{4.17}$$

By similar arguments we get corresponding estimates for the hydrogenic operators replacing V^{TF} by $\frac{z_k}{|x-r_k|} - 1$ in the above estimates. In particular, if we choose h so small that $R > \max_k\{z_k\}$ then on the support of Φ_+ we have $-z_k|x-r_k|^{-1}+1 \geq 0$. Thus we have

$$\begin{aligned} &\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|} + 1\Big]_- \\ &\geq \int_{d(u)<2R+1} \mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|} + 1 - Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_- \ell(u)^{-3} du \\ &\quad -Ch^2R^{-2}. \end{aligned} \tag{4.18}$$

We arrive at analoguous upper bounds if we utilize the density matrix

$$\gamma = \int_{d(u)<2R+1} \phi_u \chi\left(\phi_u(-h^2\Delta - V^{\mathrm{TF}})\phi_u\right)\phi_u \ell(u)^{-3} du$$

as a trial operator. I.e.,

$$\begin{aligned} \mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- &\leq \mathrm{Tr}[(-h^2\Delta - V^{\mathrm{TF}})\gamma] \\ &= \int_{d(u)<2R+1} \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u]_- \ell(u)^{-3} du. \end{aligned} \tag{4.19}$$

Similarly,

$$\begin{aligned} &\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|} + 1\Big]_- \\ &\leq \int_{d(u)<2R+1} \mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|} + 1\Big)\phi_u\Big]_- \ell(u)^{-3} du. \end{aligned} \tag{4.20}$$

We now introduce the quantities

$$\begin{aligned} D_+(u) &:= \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_- \\ &\quad -\sum_{k=1}^{M}\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big)\phi_u\Big]_- \\ D_-(u) &:= \sum_{k=1}^{M}\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1-Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_- \\ &\quad -\mathrm{Tr}[\phi_u(-h^2\Delta - V^{\mathrm{TF}})\phi_u]_-, \end{aligned}$$

and

$$\begin{aligned} D_{\mathrm{SC}}(u) &:= (2\pi h)^{-3}\int \phi_u(x)^2(p^2 - V^{\mathrm{TF}}(x))_- dpdx \\ &\quad -(2\pi h)^{-3}\sum_{k=1}^{M}\int \phi_u(x)^2\Big(p^2 - \frac{z_k}{|x-r_k|}+1\Big)_- dpdx \end{aligned}$$

Then, from (4.17), and (4.19) we have

$$\begin{aligned} &\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- - \sum_{k=1}^{M}\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- \\ &\geq \int_{d(u)<2R+1} D_+(u)\ell(u)^{-3}du - Ch^{-1/2}, \end{aligned} \tag{4.21}$$

and from (4.15) we get

$$\begin{aligned} &(2\pi h)^{-3}\int (p^2 - V^{\mathrm{TF}}(x))_- dpdx - (2\pi h)^{-3}\sum_{k=1}^{M}\int\Big(p^2 - \frac{z_k}{|x-r_k|}+1\Big)_- dpdx \\ &= \int D_{\mathrm{SC}}(u)\ell(u)^{-3}du. \end{aligned} \tag{4.22}$$

Next, we compute explicitly both the quantum and the semi-classical energies for the Coulomb potential, namely

$$\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- = \sum_{1\leq n\leq z_k/(2h)}\Big(-\frac{z_k^2}{4h^2}+n^2\Big) = -\frac{z_k^3}{12h^3}+\frac{z_k^2}{8h^2}+\mathcal{O}(h^{-1}),$$

and

$$(2\pi h)^{-3}\int\Big(p^2 - \frac{z_k}{|u-r_k|}+1\Big)_- dudp = -\frac{z_k^3}{12h^3}.$$

The first statement of the theorem is thus proven once we establish lower bounds on $D_+(u) - D_{\mathrm{SC}}(u)$ and $D_-(u) + D_{\mathrm{SC}}(u)$. Here, we have to distinguish between the region $d(u) < 2h$ and the semi-classical region, $2h < d(u) < 2R+1$.

