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Accuracy of Mean Field Approximations for Atoms and Molecules

Volker Bach

Fachbereich Mathematik MA 7-2, Technische Universität Berlin, Straße des 17. Juni 136, D-10623 Berlin, Germany

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Abstract. We estimate the accuracy of the mean field approximation induced by the Thomas–Fermi potential for the ground state energy of atoms and molecules. Taking the Dirac exchange correction into account, we show the error to be of the form $O(Z^{5/3-\delta}) + D$ for any $\delta < 2/231$ as the total nuclear charge Z becomes large. D is an electrostatic energy of the difference density that measures the deviation of the mean field ground state from self-consistency.

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 $D_N := \bigwedge_{i=1}^{N} \tilde{\mathscr{H}} \subseteq \mathscr{H}_N := \bigwedge_{i=1}^{N} \mathscr{H}$, $\mathscr{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^m$, $\tilde{\mathscr{H}} := H^2(\mathbb{R}^3) \otimes \mathbb{C}^m$. Here, $\underline{Z} := (Z_1, \ldots, Z_K)$ and $\underline{R} := (R_1, \ldots, R_K)$ denote the charges and positions of the nuclei. We will drop this dependence in our notation henceforth. Unless stated otherwise, the operators are always assumed to act as identity on $\mathbb{C}^m$.

We are interested in approximations for the ground state energy

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

The most widely used one in physics is the *Mean Field* approximation. It consists in replacing the pair potential $\sum_{1 \leqq i<j}^{N} \dfrac{1}{|x_i - x_j|}$ in (1) by an average one-body potential

$$\sum_{i=1}^{N} \int \frac{d^3 y}{|x_i - y|} \rho(y) - \frac{1}{2} D(\rho, \rho) , \tag{3}$$

where $D(f, g) := \int \frac{d^3x\, d^3y}{|x-y|} \overline{f(x)} g(y)$ induces the Coulomb norm and $\frac{1}{2}D(\rho, \rho)$ is the electrostatic energy of a nonnegative density $\rho \in L^1(\mathbb{R}^3)$. So, provided $D(\rho, \rho) < \infty$, the substitute Hamiltonian reads

$$H_N(\rho) := \sum_{i=1}^{N} \left(-\Delta_i - \sum_{j=1}^{K} \frac{Z_j}{|x_i - R_j|} + \int \frac{d^3y}{|x_i - y|} \rho(y) \right) - \frac{1}{2} D(\rho, \rho) , \tag{4}$$

and is defined on D_N. In the case of atoms and molecules with N electrons a natural candidate for ρ is the corresponding Thomas–Fermi (TF) density ρ_{TF}, and the Mean Field potential becomes the TF-potential ϕ_{TF} (see [11]). We introduce

$$h_{\mathrm{TF}} := -\Delta - \sum_{j=1}^{K} \frac{Z_j}{|x - R_j|} + \int \frac{d^3y}{|x-y|} \rho_{\mathrm{TF}} = -\Delta - \phi_{\mathrm{TF}}(x) , \tag{5}$$

self-adjointly realized on D. By general arguments $\sigma_{\mathrm{ess}}(h_{\mathrm{TF}}) = [0, \infty)$ and $\sigma_{\mathrm{disc}}(h_{\mathrm{TF}}) \subseteq (-\infty, 0)$. Moreover, if $N \geqq Z$ then the chemical potential $\mu = 0$ [11] and $|\sigma_{\mathrm{disc}}(h_{\mathrm{TF}})| < \infty$, whereas $\mu > 0$ and $|\sigma_{\mathrm{disc}}(h_{\mathrm{TF}})| = \infty$ for $N < Z$. We set $P_N := \chi_{(-\infty, 0)}[h_{\mathrm{TF}}]$ in case $\mathrm{tr}_1\{\chi_{(-\infty, 0)}[h_{\mathrm{TF}}]\} \leqq N$. Otherwise

$$P_N := \sum_{i=1}^{N} |\varphi_i\rangle \langle \varphi_i| , \tag{6}$$

is a spectral projection onto N eigenfunctions φ_i of h_{TF} with lowest possible negative eigenvalue. Note that P_N might be nonunique due to degeneracy of the N^{th} eigenvalue and we pick just any of the possible ones. We observe $\mathrm{tr}_1\{P_N\} \leqq N$. For any nonnegative trace class operator $d = \sum_i \lambda_i |\chi_i\rangle\langle\chi_i|$ on $\mathscr{H}$ with orthonormal χ_i we call $\rho[d](x) := \sum_{\sigma=1}^{m} \sum_i \lambda_i |\chi_i(x, \sigma)|^2$ the corresponding density. In particular, $\rho_N := \rho[P_N]$. We are now in the position to formulate our main result

