Commun. Math. Phys. 147, 527–548 (1992)

Communications in
Mathematical
Physics

Error Bound for the Hartree–Fock Energy of Atoms and Molecules

Volker Bach
Institut für Theoretische Physik, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Received October 25, 1991; in revised form January 2, 1992

Abstract. We estimate the error of the Hartree–Fock energy of atoms and molecules in terms of the one-particle density matrix corresponding to the exact ground state. As an application we show this error to be of order $O(Z^{5/3-\delta})$ for any $\delta < 2/21$ as the total nuclear charge Z becomes large.

1. Introduction

The nonrelativistic quantum mechanical model for an atom ($K = 1$) or molecule is given by the Hamiltonian

$$H_N(\underline{Z}, \underline{R}) := \sum_{i=1}^{N} \left(-\Delta_i - \sum_{j=1}^{K} \frac{Z_j}{|x_i - R_j|} \right) + \sum_{1 \leqq i < j}^{N} \frac{1}{|x_i - x_j|}, \tag{1}$$

acting as a self-adjoint operator on a dense domain $D_N \subseteq \bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$. Here we regard the nuclei of charge Z_j as pointcharges at fixed positions R_j, for $1 \leqq j \leqq K$. For the sake of brevity we denote $\underline{Z} := (Z_1, \ldots, Z_K)$ and $\underline{R} := (R_1, \ldots, R_K)$. The nuclei are surrounded by N electrons of spin $s = \frac{q-1}{2}$, so, in nature $q = 2$. We are interested in the ground state energy

$$E_Q(N, \underline{Z}, \underline{R}) := \inf\{\langle \Psi_N | H_N(\underline{Z}, \underline{R}) | \Psi_N \rangle \,|\, \Psi_N \in D_N,\ \|\Psi_N\| = 1\}, \tag{2}$$

which coincides with the bottom of the spectrum of $H_N(\underline{Z}, \underline{R})$. (Henceforth $\|\Psi_N\| = 1$ is assumed without further notice.) In general, $E_Q(N, \underline{Z}, \underline{R})$ is inaccessible to direct computation. Here we are concerned with the asymptotic validity of approximate theories in the limit

$$Z \to \infty, \quad N \approx Z, \quad \underline{Z}/Z \textit{ fixed}, \quad \min_{1 \leqq i < j \leqq K} |R_i - R_j| \geqq c Z^{-2/3+\varepsilon}. \tag{3}$$

To leading order $Z^{7/3}$, E_Q is given by the Thomas–Fermi energy E_{TF}, as was shown by Lieb and Simon [14]. This is followed by the Scott correction (cf. e.g. [10]) of order Z^2:

$$E_Q(Z, \underline{Z}, \underline{R}) = E_{\mathrm{TF}}(Z, \underline{Z}, \underline{R}) + \frac{q}{8} \sum_{j=1}^{K} Z_j^2 + o(Z^2) , \tag{4}$$

a result proved for neutral atoms by Hughes [6], and Siedentop and Weikard [18, 17], and for neutral molecules by Ivrii and Sigal [7]. The next correction includes exchange effects and is expected to be of the form $c_S Z^{5/3}$, where c_S is a constant proposed by Dirac [2] and corrected by Schwinger [16]. Fefferman and Seco [4] have announced a proof that

$$E_Q(N_c, Z) = E_{\mathrm{TF}}(1, 1) Z^{7/3} + \frac{q}{8} Z^2 + c_S Z^{5/3} + o(Z^{5/3}) \tag{5}$$

for atoms binding N_c electrons. Here N_c denotes the smallest integer such that $E_Q(N_c, Z) = \inf_{N \in \mathbb{N}} E_Q(N, Z)$. It is known that $Z \leqq N_c \leqq Z + o(Z)$ [5]. Also, we indicated the explicit scaling of E_{TF} in the atomic case.

In this paper we compare E_Q with the Hartree–Fock energy

$$E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) := \inf\{\langle \Psi_N | H_N(\underline{Z}, \underline{R}) | \Psi_N \rangle \,|\, \Psi_N \in SD_N \cap D_N\} , \tag{6}$$

where SD_N are the Slater determinants. We expect, of course, that E_{HF} already includes the corrections discussed above, i.e. $E_Q - E_{\mathrm{HF}} = o(Z^{5/3})$, where $o(Z^{5/3})$ might even be $O(1)$. With this goal in mind we first derive an estimate of $E_Q - E_{\mathrm{HF}}$ in terms of the one-particle density matrix γ (as defined in Sect. 2) corresponding to a ground state $\Psi_N \in D_N$ of the considered system. Actually, we do not need to use the Schrödinger equation, so Ψ_N may just as well be an *ε-approximate ground state*, i.e.

$$\langle \Psi_N | H_N(\underline{Z}, \underline{R}) | \Psi_N \rangle \leqq E_N(\underline{Z}, \underline{R}) + \varepsilon . \tag{7}$$

The estimate is as follows

Theorem 1. *Let γ be the 1-particle density matrix of an ε-approximate ground state $\Psi_N \in D_N$ of $H_N(\underline{Z}, \underline{R})$. Then, for any $0 < \delta < 1/12$,*

$$|E_Q(N, \underline{Z}, \underline{R}) - E_{\mathrm{HF}}(N, \underline{Z}, \underline{R})| \leqq d_\delta q^{2/3} Z N^{2/3} \left(\frac{\mathrm{tr}\{\gamma - \gamma^2\}}{N} \right)^{1/3 - \delta} + \varepsilon , \tag{8}$$

where $d_\delta := (857.672)\delta^{-1/3}$.

This bound is reasonable since, as $\varepsilon \to 0$, it vanishes if and only if γ is a projection or, equivalently, if $E_Q(N, \underline{Z}, \underline{R}) = \langle \Psi_N^S | H_N(\underline{Z}, \underline{R}) | \Psi_N^S \rangle$ for some Slater determinant $\Psi_N^S \in SD_N$. In the next step we estimate $\mathrm{tr}\{\gamma - \gamma^2\}$ in the limit $Z \to \infty$, using the results of the semiclassical analysis of Ivrii and Sigal [7].

Theorem 2. *Consider a molecule of nuclear charges Z_j, $1 \leqq j \leqq K$, with fixed ratios Z_j/Z, where $Z := \sum_{j=1}^K Z_j$ and $K \geqq 1$. Let $\min_{i \neq j}\{|R_i - R_j|\} \geqq c_1 Z^{-2/3+\varepsilon'}$ and $Z - c_2 Z^{1/3} \leqq N \leqq Z + c_3 Z^{5/7}$ for some constants ε', c_1, c_2, $c_3 > 0$. Let γ be the 1-particle density matrix of an ε-approximate ground state $\Psi_N \in D_N$ of $H_N(\underline{Z}, \underline{R})$. Then there exists $c > 0$, such that*

$$\mathrm{tr}\{\gamma - \gamma^2\} \leqq c \cdot Z^{5/7} . \tag{9}$$

This estimate, inserted in Theorem 1 for arbitrarily small $\varepsilon > 0$, proves

Theorem 3. *Consider a molecule of nuclear charges Z_j, $1 \leqq j \leqq K$, with fixed ratios Z_j/Z, where $Z := \sum_{j=1}^{K} Z_j$ and $K \geqq 1$. Let $\min_{i \neq j}\{|R_i - R_j|\} \geqq c_1 Z^{-2/3+\varepsilon}$ and $Z - c_2 Z^{1/3} \leqq N \leqq Z + c_3 Z^{5/7}$ for some constants ε, c_1, c_2, $c_3 > 0$. Then for any $0 < \delta < 2/21$ there exists $c_\delta > 0$ such that*

$$|E_Q(N, \underline{Z}, \underline{R}) - E_{\mathrm{HF}}(N, \underline{Z}, \underline{R})| \leqq c_\delta \cdot Z^{5/3-\delta} . \tag{10}$$

We remark that, for $N = N_c$, this result is already implicit in [4].

The paper is organized as follows. Section 2 is a collection of definitions and basic properties of fermion density matrices. In Sect. 3 we recall Lieb's extension of the Hartree–Fock variational principle [12], providing a proof which, we think, simplifies the original one. Section 4 contains an estimate of 2-body correlations in terms of $\gamma - \gamma^2$. This is the heart of the proof of Theorem 1, given in Sect. 5. The asymptotics of $Z \to \infty$ is discussed in Sect. 6, leading to the proof of Theorem 2.

2. Fermion Density Matrices

We recall definitions and basic properties of fermion density matrices. For

$$\mathscr{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^q \tag{11}$$

let $\mathscr{F}(\mathscr{H}) = \bigoplus_{N=0}^{\infty} \mathscr{H}^{(N)}$ be the corresponding fermion Fock space, i.e. $\mathscr{H}^{(0)} = \mathbb{C}$, and $\mathscr{H}^{(N)} = \bigwedge_{i=1}^{N} \mathscr{H}$ (see [20]). The annihilation and creation operators are defined as usual and obey for all $f, g \in \mathscr{H}$ the anticommutation relations

$$\begin{aligned} a(f)a^\dagger(g) + a^\dagger(g)a(f) &=: [a(f), a^\dagger(g)] = \langle f|g\rangle , \\ [a(f), a(g)] &= [a^\dagger(f), a^\dagger(g)] = 0 . \end{aligned} \tag{12}$$

Given N orthonormal elements $\chi_1, \ldots, \chi_N \in \mathscr{H}$, we compute

$$a^\dagger(\chi_1) \ldots a^\dagger(\chi_N)|0\rangle = (N!)^{-1/2} \sum_{\pi} (-1)^\pi \chi_{\pi(1)} \otimes \ldots \otimes \chi_{\pi(N)} \in \mathscr{H}^{(N)} , \tag{13}$$

the sum running over all permutations π of $(1, \ldots, N)$. These particular wavefunctions are called Slater determinants and we collect them in the set $SD_N \subseteq \mathscr{H}^{(N)}$. Given an orthonormal basis $\{\varphi_i\}_{i \in \mathbb{N}}$ of $\mathscr{H}$, we define $a_i := a(\varphi_i)$. Then the hamiltonian (1) is the restriction of

$$H = \sum_{k,l=1}^{\infty} h_{k;l} a_k^\dagger a_l + \frac{1}{2} \sum_{k,l,m,n=1}^{\infty} V_{kl;mn} a_l^\dagger a_k^\dagger a_m a_n \tag{14}$$

to $\mathscr{H}^{(N)}$. Here we denoted $h_{k;l} := \langle \varphi_k | h | \varphi_l \rangle$ and $V_{kl;mn} := \langle \varphi_k \otimes \varphi_l | V | \varphi_m \otimes \varphi_n \rangle$, with

$$h := \left(-\Delta - \sum_{j=1}^{K} \frac{Z_j}{|x - R_j|} \right) \otimes 1(\sigma_x), \quad V := \frac{1}{|x - y|} \otimes 1(\sigma_x) \otimes 1(\sigma_y) , \tag{15}$$

on $\mathscr{H}$ and $\mathscr{H} \otimes \mathscr{H}$, respectively. In particular, for a Slater determinant $\Psi_N = a_1^\dagger \ldots a_N^\dagger |0\rangle \in SD_N$ it is

$$\langle \Psi_N | H | \Psi_N \rangle = \sum_{k=1}^{N} h_{k;k} + \frac{1}{2} \sum_{k,l=1}^{N} (V_{kl;kl} - V_{kl;lk}) . \tag{16}$$

