A NEW COHERENT STATES APPROACH TO SEMICLASSICS WHICH GIVES SCOTT'S CORRECTION *

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1 Introduction

There are various highly developed methods for establishing semiclassical approximations. Probably the most refined method is based on pseudo-differential and Fourier integral operator calculi. This extremely technical approach is well suited for getting good or even sharp error estimates. Here, sharp refers to the optimal exponent of the semiclassical parameter in the error term. These sharp estimates however often require strong regularity assumptions on the operators being investigated.

A different and very simple method based on coherent states gives the leading order semiclassical asymptotics under optimal regularity assumptions.

The method of coherent states was used by Thirring [20] and Lieb [8] to give a very short and simple proof of the Thomas-Fermi energy asymptotics of large atoms and molecules; see also a recent improvement by Balodis Matesanz and Solovej [16]. This asymptotics had been first proved by Lieb and Simon in [7] using a Dirichlet-Neumann bracketing method.

Because of the Coulomb singularity of the atomic potential the pseudo-differential techniques are not immediately applicable to the Thomas-Fermi asymptotics.

In fact, although the Coulomb singularity does not affect the leading order Thomas-Fermi asymptotics, in the sense that it is purely semi-classical, it does cause the first correction to be of a non-semiclassical nature. The first correction to the Thomas-Fermi asymptotics was predicted by Scott in [18] and was later generalized to molecules and formulated as a clear mathematical conjecture in [8].

The first mathematical proof of the Scott correction for atoms was given by Hughes [4] (a lower bound) and by Siedentop and Weikard [19] (both bounds) by WKB type methods. Bach [1] proved the Scott correction for ions.

In [5], Ivrii and Sigal finally managed to apply Fourier integral operator methods to the atomic problem and proved the Scott correction for molecules, which was recently extended to matter by Balodis Matesanz [15].

In [3], Fefferman and Seco gave a rigorous derivation of the next correction (after the Scott correction) in the asymptotics of the energy of atoms. This next correction had been predicted by Dirac [2] and Schwinger [17].

As we shall explain below (see Page 12) one cannot expect to be able to derive the Scott correction using the traditional method of coherent states.

In this paper we introduce a new semiclassical approach generalizing the method of coherent states and show that this approach can be used to give a fairly simple derivation of the Scott correction for molecules.

The standard coherent states method is based on representing operators on $L^2(\mathbb{R}^n)$ as integrals of the form

$$\int_{\mathbb{R}^{2n}} a(u,q)\Pi_{u,q}\frac{dudq}{(2\pi h)^n}, \tag{1}$$

where $a(u,q)$ is a function (the symbol of the operator) on the classical phase space $\mathbb{R}^{2n}$ and $\Pi_{u,q}$ is a non-negative operator with the properties

$$\mathrm{Tr}\Pi_{u,q} = 1, \quad \int_{\mathbb{R}^{2n}} \Pi_{u,q} \frac{dudq}{(2\pi h)^n} = \mathbf{1}.$$

For the classical coherent states $\Pi_{u,q}$ is the one-dimensional projection $|u,q\rangle\langle u,q|$ onto the normalized function

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

We generalize this by representing operators in the form

$$\int \mathcal{G}_{u,q}\, \widehat{A}_{u,q}\, \mathcal{G}_{u,q} \frac{dudq}{(2\pi h)^n}. \tag{3}$$

Here $\mathcal{G}_{u,q}$ is some self-adjoint operator such that its square plays the role of $\Pi_{u,q}$ and $\widehat{A}_{u,q} = B_0(u,q) + B_1(u,q)\cdot\hat{x} - ihB_2(u,q)\cdot\nabla$ is a differential operator linear in $\hat{x}$ and $-ih\nabla$. (We have denoted by $\hat{x}$ the position operator.) We shall make an explicit choice of $\mathcal{G}_{u,q}$ in Sect. 3. In other words, we allow the symbol in the coherent state operator representation to be not just a real function on phase space but to take values in first order differential operators. If we consider, for example, a Schrödinger operator of the form $-h^2\Delta + V(\hat{x})$, where a natural choice of the coherent state symbol would be $a(u,q) = q^2 + V(u)$, then the new idea is now to choose the linear approximation

$$\widehat{A}_{u,q} = a(u,q) + \partial_u a(u,q)(\hat{x}-u) + \partial_q a(u,q)(-ih\nabla - q).$$

The representation (3) will then be a better approximation of the Schrödinger operator than (1) (see Theorem 11 for details).

In order to explain the Scott correction we consider the non-relativistic Schrödinger operator for a neutral molecule

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

We have $|Z| = \sum_{j=1}^{M} Z_j$ electrons of charges $e = -1$ and M nuclei of charges Z_j located at the fixed positions $R_1,\ldots,R_N$; we use atomic units where $\hbar^2 = m$. The number M is an arbitrary but fixed integer throughout this paper. The potential

$$V(Z,R,x) = \sum_{j=1}^{M}\frac{Z_j}{|x-R_j|} \tag{4}$$

describes the interaction of a single electron with all the nuclei. The operator $H(Z,R)$ acts as an unbounded operator in the space $\bigwedge^N L^2(\mathbb{R}^3\times\{-1,1\})$, where ±1 refer to the spin variables. We are interested in the ground state energy

$$E(Z,R) = \inf \mathrm{spec} H(Z,R)$$

and, in particular, in the asymptotic expansion for large charges. In defining the energy we have ignored the nuclear repulsion. It would simply shift the energy by a constant depending on Z and R.

The version of the Scott correction that we prove in this paper can now be stated as follows.

Theorem 1 (Scott correction). *Let $Z = |Z|(z_1, \dots, z_M)$, where $z_1, \dots, z_M > 0$ and $R = |Z|^{-1/3}(r_1, \dots, r_M)$, where $|r_i - r_j| > r_0$ for some $r_0 > 0$. Then,*

$$E(Z,R) = E^{\mathrm{TF}}(Z,R) + \tfrac{1}{2} \sum_{1 \le j \le M} Z_j^2 + \mathcal{O}(|Z|^{2-1/30}), \tag{5}$$

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

This is established in lemmas 18 and 19. In fact, one could improve slightly on the error estimate to the expense of limiting the range of Z and R, and vice verse.

It turns out that $E^{\mathrm{TF}}(Z,R)$ is of order $|Z|^{7/3}$ and the next term $\frac{1}{2}\sum_{1\le j\le M} Z_j^2$ is the Scott correction.

Part of our derivation of Theorem 1 is similar to the multi-scale analysis in [5] and we adopt their notation. Our semiclassical method, however, is very different. It does not rely on the spectral calculus, but uses only the quadratic form representation of operators. Moreover, we treat the Coulomb singularities completely differently from [5]. In treating the singularities and the region near infinity the Lieb-Thirring inequality plays an essential role.

Another virtue of our proof is that it gives an explicit trial state for the energy that is correct to an order including the Scott correction. This is, in fact, how we prove that the Scott correction is correct as an asymptotic upper bound.

This paper is organized as follows. In Sect. 2.1 we list for the convenience of the reader the analytic tools that we shall use in a crucial way. In Sect. 2.2 we review Thomas-Fermi theory. In Sect. 3 we introduce the new coherent states. In Sect. 4 we apply this new tool to prove the semi-classical expansion of the sum of the negative eigenvalues of a non-singular Schrödinger operator localized in some bounded region of space. This is the key application of our new method. The proof for the semi-classical expansion for the Thomas-Fermi potential is presented in Sect. 5. In Sect. 6 we finally prove lower and upper bound for the molecular quantum ground state energy. Some calculations concerning the new coherent states and a theorem on constructing a particular partition of unity are put into the appendices.

2 Preliminaries

2.1 Analytic tools

In this subsection we collect the main analytic tools which we shall use throughout the paper. We do not prove them here but give the standard references. Various constants are typically denoted by the same letter C, although their value might, for instance, change from one to the next line.

Let $p \geq 1$, 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 $1 \leq p \leq t \leq q \leq \infty$ we have the inclusion $L^p \cap L^q \subset L^t$, since by Hölder's inequality $\|f\|_t \leq \|f\|_p^\lambda \|f\|_q^{1-\lambda}$ 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 $\mathbf{0} \leq \gamma \leq \mathbf{1}$. 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 multiplication operators.

We also need an extension to many-particle states. Let $\psi \in \bigotimes^N L^2(\mathbb{R}^3 \times \{-1,1\})$ be an N-body wave-function. 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 (Lieb-Thirring inequality). One-body case: *Let γ be a density operator on $L^2(\mathbb{R}^n)$, then we have the Lieb-Thirring inequality*

$$\mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] \geq K_n \int \rho_\gamma^{1+2/n} \tag{6}$$

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

$$\mathrm{Tr}[(-\tfrac{1}{2}\Delta + V)\gamma] \geq -L_n \int |V_-|^{1+n/2}, \tag{7}$$

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

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

$$\left\langle \psi, \sum_{i=1}^N -\tfrac{1}{2}\Delta_i \psi \right\rangle \geq 2^{-2/3} K_3 \int \rho_\psi^{5/3}. \tag{8}$$

The original proofs of these inequalities can be found in [6].

From the min-max principle it is clear that the right side of (7) 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:

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

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

Theorem 3 (Hardy-Littlewood-Sobolev inequality). *There exists a constant C such that*

$$D(f) \leq C\,\|f\|_{6/5}^2. \tag{9}$$

The sharp constant C has been found by Lieb [11], see also [12].

In order to localize into different regions of space we shall use the standard IMS-formula

$$-\tfrac{1}{2}\theta^2\Delta - \tfrac{1}{2}\Delta\theta^2 = -\theta\Delta\theta - (\nabla\theta)^2, \tag{10}$$

which holds, by a straightforward calculation, for all bounded C^1-functions θ (here considered as a multiplication operator).

Finally we state the two inequalities which we 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 an electrostatic inequality providing us with a lower bound. This inequality is due to Lieb [10], and was improved in [13].

Theorem 4 (Lieb-Oxford inequality). *Let $\psi \in L^2(\mathbb{R}^{3N})$ be normalized, and ρ_ψ its one-electron density. Then,*

$$\left\langle \psi, \sum_{1\leq i<j\leq N} |x_i - x_j|^{-1}\psi \right\rangle \geq D(\rho_\psi) - C\int \rho_\psi^{4/3}. \tag{11}$$

The best-known numerical value is 1.68, but this does not play a role here.

An upper bound to $E(Z,R)$ is provided by a variational principle for Fermionic systems. This is also due to Lieb [9].

Theorem 5 (Lieb's Variational Principle). *Let γ be a density matrix on $L^2(\mathbb{R}^3)$ satisfying $2\mathrm{Tr}\gamma = 2\int \rho_\gamma(x)\,dx \leq Z$ (i.e., less than or equal to the number of electrons) with the kernel $\rho_\gamma(x) = \gamma(x,x)$. Then*

$$E(Z,R) \leq 2\mathrm{Tr}\Big[\big(-\tfrac{1}{2}\Delta - V(Z,R,x)\big)\,\gamma\Big] + D(2\rho_\gamma). \tag{12}$$

The factors 2 above are due to the spin degeneracy.

2.2 Thomas-Fermi theory

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

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

where V is as in (4).

By the Hardy-Littlewood-Sobolev inequality the Coulomb energy, $D(\rho)$, is finite for functions $\rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3) \subset L^{6/5}(\mathbb{R}^3)$. Therefore, the TF-energy functional is well-defined. Here we only state the properties about TF-theory which we use throughout the paper without proving them. The original proofs can be found in [7] and [8].

Theorem 6 (Thomas-Fermi minimizer). *For all* $\mathbf{z} = (z_1, \ldots, z_M) \in \mathbb{R}_+^M$ *and* $\mathbf{r} = (r_1, \ldots, r_M) \in \mathbb{R}^{3M}$ *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*

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

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

$$V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) := V(\mathbf{z}, \mathbf{r}, x) - \rho^{\mathrm{TF}} * |x|^{-1}. \tag{13}$$

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:*

$$V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) = \tfrac{1}{2}(3\pi^2)^{2/3} \rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x)^{2/3}. \tag{14}$$

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

$$V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) = h^{-4} V^{\mathrm{TF}}(h^3\mathbf{z}, h^{-1}\mathbf{r}, h^{-1}x), \tag{15}$$

$$\rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) = h^{-6} \rho^{\mathrm{TF}}(h^3\mathbf{z}, h^{-1}\mathbf{r}, h^{-1}x) \tag{16}$$

$$E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}) = h^{-7} E^{\mathrm{TF}}(h^3\mathbf{z}, h^{-1}\mathbf{r}). \tag{17}$$

By $h^{-1}\mathbf{r}$ we mean that each coordinate is scaled by h^{-1}, and likewise for $h^3\mathbf{z}$. By the TF-equation (14), the equations (15) and (16) are obviously equivalent. 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 establish the crucial estimates that we need about the TF potential. Let

$$d(x) = \min\{|x - r_k| \mid k = 1, \ldots, M\} \tag{18}$$

and

$$f(x) = \min\{d(x)^{-1/2}, d(x)^{-2}\}. \tag{19}$$

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

$$W_k(\mathbf{z}, \mathbf{r}, x) = V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) - z_k|x - r_k|^{-1}. \tag{20}$$

The function W_k can be continuously extended to $x = r_k$.

The first estimate in the next theorem is very similar to a corresponding estimate in [5].

Theorem 7 (Estimate on V^{TF}). *Let* $\mathbf{z} = (z_1, \ldots, z_M) \in \mathbb{R}_+^M$ *and* $\mathbf{r} = (r_1, \ldots, r_M) \in \mathbb{R}^{3M}$*. For all multi-indices* α *and all* x *with* $d(x) \neq 0$ *we have*

$$\left|\partial_x^\alpha V^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x)\right| \leq C_\alpha f(x)^2 d(x)^{-|\alpha|}, \tag{21}$$

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

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

$$0 \leq W_k(\mathbf{z}, \mathbf{r}, x) \leq C r_{\min}^{-1} + C, \tag{22}$$

where the constants $C > 0$ here depend on $z_1, \ldots, z_M$, and M.

Proof. Throughout the proof we shall denote all constants that depend on α, $z_1, \ldots, z_M$, M by C_α. Constants that depend on $z_1, \ldots, z_M$ we denote by C. In this proof we shall omit the dependence on $\mathbf{r}$ and $\mathbf{z}$ and simply write $V^{\mathrm{TF}}(x)$ and $W_k(x)$.