Theorem 1. *Consider a molecule of nuclear charges Z_j at positions R_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 $N \leqq Z + cZ^{1-2/77}$. Then for any $0 < \delta < 2/231$ there exists $c_\delta > 0$ such that*

$$-c_\delta K^2 \cdot Z^{5/3-\delta} \leqq E_Q(N) - \left\{ \mathrm{tr}_1\{h_{\mathrm{TF}} P_N\} - \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - c_D \int d^3x\, \rho_{\mathrm{TF}}^{4/3}(x) \right\}$$

$$\leqq c_\delta K^2 \cdot Z^{5/3-\delta} + \frac{1}{2} D(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}}) , \tag{7}$$

where $c_D := \frac{3}{4\pi} \left(\frac{6\pi^2}{m} \right)^{1/3}$.

The contribution $c_D \| \rho_{\mathrm{TF}} \|_{4/3}^{4/3}$ in $E_Q(N)$ has been proposed by Dirac [2] and is due to exchange corrections. We remark that c_δ above is independent of $\underline{Z}/Z$, K, $\underline{R}$, and N/Z. Theorem 1 states that up to errors of $O(Z^{5/3-\delta})$ the ground state energy $E_Q(N)$ can be evaluated by solving the eigenvalue problem for the Schrödinger operator h_{TF}, provided this spectral analysis yields

$$D(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}}) = O(Z^{5/3-\delta}) . \tag{8}$$

Indeed, $D^{1/2}(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}})$ is a natural norm to measure the quality of our choice $\rho = \rho_{\mathrm{TF}}$ of the Mean Field density, for it is positive definite and vanishes in case of self-consistency $\rho_N = \rho_{\mathrm{TF}}$. This indicates that $D^{1/2}(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}})$

measures the deviation of the Mean Field energy

$$E_{\mathrm{MF}}(N) := \mathrm{tr}_1\{h_{\mathrm{TF}} P_N\} - \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - c_D \int d^3x \, \rho_{\mathrm{TF}}^{4/3}(x) \tag{9}$$

from the Hartree–Fock energy $E_{\mathrm{HF}}(N)$ of the system, disregarding exchange corrections. The question how far $E_Q(N)$ then deviates from $E_{\mathrm{HF}}(N)$ has already been settled within the desired accuracy in [1] and we consider the present work as a continuation of [1]. Because of its importance for the present work we quote Theorem 1 from [1] which we are going to use here as a separate theorem.

Theorem 2. *Fix $\underline{Z}$, $\underline{R}$ and let γ be the 1-particle density matrix of a μ-approximate ground state $\psi_N \in D_N$ of H_N,* i.e. $\langle \psi_N | H_N \psi_N \rangle \leqq E_Q(N) + \mu$. *Then for any $0 < \delta < 1/12$ it holds*

$$|E_Q(N) - E_{\mathrm{HF}}(N)| \leqq d_\delta Z N^{2/3} \left(\frac{\mathrm{tr}_1\{\gamma - \gamma^2\}}{Z} \right)^{1/3 - \delta} + \mu \,, \tag{10}$$

where $d_\delta := 828 \delta^{-1/3} m^{2/3}$.

In the atomic case, i.e. $K = 1$ with $N \geqq Z$, ρ_{TF} is radially symmetric and the eigenvalue problem for h_{TF} is even one-dimensional. However, the desired accuracy $Z^{5/3-\delta}$ for $\mathrm{tr}_1\{h_{\mathrm{TF}} P_N\}$ and $D(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}})$ requires a quite delicate WKB-analysis of h_{TF}, which is interesting in its own right, but shall not concern us here. This analysis has been carried out by Fefferman and Seco [5] and we simply quote their claim (B) (p. 7) in [6] to supplement Theorem 1 in the atomic case: For $\rho' := \rho[\chi_{(-\infty, 0)}(h_{\mathrm{TF}})]$ and some $\delta > 0$ it holds

$$D(\rho' - \rho_{\mathrm{TF}}, \rho' - \rho_{\mathrm{TF}}) = O(Z^{5/3-\delta}) \,. \tag{11}$$

Fefferman and Seco also established Theorem 1 in [6] for atoms with $E_Q(N)$ replaced by $\inf_N E_Q(N)$, but their method is completely different from ours. We will prove this fact as a corollary of Theorem 1.