In the region close to the nuclei, $d(u) < 2h$, we use the estimate (2.17) on the potential, $W_k(x) = V^{\mathrm{TF}}(x) - z_k|x-r_k|^{-1}$. Then, all bounds on $D_\pm(u)$ are obtained via the LT inequality.

Secondly, let $2h < d(u) < 2R+1$. On the ball $\{x \mid |x-u| < \ell(u)\}$, the TF potential satisfies the estimate (4.16) and ϕ_u satisfies (4.15). Hence, we may use Theorem 4.1. A similar semi-classical estimate holds for the Coulomb potential, $-\frac{z_k}{|x-r_k|}+1$.

The density matrix which we choose for (4.10–4.12) to hold is constructed as follows. If $2h < d(u)$ it follows from (4.15), (4.16), and Theorem 4.1 that we may choose γ_u such that (4.3), (4.4), and (4.5) hold when $V = V^{\mathrm{TF}}$, $\phi = \phi_u$, $\ell = \ell(u)$ and $f = f(u)$.

If $d(u) \leq 2h$ we simply choose

$$\gamma_u = \chi\left[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u\right],$$

where χ is again the characteristic function of the interval $(-\infty, 0]$. I.e., γ_u is the projection onto the non-positive spectrum of $\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u$. Here we are considering ϕ_u as a multiplication operator.

Finally, we set

$$\gamma = \int_{d(u)<R} \phi_u\gamma_u\phi_u\ell(u)^{-3}du. \tag{4.23}$$

By the properties (4.15), γ is a density matrix.

□

5. Proof of main theorem

The proof of the main theorem on the molecular ground state energy is a rather standard application of the results presented in the previous Sections. We prove lower and upper bounds.

Proof of Theorem 1.1. The starting point for a lower bound is the Lieb-Oxford inequality (2.5) from which we conclude that if ψ is a Z-particle ($N = Z$) then

$$\langle\psi, H(Z,R)\psi\rangle \geq \sum_{i=1}^{Z}\left\langle\psi, \left[-\tfrac{1}{2}\Delta_i - V(Z,R,x_i)\right]\psi\right\rangle + D(\rho_\psi) - C\int\rho_\psi^{4/3}.$$

In order to bound the last term we use the many-body version of the LT inequality (2.3). For all $0 < \varepsilon < 1/2$ we have

$$\left\langle\psi, \varepsilon\sum_{i=1}^{Z} -\tfrac{1}{2}\Delta_i\psi\right\rangle - C\int\rho_\psi^{4/3} \quad\geq\quad -\varepsilon^{-1}C\int\rho_\psi = -C\varepsilon^{-1}Z.$$

Here we have used Hölder's inequality for the $\rho^{4/3}$ integral and the assumption that ψ is a Z-particle state. Thus

$$\begin{aligned}
&\langle\psi, H(Z,R)\psi\rangle \\
&\geq \quad \left\langle\psi, \sum_{i=1}^{Z}(-(1-\varepsilon)\tfrac{1}{2}\Delta_i - V(Z,R,x_i))\psi\right\rangle + D(\rho_\psi) - C\varepsilon^{-1}Z \\
&\geq \quad 2\,\mathrm{Tr}\left[-\tfrac{1}{2}(1-\varepsilon)\Delta - V^{\mathrm{TF}}(Z,R,\cdot)\right]_{-} - D(\rho^{\mathrm{TF}}(Z,R,\cdot)) - C\varepsilon^{-1}Z.
\end{aligned}$$

Here we have applied (2.8), the fact that the Coulomb kernel is positive definite such that $D(\rho - \rho^{\mathrm{TF}}) \geq 0$, and the fermionic property of the wave function.