We proceed by induction over $|\alpha|$. If $\alpha = 0$ we have the well known bound [7] that

$$0 \leq \max\{V_{r_k}^{\mathrm{TF}}(x) \mid k = 1, \ldots, M\} \leq V^{\mathrm{TF}}(x) \leq \sum_{k=1}^{M} V_{r_k}^{\mathrm{TF}}(x), \tag{23}$$

where $V_{r_k}^{\mathrm{TF}}$ denotes the Thomas-Fermi potential of a neutral atom with a nucleus placed at $r_k \in \mathbb{R}^3$ with nuclear charge z_k. This potential satisfies the bounds [7]

$$C_- \min\{z_k|x - r_k|^{-1}, |x - r_k|^{-4}\} \leq V_{r_k}^{\mathrm{TF}} \leq C_+ \min\{z_k|x - r_k|^{-1}, |x - r_k|^{-4}\}, \tag{24}$$

where $C_\pm > 0$ are universal constants (note that by scaling (15) it is enough to consider the case $z_k = 1$). We therefore get that

$$C_- \min\{z_1, \ldots, z_M, 1\} f(x)^2 \leq V^{\mathrm{TF}}(x) \leq C_+ M \max\{z_1, \ldots, z_M, 1\} f(x)^2. \tag{25}$$

This in particular gives (21) for $\alpha = 0$. Assume now that (21) has been proved for all multi-indices α with $|\alpha| < M$, for some $M > 0$. We shall first establish an estimate for the derivatives $\partial^\alpha \rho$ of the TF density ρ.

From the TF equation we have that $\rho = C(V^{\mathrm{TF}})^{3/2}$. Thus $\partial^\alpha \rho(x)$ is a sum of terms of the form

$$V^{\mathrm{TF}}(x)^{3/2-k} \partial^{\beta_1} V^{\mathrm{TF}}(x) \cdots \partial^{\beta_k} V^{\mathrm{TF}}(x)$$

where $k = 0, \ldots, |\alpha|$ and $|\beta_1| + \ldots + |\beta_k| = |\alpha|$. Thus by the induction hypothesis and (25) we have for $|\alpha| < M$ that

$$|\partial^\alpha \rho(x)| \leq C_\alpha f(x)^3 d(x)^{-|\alpha|}. \tag{26}$$

We now turn to the potential. Given α with $|\alpha| = M$. Choose some decomposition $\alpha = \beta + \alpha'$, where $|\beta| = 1$ and $|\alpha'| = M - 1$.

For all y such that $|y - x| < d(x)/2$ we write

$$\partial^{\alpha'} V^{\mathrm{TF}}(y) = -\int_{|u-x|<d(x)/2} \partial^{\alpha'} \rho(u) |y - u|^{-1} du + R(y),$$

where

$$R(y) = \partial^{\alpha'} V^{\mathrm{TF}}(y) + \int_{|u-x|<d(x)/2} \partial^{\alpha'} \rho(u) |y - u|^{-1} du$$

is a harmonic function of y for $|y-x|<d(x)/2$, since $\Delta V^{\mathrm{TF}}(y)=4\pi\rho(y)$ for such y. It follows that

$$\left|\partial^\beta R(x)\right| \le C d(x)^{-1} \sup_{|\xi-x|=d(x)/2} |R(\xi)|.$$

This can be seen by the Poisson formula

$$R(y)=\int_{|\xi-x|=d(x)/2} \frac{\frac{d(x)^2}{4}-|y-x|^2}{2\pi d(x)|\xi-y|^3} R(\xi)\, dS(\xi),$$

valid for $|y-x|<d(x)/2$. Here dS denotes the surface measure of $\{\xi : |\xi-x| = d(x)/2\}$. To estimate $\sup_{|\xi-x|=d(x)/2}|R(\xi)|$ we use the induction hypothesis, i.e., (21) and (26) for α'. Note that for $|\xi-x|\le d(x)/2$ we have that $d(x)/2\le d(\xi)\le 3d(x)/2$ and hence also that $f(\xi)\le 4f(x)$. Thus, if we also use that $f(x)\le d(x)^{-2}$ we get that

$$\sup_{|\xi-x|=d(x)/2} |R(\xi)| \le C_{\alpha'} d(x)^{-|\alpha'|} f(x)^2$$

and hence that

$$\left|\partial^\beta R(x)\right| \le C_\alpha d(x)^{-|\alpha|} f(x)^2.$$

Finally we have that

$$\left|\partial_y^\beta \int_{|u-x|<d(x)/2} \partial^{\alpha'}\rho(u)|y-u|^{-1}du\right| \le \int_{|u-x|<d(x)/2} \left|\partial^{\alpha'}\rho(u)\right| |y-u|^{-2}du$$

The estimate (21) follows since

$$\int_{|u-x|<d(x)/2} \left|\partial^{\alpha'}\rho(u)\right| |x-u|^{-2}du \le C_{\alpha'} f(x)^3 d(x)^{-|\alpha'|+1} \le C_\alpha f(x)^2 d(x)^{-|\alpha|},$$

where we have again used that $f(x)\le d(x)^{-2}$.

The estimate (22) follows from (23) and (24) if we note that the atomic potential satisfies

$$0 \le V_{r_k}^{\mathrm{TF}}(x) - z_k|x-r_k|^{-1} = \rho_{r_k}^{\mathrm{TF}} * |x|^{-1} \le C.$$

Here $\rho_{r_k}^{\mathrm{TF}}$ is the atomic density. These last estimates follow since $\rho_{r_k}^{\mathrm{TF}}$ is non-negative and bounded in $L^{5/3}$ and in L^1. $\square$

The relation of Thomas-Fermi theory to semiclassical analysis is that the semi-classical density of a gas of non-interacting electrons moving in the Thomas-Fermi potential V^{TF} is simply the Thomas-Fermi density. More precisely, the semiclassical 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

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

Here the factor two on the very left is due to the spin degeneracy. Similarly, the semiclassical 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

$$2\int \left(\frac{1}{2}p^2 - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)\right)_- \frac{dpdx}{(2\pi)^3} = -\frac{4\sqrt{2}}{15\pi^2}\int V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)^{5/2}dx = E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) + D(\rho^{\mathrm{TF}}). \tag{27}$$

In Section 5 we shall make the semiclassical approximation more precise.

3 The new coherent states

We shall now define the new coherent states (or better coherent operators[1]) discussed in the introduction. I.e., we shall define the operator $\mathcal{G}_{u,q}$ that is used to represent operators in the form (3).

The classical coherent states (2) localize in both x and p on a scale of order h. We shall choose $\mathcal{G}_{u,q}$ to localize on a longer scale. We define

$$\mathcal{G}_{u,q} := (ha)^{-n/2}\left(\frac{a}{\pi(1-ha)}\right)^n \int e^{-a/(1-ha)\,[(u-u')^2+(q-q')^2]}\,|u',q'\rangle\langle u',q'|\,du'dq'. \tag{28}$$

The new scale is $1/a > h$. Note that if we let $a \to 1/h$ then $\mathcal{G}_{u,q}^2$ converges to the projection $\Pi_{u,q} = |u,q\rangle\langle u,q|$. A straightforward calculation gives the following result.

Lemma 8 (Completeness of new coherent states). *These new coherent operators satisfy*

$$\int \mathcal{G}_{u,q}^2 \frac{dq}{(2\pi h)^n} = G_b(\hat{x}-u), \qquad \int \mathcal{G}_{u,q}^2 \frac{du}{(2\pi h)^n} = G_b(-ih\nabla - q),$$

where $\hat{x}$ denotes the operator multiplication by the position variable x. Here $G_b(v) = (b/\pi)^{n/2}\exp(-bv^2)$ with $b = 2a/(1+h^2a^2)$. Note that G_b has integral 1 and hence

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

We shall study operators that can be written in the form (3). If $\widehat{A}_{u,q} = B_0(u,q) + B_1(u,q)\cdot\hat{x} - ihB_2(u,q)\cdot\nabla$ is the operator valued symbol in (3) 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.

[1] This should not be confused with the quantum coherent operators introduced by Lieb and Solovej in [14] in order to compare two quantum systems.

More generally we shall consider operators of the form

$$\int \mathcal{G}_{u,q}\, f(\widehat{A}_{u,q})\, \mathcal{G}_{u,q} du dq, \tag{29}$$

where $f : \mathbb{R} \to \mathbb{R}$ is any polynomially bounded real function. As we shall see in the next theorem the integrand above is a traceclass operator for each (u, q). The integral above is to be understood in the weak sense, i.e., as a quadratic form. We shall consider situations where the integral defines bounded or unbounded operators.

Theorem 9 (Trace identity). *Let $f : \mathbb{R} \to \mathbb{R}$ and $V : \mathbb{R}^n \to \mathbb{R}$ be polynomially bounded, real measurable functions and*

$$\hat{A} = B_0 + B_1\hat{x} - ihB_2\nabla$$

a first order self-adjoint differential operator[2] *with $B_0 \in \mathbb{R}, B_{1,2} \in \mathbb{R}^n$. Then $\mathcal{G}_{u,q}\, f(\hat{A})\, \mathcal{G}_{u,q}\, V(\hat{x})$ is a trace class operator (when extended from $C_0^\infty(\mathbb{R}^n)$) and*

$$\begin{aligned} \mathrm{Tr}[\mathcal{G}_{u,q}\, f(\hat{A})\, \mathcal{G}_{u,q}\, V(\hat{x})] \;\; &= \;\; \int f(B_0 + B_1 v + B_2 p)\, G_b(v-u) G_b(q-p) \\ &\quad \times G_{(bh^2)^{-1}}(z) V(v + h^2 ab(u-v) + z) dv dp dz. \end{aligned}$$

In particular, $\mathrm{Tr}\Big[\mathcal{G}_{u,q}^2\Big] = 1$.

The proof is given in Appendix A. We shall need the following extension of this theorem, where we however only give an estimate on the trace. The proof is again deferred to Appendix A.

Theorem 10 (Trace estimates). *Let $f, \hat{A}$ be as in the previous theorem. Let moreover $\phi \in C^{n+4}(\mathbb{R}^n)$ be a bounded, real function with all derivatives up to order $n+4$ bounded and $V, F \in C^2(\mathbb{R}^n)$ be real functions with bounded second derivatives. Then, for $h < 1$, $1 < a < 1/h$ and $b = 2a/(1 + h^2a^2)$ we have with $\sigma(u, q) = F(q) + V(u)$ that*[3]

$$\begin{aligned} &\mathrm{Tr}[\mathcal{G}_{u,q}\, f(\hat{A})\, \mathcal{G}_{u,q}\, \phi(\hat{x})\, (F(-ih\nabla) + V(\hat{x}))\, \phi(\hat{x})] \\ &\quad = \int f(B_0 + B_1 v + B_2 p)\, G_b(v-u) G_b(q-p) \\ &\qquad \times \Big[\Big(\phi(v + h^2 ab(u-v))^2 + E_1(u,v)\Big)\sigma(v + h^2 ab(u-v), p + h^2 ab(q-p)) \\ &\qquad\qquad + E_2(u, v; q, p)\Big]\, dv dp, \end{aligned}$$

with $\|E_1\|_\infty, \|E_2\|_\infty \le Ch^2 b$ where C depends only on

$$\sup_{|\nu| \le n+4} \|\partial^\nu \phi\|_\infty, \;\; \sup_{|\nu|=2} \|\partial^\nu V\|_\infty, \;\; \text{and} \;\; \sup_{|\nu|=2} \|\partial^\nu F\|_\infty.$$

(Note that the assumption $1 < a < 1/h$ implies $1 < b < 1/h$.)

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[2]The operator $\hat{A}$ is essentially self-adjoint on Schwartz functions on $\mathbb{R}^n$.

[3]The operator $\mathcal{G}_{u,q}\, f(\hat{A})\, \mathcal{G}_{u,q}\, \phi(\hat{x})\, (F(-ih\nabla) + V(\hat{x}))\, \phi(\hat{x})$ is originally defined on, say $C_0^\infty(\mathbb{R}^n)$, but it is part of the claim of the theorem that it extends to a traceclass operator on all of $L^2(\mathbb{R}^n)$.

The above theorem shall be used to prove an upper bound on the sum of eigenvalues of the operator $F(-ih\nabla) + V(\hat{x})$, in the case when $F(p) = p^2$. This is done in Lemma 14 by constructing a trial density matrix in the form (29).

To prove a lower bound on the sum of the negative eigenvalues one approximates the Hamiltonian $F(-ih\nabla) + V(\hat{x})$ by an operator represented in the form (3). This approximation which we now formulate is also proved in Appendix A.

Theorem 11 (Coherent states representation). *Consider functions $F, V \in C^3(\mathbb{R}^n)$, 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*

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

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

$$\widehat{H}_{u,q} = \sigma(u,q) + \frac{1}{4b}\Delta\sigma(u,q) + \partial_u\sigma(u,q)(\hat{x}-u) + \partial_q\sigma(u,q)(-ih\nabla - q). \tag{30}$$

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

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

4 Semi-classical estimate of $\mathrm{Tr}\big[\phi(-h^2\Delta+V)\phi\big]_-$

In this Section we study the sum of the negative eigenvalues of Schrödinger operators with regular potentials localized in a bounded region by a localization function ϕ. This will turn out to be the key theorem in this paper. Let us recall our convention that $x_- = (x)_- = \min\{x, 0\}$. For convenience we consider balls, and we start with the unit ball.

Theorem 12 (Local semiclassics). *Let $n \geq 3$ and $\phi \in C_0^{n+4}(\mathbb{R}^n)$, be supported in a ball $B \subset \mathbb{R}^n$ of radius 1 and $V \in C^3(\overline{B})$ be a real function. Let $H = -h^2\Delta + V$, $h > 0$ and $\sigma(u,q) = q^2 + V(u)$. Then,*

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

The constant $C > 0$ here depends only on n, $\|\phi\|_{C^{n+4}}$ and $\|V\|_{C^3}$. [Here $\|V\|_{C^3} = \sup_{|\alpha|\leq 3}\|\partial^\alpha V\|_\infty$.]