Corollary 1. *Consider an atom,* i.e. $K = 1$. *There exists $c_\delta > 0$ for any $0 < \delta < 2/231$ such that*

$$\begin{aligned} -c_\delta K^2 \cdot Z^{5/3-\delta} &\leqq \inf_N E_Q(N) - \left\{ \mathrm{tr}_1\{[h_{\mathrm{TF}}]_-\} - \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - c_D \int d^3x \rho_{\mathrm{TF}}^{4/3}(x) \right\} \\ &\leqq c_\delta K^2 \cdot Z^{5/3-\delta} + \frac{1}{2} D(\rho' - \rho_{\mathrm{TF}}, \rho' - \rho_{\mathrm{TF}}) \,, \end{aligned} \tag{12}$$

where ϕ_{TF} is the neutral TF*-potential, ρ_{TF} is the neutral* TF*-density and $\rho' := \rho[\chi_{(-\infty, 0)}(h_{\mathrm{TF}})]$.*

This corollary follows if we set $N := Z + Z^{1-2/77}$ in Theorem 1, because it is known that $E_Q(N) = \inf_N E_Q(N)$ for $N \geqq Z + cZ^{1-9/56}$ [4, 15], and that $P_N = \chi_{(-\infty, 0)}[h_{\mathrm{TF}}]$ for $N \geqq Z + cZ^{2/3}$ [7].

Moreover, Fefferman and Seco compute

$$\mathrm{tr}_1\{[h_{\mathrm{TF}}]_-\} = E_{\mathrm{TF}}(1, 1) Z^{7/3} + \frac{m}{8} Z^2 + \frac{2}{9} c_D \| \rho_{\mathrm{TF}} \|_{4/3}^{4/3} + O(Z^{5/3-\delta}) \tag{13}$$

in the case of the neutral TF-atom. This justifies a claim of Schwinger [14] who predicted the total contribution in order $Z^{5/3}$ to the ground state energy of a neutral atom to be given by $\frac{11}{9} c_D \| \rho_{\mathrm{TF}} \|_{4/3}^{4/3}$, for in this case $\| \rho_{\mathrm{TF}} \|_{4/3}^{4/3} = cZ^{5/3}$ follows from scaling and $Z \leqq N \leqq Z + cZ^{2/3}$ is still considered "neutral."

This paper is organized as follows. In Sect. 2 we reformulate the Hartree–Fock- and Mean Field approximation in terms of one-particle density matrices. In Sect. 3 we derive an abstract estimate on the error term in Theorem 1, which is estimated semiclassically in Sect. 4. For this semiclassical estimate we use a coherent state method rather than invoking a result of Ivrii and Sigal [9]. This is for two reasons; first it illustrates that leading order asymptotics suffice to make our method work. And secondly, it enables us to trace back the exchange correction to the one proposed by Dirac [2] in Sect. 5. Finally, the proof of Theorem 1 is given at the end of Sect. 5.

2. One-Particle Density Matrices

We set

$$h := -\Delta - \sum_{j=1}^{K} \frac{Z_j}{|x - R_j|}, \quad V := \frac{1}{|x - y|}, \tag{14}$$

on $D := H^2(\mathbb{R}^3) \otimes \mathbb{C}^m \subseteq \mathscr{H}$ and $D \otimes D$, respectively, and write

$$H_N = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i \neq j} V_{ij}, \tag{15}$$

the indices specifying the components in $\bigotimes_{i=1}^{N} D$ the operators act on. For a normalized Slater determinant $\phi_N := (N!)^{-1/2} \sum_\pi (-1)^\pi \chi_{\pi(1)} \otimes \cdots \otimes \chi_{\pi(N)} \in D_N$ we compute

$$\langle \phi_N | H_N \phi_N \rangle = \mathrm{tr}_1 \{ h \gamma_\phi \} + \frac{1}{2} \mathrm{tr}_2 \{ V(1 - Ex)(\gamma_\phi \otimes \gamma_\phi) \} =: \varepsilon_{\mathrm{HF}}(\gamma_\phi), \tag{16}$$

where $\gamma_\phi := \sum_{i=1}^{N} |\chi_i\rangle\langle\chi_i|$ and $Ex := \sum_{i,j} |\varphi_i \otimes \varphi_j\rangle\langle\varphi_j \otimes \varphi_i|$ for any ON-basis $\{\varphi_i\}_{i \in \mathbb{N}}$ in $\mathscr{H}$. Conversely, a given $\gamma = \gamma^\dagger = \gamma^2$, $\mathrm{tr}_1\{\gamma\} = N$ can be associated with the normalized Slater determinant ϕ_N built from its eigenfunctions: $\gamma = \gamma_\phi$. The Hartree–Fock energy, i.e. the infimum of all the expectation values of the form (16), may thus be rewritten as

$$E_{\mathrm{HF}}(N) = \inf \{ \varepsilon_{\mathrm{HF}}(\gamma) \,|\, \gamma = \gamma^\dagger = \gamma^2, \mathrm{tr}_1\{\gamma\} = N, \mathrm{tr}_1\{h\gamma\} < \infty \}. \tag{17}$$