More generally, a p-body observable A is given in terms of a self-adjoint operator $A^{(p)}$ on $\bigotimes_{i=1}^{p} \mathscr{H}$ by

$$A := \frac{1}{p!} \sum_{i_1, \ldots, i_p} \sum_{j_1, \ldots, j_p} A^{(p)}_{i_1 \ldots i_p; j_1 \ldots j_p} a^\dagger_{i_p} \ldots a^\dagger_{i_1} a_{j_1} \ldots a_{j_p} . \tag{17}$$

Now, let ρ_N be an N-particle density matrix (N-pdm), i.e. $\rho_N = \sum_i |\Psi_{N,i}\rangle \lambda_i \langle \Psi_{N,i}|$ for orthonormal set $\{\Psi_{N,i}\}_{i \in \mathbb{N}} \subseteq \mathscr{H}^{(N)}$ and nonnegative numbers $0 \leqq \lambda_i \leqq 1$, $\sum_i \lambda_i = 1$. The quantum mechanical expectation of the observable A with respect to the state ρ_N may then be written as

$$\langle A \rangle := \mathrm{tr}_N\{A \rho_N\} = \frac{1}{p!} \mathrm{tr}_p\{A^{(p)} \rho_N^{(p)}\}$$

$$= \frac{1}{p!} \sum_{i_1, \ldots, i_p} \sum_{j_1, \ldots, j_p} A^{(p)}_{i_1 \ldots i_p; j_1 \ldots j_p} \langle a^\dagger_{i_p} \ldots a^\dagger_{i_1} a_{j_1} \ldots a_{j_p} \rangle . \tag{18}$$

The *reduced density matrices* $\rho_N^{(p)}$, $1 \leqq p \leqq N$, $\rho_N^{(N)} \equiv \rho_N$ are determined if (18) holds for all observables A on $\mathscr{H}^{(N)}$ of the form (17):

$$\rho^{(p)}_{N\, j_1 \ldots j_p; i_1 \ldots i_p} = \langle a^\dagger_{i_p} \ldots a^\dagger_{i_1} a_{j_1} \ldots a_{j_p} \rangle . \tag{19}$$

Of course, $\rho_N^{(p)} \geqq 0$ and $\mathrm{tr}_p\{\rho_N^{(p)}\} = N(N-1) \ldots (N-p+1)$. From the fact that $\sum_{k=1}^{\infty} a_k^\dagger a_k$ is the particle number operator, we easily deduce the recursion relation

$$\rho^{(p)}_{N\, j_1 \ldots j_p; i_1 \ldots i_p} = \frac{1}{N-p} \sum_{k=1}^{\infty} \rho^{(p+1)}_{N\, j_1 \ldots j_p, k; i_1 \ldots i_p, k} . \tag{20}$$

We call $\gamma_\rho := \rho_N^{(1)}$ the 1-pdm and $\Gamma_\rho := \rho_N^{(2)}$ the 2-pdm corresponding to ρ_N. The expectation value for H can now be written in the general form

$$\langle H \rangle = \mathrm{tr}_1\{h \gamma_\rho\} + \frac{1}{2} \mathrm{tr}_2\{V \Gamma_\rho\} . \tag{21}$$

Now, if $\rho_N = |\Psi_N\rangle\langle\Psi_N|$ and $\Psi_N = a^\dagger(\chi_1) \ldots a^\dagger(\chi_N)|0\rangle \in SD_N$ then one easily checks

$$\gamma_\rho = \sum_{i=1}^{N} |\chi_i\rangle\langle\chi_i| , \tag{22}$$

$$\Gamma_\rho = \sum_{i,j=1}^{N} |\chi_i \wedge \chi_j\rangle\langle\chi_i \wedge \chi_j|$$

$$= (\gamma_\rho \otimes \gamma_\rho) - Ex(\gamma_\rho \otimes \gamma_\rho) , \tag{23}$$

matching (21) with (16). Here,

$$Ex := \sum_{i,j} |\varphi_i \otimes \varphi_j\rangle\langle\varphi_j \otimes \varphi_i| \tag{24}$$

is the exchange operator. Note that $\frac{1}{2}(1 - Ex)$ is the projection onto $\mathscr{H} \wedge \mathscr{H}$ and it commutes with $\gamma \otimes \gamma$. So, certainly, $(1 - Ex)(\gamma \otimes \gamma)$ is self-adjoint. Finally, since $0 \leqq \rho^{(1)}_{Nk;k} = \langle a_k^\dagger a_k \rangle = 1 - \langle a_k a_k^\dagger \rangle \leqq 1$ independently of the chosen basis, we have $0 \leqq \gamma_\rho \leqq 1$. Note that, apart from the last inequality, we did not use the fermionic character of the Fock space $\mathscr{F}(\mathscr{H})$. Also, apart from the separability, we did not use the explicit structure of $\mathscr{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^q$, either. We summarize the properties of γ_ρ and Γ_ρ (cf. [1]):

$$\mathrm{tr}_1\{\gamma_\rho\} = N, \quad 0 \leqq \gamma_\rho \leqq 1 \; ; \tag{25}$$

$$\{\gamma_\rho = \gamma_\rho^2, (25)\} \Leftrightarrow \{\exists \Psi_N \in SD_N : \rho_N = |\Psi_N\rangle\langle\Psi_N|, \gamma_\rho = \rho_N^{(1)}\} \; ; \tag{26}$$

$$\Psi_N \in SD_N, \rho_N = |\Psi_N\rangle\langle\Psi_N| \Rightarrow \Gamma_\rho = (1 - Ex)(\gamma_\rho \otimes \gamma_\rho) \, . \tag{27}$$

3. Lieb's Variational Principle

In this section we define the Hartree–Fock variational principle and Lieb's variational principle and show that the latter actually is an extension of the former. Recall the definition (6) of the Hartree–Fock energy E_{HF} of the considered system:

$$E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) := \inf\{\langle\Psi_N|H_N(\underline{Z}, \underline{R})|\Psi_N\rangle | \Psi_N \in SD_N \cap D_N\} \, . \tag{28}$$

Since the trial functions vary over a smaller set, it clearly holds

$$E_Q(N, \underline{Z}, \underline{R}) \leqq E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) \, . \tag{29}$$

Using the notations and definitions of Sect. 2 and ensuring $\Psi_N \in D_N$ by $\mathrm{tr}_1\{h\gamma\} < \infty$, we may rewrite E_{HF} as

$$E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) = \inf\{\varepsilon_{\mathrm{HF}}(\gamma) | \gamma = \gamma^\dagger = \gamma^2, \mathrm{tr}_1\{\gamma\} = N, \mathrm{tr}_1\{h\gamma\} < \infty\} \, , \tag{30}$$

where we defined

$$\varepsilon_{\mathrm{HF}}(\gamma) := \mathrm{tr}_1\{h\gamma\} + \frac{1}{2}\mathrm{tr}_2\{V(1 - Ex)(\gamma \otimes \gamma)\} \, . \tag{31}$$

The Hartree–Fock variational principle is mathematically inconvenient, because the set SD_N has no linear structure. Lieb's crucial observation was, that the condition on γ_ρ to be induced by some Slater determinant $\Psi_N \in SD_N$ actually can be dropped [12]. We give an alternative proof of this result which we think is considerably simpler and more constructive than the original one.

Lemma 1. *Define $\mathscr{H}$, h, V, and $\varepsilon_{\mathrm{HF}}$ by* (11), (15), *and* (31). *Let $0 \leqq \gamma \leqq 1$, $\mathrm{tr}_1\{\gamma\} = N$ be a* 1-pdm *of finite rank. Then there exists a projection $\hat{\gamma} = \hat{\gamma}^\dagger = \hat{\gamma}^2$, $\mathrm{tr}_1\{\hat{\gamma}\} = N$, such that*

$$\varepsilon_{\mathrm{HF}}(\gamma) \geqq \varepsilon_{\mathrm{HF}}(\hat{\gamma}) \, . \tag{32}$$

Furthermore, $V > 0$ implies the strictness of the inequality (32) *unless γ is a projection itself.*

Proof. We may assume $\varepsilon_{\mathrm{HF}}(\gamma) < \infty$. Working in an eigenvector basis of γ, we may write

$$\gamma = \sum_{k=1}^{M} |\varphi_k\rangle\lambda_k\langle\varphi_k|, \quad \sum_{k=1}^{M} \lambda_k = N, \quad 0 < \lambda_k \leqq 1, \quad \langle\varphi_k|\varphi_l\rangle = \delta_{kl} \, , \tag{33}$$

for some $M < \infty$. Let us abbreviate the diagonal elements $\bar{h}_k := h_{kk} = \langle \varphi_k | h | \varphi_k \rangle$ and $\bar{V}_{kl} := V_{kl;kl} - V_{kl;lk} = \langle \varphi_k \wedge \varphi_l | V | \varphi_k \wedge \varphi_l \rangle$. Note that the positivity of V implies $\bar{V}_{kl} > 0$ for $k \neq l$, and $\bar{V}_{kk} = 0$. One easily checks

$$\varepsilon_{\mathrm{HF}}(\gamma) = \sum_{k=1}^{M} \lambda_k \bar{h}_k + \frac{1}{2} \sum_{k,l=1}^{M} \lambda_k \lambda_l \bar{V}_{kl} . \tag{34}$$

We assume that $M > N$ or, equivalently, $\gamma \neq \gamma^2$, for otherwise there is nothing to prove. Then there are at least two eigenvalues $0 < \lambda_p, \lambda_q < 1$, say, and we may assume without loss of generality,

$$\bar{h}_q + \sum_{k=1}^{M} \lambda_k \bar{V}_{kq} \leqq \bar{h}_p + \sum_{k=1}^{M} \lambda_k \bar{V}_{kp} . \tag{35}$$

Let $\delta := \min\{\lambda_p, 1 - \lambda_q\} > 0$ and define

$$\bar{\gamma} := \left(\sum_{p,q \neq k=1}^{M} |\varphi_k\rangle \lambda_k \langle \varphi_k| \right) + |\varphi_p\rangle(\lambda_p - \delta)\langle \varphi_p| + |\varphi_q\rangle(\lambda_q + \delta)\langle \varphi_q| . \tag{36}$$

By computation one checks that

$$\varepsilon_{\mathrm{HF}}(\bar{\gamma}) - \varepsilon_{\mathrm{HF}}(\gamma) = -\delta \left\{ \left(\bar{h}_p + \sum_{k=1}^{M} \lambda_k \bar{V}_{kp} \right) - \left(\bar{h}_q + \sum_{k=1}^{M} \lambda_k \bar{V}_{kq} \right) \right\} - \delta^2 \bar{V}_{pq} , \tag{37}$$

hence, $\varepsilon_{\mathrm{HF}}(\bar{\gamma}) - \varepsilon_{\mathrm{HF}}(\gamma) < 0$, according to our choice of δ. Furthermore, defining

$$n(\gamma) := |\{\lambda_k | 0 < \lambda_k < 1\}| , \tag{38}$$

we observe $n(\bar{\gamma}) \leqq n(\gamma) - 1$. After at most $M - N$ iterations of this procedure we obtain a 1-pdm $\hat{\gamma}$ which obeys $\varepsilon_{\mathrm{HF}}(\hat{\gamma}) < \varepsilon_{\mathrm{HF}}(\gamma)$ and $n(\hat{\gamma}) = 0$. But the latter means that $\hat{\gamma} = \hat{\gamma}^2$ and, hence, proves the assertion. ▌

Using an approximation argument, it is straightforward to deduce from Lemma 1 the following corollary.