With the classical coherent states the estimate one would normally prove would be that the right side above is Ch^{-n+1}. We find it instructive to sketch the proof of this here in order to make the comparison with the new method clearer.

We may assume that V is defined on all of $\mathbb{R}^n$ with bounded second and third order derivatives. We shall here assume that $h < 1$. From Theorem 11 with $a = 1/h$ we have

$$H = -h^2\Delta + V = \int [q^2 + V(u)]\, |u,q\rangle\langle u,q|\, \frac{dudq}{(2\pi h)^n} + \mathbf{E},$$

with $\|\mathbf{E}\| \le Ch$. The constant depends on the second and third order derivatives of V, which are bounded. We have here used that for $a = b = 1/h$ the first order terms in $\hat{x}$ and ∇ do not contribute (see (99) below). Moreover, the term $\Delta\sigma$ is of order h since V has bounded second order derivatives. The error term $\mathbf{E}$ can be controlled using the Lieb-Thirring inequality as in (31) below.

Then from Theorem 10 we have

$$\begin{aligned}
\mathrm{Tr}[\phi H\phi]_- \;&\ge\; \int [q^2 + V(u)]_-\, \mathrm{Tr}\Big[\phi|u,q\rangle\langle u,q|\phi\Big] \frac{dudq}{(2\pi h)^n} - Ch^{-n+1} \\
&=\; \int [q^2 + V(u)]_-\, \phi^2(u) \frac{dudq}{(2\pi h)^n} - Ch^{-n+1},
\end{aligned}$$

where C now also depends on the derivatives of ϕ.

For an upper bound we set

$$\gamma = \int \chi_{(-\infty,0]}[q^2 + V(u)]\, |u,q\rangle\langle u,q|\, \frac{dudq}{(2\pi h)^n},$$

where $\chi_{(-\infty,0]}$ denotes the characteristic function of the interval $(-\infty, 0]$. It is clear that $\mathbf{0} \le \gamma \le \mathbf{1}$. When calculating $\mathrm{Tr}[\gamma\phi H\phi]$ we may again refer to the general theorem 10 with $a = b = 1/h$. We obtain

$$\begin{aligned}
\mathrm{Tr}[\gamma\phi H\phi] \;&=\; \int \chi_{(-\infty,0]}[q^2 + V(u)]\, \mathrm{Tr}\Big[|u,q\rangle\langle u,q|\phi H\phi\Big]\, \frac{dudq}{(2\pi h)^n} \\
&\le\; \int [q^2 + V(u)]_-\, \phi^2(u)\, \frac{dudq}{(2\pi h)^n} + Ch^{-n+1}.
\end{aligned}$$

As mentioned in the Introduction it is important that we obtain errors bounded by $Ch^{-n+1+\varepsilon}$ for some $\varepsilon > 0$ as in Theorem 12. We shall prove Theorem 12 by again proving upper and lower bounds on $\mathrm{Tr}[\phi H\phi]_-$.

Lemma 13 (Lower bound on $\mathrm{Tr}(\phi H\phi)_-$). *Let $n \ge 3$, $\phi \in C_0^{n+4}(\mathbb{R}^n)$ be supported in a ball B of radius 1 and assume that $V \in C^3(\overline{B})$. Let $H = -h^2\Delta + V$, $h > 0$. Then,*

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

The constant $C > 0$ here depends only on n, $\|\phi\|_{C^{n+4}}$ and $\|V\|_{C^3}$.

Proof. Since ϕ has support in the ball B we may without loss of generality assume that $V \in C_0^3(\mathbb{R}^3)$ with the support in a ball B_2 of radius 2 and that the norm $\|V\|_{C^3}$

refers to the supremum over all of $\mathbb{R}^n$. We shall not explicitly follow how the error terms depend on $\|\phi\|_{C^3}$ and $\|V\|_{C^3}$. All constants denoted by C depend on n, $\|\phi\|_{C^3}$, $\|V\|_{C^3}$.

First note that by the Lieb-Thirring inequality we have that

$$\mathrm{Tr}[\phi H\phi]_- \geq C\|\phi\|_\infty^2 \int_{u\in B} \sigma(u,q)_- \frac{dudq}{(2\pi h)^n} \geq -Ch^{-n}.$$

Consider some fixed $0<\tau<1$ (independent of h). If $h \geq \tau$ then

$$\mathrm{Tr}[\phi H\phi]_- \geq \int \phi^2(u)\sigma(u,q)_- \frac{dudq}{(2\pi h)^n} - C\tau^{-6/5}h^{-n+6/5}.$$

We are therefore left with considering $h<\tau$. Of course one should really try to find the optimal value of τ (depending on ϕ, and V) we shall however not do that. In studying the case $h<\tau$ it will be necessary to assume that the choice of τ is small enough. We therefore now assume that $h<\tau$ and that τ is small.

From Theorem 11 we have that

$$\begin{aligned}\mathrm{Tr}[\phi H\phi]_- \quad &\geq \quad \mathrm{Tr}\left[\int \phi\,\mathcal{G}_{u,q}\widehat{H}_{u,q}\mathcal{G}_{u,q}\phi\frac{dudq}{(2\pi h)^n}\right]_- \\ &\quad +\mathrm{Tr}\left[\phi\left(-\varepsilon h^2\Delta - C(b^{-3/2}+h^2b)\right)\phi\right]_- \end{aligned} \tag{31}$$

where $0<\varepsilon<1/2$ 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 $\widetilde{\sigma}(u,q) = (1-\varepsilon)q^2 + V(u)$. We shall choose a depending on h satisfying $\tau^{-1} \leq a < h^{-1}$ and hence $\tau^{-1} \leq b < h^{-1}$. It is clear (e.g. from the Lieb-Thirring inequality) that the second trace above is estimated below by $-Ch^{-n}\varepsilon^{-n/2}(b^{-3/2}+h^2b)^{1+n/2}$. We shall choose $\varepsilon = \frac{1}{4}(b^{-3/2}+h^2b)$; note that $\varepsilon < 1/2$. Thus we find that the second trace is estimated by $-Ch^{-n}(b^{-3/2}+h^2b)$. From the variational principle we have

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

We first consider the integral over u outside the ball B_2 of radius 2, where $V=0$. Using Theorem 9 (with V replaced by ϕ^2) and $\int\phi^2 \leq C$, we get that this part of the integral is

$$\begin{aligned} &\int_{u\notin B_2} \left[(1-\varepsilon)q^2 + \frac{n}{2b}(1-\varepsilon) + 2(1-\varepsilon)q\cdot(p-q)\right]_- G_b(p-q)G_b(u-v) \\ &\qquad \times G_{(bh^2)^{-1}}(z)\phi(v+h^2ab(u-v)+z)^2 dvdpdz\frac{dudq}{(2\pi h)^n} \\ \geq\quad & C\int(1-\varepsilon)[p^2-(p-q)^2]_- G_b(p-q)\frac{dpdq}{(2\pi h)^n} \geq -Cb^{-(n+2)/2}h^{-n}, \end{aligned}$$

which for all dimensions n is bounded below by $-Cb^{-3/2}h^{-n}$. Actually it is not difficult to see that we could have inserted a factor e^{-Cb} on the right of this estimate since $u \notin B_2$ and ϕ is supported in B_1, but we do not need this here.

For the integral over $u \in B_2$ we use Theorem 10 with $F = 0$ and $V = 1$ to obtain

$$\begin{aligned}\operatorname{Tr}[\phi H \phi]_- \geq \int_{u\in B_2} & \left(\phi\left(v + h^2ab(u-v)\right)^2 + Ch^2b\right) G_b(u-v)G_b(q-p) \\ & \times [H_{u,q}(v,p)]_- \frac{dudq}{(2\pi h)^n} dpdv - Ch^{-n}(b^{-3/2} + h^2b), \end{aligned} \tag{32}$$

where

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

The rest of the proof is simply an estimate of the integral in (32). Note that by Taylor's formula for $\widetilde{\sigma}$ we have

$$H_{u,q}(v,p) \;\; \geq \;\; \widetilde{\sigma}(v,p) + \widetilde{\xi}_v(u-v, q-p) - C|u-v|(b^{-1} + |u-v|^2), \tag{33}$$

where

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

We have here used that $\Delta\widetilde{\sigma}(v,p)$ is independent of p and that $|\Delta\widetilde{\sigma}(v,0) - \Delta\widetilde{\sigma}(u,0)| \leq C|u-v|$. Since $\|V\|_{C^3} < \infty$ and thus, in particular, $\widetilde{\sigma}(v,p) \geq (1-\varepsilon)p^2 - C$ we easily get that

$$\int G_b(u-v)G_b(q-p)\,[H_{u,q}(v,p)]_-\, dpdqdv \geq -C \tag{34}$$

and hence from (32) that

$$\begin{aligned}\operatorname{Tr}[\phi H \phi]_- \geq \int_{u\in B_2} & \phi\left(v + h^2ab(u-v)\right)^2 G_b(u-v)G_b(q-p) \\ & \times [H_{u,q}(v,p)]_- \frac{dudq}{(2\pi h)^n} dpdv - Ch^{-n}(b^{-3/2} + h^2b).\end{aligned}$$

Here we have of course used the fact that the u-integration is over a bounded region. From now on we may however ignore the restriction on the u-integration. Using (33) we find after the simple change of variables $u \to u + v$ and $q \to q + p$ that

$$\begin{aligned}\operatorname{Tr}[\phi H \phi]_- \;\; \geq \;\; & \int \phi\left(v + h^2abu\right)^2 G_b(u)G_b(q) \\ & \times \left[\widetilde{\sigma}(v,p) + \widetilde{\xi}_v(u,q) - C|u|(b^{-1} + |u|^2)\right]_- \frac{dudq}{(2\pi h)^n} dpdv \\ & -Ch^{-n}(b^{-3/2} + h^2b).\end{aligned}$$

We now perform the p-integration explicitly. Recall that $\widetilde{\sigma}(v,p) = (1-\varepsilon)p^2 + V(v)$ and that $\int (p^2+s)_- dp = -\frac{2}{n+2}\omega_n |s_-|^{(n/2)+1}$, where ω_n is the volume of the unit ball in $\mathbb{R}^n$. We get

$$\begin{aligned}\mathrm{Tr}[\phi H \phi]_- \;\geq\; & -\frac{2\omega_n}{n+2}(1-\varepsilon)^{-\frac{n}{2}} \int \phi\left(v + h^2 abu\right)^2 G_b(u) G_b(q) \\ & \qquad\times \left|\left[V(v) + \widetilde{\xi}_v(u,q) - C|u|(b^{-1}+|u|^2)\right]_-\right|^{\frac{n}{2}+1} \frac{dudq}{(2\pi h)^n} dv \\ & -Ch^{-n}(b^{-3/2} + h^2 b). \end{aligned} \tag{35}$$

By expanding we find that

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

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

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

We now expand ϕ^2

$$\left|\phi\left(v+h^2abu\right)^2 - \phi(v)^2 - h^2 abu \cdot \nabla\left(\phi^2\right)(v)\right| \leq Ch^4a^2b^2|u|^2 \leq Ch^2b^2|u|^2,$$

and use the crucial identities

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

We thus arrive at

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

The lemma follows if we choose $a = \max\{h^{-4/5}, \tau^{-1}\}$ and $\varepsilon = \frac{1}{4}(b^{-3/2} + h^2 b)$. Recall that $a \leq b \leq 2a$. Thus $b^{-3/2} \leq a^{-3/2} \leq h^{6/5}$ and $h^2 b \leq 2h^2 a \leq 2\tau^{-1/5}h^{6/5}$.

$\square$

In order to prove an upper bound on $\mathrm{Tr}(\phi H\phi)_-$ we shall use that for any density matrix γ (i.e., a traceclass operator with $\mathbf{0} \leq \gamma \leq \mathbf{1}$) we have from the variational principle that $\mathrm{Tr}(\phi H\phi)_- \leq \mathrm{Tr}(\phi H\phi\gamma)$. Hence the upper bound needed to prove Theorem 12 is a consequence of the following lemma.

Lemma 14 (Construction of trial density matrix). *Let $n \geq 3$, $\phi \in C_0^{n+4}(\mathbb{R}^n)$ be supported in a ball B of radius 1, and $V \in C^3(\bar{B})$. Let $H = -h^2\Delta + V$, $h > 0$ and $\sigma(u,q) = q^2 + V(u)$. Then there exists a density matrix γ on $L^2(\mathbb{R}^n)$ such that*

$$\mathrm{Tr}[\phi H\phi\gamma] \leq \int \phi^2(u)\sigma(u,q)_- \frac{dudq}{(2\pi h)^n} + Ch^{-n+6/5}. \tag{36}$$

Moreover, the density of γ satisfies

$$\left|\rho_\gamma(x) - (2\pi h)^{-n}\omega_n \left|V(x)_-\right|^{n/2}\right| \leq Ch^{-n+9/10}, \tag{37}$$

for (almost) all $x \in B$ and

$$\left|\int \phi(x)^2\rho_\gamma(x)dx - (2\pi h)^{-n}\omega_n \int \phi(x)^2 \left|V(x)_-\right|^{n/2} dx\right| \leq Ch^{-n+6/5}, \tag{38}$$

where ω_n is the volume of the unit ball in $\mathbb{R}^n$. The constants $C > 0$ in the above estimates depend only on $n, \|\phi\|_{C^{n+4}}$, and $\|V\|_{C^3}$.

Proof. As in the lower bound we choose some fixed $0 < \tau < 1$. We have for $h \geq \tau$ that for some $C > 0$

$$\int \phi^2(u)\sigma(u,q)_- \frac{dudq}{(2\pi h)^n} + C\tau^{-6/5}h^{-n+6/5} \geq 0$$

and

$$\left|(2\pi h)^{-n}\omega_n V(x)_-\right|^{n/2} \leq C\tau^{-6/5}h^{-n+6/5},$$

If $h \geq \tau$ we may therefore choose $\gamma = 0$. We may therefore now assume that $h < \tau$ and if necessary that τ is small enough depending only on ϕ, and V. Also as in the lower bound we may assume that $V \in C_0^3(\mathbb{R}^n)$ with support in the ball $B_{3/2}$ concentric with B and of radius 3/2.