By Lieb's variational principle [12, 1], we may weaken $\gamma = \gamma^\dagger = \gamma^2$ to $0 \leqq \gamma \leqq 1$ and by weak lower semicontinuity [16] $\mathrm{tr}_1\{\gamma\} = N$ to $\mathrm{tr}_1\{\gamma\} \leqq N$ in (17), so

$$E_{\mathrm{HF}}(N) = \inf \{ \varepsilon_{\mathrm{HF}}(\gamma) \,|\, 0 \leqq \gamma \leqq 1, \mathrm{tr}_1\{\gamma\} \leqq N, \mathrm{tr}_1\{h\gamma\} < \infty \}. \tag{18}$$

We rewrite the Mean Field energy in a similar fashion. Define $0 \leqq d_{\mathrm{TF}} \leqq N$ on $\mathscr{H}$ by the integral kernel $d_{\mathrm{TF}}(x, \sigma | x', \sigma') := q^{-1} \delta_{\sigma\sigma'} \rho_{\mathrm{TF}}^{1/2}(x) \rho_{\mathrm{TF}}^{1/2}(y)$, so its diagonal summed over the spin variable equals ρ_{TF}. Then we obtain

$$E_{\mathrm{MF}}(N)=\mathrm{tr}_1\{hP_N\}+\mathrm{tr}_2\{V(d_{\mathrm{TF}}\otimes P_N)\}-\frac{1}{2}\mathrm{tr}_2\{V(d_{\mathrm{TF}}\otimes d_{\mathrm{TF}})\}-c_D\int d^3x\,\rho_{\mathrm{TF}}^{4/3}(x)$$
$$=:\tilde{E}_{\mathrm{MF}}(N)-\left[c_D\int d^3x\,\rho_{\mathrm{TF}}^{4/3}(x)-\frac{1}{2}\mathrm{tr}_2\{VEx(P_N\otimes P_N)\}\right]. \tag{19}$$

This notation makes the following lemmata completely transparent.

Lemma 1. *Let* $0\leqq\gamma\leqq 1$, $\mathrm{tr}_1\{\gamma\}\leqq N$ *and* $\mathrm{tr}_1\{h\gamma\}<\infty$. *Then*

$$\varepsilon_{\mathrm{HF}}(\gamma)\geqq\tilde{E}_{\mathrm{MF}}(N)-\frac{1}{2}\mathrm{tr}_2\{VEx(\gamma\otimes\gamma-P_N\otimes P_N)\}. \tag{20}$$

Proof.

$$\varepsilon_{\mathrm{HF}}(\gamma)+\frac{1}{2}\mathrm{tr}_2\{VEx(\gamma\otimes\gamma)\}=\mathrm{tr}_1\{h\gamma\}+\frac{1}{2}\mathrm{tr}_2\{V(\gamma\otimes\gamma)\}$$
$$\geqq\mathrm{tr}_1\{h\gamma\}+\mathrm{tr}_2\{V(d_{\mathrm{TF}}\otimes\gamma)\}-\frac{1}{2}\mathrm{tr}_2\{V(d_{\mathrm{TF}}\otimes d_{\mathrm{TF}})\}$$
$$=\mathrm{tr}_1\{h_{\mathrm{TF}}\gamma\}-\frac{1}{2}\mathrm{tr}_2\{V(d_{\mathrm{TF}}\otimes d_{\mathrm{TF}})\}$$
$$\geqq\tilde{E}_{\mathrm{MF}}(N)+\frac{1}{2}\mathrm{tr}_2\{VEx(P_N\otimes P_N)\}.\ \blacksquare \tag{21}$$

A similar estimate in the opposite direction is as follows.