Corollary 1 (*Lieb's variational principle*).

$$E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) = \inf\{\varepsilon_{\mathrm{HF}}(\gamma) | 0 \leqq \gamma \leqq 1, \mathrm{tr}_1\{\gamma\} = N, \mathrm{tr}_1\{h\gamma\} < \infty\} . \tag{39}$$

Now, we apply Lieb's variational principle to a particular trial 1-pdm. Let $\rho_N := |\Psi_N\rangle\langle\Psi_N|$, where Ψ_N is an ε-approximate ground state of the molecule we consider. By Lieb's variational principle it holds

$$E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) \leqq \mathrm{tr}_1\{h\gamma_\rho\} + \frac{1}{2}\mathrm{tr}_2\{V(1 - Ex)(\gamma_\rho \otimes \gamma_\rho)\} . \tag{40}$$

Thus we have the following bound:

$$\begin{aligned} 0 &\geqq E_Q(N, \underline{Z}, \underline{R}) - E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) \\ &\geqq \mathrm{tr}_1\{h\gamma_\rho\} + \frac{1}{2}\mathrm{tr}_2\{V\Gamma_\rho\} - \varepsilon - \mathrm{tr}_1\{h\gamma_\rho\} + \frac{1}{2}\mathrm{tr}_2\{V(1 - Ex)(\gamma_\rho \otimes \gamma_\rho)\} \\ &= \frac{1}{2}\mathrm{tr}_2\{V[\Gamma_\rho - (1 - Ex)(\gamma_\rho \otimes \gamma_\rho)]\} - \varepsilon . \end{aligned} \tag{41}$$

In fact, the last expression is exactly what we are going to consider in the following section.

4. Correlation Estimate for Fermions

In this section we give a lower bound on the truncated 2-pdm of an N-fermion system. The interaction is assumed to factorize into projections in each particle variable.

Assume for the moment that $\rho_N^S = |\Psi_N\rangle\langle\Psi_N|$ where $\Psi_N = a^\dagger(\chi_1) \ldots a^\dagger(\chi_N)|0\rangle \in SD_N$ is a Slater determinant. As mentioned in (27), $\Gamma_\rho = (\gamma_\rho \otimes \gamma_\rho) - Ex(\gamma_\rho \otimes \gamma_\rho)$. We expect the N-pdm ρ_N we will deal with later on to be very close to such a ρ_N^S, in some appropriate sense. Therefore it is reasonable to call Γ_ρ^T, defined by

$$\Gamma_\rho^T := \Gamma_\rho - (1 - Ex)(\gamma_\rho \otimes \gamma_\rho) , \tag{42}$$

the *truncated* 2-pdm. Note that we cannot expect Γ_ρ^T to have a definiteness, for Coleman [1] constructed an N-pdm ρ_N with BCS type wavefunctions for which Γ_ρ and, therefore, also Γ_ρ^T had an eigenvalue of order N and, on the other hand, $\mathrm{tr}_2\{\Gamma_\rho^T\} = -\mathrm{tr}_1\{\gamma_\rho - \gamma_\rho^2\} \leqq 0$.

In practice, we have nonnegative pair interactions $V \geqq 0$ acting on $\mathscr{H} \otimes \mathscr{H}$ and wish to bound $\mathrm{tr}_2\{V\Gamma_\rho^T\}$. As shown in Sect. 3 we get upper bounds by means of Lieb's variational principle. Our goal is to obtain lower bounds on $\mathrm{tr}_2\{V\Gamma_\rho^T\}$, too, at least for suitable V. The lower bound we will prove is as follows.

Theorem 4. *Let $\mathscr{H}$ be a separable Hilbert space and $\mathscr{F}(\mathscr{H})$ the corresponding fermion Fock space. Let ρ_N be an N-*pdm, *and denote the corresponding* 1- *and* 2-pdm *by γ and Γ, respectively* (*see Sect.* 2). *Let $X = X^\dagger = X^2$ be an orthogonal projection on $\mathscr{H}$. Then*

$$\mathrm{tr}_2\{(X \otimes X)\Gamma^T\} \geqq -\mathrm{tr}_1\{X\gamma\} \cdot \min\{1, 7.554[\mathrm{tr}_1\{X(\gamma - \gamma^2)\}]^{1/2}\} . \tag{43}$$

Proof. For the proof of Theorem 4, an appropriate choice of the orthonormal basis $\{\varphi_i\}_{i\in\mathbb{N}} \subseteq \mathscr{H}$ is crucial. We choose $\{\varphi_i\}_{i\in\mathbb{N}}$ to consist of the eigenfunctions of γ: $\gamma\varphi_i = \lambda_i\varphi_i$. For $\lambda_i > 0$, φ_i is called a natural orbital of γ_ρ. Recall that the general property (25) of γ_ρ implies $\sigma(\gamma_\rho)\backslash\{0\} = \sigma_{\mathrm{disc}}(\gamma_\rho)\backslash\{0\}$ and we obtain $\{\varphi_i\}_{i\in\mathbb{N}}$ by adding some discrete ON-basis of $\mathrm{Ker}(\gamma_\rho)$, whose eigenvalues are set to 0, to the natural orbitals. Also, we remark that for this particular basis we have

$$\langle a_k^\dagger a_m \rangle = \langle \varphi_m | \gamma | \varphi_k \rangle = \delta_{mk}\lambda_k . \tag{44}$$

We denote $X_{km} := \langle \varphi_k | X | \varphi_m \rangle$. We have

$$\begin{aligned} \mathrm{tr}_2\{(X \otimes X)\Gamma^T\} &= \mathrm{tr}_2\{(X \otimes X)[\Gamma - (1 - Ex)(\gamma \otimes \gamma)]\} \\ &= \sum_{k,l,m,n} X_{km}X_{ln}\{\langle a_l^\dagger a_k^\dagger a_m a_n\rangle - \langle a_k^\dagger a_m\rangle\langle a_l^\dagger a_n\rangle + \langle a_k^\dagger a_n\rangle\langle a_l^\dagger a_m\rangle\} \\ &= \sum_{k,l,m,n} X_{km}X_{ln}\{\langle a_l^\dagger a_k^\dagger a_m a_n\rangle\} - \sum_{k,l} X_{kk}X_{ll}\lambda_k\lambda_l + \sum_{k,l} |X_{kl}|^2\lambda_k\lambda_l . \end{aligned} \tag{45}$$

For the sake of comprehensibility we break up the proof into several lemmata. We start with the left part of inequality (43).

Lemma 2.

$$\mathrm{tr}_2\{(X \otimes X)\Gamma^T\} \geqq -\mathrm{tr}_1\{X\gamma\} . \tag{46}$$

Proof of Lemma 2. We follow the usual method of the mean field approximation, known from quantum mechanics. More precisely

$$\begin{aligned}
&\mathrm{tr}_2\{(X \otimes X)\Gamma^T\} \\
&= \sum_{k,l,m,n} X_{km}X_{ln}(\langle a_l^\dagger a_k^\dagger a_m a_n\rangle - \langle a_k^\dagger a_m\rangle\langle a_l^\dagger a_n\rangle) + \sum_{k,l} |X_{kl}|^2\lambda_k\lambda_l \\
&= \left\langle \left[\sum_{k,m} X_{mk}(a_m^\dagger a_k - \langle a_m^\dagger a_k\rangle)\right]^\dagger \left[\sum_{k,m} X_{mk}(a_m^\dagger a_k - \langle a_m^\dagger a_k\rangle)\right]\right\rangle \\
&\quad - \sum_{k,l,m,n} X_{km}X_{ln}[a_m, a_l^\dagger]\langle a_k^\dagger a_n\rangle + \sum_{k,l} |X_{kl}|^2\lambda_k\lambda_l \\
&\geqq -\sum_{k,l} |X_{kl}|^2\lambda_k(1-\lambda_l) \geqq -\sum_k X_{kk}\lambda_k . \quad \blacksquare
\end{aligned} \tag{47}$$

Note that in the last line the exchange term $\sum_{k,l}|X_{kl}|^2\lambda_k\lambda_l$ partially cancels the self energy $\sum_k X_{kk}\lambda_k$ as long as λ_l is close enough to 1. Indeed, this is the main idea for proving Theorem 4. It suggests to treat large and small λ_k separately. To this end we fix a number $0 < \tau < 1$ and introduce the operators

$$c_p := \sum_{k<\tau} X_{pk}a_k, \quad d_p := \sum_{k \geqq \tau} X_{pk}a_k , \tag{48}$$

where $k < \tau$ and $k \geqq \tau$ denote $\lambda_k < \tau$ and $\lambda_k \geqq \tau$, respectively. We compute their anticommutation relations and quadratic expectation values. For all $p, q \in \mathbb{N}$ we have

$$\begin{aligned}
0 &= [c_p, c_q] = [c_p^\dagger, c_q^\dagger] = [d_p, d_q] = [d_p^\dagger, d_q^\dagger] \\
&= [c_p, d_q^\dagger] = [c_p^\dagger, d_q] = [c_p, d_q] = [c_p^\dagger, d_q^\dagger] ,
\end{aligned} \tag{49}$$

$$\begin{aligned}
0 &= \langle c_p c_q\rangle = \langle c_p^\dagger c_q^\dagger\rangle = \langle d_p d_q\rangle = \langle d_p^\dagger d_q^\dagger\rangle \\
&= \langle c_p^\dagger d_q\rangle = \langle d_p^\dagger c_q\rangle = \langle c_p d_q\rangle = \langle c_p^\dagger d_q^\dagger\rangle .
\end{aligned} \tag{50}$$

The nonvanishing contributions are

$$\begin{aligned}
[d_p^\dagger, d_q] &= \sum_{k,l \geqq \tau} X_{kp}X_{ql}[a_k^\dagger, a_l] = \sum_{k \geqq \tau} X_{kp}X_{qk} , \\
[c_p^\dagger, c_q] &= \sum_{k,l < \tau} X_{kp}X_{ql}[a_k^\dagger, a_l] = \sum_{k<\tau} X_{kp}X_{qk} , \\
\langle d_p^\dagger d_q\rangle &= \sum_{k,l \geqq \tau} X_{kp}X_{ql}\langle a_k^\dagger a_l\rangle = \sum_{k \geqq \tau} X_{kp}X_{qk}\lambda_k , \\
\langle c_p^\dagger c_q\rangle &= \sum_{k,l<\tau} X_{kp}X_{ql}\langle a_k^\dagger a_l\rangle = \sum_{k<\tau} X_{kp}X_{qk}\lambda_k .
\end{aligned} \tag{51}$$