In analogy to the previous proof for the lower bound we now for each (u,q) define an operator $\hat{h}_{u,q}$ by

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

The corresponding function is

$$h_{u,q}(v,p) = \begin{cases} \sigma(u,q) + \frac{1}{4b}\Delta\sigma(u,q) + \partial_u\sigma(u,q)(v - u) + \partial_q\sigma(u,q)(p - q) & \text{, if } u \in B_2 \\ 0 & \text{, if } u \notin B_2 \end{cases}.$$

Recall that $b = 2a/(1 + h^2a^2)$ (i.e., in particular $a \leq b \leq 2a$) and as in the lower bound we shall choose $a = \max\{h^{-4/5}, \tau^{-1}\}$

Similar to (33) we have for $u \in B_2$ that

$$|h_{u,q}(v,p) - \sigma(v,p) - \xi_v(u-v, q-p)| \leq C|u-v|(b^{-1} + |u-v|^2), \tag{39}$$

where

$$\xi_v(u,q) = \frac{1}{4b}\Delta\sigma(v,0) - q^2 - \tfrac{1}{2}\sum_{i,j}\partial_i\partial_j V(v)u_iu_j.$$

We have here used that $\Delta\sigma(v,p)$ is independent of p.

If we let $\chi = \chi_{(-\infty,0]}$ be the characteristic function of $(-\infty, 0]$ we now define

$$\gamma = \int \mathcal{G}_{u,q}\,\chi[\hat{h}_{u,q}]\,\mathcal{G}_{u,q}\,\frac{dudq}{(2\pi h)^n}. \tag{40}$$

Since $\mathbf{0} \leq \chi[\hat{h}_{u,q}] \leq \mathbf{1}$ it is obvious that $\mathbf{0} \leq \gamma \leq \mathbf{1}$. Moreover, by Theorem 9 and (39), γ is easily seen to be a traceclass operator with density

$$\rho_\gamma(x) = \int \chi\left(h_{u,q}(v,p)\right) G_b(u-v)G_b(p-q)G_{(bh^2)^{-1}}(x - v - h^2ab(u-v))dvdp\frac{dudq}{(2\pi h)^n}.$$

If we change variables $u \to u + v$, $q \to q + p$ and perform the p-integration we find that

$$\begin{aligned}\rho_\gamma(x) &= \omega_n \int_{u\in B_2 - v} \Xi(v,u,q)G_b(u)G_b(q)G_{(bh^2)^{-1}}(x - v - h^2abu)dv\frac{dudq}{(2\pi h)^n}\\ &= \omega_n \int_{(1-h^2ab)u\in B_2-v} \Xi(v - h^2abu, u, q)G_b(u)G_b(q)G_{(bh^2)^{-1}}(x-v)dv\frac{dudq}{(2\pi h)^n}\end{aligned} \tag{41}$$

where $\Xi(v,u,q) = \omega_n^{-1}\int \chi(h_{(u+v,q+p)}(v,p))\,dp \geq 0$. From equation (39) we have

$$\left|\Xi(v,u,q)^{2/n} - \left|\Big(V(v) + \xi_v(u,q)\Big)_-\right|\right| \leq C|u|(b^{-1} + |u|^2), \tag{42}$$

for all $v, q \in \mathbb{R}^n$ and $u \in B_2 - v$. Since

$$|\xi_v(u,q) - \xi_{v-h^2abu}(u,q)| \leq Ch^2ab|u|(b^{-1} + |u|^2)$$

we therefore also have

$$\begin{aligned}\left|\Xi(v - h^2abu, u, q)^{2/n} - \left|\Big(V(v) + \eta_v(u,q)\Big)_-\right|\right| &\leq Ch^4a^2b^2|u|^2\\ &\quad + C(1 + h^2ab)|u|(b^{-1} + |u|^2),\end{aligned}$$

where

$$\eta_v(u,q) = \xi_v(u,q) - h^2ab\nabla V(v)\cdot u.$$

Hence from (41)

$$\left|\rho_\gamma(x)^{\frac{2}{n}} - \Big(\omega_n \int\limits_{(1-h^2ab)u\in B_2-v} \Big|\Big(V(v)+\eta_v(u,q)\Big)_-\Big|^{\frac{n}{2}} G_b(u)G_b(q)G_{(bh^2)^{-1}}(x-v)dv\frac{dudq}{(2\pi h)^n}\Big)^{\frac{2}{n}}\right|$$
$$\leq Ch^{-2}(h^4a^2b+b^{-3/2}) \leq Ch^{-2+6/5}, \quad (43)$$

where C may depend on τ.

We now use that for all $x, y \in \mathbb{R}$ and all $n \geq 3$ we have

$$\big||x_-|^{\frac{n}{2}} - |y_-|^{\frac{n}{2}} + \tfrac{n}{2}|y_-|^{\frac{n}{2}-1}(x-y)\big| \leq \begin{cases} C|x-y|^{\frac{3}{2}}, & n=3 \\ C(|x|^{\frac{n}{2}-2}+|y|^{\frac{n}{2}-2})|x-y|^2, & n\geq 4 \end{cases} \quad (44)$$

where C depends on n. This gives for $n=3$ (it is left to the reader to write down the estimates for $n \geq 4$)

$$\left|\Big|\Big(V(v)+\eta_v(u,q)\Big)_-\Big|^{\frac{3}{2}} - |V(v)_-|^{\frac{3}{2}} + \tfrac{3}{2}|V(v)_-|^{\frac{1}{2}}\eta_v(u,q)\right| \leq C|\eta_v(u,q)|^{\frac{3}{2}}. \quad (45)$$

It is now again crucial that $\int \eta_v(u,q)G_b(u)G_b(q)dudq = 0$ and hence for $v \in \operatorname{supp}(V) \subseteq B_{3/2}$

$$\Big|\int\limits_{(1-h^2ab)u\in B_2-v} \eta_v(u,q)G_b(u)G_b(q)dudq\Big| \leq Ce^{-b/5} \leq Ch^{6/5}. \quad (46)$$

Combining (43), (45), (46), and $|\eta_v(u,q)| \leq C(b^{-1}+|u|^2+|q|^2+h^2ab|u|)$ we obtain

$$\Big|\rho_\gamma(x) - (2\pi h)^{-3}\omega_3 \int |V(v)_-|^{3/2} G_{(bh^2)^{-1}}(x-v)dv\Big|$$
$$\leq \; Ch^{-3}(e^{-b/5}+h^3a^{3/2}b^{3/4}+b^{-3/2}+h^{6/5}) \leq Ch^{-3+6/5}, \quad (47)$$

where we have again removed the condition $(1-h^2ab)u \in B_2 - v$ paying a price of $Ch^{-3}e^{-b/5}$.

A simple Taylor expansion of ϕ^2 gives

$$\Big|\phi(x)^2 - \int \phi(v)^2 G_{(bh^2)^{-1}}(x-v)dv\Big| \leq Cbh^2 \leq Ch^{6/5},$$

where we have again used that $\int vG_{(bh^2)^{-1}}(v)dv = 0$. This immediately gives (38).

Finally, using again (44) we get

$$\Big||V(x+v)_-|^{\frac{3}{2}} - |V(x)_-|^{\frac{3}{2}} + \tfrac{3}{2}|V(x)_-|^{\frac{1}{2}}\nabla V(x)\cdot v\Big| \leq C(|v|^{\frac{3}{2}}+|v|^2),$$

and hence from (47)

$$\Big|\rho_\gamma(x) - (2\pi h)^{-3}\omega_n|V(x)_-|^{3/2}\Big| \leq Ch^{-3}(h^{6/5}+(bh^2)^{3/4}) \leq Ch^{-3+9/10}.$$

We must now calculate $\mathrm{Tr}(\gamma\phi H\phi) = \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) + \mathrm{Tr}(\gamma\phi V\phi)$ for $n \geq 3$. From the argument leading to (38) we have

$$(2\pi h)^n \mathrm{Tr}(\gamma\phi V\phi) \leq -\omega_n \int \phi(x)^2 |V(x)_-|^{\frac{n}{2}+1} dx + Ch^{-n+6/5}. \tag{48}$$

From Theorem 10 we have

$$\begin{aligned}(2\pi h)^n \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) \;=\; & \int \chi(h_{u,q}(v,p))\, G_b(u-v)G_b(q-p)\Big[E_2 + \\ & (\phi(v+h^2ab(u-v))^2 + E_1)(p+h^2ab(q-p))^2\Big] dudqdvdp,\end{aligned}$$

where E_1, E_2 are functions such that $\|E_1\|_\infty, \|E_2\|_\infty \leq Ch^2b$. Since

$$\int \chi(h_{u,q}(v,p))\, G_b(u-v)G_b(q-p)(1+p^2) dudqdvdp \leq C,$$

(note that it is important here that $h_{u,q}(v,p) = 0$ unless $u \in B_2$) we get

$$\begin{aligned}& (2\pi h)^n \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) \\ & \leq \int \chi(h_{u,q}(v,p))\, G_b(u-v)G_b(q-p)\phi(v+h^2ab(u-v))^2 \\ & \quad \times (p+h^2ab(q-p))^2 dudqdvdp + Cbh^2.\end{aligned}$$

From (39) we may now conclude that

$$\begin{aligned}(2\pi h)^n \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) \;\leq\; & \int \chi(\sigma(v,p) + \xi_v(u,q) - C|u|(b^{-1}+|u|^2))\, G_b(u)G_b(q) \\ & \times \phi(v+h^2abu)^2(p+h^2abq)^2 dudqdvdp + Cbh^2.\end{aligned} \tag{49}$$

We now perform the p-integration in (49) and arrive at

$$\begin{aligned}(2\pi h)^n \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) \;\leq\; & \frac{n}{n+2}\omega_n \int \Big| \big(V(v) + \xi_v(u,q) - C|u|(b^{-1}+|u|^2)\big)_- \Big|^{\frac{n}{2}+1} \\ & \times G_b(u)G_b(q)\phi(v+h^2abu)^2 dudqdv + Cbh^2,\end{aligned} \tag{50}$$

where we have used that the integral over the term containing $q \cdot p$ vanishes and the integral over the term containing $(h^2abq)^2$ is bounded by $h^4a^2b \leq h^2b$.

We now expand the integrand in (50) in the same way as we did the integrand in (35). We finally obtain

$$(2\pi h)^n \mathrm{Tr}(\gamma\phi(-h^2\Delta)\phi) \leq \frac{n}{n+2}\omega_n \int |V(v)_-|^{\frac{n}{2}+1}\, \phi(v)^2 dv + Ch^{6/5},$$

which together with (48) gives (36). $\square$

We shall need the generalization of Theorem 12 and Lemma 14 to a ball of arbitrary radius. We also require to know how the error term depends more explicitly on the potential.

Corollary 15 (Rescaled 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*

$$\left|\mathrm{Tr}[\phi H \phi]_- - (2\pi h)^{-n} \int \phi(u)^2 \sigma(u,q)_-\, dudq\right| \leq C h^{-n+6/5} f^{n+4/5} \ell^{n-6/5}, \tag{51}$$

where the constant C depends only on

$$\sup_{|\alpha| \leq n+4} \|\ell^{|\alpha|}\partial^\alpha \phi\|_\infty, \qquad \textit{and} \qquad \sup_{|\alpha|\leq 3} \|f^{-2}\ell^{|\alpha|}\partial^\alpha V\|_\infty. \tag{52}$$

Moreover, there exists a density matrix γ such that

$$\mathrm{Tr}[\phi H \phi \gamma] \leq (2\pi h)^{-n} \int \phi(u)^2 \sigma(u,q)_-\, dudq + C h^{-n+6/5} f^{n+4/5} \ell^{n-6/5} \tag{53}$$

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

$$\left|\rho_\gamma(x) - (2\pi h)^{-n}\omega_n \left|V(x)_-\right|^{n/2}\right| \leq C h^{-n+9/10} f^{n-9/10} \ell^{-9/10}, \tag{54}$$

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

$$\left|\int \phi(x)^2 \rho_\gamma(x) dx - (2\pi h)^{-n}\omega_n \int \phi(x)^2 \left|V(x)_-\right|^{n/2} dx\right| \leq C h^{-n+6/5} f^{n-6/5} \ell^{n-6/5}, \tag{55}$$

where the constants $C > 0$ in the above estimates again depend only on the parameters in (52).

Proof. This is a simple rescaling argument. Introducing the unitary operator $(U\psi)(x) = \ell^{-n/2}\psi(\ell^{-1}x)$ we see that $\phi H \phi$ is unitarily equivalent to the operator

$$U^*\phi H \phi U = f^2 \phi_\ell(-h^2 f^{-2}\ell^{-2}\Delta + V_{f,\ell})\phi_\ell,$$

where $\phi_\ell(x) = \phi(\ell x)$, and $V_{f,\ell}(x) = f^{-2}V(\ell x)$. Thus

$$\mathrm{Tr}[\phi H \phi]_- = f^2 \mathrm{Tr}[\phi_\ell(-h^2 f^{-2}\ell^{-2}\Delta + V_{f,\ell})\phi_\ell]_-.$$

Note that ϕ_ℓ and $V_{f,\ell}$ are defined in a ball of radius 1 and that for all α

$$\|\partial^\alpha \phi_\ell\|_\infty = \|\ell^{|\alpha|}\partial^\alpha \phi\|_\infty, \qquad \text{and} \qquad \|\partial^\alpha V_{f,\ell}\|_\infty = \|f^{-2}\ell^{|\alpha|}\partial^\alpha V\|_\infty.$$

It follows from Theorem 12 that

$$\left|\mathrm{Tr}[\phi H \phi]_- - (2\pi h f^{-1}\ell^{-1})^{-n} \int \phi_\ell(u)^2 f^2 \sigma_{f,\ell}(u,q)_-\, dudq\right| \leq C f^2 (h f^{-1}\ell^{-1})^{-n+6/5}, \tag{56}$$

where $\sigma_{f,\ell}(u,q) = q^2 - V_{f,\ell}(u)$ and where the constant C only depends on the parameters in (52). A simple change of variables gives

$$(2\pi h f^{-1}\ell^{-1})^{-n}\int \phi_\ell(u)^2 f^2 \sigma_{f,\ell}(u,q)_-\,dudq = (2\pi h)^{-n}\int \phi(u)^2\sigma(u,q)_-\,dudq.$$

Thus (51) follows.