If we now use the scaling property (2.10) we find that

$$\mathrm{Tr}\left[-\tfrac{1}{2}(1-\varepsilon)\Delta - V^{\mathrm{TF}}(Z,R,\cdot)\right]_{-} = |Z|^{4/3}\mathrm{Tr}\left[-\tfrac{1}{2}(1-\varepsilon)|Z|^{-2/3}\Delta - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right]_{-},$$

where $\mathbf{z} = (z_1, \ldots, z_M)$ and $\mathbf{r} = (r_1, \ldots, r_M)$. Using now (4.9) (with $h = \sqrt{\frac{1-\varepsilon}{2}} \cdot |Z|^{-1/3}$) and (2.18) we see that

$$\begin{aligned} &2\mathrm{Tr}\big[-\tfrac{1}{2}(1-\varepsilon)\Delta - V^{\mathrm{TF}}(Z,R,\cdot)\big]_- \\ &= (1-\varepsilon)^{-3/2}|Z|^{7/3}\left(E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) + D(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) + (1-\varepsilon)^{-1}\frac{|Z|^2}{2}\sum_{k=1}^M z_k^2 \\ &\quad + O(|Z|^{2-1/30}) \\ &= (1-\varepsilon)^{-3/2}\left(E^{\mathrm{TF}}(Z,R) + D(\rho^{\mathrm{TF}}(Z,R,\cdot)\right) + \tfrac{1}{2}(1-\varepsilon)^{-1}\sum_{k=1}^M Z_k^2 \\ &\quad + O(|Z|^{2-1/30}). \end{aligned}$$

We have here used the TF scaling $E^{\mathrm{TF}}(Z,R) = |Z|^{7/3}E^{\mathrm{TF}}(\mathbf{z},\mathbf{r})$ and $D(\rho^{\mathrm{TF}}\,(Z,R,\cdot)$ $= |Z|^{7/3}D\left(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right)$. Choosing $\varepsilon = |Z|^{-2/3}$ completes the proof of the lower bound.

The starting point for an upper bound is Lieb's variational principle, Theorem 2.4. By a simple rescaling the variational principle states that for any density matrix γ on $L^2(\mathbb{R}^3)$ with $2\mathrm{Tr}\gamma \le Z$ we have

$$E(Z,R) \le |Z|^{4/3}\left(2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V(\mathbf{z},\mathbf{r},x)\right)\gamma\right] + |Z|D(2|Z|^{-1}\rho_\gamma)\right).$$

As for the lower bound we bring the TF-potential into play,

$$\begin{aligned} |Z|^{-4/3}E(Z,R) &\le 2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V(\mathbf{z},\mathbf{r},x)\right)\gamma\right] + |Z|D(2|Z|^{-1}\rho_\gamma) \\ &= 2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)\right)\gamma\right] \\ &\quad + |Z|D\left(2|Z|^{-1}\rho_\gamma - \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) - |Z|D(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)). \end{aligned} \tag{5.1}$$

We now choose a density matrix $\widetilde{\gamma}$ according to Theorem 4.2 with $h = \sqrt{1/2}|Z|^{-1/3}$. Note that with this choice of h we have that

$$(6\pi^2h^3)^{-1}V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)^{3/2} = |Z|\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)/2.$$

Since $\int \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x) = \sum_{j=1}^M z_j = 1$ we see from (4.12) that

$$2\mathrm{Tr}\widetilde{\gamma} \le |Z| + C|Z|^{2/3-1/15} = |Z|(1 + C|Z|^{-1/3-1/15}).$$

Thus if we define $\gamma = (1 + C|Z|^{-1/3-1/15})^{-1}\widetilde{\gamma}$ we see that the condition $2\mathrm{Tr}\gamma \le |Z|$ is satisfied.

Using (4.11) we conclude that

$$|Z|D\left(2|Z|^{-1}\rho_{\widetilde{\gamma}} - \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) \le C|Z|^{2/3-4/15},$$

and thus

$$|Z|D\left(2|Z|^{-1}\rho_\gamma - \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) \le C|Z|^{2/3-4/15}, \tag{5.2}$$

where we have used that $D\left(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) \le C$.