We may rewrite $\mathrm{tr}_2\{(X \otimes X)\Gamma\}$ as follows:

$$\begin{aligned}
&\mathrm{tr}_2\{(X \otimes X)\Gamma\} \\
&= \sum_{p,q} \left\langle \left(\sum_l X_{pl} a_l\right)^\dagger \left(\sum_k X_{qk} a_k\right)^\dagger \left(\sum_m X_{qm} a_m\right)\left(\sum_n X_{pn} a_n\right)\right\rangle \\
&= \sum_{p,q} \langle (c_p^\dagger + d_p^\dagger)(c_q^\dagger + d_q^\dagger)(c_q + d_q)(c_p + d_p)\rangle \\
&= (\text{Main Part}) + (\text{Remainder}) \,,
\end{aligned} \tag{52}$$

where

$$\mathrm{MP} = \text{Main Part} := \sum_{p,q} \langle d_p^\dagger (c_q^\dagger + d_q^\dagger) d_q (c_p + d_p)\rangle \tag{53}$$

and

$$\begin{aligned}
\mathrm{R} &= \text{Remainder} \\
&:= \sum_{p,q} \{\langle c_p^\dagger (c_q^\dagger + d_q^\dagger) d_q (c_p + d_p)\rangle + \langle d_p^\dagger (c_q^\dagger + d_q^\dagger) c_q (c_p + d_p)\rangle \\
&\quad + \langle c_p^\dagger (c_q^\dagger + d_q^\dagger) c_q (c_p + d_p)\rangle\} \\
&= \sum_{p,q} \{2\mathrm{Re}\langle c_p^\dagger (c_q^\dagger + d_q^\dagger) d_q (c_p + d_p)\rangle + \langle c_p^\dagger (c_q^\dagger + d_q^\dagger) c_q (c_p + d_p)\rangle\} \,.
\end{aligned} \tag{54}$$

Now we start proving the right part of (43) in Theorem 4 by estimating the *Main Part*. In fact, MP is large enough to cancel $\mathrm{tr}_2\{(X \otimes X)(1 - Ex)(\gamma \otimes \gamma)\}$. We claim

Lemma 3.

$$\begin{aligned}
&\mathrm{MP} - \mathrm{tr}_2\{(X \otimes X)(1 - Ex)(\gamma \otimes \gamma)\} \\
&\qquad \geqq -\left(\frac{2}{1-\tau} + \frac{1}{\tau}\right)\cdot \mathrm{tr}_1\{X\gamma\}\cdot \mathrm{tr}_1\{X(\gamma - \gamma^2)\} \,.
\end{aligned} \tag{55}$$

Proof of Lemma 3. We proceed as in Lemma 2.

$$\mathrm{MP} = \sum_{p,q} \langle (c_q^\dagger + d_q^\dagger) d_q d_p^\dagger (c_p + d_p)\rangle - \sum_{p,q} ([d_p^\dagger, d_q]\langle (c_q^\dagger + d_q^\dagger)(c_p + d_p)\rangle) \,. \tag{56}$$

Observe that $\sum_q \langle d_q^\dagger (c_q + d_q)\rangle = \sum_{k \geqq \tau} X_{kk}\lambda_k$. So, abbreviating $A := \sum_q [d_q^\dagger (c_q + d_q) - \langle d_q^\dagger (c_q + d_q)\rangle]$, we obtain

$$\begin{aligned}
\mathrm{MP} &= \langle A^\dagger A\rangle + \left(\sum_{k \geqq \tau} X_{kk}\lambda_k\right)^2 - \sum_{k \geqq \tau; l} |X_{kl}|^2 \lambda_l \\
&\geqq \left(\sum_k X_{kk}\lambda_k\right)^2 - \sum_{k,l} |X_{kl}|^2 \lambda_k \lambda_l - 2\left(\sum_k X_{kk}\lambda_k\right)\left(\sum_{k<\tau} X_{kk}\lambda_k\right) \\
&\quad - \sum_{k \geqq \tau; l} |X_{kl}|^2 (1 - \lambda_k)\lambda_l \\
&\geqq \left(\sum_k X_{kk}\lambda_k\right)^2 - \sum_{k,l} |X_{kl}|^2 \lambda_k \lambda_l - \frac{1}{\tau} \sum_{k \geqq \tau; l} |X_{kl}|^2 (\lambda_k - \lambda_k^2)\lambda_l \\
&\quad - \frac{2}{1-\tau}\left(\sum_k X_{kk}\lambda_k\right)\left(\sum_{k<\tau} X_{kk}(\lambda_k - \lambda_k^2)\right) .
\end{aligned} \tag{57}$$

Using $|X_{kl}|^2 \leqq X_{kk}X_{ll}$ and letting the sums run over their entire range, we arrive at the assertion. ∎

In the next step we estimate the *Remainder*. Again we cast this into a lemma. Note that $[d_p^\dagger, d_p] = \sum_{k\geqq\tau}|X_{kp}|^2 \leqq \tau^{-1}\sum_{k\geqq\tau}|X_{kp}|^2\lambda_k \leqq \tau^{-1}\langle d_p^\dagger d_p\rangle$, of which there is no analogue for $[c_p^\dagger, c_p]$. Thus, one could summarize the strategy of the proof of the following lemma as *avoiding anticommutators of type* $[c_p^\dagger, c_p]$ *in the estimates.*

Lemma 4.

$$R \geqq -\left\{\left(\frac{3}{\tau(1-\tau)} + \frac{3}{\tau^{3/2}(1-\tau)^{1/2}}\right)(\mathrm{tr}_1\{X(\gamma-\gamma^2)\})^{1/2} + \frac{2}{\tau^{1/2}(1-\tau)^{1/2}}\left(1 + \frac{1}{\tau(1-\tau)}\mathrm{tr}_1\{X(\gamma-\gamma^2)\}\right)^{1/2}\right\} \cdot \mathrm{tr}_1\{X\gamma\}\cdot(\mathrm{tr}_1\{X(\gamma-\gamma^2)\})^{1/2}. \tag{58}$$

Proof of Lemma 4. First observe that by expanding and relabelling

$$\sum_{p,q}\langle c_p^\dagger(c_q^\dagger + d_q^\dagger)c_q(c_p + d_p)\rangle = \sum_{p,q}(\langle c_p^\dagger c_q^\dagger c_q c_p\rangle + \langle c_p^\dagger d_q^\dagger c_q d_p\rangle + 2\mathrm{Re}\langle c_p^\dagger d_q^\dagger c_q c_p\rangle)\,. \tag{59}$$

Hence, after some algebra, anticommutations, and dropping of vanishing expectation values,

$$R = \sum_{p,q}(\langle c_p^\dagger c_q^\dagger c_q c_p\rangle + 4\mathrm{Re}\langle c_p^\dagger d_q^\dagger c_q c_p\rangle + 2\langle c_p^\dagger d_q^\dagger d_q c_p\rangle) \tag{60}$$

$$+ \sum_{p,q}\langle c_p^\dagger d_p d_q^\dagger c_q\rangle - \sum_{p,q}[d_q^\dagger, d_p]\langle c_p^\dagger c_q\rangle \tag{61}$$

$$+ \sum_{p,q}2\mathrm{Re}\langle c_p^\dagger d_q d_p d_q^\dagger\rangle + 2\mathrm{Re}\left\langle\left(\sum_p c_p^\dagger d_p\right)\left(\sum_p c_p^\dagger d_p\right)\right\rangle\,. \tag{62}$$

We estimate the above sum term by term, merely using the Cauchy–Schwarz inequality $|\langle AB\rangle|^2 \leqq \langle AA^\dagger\rangle\langle B^\dagger B\rangle$. But before doing so, let us single out an estimate which will be used over and over again. Written in a somewhat redundant way, it holds

$$\left|\sum_{p,q}\langle c_p^\dagger d_q^\dagger d_q c_p\rangle\right| + \left|\sum_{p,q}\langle c_p^\dagger d_q d_q^\dagger c_p\rangle\right| \leqq \frac{1}{\tau(1-\tau)}\left(\sum_k X_{kk}\lambda_k\right)\left(\sum_k X_{kk}(\lambda_k - \lambda_k^2)\right), \tag{63}$$

because the left-hand side of (63) equals

$$\sum_{p,q}\langle c_p^\dagger c_p\rangle[d_q^\dagger, d_q] = \left(\sum_{k<\tau}X_{kk}\lambda_k\right)\left(\sum_{k\geqq\tau}X_{kk}\right) \leqq \frac{1}{\tau(1-\tau)}\left(\sum_{k<\tau}X_{kk}(\lambda_k - \lambda_k^2)\right)\left(\sum_{k\geqq\tau}X_{kk}\lambda_k\right). \tag{64}$$

Hence, completing the square and using (63), the sum in the right-hand side of (60) is bounded from below by

$$\sum_{p,q} (\langle c_p^\dagger c_q^\dagger c_q c_p\rangle - 4\langle c_p^\dagger c_q^\dagger c_q c_p\rangle^{1/2}\langle c_p^\dagger d_q^\dagger d_q c_p\rangle^{1/2} + 2\langle c_p^\dagger d_q^\dagger d_q c_p\rangle)$$
$$\geqq -2\sum_{p,q}\langle c_p^\dagger d_q^\dagger d_q c_p\rangle$$
$$\geqq -\frac{2}{\tau(1-\tau)}\left(\sum_k X_{kk}(\lambda_k - \lambda_k^2)\right)\left(\sum_k X_{kk}\lambda_k\right). \tag{65}$$

The first sum in (61) is obviously nonnegative and the second sum is explicitly computable. After doing the p, q summation the second sum in (61) yields

$$-\sum_{k\geqq\tau}\sum_{l<\tau}|X_{kl}|^2\lambda_l \geqq -\frac{1}{\tau(1-\tau)}\left(\sum_k X_{kk}(\lambda_k-\lambda_k^2)\right)\left(\sum_k X_{kk}\lambda_k\right). \tag{66}$$

The estimate on the first sum in (62) goes as follows:

$$\sum_{p,q} 2\mathrm{Re}\langle c_p^\dagger d_q d_p d_q^\dagger\rangle \geqq -2\sum_{p,q}(\langle c_p^\dagger d_q d_q^\dagger c_p\rangle^{1/2}\langle d_q d_p^\dagger d_p d_q^\dagger\rangle^{1/2})$$
$$\geqq -2\left(\sum_{p,q}\langle c_p^\dagger d_q d_q^\dagger c_p\rangle\right)^{1/2}\left(\sum_{p,q}\langle d_q d_p^\dagger d_p d_q^\dagger\rangle\right)^{1/2}. \tag{67}$$