To find the appropriate density matrix γ. We begin with the corresponding density matrix $\gamma_{f,\ell}$ for $\phi_\ell(-h^2f^{-2}\ell^{-2}\Delta + V_{f,\ell})\phi_\ell$, i.e. the density matrix, which according to Lemma 14 satisfies the three estimates

$$\begin{aligned}\mathrm{Tr}\left[\phi_\ell(-h^2f^{-2}\ell^{-2}\Delta + V_{f,\ell})\phi_\ell\gamma_{f,\ell}\right] \;&\leq\; (2\pi h f^{-1}\ell^{-1})^{-n}\int \phi_\ell^2(u)\sigma_{f,\ell}(u,q)_-\,dudq \\ &\quad + C(hf^{-1}\ell^{-1})^{-n+6/5},\end{aligned}$$

$$\left|\rho_{\gamma_{f,\ell}}(x) - (2\pi h f^{-1}\ell^{-1})^{-n}\omega_n |V_{f,\ell}(x)_-|^{n/2}\right| \leq C(hf^{-1}\ell^{-1})^{-n+9/10},$$

$$\left|\int \phi_\ell^2\rho_{\gamma_{f,\ell}} - (2\pi h f^{-1}\ell^{-1})^{-n}\omega_n\int \phi_\ell(x)^2|V_{f,\ell}(x)_-|^{n/2}dx\right| \leq C(hf^{-1}\ell^{-1})^{-n+6/5}.$$

The density matrix $\gamma = U\gamma_{f,\ell}U^*$ whose density is $\rho_\gamma(x) = \ell^{-n}\rho_{\gamma_{f,\ell}}(x/\ell)$ then satisfies the properties (53–55). $\square$

5 Semiclassics for the Thomas-Fermi potential

We shall consider the semiclassical approximation for a Schrödinger operator with the Thomas-Fermi potential $V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)$, i.e., $-h^2\Delta - V^{\mathrm{TF}}$. We shall throughout this section simply write $V^{\mathrm{TF}}(x)$ instead of $V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)$. Recall that $V^{\mathrm{TF}}(x) > 0$.

The main result we shall prove here is the Scott correction to the semiclassical expansion for this potential.

Theorem 16 (Scott corrected semiclassics). *For all $h > 0$ and all $r_1,\ldots,r_M \in \mathbb{R}^3$ with $\min_{k\neq m}|r_m - r_k| > r_0 > 0$ we have*

$$\left|\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- - (2\pi h)^{-3}\int (p^2 - V^{\mathrm{TF}}(u))_-\,dudp - \frac{1}{8h^2}\sum_{k=1}^M z_k^2\right| \leq Ch^{-2+\frac{1}{10}}, \tag{57}$$

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

$$\mathrm{Tr}\left[(-h^2\Delta - V^{\mathrm{TF}})\gamma\right] \leq \mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}\right]_- + Ch^{-2+1/10}, \tag{58}$$

and such that

$$D\left(\rho_\gamma - \frac{1}{6\pi^2h^3}(V^{\mathrm{TF}})^{3/2}\right) \leq Ch^{-5+4/5} \tag{59}$$

and

$$\int \rho_\gamma \le \frac{1}{6\pi^2 h^3}\int V^{\mathrm{TF}}(x)^{3/2}dx + Ch^{-2+1/5}, \tag{60}$$

with C depending on the same parameters as before.

Note that if we choose $h = 2^{-1/2}$ we have from (14) that $(6\pi^2h^3)^{-1}(V^{\mathrm{TF}})^{3/2} = \rho^{\mathrm{TF}}/2$. The factor $1/2$ on the right is due to the fact that we have not included spin degeneracy in Theorem 16.

In order to prove this theorem we shall compare with semiclassics for hydrogen like atoms.

Lemma 17 (Hydrogen comparison). *For all $h > 0$ and all $r_1, \ldots, r_M \in \mathbb{R}^3$ with $\min_{k\neq m}|r_m - r_k| > r_0 > 0$ we have*

$$\begin{aligned}&\Big|\mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}(\hat{x})\right]_- - (2\pi h)^{-3}\int \left(p^2 - V^{\mathrm{TF}}(u)\right)_- dudp\\ &\qquad -\sum_{k=1}^M\left(\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- - (2\pi h)^{-3}\int\Big(p^2 - \frac{z_k}{|u-r_k|}+1\Big)_- dudp\right)\Big|\\ &\le\ Ch^{-2+1/10},\end{aligned} \tag{61}$$

where $C > 0$ depends only on $z_1, \ldots, z_M$, M and r_0.

The first estimate in Theorem 16 follows from Lemma 17 combined with the exact calculations for hydrogen

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

and

$$(2\pi h)^{-3}\int\Big(p^2 - \frac{z_k}{|u-r_k|}+1\Big)_- dudp = -\frac{32\pi^2 z_k^3}{15(2\pi h)^3}\frac{\Gamma(7/2)\Gamma(1/2)}{\Gamma(4)} = -\frac{z_k^3}{12h^3}.$$

Before giving the proof of Lemma 17 we introduce the function

$$\ell(x) = \tfrac12\Big(1+\sum_{k=1}^M(|x-r_k|^2+\ell_0^2)^{-1/2}\Big)^{-1} \tag{62}$$

where $0 < \ell_0 < 1$ is a parameter that we shall choose explicitly in (76) below. Note that ℓ is a smooth function with

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

Note also that in terms of the function $d(x)$ from (18) we have

$$\tfrac12(1+M)^{-1}\ell_0 \le \tfrac12(1+M(d(x)^2+\ell_0^2)^{-1/2})^{-1} \le \ell(x) \le \tfrac12(d(x)^2+\ell_0^2)^{1/2}. \tag{63}$$

Note in particular that we have

$$\ell(x) \geq \tfrac{1}{2}(1+M)^{-1} \min\{d(x), 1\}. \tag{64}$$

We fix a localization function $\phi \in C_0^\infty(\mathbb{R}^3)$ with support in $\{|x| < 1\}$ and such that $\int \phi(x)^2 dx = 1$. According to Theorem 22 we can 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

$$\int \phi_u(x)^2 \ell(u)^{-3} du = 1 \quad \text{and} \quad \|\partial^\alpha \phi_u\|_\infty \leq C\ell(u)^{-|\alpha|}, \tag{65}$$

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

Moreover, from (21) in Theorem 7 we know that for all $u \in \mathbb{R}^n$ with $d(u) > 2\ell_0$ the TF-potential V^{TF} satisfies

$$\sup_{|x-u|<\ell(u)} |\partial^\alpha V^{\mathrm{TF}}(x)| \leq Cf(u)^2 \ell(u)^{-|\alpha|}, \tag{66}$$

where $C > 0$ depends only on α, $z_1, \ldots, z_M$, and M. We have here used the fact that if $d(u) > 2\ell_0$ then $\ell(u) \leq \sqrt{5}d(u)/4$ and hence for all x with $|x-u| < \ell(u)$ we have (note that $d(u) \leq d(x) + |x-u|$ and $\sqrt{5}/4 < 1$)

$$\ell(u) < Cd(x) \quad \text{and} \quad f(x) \leq Cf(u).$$

Proof of Lemma 17. We note first that we may if necessary assume that h is smaller than some constant depending only on the parameters $z_1, \ldots, z_M$, M, r_0. This follows from the Lieb-Thirring inequality (7) and the estimate on V^{TF} given in (21) for $\alpha = 0$.

In order to control the region far away from all the nuclei we introduce localization functions $\theta_-, \theta_+ \in C^\infty(\mathbb{R})$ such that

1. $\theta_-^2 + \theta_+^2 = 1$,
2. $\theta_-(t) = 1$ if $t < 1$ and $\theta_-(t) = 0$ if $t > 2$.

Let

$$R = h^{-1/2} \tag{67}$$

and define $\Phi_\pm(x) = \theta_\pm(d(x)/R)$. Then $\Phi_-^2 + \Phi_+^2 = 1$. 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

$$\|\mathcal{I}\|_\infty \leq CR^{-2}.$$

Using the IMS-formula (10) we find that

$$-h^2\Delta - V^{\mathrm{TF}} = \Phi_-(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_- + \Phi_+(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_+$$

From the Lieb-Thirring inequality the estimates on $\mathcal{I}$ and the bound $V^{\mathrm{TF}}(x) \leq Cd(x)^{-4}$ (see (21) with $\alpha = 0$) we find

$$\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- \geq \mathrm{Tr}[\Phi_-(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I})\Phi_-]_- - C(h^{-3}R^{-7} + h^2R^{-2}).$$

On the support of Φ_- we now use the localization functions ϕ_u. Again using the IMS formula (10) we obtain from (65) that

$$\begin{aligned}&\Phi_- \left(-h^2\Delta - V^{\mathrm{TF}} - h^2\mathcal{I}\right)\Phi_- \\ &\quad\geq \int \Phi_-\phi_u \left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2(\ell(u)^{-2} + R^{-2})\right)\phi_u\Phi_-\ell(u)^{-3}du.\end{aligned}$$

We have here used that if the supports of ϕ_u and $\phi_{u'}$ overlap then $|u-u'| \leq \ell(u)+\ell(u')$ and thus

$$\ell(u) \leq \ell(u') + \|\nabla\ell\|_\infty(\ell(u) + \ell(u')).$$

Therefore, since $\|\nabla\ell\|_\infty < 1$, we have that $\ell(u) \leq C\ell(u')$ and thus $\ell(u')^{-2} \leq C\ell(u)^{-2}$.

From the variational principle we now get

$$\begin{aligned}&\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- \\ &\quad\geq \int_{d(u)<2R+1} \mathrm{Tr}[\phi_u \left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_-\ell(u)^{-3}du \\ &\quad\quad -C(h^{-3}R^{-7} + h^2R^{-2}),\end{aligned} \tag{68}$$

where we have restricted the integral according to the support of Φ_- and ϕ_u and used that, since we may assume that h is so small that $R > C$, then $\ell(u)^{-2} \geq CR^{-2}$. Note that there is no need to write Φ_- on the right, since in general $\mathrm{Tr}(\Phi_-A\Phi_-)_- \geq \mathrm{Tr}A_-$ for any selfadjoint operator A.

In a very similar manner we get corresponding estimates for the hydrogenic operators. 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

$$\begin{aligned}&\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x} - r_k|} + 1\Big]_- \\ &\quad\geq \int_{d(u)<2R+1} \mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x} - r_k|} + 1 - Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_-\ell(u)^{-3}du \\ &\quad\quad -Ch^2R^{-2}.\end{aligned} \tag{69}$$

We shall now get upper bounds similar to (68) and (69). If we again denote by χ the characteristic function of the interval $(-\infty, 0]$ we see from (65) that

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

defines a density matrix. If we use it as a trial density matrix to get an upper bound we obtain

$$\begin{aligned}\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- &\leq \mathrm{Tr}[(-h^2\Delta - V^{\mathrm{TF}})\gamma] \\ &= \int\limits_{d(u)<2R+1} \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u]_-\ell(u)^{-3}du. \qquad (70)\end{aligned}$$

Similarly,

$$\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- \leq \int\limits_{d(u)<2R+1} \mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big)\phi_u\Big]_-\ell(u)^{-3}du. \quad (71)$$

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 (68), (69),(70), and (71) we have

$$\begin{aligned}\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- - \sum_{k=1}^{M}\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- &\geq \int_{d(u)<2R+1} D_+(u)\ell(u)^{-3}du \\ &\quad -C(h^2R^{-2}+h^{-3}R^{-7}) \quad (72)\end{aligned}$$

and

$$\begin{aligned}\sum_{k=1}^{M}\mathrm{Tr}\Big[-h^2\Delta - \frac{z_k}{|\hat{x}-r_k|}+1\Big]_- - \mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- &\geq \int_{d(u)<2R+1} D_-(u)\ell(u)^{-3}du \\ &\quad -Ch^2R^{-2}, \qquad (73)\end{aligned}$$

and from (65)

$$\begin{aligned}(2\pi h)^{-3}\int(p^2 - V^{\mathrm{TF}}(x))_- dpdx - (2\pi h)^{-3}\sum_{k=1}^{M}\int\Big(p^2 - \frac{z_k}{|x-r_k|}+1\Big)_- dpdx \\ = \int D_{\mathrm{SC}}(u)\ell(u)^{-3}du. \qquad (74)\end{aligned}$$

The same estimates which led to (68) and (69) give

$$\left|\int D_{\rm SC}(u)\ell(u)^{-3}du - \int_{d(u)<2R+1} D_{\rm SC}(u)\ell(u)^{-3}du\right| \le Ch^{-3}R^{-7}. \tag{75}$$

We shall prove the lemma by establishing lower bounds on $D_+(u) - D_{\rm SC}(u)$ and $D_-(u) + D_{\rm SC}(u)$.