Finally, if we use (4.9), (4.10), and (2.18) we arrive at

$$\begin{aligned} 2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)\right)\widetilde{\gamma}\right] &\le |Z|\left(E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) + D(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) \\ &\quad + \frac{|Z|^{2/3}}{2}\sum_{k=1}^M z_k^2 + O(|Z|^{2/3-1/30}). \end{aligned}$$

Since $E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) \le C$ and $D\left(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) \le C$ we see that the same estimate holds for $\widetilde{\gamma}$ replaced by γ. If we insert this estimate together with (5.2) into (5.1) and use again that $E^{\mathrm{TF}}(Z,R) = |Z|^{7/3}E^{\mathrm{TF}}(\mathbf{z},\mathbf{r})$ we arrive at the upper bound. $\square$

References

[B] V. Bach: *A proof of Scott's conjecture for ions*, Rep. Math. Phys., **28** 213–248 (1989)

[H] W. Hughes: *An atomic energy bound that gives Scott's correction*, Adv. Math., **79** 213–270 (1990)

[IS] V.I. Ivrii and I.M. Sigal: *Asymptotics of the ground state energies of large Coulomb systems*, Ann. of Math. (2) **1**38, 243–335 (1993)

[L1] E.H. Lieb: *Thomas-Fermi theories and related theories of atoms and molecules*, Rev. Mod. Phys. **5**3, 603–641 (1981)

[L2] E.H. Lieb: *Variational principle for many-fermion systems*, Phys. Rev. Lett, vol. **4**6, 457–459 (1981), or in *The stability of matter: from atoms to stars*, Springer (1991)

[L3] E.H. Lieb: *A lower bound for Coulomb energies*, Phys. Lett. **7**0A, 444–446 (1979)

[L4] E.H. Lieb: *Sharp constants in the Hardy-Littlewood-Sobolev and related inequalities*, Ann. of Math., **1**18 no. 2, 349–374, (1983)

[LL] E.H. Lieb and M. Loss: *Analysis*, Graduate studies in Mathematics, vol. **1**4 (2001)

[LO] E.H. Lieb and S. Oxford: *An improved lower bound on the indirect Coulomb energy*, Int. J. Quant. Chem. **1**9, 427–439 (1981)

[LSi] E.H. Lieb and B. Simon: *Thomas-Fermi theory of atoms, molecules and solids*, Adv. in Math., **2**3, 22–116, (1977)

[LSo] E.H. Lieb and J.P. Solovej: *Quantum coherent operators: A generalization of coherent states*, Lett. Math. Phys., **22**, 145–154 (1991)

[M] P. Balodis Matesanz: *A proof of Scott correction for Matter*, preprint mp-arc/02-62

[MS] P. Balodis Matesanz and J.P. Solovej: *On the asymptotic exactness of Thomas-Fermi theory in the thermodynamic limit*, Ann. Henri Poincare, **1**, 281–306 (2000)

[LT] E.H. Lieb and W.E. Thirring: *Inequalities for the moments of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities,* in Studies in mathematical physics, (E. Lieb, B. Simon, and A.S. Wightman, eds.), Princeton Univ. Press, Princeton, New Jersey, 269–330 (1976)

[SW] H. Siedentop and R. Weikard: *On the leading energy correction for the statistical model of an atom: interacting case*, Comm. Math. Phys. **1**12, 471–490 (1987), *On the leading correction of the Thomas-Fermi model: lower bound*, Invent. Math. **9**7, 159–193 (1990), and *A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators*, Ann. Sci. École Norm. Sup. (4), vol. **24**, no. 2, 215–225 (1991)

[SS] J.P. Solovej and W.L. Spitzer: *New coherent states approach to semiclassics which gives Scott's correction,* preprint mp-arc/02-357, or math-ph/0208044 (2002)

[T] W. Thirring: *A lower bound with the best possible constant for Coulomb Hamiltonians*, Commun. Math. Phys., **7**9 no. 1, 1–7, (1981)

Department of Mathematics, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

E-mail address: `solovej@math.ku.dk`

Department of Mathematics, University of California, One Shields Avenue, Davis 95616-8366, USA

E-mail address: `spitzer@math.ucdavis.edu`