Now, the first factor is taken care of by (63) and in the second factor we again anticommute $d_p^\dagger$ and d_p and use $\langle d_q d_q^\dagger\rangle = [d_q^\dagger, d_q] - \langle d_q^\dagger d_q\rangle$. Hence we obtain

$$\sum_{p,q}\langle d_q d_p^\dagger d_p d_q^\dagger\rangle \leqq \left(\sum_p [d_p^\dagger, d_p]\right)\left(\sum_q([d_q^\dagger, d_q] - \langle d_q^\dagger d_q\rangle)\right)$$
$$= \left(\sum_{k\geqq\tau} X_{kk}\right)\left(\sum_{k\geqq\tau} X_{kk}(1-\lambda_k)\right)$$
$$\leqq \frac{1}{\tau^2}\left(\sum_k X_{kk}\lambda_k\right)\left(\sum_k X_{kk}(\lambda_k-\lambda_k^2)\right). \tag{68}$$

The above product therefore leads to the inequality

$$\sum_{p,q} 2\mathrm{Re}\langle c_p^\dagger d_q d_p d_q^\dagger\rangle \geqq -\frac{2}{\tau^{3/2}(1-\tau)^{1/2}}\left(\sum_k X_{kk}\lambda_k\right)\left(\sum_k X_{kk}(\lambda_k-\lambda_k^2)\right). \tag{69}$$

It remains to estimate $2\mathrm{Re}\langle(\sum_p c_p^\dagger d_p)^2\rangle$ which will actually give the leading error term. As the way we write this term suggests, we use the Cauchy–Schwarz inequality on the embraced operator, yielding the lower bound

$$-2\left(\sum_{p,q}\langle c_p^\dagger d_p d_q^\dagger c_q\rangle\right)^{1/2}\left(\sum_{p,q}\langle d_q^\dagger c_q c_p^\dagger d_p\rangle\right)^{1/2}. \tag{70}$$

Now, observe that

$$\sum_{p,q}\langle c_p^\dagger d_p d_q^\dagger c_q\rangle \leqq \left(\sum_p\langle c_p^\dagger d_p d_p^\dagger c_p\rangle^{1/2}\right)^2$$
$$\leqq \left(\sum_p\langle c_p^\dagger c_p\rangle^{1/2}[d_p^\dagger, d_p]^{1/2}\right)^2$$
$$\leqq \sum_{p,q}\langle c_p^\dagger c_p\rangle[d_q^\dagger, d_q], \tag{71}$$

so, again, (63) applies. After an anticommutation, a similar argument is used to estimate the other factor

$$\sum_{p,q} \langle d_q^\dagger c_q c_p^\dagger d_p \rangle = \sum_{p,q} (\langle d_q^\dagger d_p \rangle [c_p^\dagger, c_q]) - \sum_{p,q} \langle c_p^\dagger d_q^\dagger d_p c_q \rangle$$
$$\leqq \sum_{k \geqq \tau} \sum_{l < \tau} |X_{kl}|^2 \lambda_k + \sum_{p,q} \langle c_p^\dagger d_q^\dagger d_q c_p \rangle$$
$$\leqq \left(\sum_k X_{kk} \lambda_k \right) \left[1 + \frac{1}{\tau(1-\tau)} \left(\sum_k X_{kk} (\lambda_k - \lambda_k^2) \right) \right]. \tag{72}$$

Lemma 4 is proved by collecting all these estimates. ▮

Taking into account all the estimates from Lemma 2, 3 and 4 and denoting $\mathrm{tr}_1\{X(\gamma - \gamma^2)\} =: a^2$, $\mathrm{tr}_1\{X\gamma\} =: b$ and $g^{-1} := \tau(1-\tau)$, we arrive at

$$\mathrm{tr}_2\{(X \otimes X)\Gamma^T\}$$
$$\geqq -b \cdot \min \left\{ 1, a \left[\left(2\tau g + \frac{1}{\tau} + 3g + \frac{2}{\tau} g^{1/2} \right) a + 2 g^{1/2} (1 + g a^2)^{1/2} \right] \right\}. \tag{73}$$

We just describe in words how to get from here to the final inequality. Note that the term in brackets, let us call it $F(a, \tau)$, is monotonically increasing in a. Also we only consider the range of a, where $aF(a, \tau) \leqq 1$. This leads to the range $0 \leqq a \leqq a_0(\tau)$ for an explicitly given function $a_0(\tau)$. But then $aF(a, \tau) \leqq aF(a_0(\tau), \tau) = a a_0^{-1}(\tau)$ and it remains to optimize with respect to τ, which gives $\tau_{\mathrm{opt}} = 0.533$ and $a_0^{-1}(\tau_{\mathrm{opt}}) = 7.554$, and the above inequality reduces to the desired result. ▮

5. Error Bound for the Hartree–Fock Energy

The next task we undertake is the application of the fairly abstract result of Sect. 4 to the Coulomb interaction in atoms and molecules.

5.1. Application of the Correlation Estimate. As explained in Sect. 3 we have

$$0 \geqq E_Q(N, \underline{Z}, \underline{R}) - E_{\mathrm{HF}}(N, \underline{Z}, \underline{R}) \geqq \frac{1}{2} \mathrm{tr}_2\{V \Gamma_\rho^T\} - \varepsilon, \tag{74}$$

where Γ_ρ^T is the truncated 2-pdm of an N-pdm $\rho_N = |\Psi_N\rangle\langle\Psi_N|$, $\Psi_N \in D_N$ being an ε-approximate ground state of the molecule in question. $V := \frac{1}{|x-y|} \otimes 1(\sigma_x) \otimes 1(\sigma_y)$ is the Coulomb interaction on $\mathscr{H} \otimes \mathscr{H}$. We use the decomposition

$$\frac{1}{|x-y|} = \frac{1}{\pi} \int d^3 z \int_0^\infty \frac{dr}{r^5} \chi_{B(r,z)}(x) \chi_{B(r,z)}(y), \tag{75}$$

which was introduced by Fefferman and de la Llave [3]. Here, $\chi_{B(r,z)}$ is the characteristic function of $\{x \in \mathbb{R}^3 | |x - z| \leqq r\}$. We denote the multiplication operator on $\mathscr{H}$ corresponding to $\chi_{B(r,z)} \otimes 1(\sigma)$ by $X_{(r,z)}$. Note that clearly $X_{(r,z)} = X^+_{(r,z)} = X^2_{(r,z)}$.

Furthermore we define

$$\rho(x) := \sum_{\sigma=1}^{q} \gamma_\rho(x, \sigma | x, \sigma) , \tag{76}$$

$$\rho_T(x) := \sum_{\sigma=1}^{q} \{\gamma_\rho(x, \sigma | x, \sigma) - \gamma_\rho^2(x, \sigma | x, \sigma)\} , \tag{77}$$

so ρ is the one-particle density of the ε-approximate ground state Ψ_N and we call ρ_T the *truncated one-particle density.* With the above notations we can prove the following estimate.

Lemma 5. *Assume* (15), (75) *and* (76). *For any* $0 < \delta \leqq 5/24$ *it holds*

$$\frac{1}{2}\operatorname{tr}_2\{V\Gamma_\rho^T\} \geqq -c_\delta\left(\int \rho^{5/3}(x)d^3x\right)^{1/2}\left(\int \rho(x)d^3x\right)^{1/2}\left(\frac{\int \rho_T(x)\,d^3x}{\int \rho(x)d^3x}\right)^{1/3-\delta} , \tag{78}$$

where $c_\delta := (185.417)(7.554)^{2/3}\delta^{-1/3}$.

Proof. The first step consists in applying Theorem 4 to $X := X_{(r,z)}$ and superimposing all the obtained estimates.

$$\begin{aligned}
\frac{1}{2}\operatorname{tr}_2\{V\Gamma_\rho^T\} &= \frac{1}{2\pi}\int d^3z \int_0^\infty \frac{dr}{r^5}\operatorname{tr}_2\{(X_{(r,z)} \otimes X_{(r,z)})\Gamma_\rho^T\} \\
&\geqq -\frac{1}{2\pi}\int d^3z \int_0^\infty \frac{dr}{r^5}\operatorname{tr}_1\{X_{(r,z)}\gamma_\rho\} \\
&\quad \cdot \min\{1, \alpha(\operatorname{tr}_1\{X_{(r,z)}(\gamma_\rho - \gamma_\rho^2)\})^{1/2}\} \\
&= -\frac{1}{2\pi}\int d^3z \int_0^\infty \frac{dr}{r^5}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right) \\
&\quad \cdot \min\left\{1, \alpha\left(\int_{|x-z|\leqq r} \rho_T(x)d^3x\right)^{1/2}\right\} \\
&\geqq -\frac{1}{2\pi}\int d^3z \left\{\int_0^{R(z)} \frac{dr}{r^5}\,\alpha\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right)\left(\int_{|x-z|\leqq r} \rho_T(x)d^3x\right)^{1/2}\right. \\
&\quad \left. + \int_{R(z)}^\infty \frac{dr}{r^5}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right)\right\} ,
\end{aligned} \tag{79}$$

for any measurable choice of $R(z)$, with $\alpha := 7.554$. We proceed analogously to Lieb [8] introducing the Hardy–Littlewood maximal functions of ρ and ρ_T.

$$M(z) := \sup_{r>0}\left\{\frac{3}{4\pi r^3}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right)\right\} , \tag{80}$$

$$M_T(z) := \sup_{r>0}\left\{\frac{3}{4\pi r^3}\left(\int_{|x-z|\leqq r} \rho_T(x)d^3x\right)\right\} . \tag{81}$$