We consider first u with $d(u) \le 2\ell_0$, where ℓ_0 is the parameter that occurs in the definition (62) of ℓ. We choose

$$\ell_0 = h, \tag{76}$$

where we assume that h is small enough to ensure that $\ell_0 < 1$. In fact, we may also assume that $\ell_0 < r_0/8$. If k is such that $d(u) = |u - r_k|$ we get from (63) that

$$|u - r_k| + \ell(u) = d(u) + \ell(u) \le d(u) + \tfrac{1}{2}(d(u)^2 + \ell_0^2)^{1/2} < 4\ell_0 < r_0/2.$$

Thus for all x with $|x-u| < \ell(u)$, i.e., for all x in the support of ϕ_u we must have that $|x - r_k| < r_0/2$ and hence $|x - r_j| \ge r_0/2$. Thus $d(x) = |x - r_k|$ and of the nuclear positions $r_1, \ldots, r_M$ only r_k may be contained in the support of ϕ_u. Since the function $W_k(x) = V^{\rm TF}(x) - z_k|x - r_k|^{-1}$ satisfies the estimate (22) on the support of ϕ_u we have for $0 < \varepsilon < 1/2$ that

$$\begin{aligned}
&\mathrm{Tr}\Big[\phi_u(- h^2\Delta - V^{\rm TF} - Ch^2\ell(u)^{-2})\phi_u\Big]_- \\
&\ge \ \mathrm{Tr}\Big[\phi_u\Big(- (1-\varepsilon)h^2\Delta - (1-\varepsilon)\frac{z_k}{|\hat{x} - r_k|} + (1-\varepsilon)\Big)\phi_u\Big]_- \\
&\quad + \mathrm{Tr}\Big[\phi_u\Big(- \varepsilon h^2\Delta - \varepsilon\frac{z_k}{|\hat{x} - r_k|} - (1-\varepsilon) - W_k(x) - Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_- \\
&\ge \ \mathrm{Tr}\Big[\phi_u\Big(- h^2\Delta - \frac{z_k}{|\hat{x} - r_k|} + 1\Big)\phi_u\Big]_- \\
&\quad -Ch^{-3}[\varepsilon\ell(u)^{1/2} + \varepsilon^{-3/2}\ell(u)^3(1 + r_0^{-5/2}) + h^5\varepsilon^{-3/2}\ell(u)^{-2}],
\end{aligned}$$

where in the last line we have used the Lieb-Thirring inequality (7) and the fact that $\mathrm{Tr}[\ldots]_- \le 0$. We therefore have that

$$D_+(u) \ge -Ch^{-3}[\varepsilon\ell(u)^{1/2} + \varepsilon^{-3/2}\ell(u)^3 + h^5\varepsilon^{-3/2}\ell(u)^{-2}]. \tag{77}$$

The quantity $D_-(u)$ is estimated in essentially the same way. We get

$$\begin{aligned}
&\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - \frac{z_k}{|\hat{x} - r_k|} + 1 - Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_- \\
&\ge \ \mathrm{Tr}\Big[\phi_u\Big(-(1-\varepsilon)h^2\Delta - (1-\varepsilon)V^{\rm TF}\Big)\phi_u\Big]_- \\
&\quad + \mathrm{Tr}\Big[\phi_u\Big(-\varepsilon h^2\Delta - \varepsilon\frac{z_k}{|\hat{x} - r_k|} + (1-\varepsilon)W_k - Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_- \\
&\ge \ \mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta - V^{\rm TF}\Big)\phi_u\Big]_- \\
&\quad -Ch^{-3}[\varepsilon\ell(u)^{1/2} + \varepsilon^{-3/2}\ell(u)^3 + h^5\varepsilon^{-3/2}\ell(u)^{-2}],
\end{aligned}$$

and again by the Lieb-Thirring inequality

$$\sum_{j,j\neq k}\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta-\frac{z_k}{|\hat{x}-r_j|}+1-Ch^2\ell(u)^{-2}\Big)\phi_u\Big]_-\geq -Ch^{-3}[\ell(u)^3+h^5\ell(u)^{-2}].$$

Therefore $D_-(u)$ satisfies an estimate similar to (77). Since $d(u)\leq 2\ell_0$ and $\ell_0<1$ we have that $C^{-1}\ell_0\leq\ell(u)\leq C\ell_0$. Hence we can replace $\ell(u)$ by ℓ_0 in the above estimates if we change the constant C. If we now choose $\varepsilon=\ell_0^{-1}h^2$ (with the choice (76) we may assume that h is so small that, indeed, $\varepsilon<1/2$) we get

$$D_+(u),D_-(u)\geq -Ch^{-3}[h^2\ell_0^{-1/2}+h^{-3}\ell_0^{9/2}]. \tag{78}$$

By an identical argument using $(x+y)_-\geq x_-+y_-$ we get that for u with $d(u)\leq 2\ell_0$ we have

$$|D_{\rm SC}(u)|\leq Ch^{-3}[h^2\ell_0^{-1/2}+h^{-3}\ell_0^{9/2}]. \tag{79}$$

We next consider u such that $2\ell_0<d(u)\leq 2R+1$. We choose again $0<\varepsilon<1/2$ (not necessarily the same as before) and use the Lieb-Thirring inequality to arrive at

$$\begin{aligned} D_+(u) \;\geq\;& \mathrm{Tr}[\phi_u\left(-(1-\varepsilon)h^2\Delta-V^{\rm TF}\right)\phi_u]_- \\ & -\sum_{k=1}^{M}\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta-\frac{z_k}{|\hat{x}-r_k|}+1\Big)\phi_u\Big]_- -C\varepsilon^{-3/2}h^2\ell(u)^{-2}. \end{aligned}\tag{80}$$

Since $V^{\rm TF}$ satisfies the estimate (66) on the ball $\{x\mid |x-u|<\ell(u)\}$ and ϕ_u satisfies (65) we may use Corollary 15 to conclude that

$$\begin{aligned}\Big|\mathrm{Tr}[\phi_u\left(-(1-\varepsilon)h^2\Delta-V^{\rm TF}\right)\phi_u]_- -(2\pi(1-\varepsilon)^{1/2}h)^{-3}\int\phi_u^2(x)(p^2-V^{\rm TF}(x))_-dxdp\Big| \\ \leq Ch^{-3}h^{6/5}f(u)^{19/5}\ell(u)^{9/5},\end{aligned}$$

where C depends only on $z_1,\ldots,z_M$ and M. Hence again using (66) we obtain

$$\begin{aligned}\mathrm{Tr}[\phi_u\left(-(1-\varepsilon)h^2\Delta-V^{\rm TF}\right)\phi_u]_- \;\geq\;& (2\pi h)^{-3}\int\phi_u^2(x)(p^2-V^{\rm TF}(x))_-dxdp \\ & -Ch^{-3}(\varepsilon f(u)^5\ell(u)^3+h^{6/5}f(u)^{19/5}\ell(u)^{9/5}).\end{aligned}\tag{81}$$

If $d(u)>\max_k\{z_k\}+1$ then we have that for all $k=1,\ldots,M$ that

$$\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta-\frac{z_k}{|\hat{x}-r_k|}+1\Big)\phi_u\Big]_-=0\quad\text{and}\quad\int\phi_u(x)^2\Big(p^2-\frac{z_k}{|x-r_k|}+1\Big)_-dpdx=0.$$

On the other hand, if $2\ell_0<d(u)<\max_k\{z_k\}+1$ then for all $k=1,\ldots,M$ the potential $z_k|x-r_k|^{-1}-1$ satisfies a bound similar to (66) and we may again use Corollary 15 to conclude that for all u with $d(u)>2\ell_0$ we have

$$\begin{aligned}\Big|\mathrm{Tr}\Big[\phi_u\Big(-h^2\Delta-\frac{z_k}{|\hat{x}-r_k|}+1\Big)\phi_u\Big]_- -(2\pi h)^{-3}\int\phi_u^2(x)\Big(p^2-\frac{z_k}{|x-r_k|}+1\Big)_-dxdp\Big| \\ \leq Ch^{-3}h^{6/5}f(u)^{19/5}\ell(u)^{9/5}.\end{aligned}\tag{82}$$

Hence from (80), (81), and (82) we have for all u with $2\ell_0 < d(u) \leq 2R+1$ that

$$\begin{aligned} D_+(u) - D_{\mathrm{SC}}(u) &\geq -Ch^{-3}(\varepsilon^{-3/2}h^5\ell(u)^{-2} + \varepsilon f(u)^5\ell(u)^3 + h^{6/5}f(u)^{19/5}\ell(u)^{9/5}) \\ &= -Ch^{-3}(h^2 f(u)^3\ell(u) + h^{6/5}f(u)^{19/5}\ell(u)^{9/5}), \end{aligned} \tag{83}$$

where we have chosen $\varepsilon = ch^2\ell(u)^{-2}f(u)^{-2}$. Note that from the property (64) of ℓ and the definition (19) of f we have

$$\varepsilon \leq cCh^2 \max\{d(u)^{-1}, d(u)^4\} \leq cCh^2 \max\{\ell_0^{-1}, (2R+1)^4\}.$$

We see that with the choice of R in (67) and of ℓ_0 in (76) we may assume that h and c are chosen small enough so that $\varepsilon < 1/2$.

In a completely similar way we get for all u with $2\ell_0 < d(u) \leq 2R+1$ that

$$D_-(u) + D_{\mathrm{SC}}(u) \geq -Ch^{-3}(h^2 f(u)^3\ell(u) + h^{6/5}f(u)^{19/5}\ell(u)^{9/5}). \tag{84}$$

If we now combine (78),(79), (83), and (84) we obtain

$$\begin{aligned} &\int\limits_{d(u)\leq 2R+1} [D_\pm(u) \mp D_{\mathrm{SC}}(u)]\ell(u)^{-3}du \\ &\quad\geq -Ch^{-3}[h^2\ell_0^{-1/2} + h^{-3}\ell_0^{9/2}] \\ &\qquad -Ch^{-3} \int\limits_{2\ell_0\leq d(u)\leq 2R+1} (h^2 f(u)^3\ell(u)^{-2} + h^{6/5}f(u)^{19/5}\ell(u)^{-6/5})du, \end{aligned} \tag{85}$$

where we have used that the volume of the set of u for which $d(u) \leq 2\ell_0$ is bounded by $C\ell_0^3$ and that from (63), $\ell(u) \geq C^{-1}\ell_0$. Using again the property (64) of ℓ and the definition (19) of f we see that the last integral in (85) is bounded by

$$\begin{aligned} & Ch^{-3} \int\limits_{2\ell_0\leq d(u)\leq 2R+1} h^2 \min\{d(u)^{-7/2}, d(u)^{-6}\} + h^{6/5}\min\{d(u)^{-31/10}, d(u)^{-38/5}\}du \\ \leq\ & Ch^{-3} \int\limits_{2\ell_0\leq |u|} h^2 \min\{|u|^{-7/2}, |u|^{-6}\} + h^{6/5}\min\{|u|^{-31/10}, |u|^{-38/5}\}du \\ \leq\ & Ch^{-1}\ell_0^{-1/2} + Ch^{-9/5}\ell_0^{-1/10}. \end{aligned}$$

Thus if we combine (72), (73), (74) ,(75), and (85) we see that the left side of the main inequality (61) is bounded by

$$\begin{aligned} &C(h^{-1}\ell_0^{-1/2} + h^{-9/5}\ell_0^{-1/10} + h^{-6}\ell_0^{9/2} + h^2R^{-2} + Ch^{-3}R^{-7}) \\ &\quad\leq C(h^{-3/2} + h^{-19/10} + h^{-3/2} + h^3 + h^{1/2}) \leq Ch^{-2+1/10}. \end{aligned}$$

Note that the choice of ℓ_0 has not been optimized. $\square$

Proof of Theorem 16. As mentioned just after the statement of Lemma 17 the first estimate in the theorem is a consequence of the lemma. It remains to prove the existence of a density matrix γ with the stated properties.

We note first that we may as before, if necessary, assume that h is smaller than some constant depending only on the parameters $z_1, \ldots, z_M$, M, and r_0. Otherwise we simply choose $\gamma = 0$. That this is an acceptable choice follows from the Lieb-Thirring inequality (7) and the fact that the estimate (21) for $\alpha = 0$ implies that $D\left(\left(V^{\mathrm{TF}}\right)^{3/2}\right) \leq C$.

To construct γ we shall again use the localization family ϕ_u with the properties given in (65). As in the previous lemma we shall choose $R = h^{-1/2}$ and $\ell_0 = h$ (although it is not a requirement that they should be as before). We shall choose γ of the form

$$\gamma = \int_{d(u)<R} \phi_u \gamma_u \phi_u \ell(u)^{-3} du, \tag{86}$$

where γ_u is a family of density matrices which we shall now choose. Note that the first condition in (65) implies that γ is then a density matrix.

If $2\ell_0 < d(u)$ it follows from (65), (66), and Corollary 15 that we may choose γ_u such that (53), (54), and (55) hold when $V = V^{\mathrm{TF}}$, $\phi = \phi_u$, $\ell = \ell(u)$ and $f = f(u)$.

If $d(u) \leq 2\ell_0$ 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.

We shall first prove that for $d(u) \leq 2\ell_0$ we have

$$\int \left(\phi_u^2 \rho_{\gamma_u}\right)^{5/3} \leq C h^{-5} \ell_0^{1/2}. \tag{87}$$

From the Lieb-Thirring inequality (7) and the estimate (21) with $\alpha = 0$, we conclude that

$$0 \geq \mathrm{Tr}\left(\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u\gamma_u\right) \geq \tfrac{1}{2}\mathrm{Tr}\left(-h^2\Delta(\phi_u\gamma_u\phi_u)\right) - Ch^{-3}\ell_0^{1/2},$$

where we have used that $d(u) \leq 2\ell_0$ implies that $\ell(u) \leq C\ell_0$. The density of the operator $\phi_u\gamma_u\phi_u$ is $\phi_u^2\rho_{\gamma_u}$. Thus, using the Lieb-Thirring inequality in the formulation (6) we arrive at (87).

Using (87), Hölder's inequality, the support property for ϕ_u, (63), and the second property in (65) we arrive at the estimates

$$\|\phi_u^2\rho_{\gamma_u}\|_1 \leq Ch^{-3}\ell(u)^{3/2} \quad \text{and} \quad \|\phi_u^2\rho_{\gamma_u}\|_{6/5} \leq Ch^{-3}\ell(u), \tag{88}$$

for u with $d(u) \leq 2\ell_0$. For these u we also have

$$\|\phi_u^2(V^{\mathrm{TF}})^{3/2}\|_1 \leq C\ell_0^{3/2} \quad \text{and} \quad \|\phi_u^2(V^{\mathrm{TF}})^{3/2}\|_{6/5} \leq C\ell_0, \tag{89}$$

where we have used that from (21) with $\alpha = 0$, $V^{\mathrm{TF}}(x) \leq Cd(x)^{-1}$.