Recall that in general, if $f \in L^1(\mathbb{R}^3)$, then its maximal function $M_f(z) := \sup_{r>0}\{3(4\pi r^3)^{-1}(\int_{|x-z|\leqq r}|f(x)|d^3x)\} < \infty$ on $\mathbb{R}^3$ a.e. and fulfills the maximal inequality

$$\int M_f^p(z)d^3z \leqq \frac{96}{\pi}\frac{p}{p-1}\int |f(z)|^p d^3z \tag{82}$$

for all $p > 1$ (cf. [19], pp. 58). By means of M and M_T we find for any $q > 1/3$

$$\begin{aligned}
&\int_0^{R(z)} \frac{dr}{r^5}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right)\left(\int_{|x-z|\leqq r} \rho_T(x)d^3x\right)^q \\
&\leqq \left(\frac{4\pi}{3}\right)^{1+q} M(z)M_T^q(z)\int_0^{R(z)} r^{3q-2}dr \\
&= \left(\frac{4\pi}{3}\right)^{1+q}\frac{R^{3q-1}(z)}{3q-1}M(z)M_T^q(z)\,,
\end{aligned} \tag{83}$$

and similarly

$$\int_{R(z)}^{\infty} \frac{dr}{r^5}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right) \leqq \frac{4\pi}{3}\frac{M(z)}{R(z)}\,, \tag{84}$$

on $\mathbb{R}^3$ a.e. Thus we obtain

$$\begin{aligned}
&\int_0^{\infty} \frac{dr}{r^5}\left(\int_{|x-z|\leqq r} \rho(x)d^3x\right)\min\left\{1, \alpha\left(\int_{|x-z|\leqq r} \rho_T(x)d^3x\right)^{1/2}\right\} \\
&\leqq \frac{4\pi}{3}M(z)\left\{\frac{c_q}{3q-1}M_T^q(z)R^{3q-1}(z) + R^{-1}(z)\right\},
\end{aligned} \tag{85}$$

where $c_q = (4\pi/3)^q\alpha$. An optimization yields $R(z) = c_q^{-1/3q}M_T^{-1/3}(z)$ and bounds the right-hand side of the inequality above by

$$\frac{12\pi q}{3(3q-1)}c_q^{1/3q}M(z)M_T^{1/3}(z)\,. \tag{86}$$

Observe that there is no dependence of the estimate (86) on q apart from an overall constant. In this respect, a substitution of $(\mathrm{tr}_1\{X(\gamma-\gamma^2)\})^{1/2}$ by $\mathrm{tr}_1\{X(\gamma-\gamma^2)\}$ in Theorem 4 would not have yielded a better result. Inserting the actual value $q = 1/2$ we obtain

$$\frac{1}{2}\mathrm{tr}_2\{V\Gamma_\rho^T\} \geqq -\frac{3}{2\pi}\left(\frac{4\pi}{3}\right)^{4/3}\alpha^{2/3}\int M(z)M_T^{1/3}(z)d^3z\,. \tag{87}$$

We fix $0 < \varepsilon \leqq 1/12$ and apply the Hölder and the maximal inequality (82) to the right hand of (87). This gives

$$\begin{aligned}
\int M(z)M_T^{1/3}(z)d^3z &\leqq \left(\int [M(z)]^{\frac{3}{2+3\varepsilon}}d^3z\right)^{2/3+\varepsilon}\left(\int [M_T(z)]^{\frac{1}{1-3\varepsilon}}d^3z\right)^{1/3-\varepsilon} \\
&\leqq \left(\frac{96}{\pi}\right)\left(\frac{8}{3}\right)^{1/3}\varepsilon^{-1/3}\left(\int [\rho(x)]^{\frac{3}{2+3\varepsilon}}d^3x\right)^{2/3+\varepsilon} \\
&\quad\cdot\left(\int [\rho_T(x)]^{\frac{1}{1-3\varepsilon}}d^3x\right)^{1/3-\varepsilon}.
\end{aligned} \tag{88}$$

Applying the Hölder inequality again, we find

$$\int [\rho(x)]^{\frac{3}{2+3\varepsilon}} d^3x \leqq \left(\int \rho^{5/3}(x) d^3x \right)^{\frac{3(1-3\varepsilon)}{2(2+3\varepsilon)}} \left(\int \rho(x) d^3x \right)^{\frac{1+15\varepsilon}{2(2+3\varepsilon)}}, \tag{89}$$

$$\int [\rho_T(x)]^{\frac{1}{1-3\varepsilon}} d^3x \leqq \left(\int \rho_T^{5/3}(x) d^3x \right)^{\frac{9\varepsilon}{2(1-3\varepsilon)}} \left(\int \rho_T(x) d^3x \right)^{\frac{2-15\varepsilon}{2(1-3\varepsilon)}}. \tag{90}$$

We exploit $\rho_T^{5/3} \leqq \rho^{5/3}$ and get

$$\left(\int [\rho(x)]^{\frac{3}{2+3\varepsilon}} d^3x \right)^{2/3+\varepsilon} \left(\int [\rho_T(x)]^{\frac{1}{1-3\varepsilon}} d^3x \right)^{1/3-\varepsilon}$$

$$\leqq \left(\int \rho^{5/3}(x) d^3x \right)^{1/2} \left(\int \rho(x) d^3x \right)^{1/2} \left(\frac{\int \rho_T(x) d^3x}{\int \rho(x) d^3x} \right)^{1/3-5\varepsilon/2}. \tag{91}$$

Combining these estimates, we prove the assertion (78) above. ▮

5.2. A Simple Bound on the Kinetic Energy. We need to bound the kinetic energy $\langle \Psi_N | \sum_{i=1}^N -\Delta_i | \Psi_N \rangle$ in order to prove Theorem 1. Our goal is to use as little information as possible about the system, i.e. about Ψ_N, N, $\underline{Z}$, and $\underline{R}$. We derive our bound essentially by reproducing a similar result of Lieb [10].

Lemma 6. *Let $q \leqq N$ and $\Phi_N \in D_N$ such that $\langle \Phi_N | H_N(\underline{Z}, \underline{R}) | \Phi_N \rangle \leqq 0$. Then*

$$\left\langle \Phi_N \left| \sum_{i=1}^N -\Delta_i \right| \Phi_N \right\rangle \leqq 2q^{2/3} Z^2 N^{1/3}. \tag{92}$$

Proof. Dropping the Coulomb interaction of the electrons, we have

$$\begin{aligned} 0 &\geqq \left\langle \Phi_N \left| \sum_{i=1}^N \left(-\Delta_i - \sum_{j=1}^K \frac{Z_j}{|x_i - R_j|} \right) \right| \Phi_N \right\rangle \\ &= \frac{1}{2} \left\langle \Phi_N \left| \sum_{i=1}^N -\Delta_i \right| \Phi_N \right\rangle \\ &\quad + \sum_{j=1}^K \frac{Z_j}{2Z} \left\langle \Phi_N \left| \sum_{i=1}^N \left(-\Delta_i - \frac{2Z}{|x_i - R_j|} \right) \right| \Phi_N \right\rangle \\ &\geqq \frac{1}{2} \left\langle \Phi_N \left| \sum_{i=1}^N -\Delta_i \right| \Phi_N \right\rangle - \sum_{j=1}^K \frac{Z_j}{2Z} \frac{(2Z)^2}{4} q \left(\frac{N}{q} \right)^{1/3}. \end{aligned} \tag{93}$$

In the last step we just added up the eigenvaues of the Bohr atom. ▮

We are now in position to prove Theorem 1

Proof of Theorem 1. We recall the Lieb–Thirring inequality [15], which bounds $\int \rho^{5/3}$ by the kinetic energy. Namely, denoting $c_{\mathrm{LT}} := 2.7709 q^{-2/3}$ (see [9] for this value), it holds

$$c_{\mathrm{LT}} \int \rho_\Phi^{5/3}(x) d^3x \leqq \left\langle \Phi_N \left| \sum_{i=1}^N -\Delta_i \right| \Phi_N \right\rangle, \tag{94}$$

where ρ_Φ is the one-particle density of $\Phi_N \in D_N$. Inserting the Lieb–Thirring inequality into Lemmas 2 and 6 we thus complete the proof of Theorem 1. ∎

6. Asymptotics for Large Z

Our goal in this section is to derive Theorem 2. The idea underlying our proof is that Ψ_N is not only the ground state of $H_N(\underline{Z}, \underline{R})$, but it is an α-approximate ground state of a suitable one-body Hamiltonian which approximates $H_N(\underline{Z}, \underline{R})$, too, where $\alpha = o(Z^{7/3})$. However, the exact ground state Φ_N, say, of such a one-body Hamiltonian is a Slater determinant and the corresponding 1-pdm is a projection. Therefore, we expect γ to be close to a projection. It is here that we use semiclassical results, namely the considered one-body Hamiltonian is suggested by Thomas–Fermi theory.

We assume the existence of ε, c_1, c_2, $c_3 \geqq 0$ such that

$$\min\{|R_i - R_j| \,|\, 1 \leqq i < j \leqq K\} \geqq c_1 Z^{-2/3+\varepsilon} , \qquad Z - c_2 Z^{1/3} \leqq N \leqq Z + c_3 Z^{5/7} , \tag{95}$$

hold throughout this section without further notice.

6.1. The Semiclassical Results of Ivrii and Sigal. Let $\phi_{\mathrm{TF}} := \phi_{\mathrm{TF}}(Z, \underline{Z}, \underline{R})$ be the Thomas–Fermi potential of a neutral molecule with nuclei $\underline{Z}$ at positions $\underline{R}$ (cf. [10]) and define

$$H := (-\Delta - \phi_{\mathrm{TF}}(x)) \otimes 1(\sigma) \tag{96}$$

self-adjointly on $D \subseteq \mathscr{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^q$. For all $\alpha > 0$ we define the spectral projections $P_\alpha := \chi_{(-\infty, -\alpha]}(H)$ and $P_0 := \chi_{(-\infty, 0)}(H)$. For $E \geqq 0$ we then denote

$$H_E := P_E H P_E . \tag{97}$$

We define the energy $e \geqq 0$ as follows:

$$-e := \begin{cases} Z^{\mathrm{th}} \text{ eigenvalue of } H & \text{if } \operatorname{tr}\{P_0\} > Z \\ 0 & \text{if } \operatorname{tr}\{P_0\} \leqq Z . \end{cases} \tag{98}$$

In other words, if H has at least Z negative eigenvalues (counting multiplicities) then $-e$ is the Z^{th} eigenvalue and otherwise $e = 0$. Since $M := \operatorname{tr}\{P_e\} \leqq Z$, P_e certainly has an integral kernel and we define the corresponding one-particle density by $\rho_M(x) := \sum_{\sigma=1}^q P_e(x, \sigma | x, \sigma)$ on $\mathbb{R}^3$ a.e. Note that $\int \rho_M(x) d^3x = M$. Furthermore, we set for $f, g \in L^1(\mathbb{R}^3)$

$$D(f, g) := \int \frac{d^3x\, d^3y}{|x - y|} f^*(x) g(y) . \tag{99}$$

Let us quote the results of Ivrii and Sigal in form of a lemma (cf. [7], Thm. 2.4 and Lemma 2.8)

Lemma 7. (*Ivrii and Sigal*). *Let* $\min\{|R_i - R_j| \,|\, 1 \leqq i < j \leqq K\} \geqq \hat{c} Z^{-2/3+\varepsilon}$ *for some* $\hat{c}, \varepsilon > 0$. *Then, for some* $c > 0$ *and for all* $\alpha \geqq 0$,

(i) $D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) \leqq c Z^{5/3}$,
(ii) $\operatorname{tr}\{P_\alpha\} = c_{sc} \int [\phi_{\mathrm{TF}}(x) - \alpha]_+^{3/2} d^3x + O(Z^{2/3})$, *where* $c_{sc} := 6\pi^2 q^{-1}$.

6.2. The Energy Truncation. Our first result in this section is an estimate on the energy expectation of γ with respect to H. We claim

Lemma 8. *Let γ be the* 1-pdm *of an ε-approximate ground state of $H_N(\underline{Z}, \underline{R})$ with $\varepsilon \leqq \tilde{c}Z^{5/3}$. Then, for some $c \geqq 0$,*

$$\operatorname{tr}\{H\gamma\} \leqq \operatorname{tr}\{H_e\} + cZ^{5/3} . \tag{100}$$

Proof. By the variational principle for $H_M(\underline{Z}, \underline{R})$ and the Lieb–Oxford inequality [13]

$$\left\langle \Psi_N \left| \sum_{1 \leqq i < j \leqq N} \frac{1}{|x-y|} \right| \Psi_N \right\rangle \geqq \frac{1}{2} D(\rho, \rho) - (1.68) \int \rho^{4/3}(x) d^3x , \tag{101}$$

we obtain

$$\begin{aligned}
\operatorname{tr}\{H_e\} &= \operatorname{tr}\{hP_e\} + D(\rho_{\mathrm{TF}}, \rho_M) \\
&= \operatorname{tr}\{hP_e\} + \frac{1}{2} D(\rho_M, \rho_M) + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\
&\quad - \frac{1}{2} D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) \\
&\geqq E_Q(M, \underline{Z}, \underline{R}) + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \frac{1}{2} D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) \\
&\geqq \operatorname{tr}\{h\gamma\} + \frac{1}{2} D(\rho, \rho) - [E_Q(N, \underline{Z}, \underline{R})] - E_Q(\underline{M}, \underline{Z}, \underline{R})] - \varepsilon \\
&\quad - (1.68) \int \rho^{4/3}(x) d^3x + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \frac{1}{2} D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) \\
&\geqq \operatorname{tr}\{H\gamma\} - [E_Q(N, \underline{Z}, \underline{R}) - E_Q(M, \underline{Z}, \underline{R})] - \varepsilon \\
&\quad - (1.68) \int \rho^{4/3}(x) d^3x - \frac{1}{2} D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) .
\end{aligned} \tag{102}$$

Now, Lemma 7(i) states $D(\rho_M - \rho_{\mathrm{TF}}, \rho_M - \rho_{\mathrm{TF}}) \leqq cZ^{5/3}$ and using Lemma 6 yields

$$\int \rho^{4/3}(x) d^3x \leqq \left(\int \rho^{5/3}(x) d^3x\right)^{1/2} \left(\int \rho(x) d^3x\right)^{1/2} \leqq cZ^{5/3} . \tag{103}$$

Next, denoting $E_N := E_Q(N, \underline{Z}, \underline{R})$, we show for all $N \geqq 3$

$$\left| \frac{E_N}{N} \right| \leqq \left| \frac{E_{N-1}}{N-1} \right| . \tag{104}$$

Namely, setting $h_i := -\Delta_i + \sum_{j=1}^{K} Z_j |x_i - R_j|^{-1}$ and using an ε'-approximate ground state $\Psi_N \in D_N$ of $H_N(\underline{Z}, \underline{R})$ for a suitably small $\varepsilon' > 0$, we infer

$$\begin{aligned}
E_N &\geqq \langle \Psi_N | h_1 + (N-1)|x_1 - x_2|^{-1} | \Psi_N \rangle - \varepsilon' \\
&\quad + \left\langle \Psi_N \left| \sum_{i=2}^{N} h_i + \sum_{2 \leqq i < j \leqq N} \frac{1}{|x_i - x_j|} \right| \Psi_N \right\rangle \\
&\geqq N^{-1} E_N + E_{N-1} .
\end{aligned} \tag{105}$$

Now, if $N \geqq M$, we already arrive at the claim. Conversely assume $N < M$. Then, by (104),

$$E_N - E_M \leqq (M - N) \left| \frac{E_N}{N} \right| \leqq cZ^{1/3} \cdot Z^{4/3} . \quad \blacksquare \tag{106}$$

We remark that $\operatorname{tr}\{H\gamma\}$ and $\operatorname{tr}\{H_e\}$ are both of order $Z^{7/3}$. Thus one may interpret Lemma 8 as stating that γ cannot deviate much from $P_e = P_e^2$. It hence implicitly asserts the smallness of $\gamma - \gamma^2$. We introduce a cut-off in energy to make this explicit.

Lemma 9. *Let $E > e$. Then, for some $c > 0$,*

$$\operatorname{tr}\{P_E(\gamma - \gamma^2)\} \leqq c\,\frac{Z^{5/3}}{E} + \frac{e}{E} \operatorname{tr}\{P_0 - P_e\} . \tag{107}$$

Proof. We observe that $0 \geqq \operatorname{tr}\{H_0(P_e - \gamma)^2\}$ implies $\operatorname{tr}\{(-H_0)(\gamma - \gamma^2)\} \leqq \operatorname{tr}\{(-H_e)(1 - \gamma)\}$. This inequality, $0 \leqq \gamma \leqq 1$, and $H_0 - H \leqq 0 \leqq -H_E \leqq -H_e \leqq -H_0$ yield

$$\begin{aligned} E \operatorname{tr}\{P_E(\gamma - \gamma^2)\} &\leqq \operatorname{tr}\{(-H_E)(\gamma - \gamma^2)\} \leqq \operatorname{tr}\{(-H_e)(\gamma - \gamma^2)\} \\ &\leqq \operatorname{tr}\{(-H_e)(1 - \gamma)\} \\ &\leqq -\operatorname{tr}\{H_e\} + \operatorname{tr}\{H\gamma\} - \operatorname{tr}\{(H_0 - H_e)\gamma\} \\ &\leqq cZ^{5/3} + e \operatorname{tr}\{P_0 - P_e\} , \end{aligned} \tag{108}$$

applying Lemma 8 in the last estimate. $\blacksquare$

As will be shown next, Lemma 8 does not only supply a bound on $\operatorname{tr}\{P_E(\gamma - \gamma^2)\}$, but also on $\operatorname{tr}\{(1 - P_E)(\gamma - \gamma^2)\}$. Intuitively this is clear provided there are approximately Z eigenvalues of H below $-E$. More specifically, we will prove

Lemma 10. *Let $E > e$. Then, for some $c > 0$,*

$$\begin{aligned} \operatorname{tr}\{(1 - P_E)(\gamma - \gamma^2)\} \leqq Z - \operatorname{tr}\{P_E\} + cZ^{5/7} + c\,\frac{Z^{5/3}}{E} \\ + \frac{e}{E} \operatorname{tr}\{P_0 - P_e\} . \end{aligned} \tag{109}$$

Proof. As in the proof of Lemma 9 we observe

$$E \operatorname{tr}\{P_E(1 - \gamma)\} \leqq \operatorname{tr}\{(-H_e)(1 - \gamma)\} \leqq cZ^{5/3} + e \operatorname{tr}\{P_0 - P_e\} . \tag{110}$$

Also,

$$\operatorname{tr}\{(1 - P_E)\gamma\} = N - \operatorname{tr}\{P_E\} + \operatorname{tr}\{P_E(1 - \gamma)\} . \tag{111}$$

These two inequalities (110), (111) imply the assertion, since $\gamma \geqq \gamma - \gamma^2$ and $N \leqq Z + cZ^{5/7}$. $\blacksquare$

Now we will put these estimates together and insert the bound (ii) of Lemma 7 on $\operatorname{tr}\{P_\alpha\}$, $\alpha \geqq 0$.

Lemma 11. *Let $E > e$. Then, for some c, $c' > 0$,*

$$\operatorname{tr}\{\gamma - \gamma^2\} \leqq cZ^{5/7} + c' \frac{Z^{5/3}}{E} + 3c_{sc} \int \{\phi_{\mathrm{TF}}^{3/2}(x) - [\phi_{\mathrm{TF}}(x) - E]_+^{3/2}\} d^3x . \quad (112)$$

Proof. We add up the estimates from Lemma 9 and 10. This yields

$$\operatorname{tr}\{\gamma - \gamma^2\} \leqq Z - \operatorname{tr}\{P_E\} + c\frac{Z^{5/3}}{E} + c_1 Z^{5/7} + 2\frac{e}{E}\operatorname{tr}\{P_0 - P_e\} . \quad (113)$$

By (ii) of Lemma 7 and Thomas–Fermi theory (cf. [11]) it holds

$$Z = c_{sc} \int \phi_{\mathrm{TF}}^{3/2}(x) d^3x = \operatorname{tr}\{P_0\} + O(Z^{2/3}) , \quad (114)$$

which implies

$$\frac{e}{E}\operatorname{tr}\{P_0 - P_e\} \leqq Z - \operatorname{tr}\{P_E\} + cZ^{2/3} . \quad (115)$$

On the other hand, (ii) of Lemma 7 also asserts

$$\operatorname{tr}\{P_E\} \geqq c_{sc} \int [\phi_{\mathrm{TF}}(x) - E]_+^{3/2} d^3x - cZ^{2/3} , \quad (116)$$

thus establishing Lemma 11. ▮

6.3. The Semiclassical Number of Particles. As we have seen in the section before it remains to bound

$$c_{sc} \int \{\phi_{\mathrm{TF}}^{3/2}(x) - [\phi_{\mathrm{TF}}(x) - E]_+^{3/2}\} d^3x \quad (117)$$

and to assure $E > e$. We will do this by means of Lemma 12 below. Let us emphasize that the only parameters which enter in our estimate are Z and K. Nothing needs to be assumed about $\underline{Z}/Z$ and $\underline{R}$.

Lemma 12. *Let $\phi_{\mathrm{TF}} := \phi_{\mathrm{TF}}(Z, \underline{Z}, \underline{R})$ be the Thomas–Fermi potential of a neutral molecule with nuclei Z_j at positions R_j for $1 \leqq j \leqq K$. Let furthermore $Z := \sum_{j=1}^K Z_j$ and $0 < E \leqq o(Z^{4/3})$. Then, for sufficiently large Z,*

$$\frac{2\pi}{3}\left(\frac{3c_{sc}}{\pi}\right)^{3/2} E^{3/4} \leqq \int \{\phi_{\mathrm{TF}}^{3/2}(x) - [\phi_{\mathrm{TF}}(x) - E]_+^{3/2}\} d^3x \quad (118)$$

$$\leqq \frac{16\pi}{3} K^{7/4} \left(\frac{3c_{sc}}{\pi}\right)^{3/2} E^{3/4} . \quad (119)$$

Proof. Let ϕ_Z be the Thomas–Fermi potential of a neutral atom at the origin. Using the maximum principle (cf. [11]) one sees that for all $1 \leqq j \leqq K$ and $x \in \mathbb{R}^3$ a.e.,

$$\phi_{Z_j}(x - R_j) \leqq \phi_{\mathrm{TF}}(x) \leqq \sum_{j=1}^{K} \phi_{Z_j}(x - R_j) . \quad (120)$$

We prove the inequality (118). Observe that $\phi^{3/2} - [\phi - E]_+^{3/2}$ is monotone in ϕ. Since at least one of the nuclei, the j^{th}, say, has charge $Z_j \geqq Z/K$, we derive