We are now ready to prove that the density matrix γ has the stated properties. We begin with proving (60). The density of γ is

$$\rho_\gamma(x) = \int_{d(u)<R} \phi_u(x)^2 \rho_{\gamma_u}(x)\ell(u)^{-3} du.$$

From (55) we see that for $d(u) > 2\ell_0$ we have

$$\int \phi_u(x)^2 \rho_{\gamma_u}(x) dx \leq \frac{1}{6\pi^2 h^3} \int \phi_u(x)^2 V^{\mathrm{TF}}(x)^{3/2} dx + Ch^{-2+1/5} f(u)^{9/5} \ell(u)^{9/5}$$

and from (88) and (89) we get for $d(u) \leq 2\ell_0$ that

$$\int \phi_u(x)^2 \rho_{\gamma_u}(x) dx \leq \frac{1}{6\pi^2 h^3} \int \phi_u(x)^2 V^{\mathrm{TF}}(x)^{3/2} dx + Ch^{-3} \ell_0^{3/2}.$$

Hence using the first property of ϕ_u in (65) we obtain

$$\begin{aligned}
\int \rho_\gamma(x) dx &\leq \frac{1}{6\pi^2 h^3} \int V^{\mathrm{TF}}(x)^{3/2} dx + Ch^{-3} \int_{d(u)\leq 2\ell_0} \ell_0^{3/2} \ell(u)^{-3} du \\
&\quad + C \int_{2\ell_0 < d(u) < R} h^{-2+1/5} f(u)^{9/5} \ell(u)^{-6/5} du \\
&\leq \frac{1}{6\pi^2 h^3} \int V^{\mathrm{TF}}(x)^{3/2} dx + Ch^{-3} \ell_0^{3/2} \\
&\quad + Ch^{-2+1/5} \int_{2\ell_0 < d(u) < R} \min\{d(u)^{-21/10}, d(u)^{-18/5}\} du \\
&\leq \frac{1}{6\pi^2 h^3} \int V^{\mathrm{TF}}(x)^{3/2} dx + Ch^{-2+1/5},
\end{aligned}$$

where we have inserted the choice $\ell_0 = h$, used that h is small, and controlled the integral over the region $2\ell_0 < d(u) < R$ in a way similar to the integral in (85), using the properties (19) and (64) of f and ℓ.

We now come to the proof of (59). If we use the Hardy-Littlewood-Sobolev inequality (9) we see that it is enough to estimate the 6/5 norm

$$\begin{aligned}
\left\| \rho_\gamma - \frac{1}{6\pi^2 h^3} (V^{\mathrm{TF}})^{3/2} \right\|_{6/5} &\leq \int_{d(u)<R} \left\| \phi_u^2 \left(\rho_{\gamma_u} - \frac{1}{6\pi^2 h^3} (V^{\mathrm{TF}})^{3/2} \right) \right\|_{6/5} \ell(u)^{-3} du \\
&\quad + \int_{d(u)>R} \left\| \frac{1}{6\pi^2 h^3} (V^{\mathrm{TF}})^{3/2} \phi_u^2 \right\|_{6/5} \ell(u)^{-3} du.
\end{aligned}$$

If we use (88) and (89) when u with $d(u) \leq 2\ell_0$, (54) when $2\ell_0 < d(u) < R$, and (66) when $d(u) > R$ we obtain

$$\begin{aligned}
\left\| \rho_\gamma - \frac{1}{6\pi^2 h^3} (V^{\mathrm{TF}})^{3/2} \right\|_{6/5} &\leq Ch^{-3} \ell_0 + Ch^{-21/10} \int\limits_{2\ell_0 < d(u) < R} f(u)^{21/10} \ell(u)^{-7/5} du \\
&\quad + Ch^{-3} \int_{d(u)>R} f(u)^3 \ell(u)^{-1/2} du.
\end{aligned}$$

Using as before the properties (19) and (64) we see that the first integral above is bounded by a constant and the second integral (since we may assume that $R > 1$) is bounded by R^{-3}. Thus using the Hardy-Littlewood-Sobolev inequality (9) we obtain

$$D\left(\rho_\gamma - \frac{1}{6\pi^2 h^3}(V^{\mathrm{TF}})^{3/2}\right) \leq C\left\|\rho_\gamma - \frac{1}{6\pi^2 h^3}(V^{\mathrm{TF}})^{3/2}\right\|_{6/5}^2 \leq C(h^{-5+4/5} + h^{-6}R^{-6}).$$

Finally we turn to proving (58). From the definition of γ, (51) and (53) we obtain

$$\begin{aligned}\mathrm{Tr}\left[(-h^2\Delta - V^{\mathrm{TF}})\gamma\right] &= \int_{d(u)<R} \mathrm{Tr}\left[\phi_u\gamma_u\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\right]\ell(u)^{-3}du \\ &\leq \int_{d(u)<R} \mathrm{Tr}\left[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u\right]_-\ell(u)^{-3}du \\ &\quad + Ch^{-2+1/5}\int_{2\ell_0<d(u)<R} f(u)^{19/5}\ell(u)^{-6/5}du. \qquad (90)\end{aligned}$$

On the other hand, from (68) (used with $2R+1$ replaced by R) we get

$$\begin{aligned}\mathrm{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- &\geq \int_{d(u)<R} \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_-\ell(u)^{-3}du \\ &\quad -C(h^2R^{-2} + h^{-3}R^{-7}). \qquad (91)\end{aligned}$$

Appealing to the Lieb-Thirring inequality (7) we see that for all $0 < \varepsilon < 1$ we have

$$\begin{aligned}\mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_- &\geq (1-\varepsilon)\mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u]_- \\ &\quad - C\varepsilon^{-3/2}h^2\ell(u)^{-2} \\ &\quad -C\varepsilon h^{-3}\int_{|x-u|<\ell(u)}(V^{\mathrm{TF}}(x))^{5/2}dx.\end{aligned}$$

Using (21) and (66) both with $\alpha = 0$ we find that

$$\int_{|x-u|<\ell(u)} V^{\mathrm{TF}}(x)^{5/2}dx \leq \begin{cases} C\ell_0^{1/2}, & \text{if } d(u) \leq 2\ell_0 \\ Cf(u)^5\ell(u)^3, & \text{if } d(u) > 2\ell_0 \end{cases}.$$

If $d(u) \leq 2\ell_0$ we choose $\varepsilon = c\ell_0^{-1}h^2$ (as we did just before (78)) and we get

$$\begin{aligned}\mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_- &\geq \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u]_- \\ &\quad - Ch^{-1}\ell_0^{-1/2} \qquad (92)\end{aligned}$$

If $d(u) > 2\ell_0$ we choose $\varepsilon = h^2\ell(u)^{-2}f(u)^{-2}$ (as we did just after (83)) and we get

$$\begin{aligned}\mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}} - Ch^2\ell(u)^{-2}\right)\phi_u]_- &\geq \mathrm{Tr}[\phi_u\left(-h^2\Delta - V^{\mathrm{TF}}\right)\phi_u]_- \\ &\quad - Ch^{-1}f(u)^3\ell(u) \qquad (93)\end{aligned}$$

Thus from (90), (91), (92), and (93) we get

$$\begin{aligned}\operatorname{Tr}\left[(-h^2\Delta - V^{\mathrm{TF}})\gamma\right] \;&\leq\; \operatorname{Tr}[-h^2\Delta - V^{\mathrm{TF}}]_- + C(h^{-1}\ell_0^{-1/2} + h^2R^{-2} + h^{-3}R^{-7})\\ &\quad + C\int\limits_{d(u)<R} h^{-2+1/5}f(u)^{19/5}\ell(u)^{-6/5} + h^{-1}f(u)^3\ell(u)^{-2}du.\end{aligned}$$

The estimate (58) now follows from a calculation almost identical to the one given right after (85).

□

6 Proof of the Scott correction for the molecular ground state energy

The proof of the Scott correction Theorem 1 is now a fairly standard application of the results in the previous sections. We begin with giving the proof of the lower bound.

Lemma 18 (Lower bound). *Let R and Z be as in the statement of Theorem 1. Then, the ground state energy for a neutral molecule satisfies*

$$E(Z,R) \geq E^{\mathrm{TF}}(Z,R) + \tfrac{1}{2}\sum_j Z_j^2 + \mathcal{O}(|Z|^{2-1/30}).$$

Proof. The starting point is the Lieb-Oxford inequality (11), from which we conclude that if ψ is a Z-particle ($N = Z$) wave function we have

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

In order to bound the last term we use the many-body version of the Lieb-Thirring inequality (8). For all $0<\varepsilon<1/2$ we have

$$\begin{aligned}\Big\langle \psi, \varepsilon\sum_{i=1}^{Z} -\tfrac{1}{2}\Delta_i\psi\Big\rangle - C\int\rho_\psi^{4/3} \;&\geq\; \varepsilon\int\rho_\psi^{5/3} - C\int\rho_\psi^{4/3}\\ &\geq\; \varepsilon\int\rho_\psi^{5/3} - C\left(\int\rho_\psi^{5/3}\right)^{1/2}\left(\int\rho_\psi\right)^{1/2}\\ &\geq\; -\varepsilon^{-1}C\int\rho_\psi = -C\varepsilon^{-1}Z.\end{aligned}$$

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

$$\langle \psi, H(Z,R)\psi\rangle \;\geq\; \left\langle \psi, \sum_{i=1}^{Z}(-(1-\varepsilon)\tfrac{1}{2}\Delta_i - V(Z,R,x_i))\psi\right\rangle + D(\rho_\psi) - C\varepsilon^{-1}Z$$

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

Here we have applied (13), 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 (15) we find that

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

where $\mathbf{z} = (z_1,\ldots,z_M)$ and $\mathbf{r} = (r_1,\ldots,r_M)$. Using now (57) (with $h = \sqrt{(1-\varepsilon)/2}|Z|^{-1/3}$) and (27) we see that

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

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 lemma. □

Lemma 19 (Upper bound). *Let R and Z satisfy the conditions from Theorem 1. Then, the ground state energy for a neutral molecule satisfies*

$$
E(Z,R) \leq E^{\mathrm{TF}}(Z,R) + \tfrac{1}{2}\sum_j Z_j^2 + \mathcal{O}(|Z|^{2-1/30}).
$$

Proof. The starting point now is Lieb's variational principle, Theorem 5. By a simple rescaling the variational principle states that for any density matrix γ on $L^2(\mathbb{R}^3)$ with $2\mathrm{Tr}\gamma \leq Z$ we have

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

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

$$
\begin{aligned}
|Z|^{-4/3}E(Z,R) &\leq 2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V(\mathbf{z},\mathbf{r},x)\right)\gamma\right] + |Z|D(2|Z|^{-1}\rho_\gamma) \\
&= 2\mathrm{Tr}\left[\left(-\tfrac{1}{2}|Z|^{-2/3}\Delta - V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},x)\right)\gamma\right] \\
&\quad +|Z|D\left(2|Z|^{-1}\rho_\gamma - \rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)\right) - |Z|D(\rho^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)). \quad (94)
\end{aligned}
$$

We now choose a density matrix $\widetilde{\gamma}$ according to Theorem 16 with $h = \sqrt{1/2}|Z|^{-1/3}$. Note that with this choice of h we have that

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

Since $\int \rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, x) = \sum_{j=1}^{M} z_j = 1$ we see from (60) that

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

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

Using (59) we see that

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

and thus

$$\begin{aligned}
&|Z| D\left(2|Z|^{-1}\rho_{\gamma} - \rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, \cdot)\right) \\
&\quad\leq \; C|Z|(1 + C|Z|^{-1/3-1/15})^{-2} D\left(2|Z|^{-1}\rho_{\widetilde{\gamma}} - \rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, \cdot)\right) \\
&\qquad + C|Z|^{1/3-2/15} D\left(\rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, \cdot)\right) \leq C|Z|^{2/3-4/15}, \qquad (95)
\end{aligned}$$

where we have used the triangle inequality for $\sqrt{D}$, and that $D\left(\rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, \cdot)\right) \leq C$.

Finally, if we use (57), (58), and (27) we arrive at

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

Since $E^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}) \leq C$ and $D\left(\rho^{\mathrm{TF}}(\mathbf{z}, \mathbf{r}, \cdot)\right) \leq C$ we see that the same estimate holds for $\widetilde{\gamma}$ replaced by γ. If we insert this estimate together with (95) into (94) 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 in the lemma. $\square$

A Appendix: Results on the new coherent states

Before we prove the trace formula (10) and the representation (11) we need some simple lemmas. The proof of the first one is a straightforward calculation which it is left to the reader to check.

Lemma 20. *Let $\mathcal{G}_{u,q}$ be defined as in (28), then its integral kernel is*

$$\mathcal{G}_{u,q}(x, y) = (\pi h)^{-n/2} e^{-a\left(\frac{x+y}{2} - u\right)^2 + iq(x-y)/h - \frac{1}{4h^2 a}(x-y)^2}. \qquad (96)$$

Lemma 21. *Let $B_0 \in \mathbb{R}, B_{1,2} \in \mathbb{R}^n$ and $\hat{A} = B_0 + B_1\hat{x} - ihB_2\nabla$ be a linear combination of the identity, multiplication and momentum operator. Let f be a polynomially bounded, measurable function on $\mathbb{R}^n$ with values in $\mathbb{R}$. Then,*

$$f(B_0 + B_1\hat{x} - ihB_2\nabla)(x,y) = \int f(B_0 + B_1\left(\tfrac{x+y}{2}\right) + B_2p)e^{ip(x-y)/h}\frac{dp}{(2\pi h)^n}$$

as a distributional kernel.

Proof. First assume that B_1 and B_2 are not orthogonal. By applying the unitary transformation $(U\psi)(x) = \exp[-\frac{i}{2hB_1\cdot B_2}(B_1x)^2]\psi(x)$ and the Spectral Theorem we get $U^{-1}f(B_0 + B_1\hat{x} - ihB_2\nabla)U = f(B_0 - ihB_2\nabla)$. Hence,

$$\begin{aligned} & f(B_0 + B_1\hat{x} - ihB_2\nabla)(x,y) \\ &= \int f(B_0 + B_2p)\,e^{-\frac{i}{2hB_1\cdot B_2}((B_1x)^2-(B_1y)^2)+ip(x-y)/h}\,\frac{dp}{(2\pi h)^n} \\ &= \int f(B_0 + B_1\left(\tfrac{x+y}{2}\right) + B_2p)\,e^{ip(x-y)/h}\,\frac{dp}{(2\pi h)^n}. \end{aligned}$$

The case $B_1 \cdot B_2 = 0$ follows then, say by continuity. $\square$

Proof of Theorem 9. The proof is actually a fairly standard exercise in calculations with Fourier integrals, but we shall do it here carefully.