$\phi_{\mathrm{TF}}(x) \geqq \phi_{Z_j}(x - R_j) \geqq \phi_{Z/K}(x - R_j)$, and hence, using $\phi_Z(x) = Z^{4/3}\phi_1(Z^{1/3}x)$,

$$\begin{aligned}
&\int \{\phi_{\mathrm{TF}}^{3/2}(x) - [\phi_{\mathrm{TF}}(x) - E]_+^{3/2}\} d^3x \\
&\quad \geqq \int \{\phi_{Z/K}^{3/2}(x - R_j) - [\phi_{Z/K}(x - R_j) - E]_+^{3/2}\} d^3x \\
&\quad = \hat{Z} \int \{\phi_1^{3/2}(x) - [\phi_1(x) - \hat{E}]_+^{3/2}\} d^3x\,, \qquad (121)
\end{aligned}$$

where $\hat{Z} := Z/K$ and $\hat{E} := E/\hat{Z}^{4/3} = o(1)$. As a result of Thomas–Fermi theory, $\phi_1(x)$ is a function of $|x|$ and decreases monotonically in $|x|$. Furthermore, $\phi_1(x) \leqq (3/\pi)^2 c_{sc}^2 |x|^{-4} =: \tilde{c}^{2/3}|x|^{-4}$ and, indeed, for $|x|$ sufficiently large,

$$2^{-2/3}\frac{\tilde{c}^{2/3}}{|x|^4} \leqq \phi_1(x) \leqq \frac{\tilde{c}^{2/3}}{|x|^4}\,, \qquad (122)$$

(cf. [11]). Therefore, $\hat{E} = o(1)$ implies $\phi_1(x) \geqq \tilde{c}2^{-2/3}|x|^{-4}$ on

$$A := \{x \in \mathbb{R}^3 | \phi_1(x) \leqq E\} \supseteq \{x \in \mathbb{R}^3 | \tilde{c}^{2/3}|x|^{-4} \leqq E\} =: B\,. \qquad (123)$$

This yields

$$\begin{aligned}
\int \{\phi_1^{3/2}(x) - [\phi_1(x) - \hat{E}]_+^{3/2}\} d^3x &\geqq \int_A \phi_1^{3/2}(x) d^3x \geqq \int_A \frac{\tilde{c}}{2}|x|^{-6} d^3x \\
&\geqq \int_B \frac{\tilde{c}}{2}|x|^{-6} d^3x \\
&= 4\pi\frac{\tilde{c}}{2}\int_{\tilde{c}^{1/6}\hat{E}^{-1/4}}^{\infty} \frac{dr}{r^4} = \frac{4\pi}{6}\tilde{c}^{1/2}\hat{E}^{3/4}\,. \qquad (124)
\end{aligned}$$

Applying these estimates, the inequality (118) follows.

Now, we prove the inequality (119). We divide the space into the K regions, $1 \leqq j \leqq K$,

$$A_j := \{x \in \mathbb{R}^3 | \forall 1 \leqq i \leqq K : |x - R_j| \leqq |x - R_i|\}\,. \qquad (125)$$

On A_j, we estimate

$$\varphi_{\mathrm{TF}}(x) \leqq \sum_{i=1}^{K} \phi_{Z_i}(x - R_i) \leqq \sum_{i=1}^{K} \phi_{Z_i}(x - R_j) \leqq K\phi_Z(x - R_j)\,. \qquad (126)$$

Hence it follows, with $\hat{E} := EK^{-1}Z^{-4/3}$,

$$\begin{aligned}
&\int \{\phi_{\mathrm{TF}}^{3/2}(x) - [\phi_{\mathrm{TF}}(x) - E]_+^{3/2}\} d^3x \\
&\quad \leqq \sum_{j=1}^{K}\int_{A_j} \{K^{3/2}\phi_Z^{3/2}(x - R_j) - [K\phi_Z(x - R_j) - E]_+^{3/2}\} d^3x \\
&\quad \leqq \sum_{j=1}^{K}\int \{K^{3/2}\phi_Z^{3/2}(x - R_j) - [K\phi_Z(x - R_j) - E]_+^{3/2}\} d^3x \\
&\quad = K^{5/2}Z\int \{\phi_1^{3/2}(x) - [\phi_1(x) - \hat{E}]_+^{3/2}\} d^3x
\end{aligned}$$

$$\leqq K^{5/2}Z\int\{\tilde{c}|x|^{-6}-[\tilde{c}^{2/3}|x|^{-4}-\hat{E}]_+^{3/2}\}d^3x$$

$$\leqq 4\pi K^{5/2}Z\left\{\hat{E}\int_0^{\tilde{c}^{1/6}\hat{E}^{-1/4}}\tilde{c}^{1/3}\,dr+\tilde{c}\int_{\tilde{c}^{1/6}\hat{E}^{-1/4}}^{\infty}\frac{dr}{r^4}\right\}$$

$$=4\pi K^{5/2}Z\,\frac{4\tilde{c}^{1/2}}{3}\,\hat{E}^{3/4}\,. \tag{127}$$

This establishes inequality (119) and hence Lemma 12. ∎

We are now in position to prove Theorem 2

Proof of Theorem 2. In order to apply Lemma 11 we need to have an upper bound on e. First, assume that $e \geqq cZ$ for some $c>0$. Then $\mathrm{tr}\{P_e\}=Z$, by definition. Again applying (ii) of Lemma 7, this implies

$$c_{sc}\int\{\phi_{\mathrm{TF}}^{3/2}(x)-[\phi_{\mathrm{TF}}(x)-e]_+^{3/2}\}d^3x\leqq Z-\mathrm{tr}\{P_e\}+c'Z^{2/3}\leqq c'Z^{2/3}\,. \tag{128}$$

By the monotonicity in e, (128) would still hold true if we replaced e by cZ on the left-hand side. Now, by Lemma 12, we know that for $\bar{E}=o(Z^{4/3})$,

$$2\left(\frac{3}{\pi}\right)^{1/2}c_{sc}^{5/2}\bar{E}^{3/4}\leqq c_{sc}\int\{\phi_{\mathrm{TF}}^{3/2}(x)-[\phi_{\mathrm{TF}}(x)-\bar{E}]_+^{3/2}\}d^3x\,. \tag{129}$$

Hence, setting $\bar{E}:=cZ$, (128) lead to the contradiction $Z^{3/4}\leqq \mathrm{const}\,Z^{2/3}$. Therefore, $e=o(Z)\leqq o(Z^{4/3})$. This assures we may set $\bar{E}:=e$ in (129) which, together with (128), implies

$$e\leqq cZ^{8/9}\,. \tag{130}$$

Now, using Lemma 12, we derive from Lemma 11,

$$\mathrm{tr}\{\gamma-\gamma^2\}\leqq cZ^{5/7}+c'\frac{Z^{5/3}}{E}+3c_{sc}\int\{\phi_{\mathrm{TF}}^{3/2}(x)-[\phi_{\mathrm{TF}}(x)-E]_+^{3/2}\}d^3x$$

$$\leqq cZ^{5/7}+c'\frac{Z^{5/3}}{E}+c''E^{3/4}$$

$$\leqq cZ^{5/7}\,, \tag{131}$$

choosing $E:=Z^{20/21}=o(Z^{4/3})$. This choice is justified for sufficiently large Z, since $E=Z^{20/21}>cZ^{8/9}\geqq e$. ∎

We would like to emphasize that the method of proving Theorem 2 is not intrinsically semiclassical, despite the fact we use results from semiclassical analysis. Indeed, if we had substituted H by some other one-body Hamiltonian $\tilde{H}$, say, we could have proved $\mathrm{tr}\{\gamma-\gamma^2\}=o(Z)$, provided its ground state energy agrees with E_Q in leading order. Of course, we needed to have some explicit access to spectral functions of $\tilde{H}$ as well, which is why we chose $H=(-\Delta-\phi_{\mathrm{TF}}(x))\otimes 1(\sigma)$.

Acknowledgements. It is a pleasure to thank W. Hunziker and I.M. Sigal for helpful discussions and comments. I also appreciate W. Hunziker's very constructive proofreading. Furthermore, I thank H. Siedentop, J.-P. Solovej, and M.B. Ruskai for various discussions and supplementary material.

References

1. Coleman, A.J.: Structure of fermion density matrices. Rev. Mod. Phys. **35**(3), 668–689 (1963)
2. Dirac, P.A.M.: Note on exchange phenomena in the Thomas–Fermi atom. Proc. Cambridge Philos. Soc. **26**, 376–385 (1931)
3. Fefferman, C.L., de la Llave, R.: Relativistic stability of matter – I. Revista Matematica Iberoamericana, **2**(1, 2), 119–161 (1986)
4. Fefferman, C.L., Seco, L.A.: The ground-state energy of a large atom. Bull. A.M.S. (1990)
5. Fefferman, C.L., Seco, L.A.: An upper bound for the number of electrons in a large ion. Proc. Nat. Acad. Sci. USA, **86**, 3464–3465 (1989)
6. Hughes, W.: An Atomic Energy Lower Bound that Gives Scott's Correction. PhD thesis, Princeton, Department of Mathematics, 1986
7. Ivrii, V.Ja., Sigal, I.M.: Asymptotics of the ground state energies of large Coulomb systems. Annals Math. (to appear)
8. Lieb, E.H.: A lower bound for Coulomb energies. Phys. Lett. **70A**, 444–446 (1979)
9. Lieb, E.H.: On characteristic exponents in turbulence. Commun. Math. Phys. **92**, 473–480 (1984)
10. Lieb, E.H.: The stability of matter. Rev. Mod. Phys. **48**, 653–669 (1976)
11. Lieb, E.H.: Thomas–Fermi and related theories of atoms and molecules. Rev. Mod. Phys. **53**, 603–604 (1981)
12. Lieb, E.H.: Variational principle for many-fermion systems. Phys. Rev. Lett. **46**(7), 457–459 (1981)
13. Lieb, E.H., Oxford, S.: An improved lower bound on the indirect Coulomb energy. Int. J. Quantum Chem. **19**, 427–439 (1981)
14. Lieb, E.H., Simon, B.: The Thomas-Fermi theory of atoms, molecules and solids. Adv. Math. **23**, 22–116 (1977)
15. Lieb, E.H., Thirring, W.E.: Inequalities for the moments of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities. In Lieb, E.H., Simon, B., Wightman, A.S. (eds.), Studies in Mathematical Physics: Essays in Honor of Valentine Bargmann. Princeton, NJ: Princeton University Press 1976
16. Schwinger, J.: Thomas–Fermi model: The second correction. Phys. Rev. A **24**(5), 2353–2361 (1981)
17. Siedentop, H.K.H., Weikard, R.: A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators. Ann. Scient. Ec. Norm. Sup. **24**, 215–225 (1991)
18. Siedentop, H.K.H., Weikard, R.: On the leading energy correction for the statistical model of the atom: Interacting case. Commun. Math. Phys. **112**, 471–490 (1987)
19. Stein, E.M., Weiss, G.: Introduction to Fourier Analysis on Euclidean Spaces. Princeton, New Jersey: Princeton University Press, 2 edition, 1971
20. Thirring, W.: Lehrbuch der Mathematischen Physik 4: Quantenmechanik großer Systeme. Wien, New York: Springer, 1 edition, 1980

Communicated by B. Simon