Let us for simplicity call $\mathcal{G} = \mathcal{G}_{u,q}$. Since f is polynomially bounded we have that $(1+\hat{A}^{2N})^{-1}f(\hat{A})$ extends to a bounded operator when N is a large enough integer. From the explicit expression (96) for the integral kernel of $\mathcal{G}$ we immediately see that $(1+\hat{A}^{2N})\mathcal{G}(x,y)$ is in $L^2(\mathbb{R}^n \times \mathbb{R}^n)$. Thus, the operator $(1+\hat{A}^{2N})\mathcal{G}$ is Hilbert-Schmidt. It follows that $f(\hat{A})\mathcal{G}$ is Hilbert-Schmidt. Likewise $(1+|x|)^{-M}V(x)$ is bounded for M large enough. and thus $\mathcal{G}V(\hat{x})$ extends to a Hilbert-Schmidt operator. Moreover if we define

$$f_\varepsilon(s) = f(s)e^{-\varepsilon s^2} \text{ and } V_\varepsilon(x) = V(x)e^{-\varepsilon x^2},$$

we have

$$\lim_{\varepsilon\to 0}\mathrm{Tr}\left[\mathcal{G}f_\varepsilon(\hat{A})\mathcal{G}V_\varepsilon\right] = \mathrm{Tr}\left[\mathcal{G}f(\hat{A})\mathcal{G}V\right].$$

The trace on the left can be immediately calculated from Lemmas 20 and 21. $\square$

Proof of Theorem 10. We proceed as in the previous proof. We consider first the case $V = 0$. We have that $(1-h^2\Delta)^{-1}F(-ih\nabla)$ is a bounded operator and thus $\phi F(-ih\nabla)\phi\mathcal{G}$ is a Hilbert-Schmidt operator. It follows moreover that if we define

$$f_\varepsilon(s) = f(s)e^{-\varepsilon s^2} \text{ and } F_\varepsilon(p) = F(p)e^{-\varepsilon p^2},$$

then the operators

$$f_\varepsilon(\hat{A})\mathcal{G} \text{ and } \phi F_\varepsilon(-ih\nabla)\phi\mathcal{G}$$

converge in Hilbert-Schmidt norm as $\varepsilon \to 0$. We therefore have

$$\mathrm{Tr}[\mathcal{G}\, f(\hat{A})\, \mathcal{G}\, \phi F(-ih\nabla)\phi] = \lim_{\varepsilon\to 0}\lim_{\delta\to 0} \mathrm{Tr}[\mathcal{G}\, f_\delta(\hat{A})\, \mathcal{G}\, \phi F_\varepsilon(-ih\nabla)\phi].$$

The trace on the right can be written as an absolutely convergent integral

$$\begin{aligned} &(2\pi h)^{2n}\mathrm{Tr}[\mathcal{G}\, f_\delta(\hat{A})\, \mathcal{G}\, \phi F_\varepsilon(-ih\nabla)\phi] \\ &= \int f_\delta(B_0 + B_1\tfrac{x+y}{2} + B_2 p)e^{ip(x-y)/h+i\eta(z-z')/h}\mathcal{G}_{u,q}(y,z)\mathcal{G}_{u,q}(z'x) \\ &\quad \times \phi(z)\phi(z')F_\varepsilon(\eta)\, d\eta dx dy dz dz' dp \end{aligned}$$

We now perform the integration in the variable $x-y$ and we rename the integration variable $(x+y)/2$ as v. We subsequently change variables so that (z, z', η) are replaced by $(z + h^2ab(u-v)+v, z'+h^2ab(u-v)+v, \eta+p+h^2(ab)(q-p))$. This eventually gives

$$\begin{aligned} &(2\pi h)^{2n}(\pi/4b)^{n/2}\mathrm{Tr}[\mathcal{G}\, f_\delta(\hat{A})\, \mathcal{G}\, \phi F_\varepsilon(-ih\nabla)\phi] \\ &= \int f_\delta(B_0 + B_1 v + B_2 p)F_\varepsilon(\eta + w(p,q))e^{-b(p-q)^2-b(u-v)^2} \qquad (97) \\ &\quad \times \phi(z+w(v,u))\phi(z'+w(v,u))e^{i\eta(z-z')/h}e^{-b\left(\frac{z-z'}{2}\right)^2-\frac{1}{4h^2b}(z+z')^2}\, dz dz' d\eta dv dp, \end{aligned}$$

where to avoid lengthy expressions we have introduced the function $w(s,t) = s + h^2ab(t-s)$ for $s,t\in\mathbb{R}^n$. We now expand $F(w(p,q)+\eta)$ around $w(p,q)$. I.e., we write

$$F_\varepsilon(w(p,q)+\eta) = \Big[F(w(p,q)) + \eta\cdot\nabla F(w(p,q)) + R_F(w(p,q),\eta)\Big]e^{-\varepsilon(w(p,q)+\eta)^2},$$

where according to the assumption that all second derivatives of F are bounded we have that the remainder term satisfies $|R_F(p+h^2ab(q-p),\eta)| \le C\eta^2$, with a constant depending on the bound on the second derivatives of F. We shall estimate the error coming from the remainder term below, but we first consider the contribution from the two main terms. If we insert the two main terms in the expansion into the integral (97) above we see that they give integrals in which the η integration can be performed explicitly. After letting $\delta, \varepsilon \to 0$ we obtain for these leading terms

$$(2\pi h)^n \int \begin{aligned} &f(B_0 + B_1 v + B_2 p)F(w(p,q))e^{-b(p-q)^2-b(u-v)^2} \\ &\phi(z+w(v,u))^2 e^{-\frac{1}{h^2b}z^2}\, dz dv dp. \end{aligned} \qquad (98)$$

Here we may now expand the function ϕ^2

$$\phi(z+w(v,u))^2 = \phi(w(v,u))^2 + z\cdot\nabla\phi(w(v,u))^2 + R_\phi(w(v,u),z),$$

where $|R_\phi(h^2ab(u-v)+v,z)| \le Cz^2$ with a constant that depends on the bound on ϕ, and its first and second derivatives. Hence the integral in (98) may be written as

$$(2\pi h)^n(b/4\pi)^{n/2}\int \begin{aligned} &f(B_0 + B_1 v + B_2 p)e^{-b(p-q)^2-b(u-v)^2}F(w(p,q)) \\ &\times \left[\phi(w(v,u))^2 + E_1(u,v)\right] dv dp, \end{aligned}$$

where $|E_1(u,v)| \le Ch^2 b$.

We now return to estimating the contribution from the remainder term R_F. Note that for all integers $1 \le k \le (n/2)+2$ we have

$$\begin{aligned}
&(1+\eta^2/(bh^2))^k \left| \int \phi(z+w(v,u))\psi(z'+w(v,u)) e^{i\eta(z-z')/h} e^{-b\left(\frac{z-z'}{2}\right)^2}\, d(z-z') \right| \\
\le\ & C \int \left| (1-b^{-1}\Delta_{z-z'})^k \left(\phi(z+w(v,u))\phi(z'+w(v,u)) e^{-b\left(\frac{z-z'}{2}\right)^2} \right) \right| d(z-z') \\
\le\ & C b^{-n/2},
\end{aligned}$$

where we have used that $b > 1$. Here the constant depends on the bound on ϕ, and its first $n+4$ derivatives. Thus the relevant contribution to the integral (97) coming from the error term R_F can be estimated by

$$\begin{aligned}
&\left| \int R_F(p + h^2 ab(q-p), \eta) \phi(z+w(v,u))\phi(z'+w(v,u)) e^{i\eta(z-z')/h} \right. \\
&\left. \times\, e^{-b\left(\frac{z-z'}{2}\right)^2 - \frac{1}{4h^2 b}(z+z')^2}\, dz dz' d\eta \right| \\
&\le C b^{-n/2} \int (1+\eta^2/(bh^2))^{-k} \eta^2 e^{-\frac{1}{h^2 b}\tilde{z}^2}\, d\tilde{z} d\eta \le C b^{n/2} h^{2n} b h^2,
\end{aligned}$$

where we have chosen k so as to make the integral finite. We can always do this without violating $1 \le k \le (n/2)+2$. Thus after taking the limit $\delta \to 0$ we obtain the statement of the theorem.

The case when $F = 0$ and $V \ne 0$ is similar but much simpler since we may start with Theorem 9 and expand V. $\square$

Proof of theorem 11. Since σ is a sum of a function of q and a function of u it is enough to consider only one of the terms, say, V. Let as before $G_b(x) = (b/\pi)^{n/2} e^{-bx^2}$. It follows immediately from (96) that

$$\begin{aligned}
\int \mathcal{G}_{u,q}^2 \frac{dq}{(2\pi h)^n} &= G_b(\hat{x}-u), \\
\int \mathcal{G}_{u,q}(\hat{x}-u)\mathcal{G}_{u,q} \frac{dq}{(2\pi h)^n} &= (1-h^2 ab)(\hat{x}-u) G_b(\hat{x}-u).
\end{aligned} \tag{99}$$

As a consequence we have

$$\begin{aligned}
V(\hat{x}) - \int \mathcal{G}_{u,q}\Big(V(u) + \tfrac{1}{4b}\Delta V(u) + \nabla V(u)\cdot(\hat{x}-u)\Big)\mathcal{G}_{u,q} \frac{du dq}{(2\pi h)^n} \\
= \int G_b(\hat{x}-u)\Big(V(\hat{x}) - \Big(V(u) + \tfrac{1}{4b}\Delta V(u) \\
+ (1-h^2 ab)\nabla V(u)\cdot(\hat{x}-u)\Big)\Big) du.
\end{aligned}$$

Using Taylors' formula we have

$$V(x) = V(u) + \nabla V(u)\cdot(x-u) + \tfrac{1}{2}\sum_{ij}\partial_i\partial_j V(x)(x_i-u_i)(x_j-u_j) - \mathcal{R}_1(x,u)$$

where

$$\mathcal{R}_1(x,u) = \tfrac{1}{2}\int_0^1 \sum_{i,j,k}\partial_i\partial_j\partial_k V(u+t(x-u))(x_i-u_i)(x_j-u_j)(x_k-u_k)(1-(1-t)^2)dt.$$

Since $\int x_i x_j G_b(x)dx = \frac{1}{2b}\delta_{ij}$ we have

$$\begin{aligned} V(\hat{x}) - &\int \mathcal{G}_{u,q}\left(V(u) + \tfrac{1}{4b}\Delta V(u) + \nabla V(u)\cdot(\hat{x}-u)\right)\mathcal{G}_{u,q}\frac{dudq}{(2\pi h)^n} \\ = &\int G_b(\hat{x}-u)\Big(\tfrac{1}{4b}\left(\Delta V(\hat{x}) - \Delta V(u)\right) + h^2 ab\nabla V(u)\cdot(\hat{x}-u) - \mathcal{R}_1(\hat{x},u)\Big)du \\ = &\int G_b(\hat{x}-u)\left(\tfrac{1}{4b}\left(\Delta V(\hat{x}) - \Delta V(u)\right) - \tfrac{1}{2}h^2 a\Delta V(u) - \mathcal{R}_1(\hat{x},u)\right)du \end{aligned}$$

where the last identity follows by integration by parts. The theorem now follows easily since $a \le b$ and

$$\Delta V(x) - \Delta V(u) = \int_0^1 \sum_i \partial_i \Delta V(u+t(x-u))(x_i-u_i)dt.$$

□

B Appendix: A localization theorem

Theorem 22. *Consider $\phi \in C_0^\infty(\mathbb{R}^n)$ with support in the ball $\{|x| \le 1\}$ and satisfying $\int \phi^2(x)\,dx = 1$. Assume that $\ell : \mathbb{R}^n \to \mathbb{R}$ is a C^1 map satisfying $0 < \ell(u) \le 1$ and $\|\nabla \ell\|_\infty < 1$. Let $J(x,u)$ be the Jacobian of the map $u \mapsto \frac{x-u}{\ell(u)}$, i.e.*

$$J(x,u) = \ell(u)^{-n}\left|\det\left[\frac{(x_i-u_i)\partial_j\ell(u)}{\ell(u)} + \delta_{ij}\right]_{ij}\right|.$$

We set $\phi_u(x) := \phi\Big(\frac{x-u}{\ell(u)}\Big)\sqrt{J(x,u)}\ell(u)^{n/2}$. Then, for all $x \in \mathbb{R}^n$

$$\int_{\mathbb{R}^n} \phi_u^2(x)\ell(u)^{-n}\,du = 1 \tag{100}$$

and for all multi-indices α we have

$$\|\partial^\alpha \phi_u\|_\infty \le \ell(u)^{-|\alpha|}C_\alpha \max_{|\beta|\le|\alpha|}\|\partial^\beta\phi\|_\infty, \tag{101}$$

where C_α depends only on α.

Proof. In order to prove (100) it is of course enough to consider the case $x = 0$. The identity follows from the change of variables formula if we can show that the map $F : \mathbb{R}^n \to \mathbb{R}^n$ given by $F(u) = -u/\ell(u)$ is a bijection of $F^{-1}(\{|x| \leq 1\})$ onto $\{|x| \leq 1\}$.

The map is, in fact, onto $\mathbb{R}^n$ since $F(0) = 0$ and $|F(u)| \geq |u|$. Hence for all $u \in \mathbb{R}^n$ there exists $t \in \mathbb{R}$ with $-1 \leq t \leq 0$ such that $F(tu) = u$.

That the map is also injective on $F^{-1}(\{|x| \leq 1\})$ follows since for $u \neq 0$ we may write $F(tu) = -g(t)u$ and the map $g : \mathbb{R} \to \mathbb{R}$ is monotone increasing for all t for which $|g(t)||u| \leq 1$. In fact, $g(t) = t/\ell(tu)$ and thus

$$\begin{aligned} g'(t) &= \ell(tu)^{-1} - t\ell(tu)^{-2}\nabla\ell(tu)\cdot u = \ell(tu)^{-1}[1 - t\ell(tu)^{-1}\nabla\ell(tu)\cdot u] \\ &\geq \ell(tu)^{-1}[1 - \|\nabla\ell\|_\infty |g(t)||u|] > 0. \end{aligned}$$

Note that $\phi_u(x) = \widetilde{\phi}_u\left(\frac{x-u}{\ell(u)}\right)$, where

$$\widetilde{\phi}_u(x) = \phi(x)\left|\det\left[x_i\partial_j\ell(u) + \delta_{ij}\right]_{ij}\right|.$$

The estimates (101) follow since $\|\partial^\alpha\widetilde{\phi}_u\|_\infty \leq C\max_{|\beta|\leq|\alpha|}\|\partial^\beta\phi\|_\infty$. □

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