Lemma 2.

$$E_{\mathrm{HF}}(N)\leqq\tilde{E}_{\mathrm{MF}}(N)+\frac{1}{2}D(\rho_N-\rho_{\mathrm{TF}},\rho_N-\rho_{\mathrm{TF}}). \tag{22}$$

Proof. We estimate

$$E_{\mathrm{HF}}\leqq\varepsilon_{\mathrm{HF}}(P_N)$$
$$=\mathrm{tr}_1\{hP_N\}+\frac{1}{2}\mathrm{tr}_2\{V(1-Ex)(P_N\otimes P_N)\}$$
$$\leqq\mathrm{tr}_1\{h_{\mathrm{TF}}P_N\}+\frac{1}{2}\mathrm{tr}_2\{V[(P_N-d_{\mathrm{TF}})\otimes(P_N-d_{\mathrm{TF}})]\}$$
$$-\frac{1}{2}\mathrm{tr}_2\{VEx(P_N\otimes P_N)\}. \tag{23}$$

Here enters $\mathrm{tr}_1\{P_N\}\leqq N$. $\blacksquare$

3. Exchange Estimates

From Lemmas 1 and 2 we see that the error bound in Theorem 1 essentially asserts the smallness of

$$\frac{1}{2}\mathrm{tr}_2\{VEx(\gamma\otimes\gamma-P_N\otimes P_N)\}, \tag{24}$$

provided $\varepsilon_{\mathrm{HF}}(\gamma) - E_{\mathrm{HF}}(N)$ is small enough, and

$$\frac{1}{2}\mathrm{tr}_2\{VEx(P_N \otimes P_N)\} = c_D \int \rho_{\mathrm{TF}}^{4/3}(x) d^3x \ . \tag{25}$$

We estimate the above quantities by means of the following lemma.

Lemma 3. *Let $0 \leqq a, b \leqq 1$, $\mathrm{tr}_1\{a\}, \mathrm{tr}_1\{b\} < \infty$ and $X = X^2$ be bounded self-adjoint operators on $\mathscr{H}$. Then*

$$|\mathrm{tr}_2\{(X \otimes X)Ex(a \otimes a - b \otimes b)\}| \leqq (\mathrm{tr}_1\{X(a-b)^2\})^{1/2} \cdot \min\{(2\mathrm{tr}_1\{X(a+b)\})^{1/2}, \mathrm{tr}_1\{X(a+b)\}\} \ . \tag{26}$$

Proof. Let E, F be trace class and $\{\varphi_i\}_{i \in \mathbb{N}}$ an ON-basis in $\mathscr{H}$. Then

$$\begin{aligned} \mathrm{tr}_2\{Ex(E \otimes F)\} &= \sum_{i,j=1}^{\infty} \langle \varphi_i \otimes \varphi_j | (E \otimes F) \varphi_j \otimes \varphi_i \rangle \\ &= \sum_{i,j=1}^{\infty} \langle \varphi_i | E | \varphi_j \rangle \langle \varphi_j | F | \varphi_i \rangle = \mathrm{tr}_1\{EF\} \ . \end{aligned} \tag{27}$$

Hence,

$$\begin{aligned} |\mathrm{tr}_2\{(X \otimes X)Ex(a \otimes a - b \otimes b)\}| &= |\mathrm{tr}_1\{aXaX - bXbX\}| \\ &= |\mathrm{tr}_1\{(a-b)X(a+b)X\}| \\ &= |\mathrm{tr}_1\{(a-b)X[X(a+b)X]\}| \\ &\leqq (\mathrm{tr}_1\{X(a-b)^2\})^{1/2}(\mathrm{tr}_1\{[X(a+b)X]^2\})^{1/2} \ . \end{aligned} \tag{28}$$

Observe that $0 \leqq XFX \leqq 2$ implies

$$\mathrm{tr}_1\{[XFX]^2\} \leqq 2\mathrm{tr}_1\{XFX\} = 2\mathrm{tr}_1\{XF\} \ . \tag{29}$$

On the other hand,

$$\mathrm{tr}_1\{[XFX]^2\} \leqq (\mathrm{tr}_1\{XFX\})^2 \ , \tag{30}$$

because of $0 \leqq XFX$. This, inserted in (28) proves the assertion. ∎

Patterned after Lemma 5 in [1], we can exploit Lemma 3 to show

Lemma 4. *Let $0 \leqq a, b \leqq 1$, $\mathrm{tr}_1\{a\}, \mathrm{tr}_1\{b\} < \infty$ be bounded self-adjoint operators on $\mathscr{H}$. Then, for any $\varepsilon > 0$,*

$$|\mathrm{tr}_2\{(VEx(a \otimes a - b \otimes b)\}| \leqq C_\varepsilon \left(\frac{\mathrm{tr}_1\{(a-b)^2\}}{\mathrm{tr}_1\{a+b\}} \right)^{1/2-\varepsilon} \|\rho[a+b]\|_1^{1/2} \, \|\rho[a+b]\|_{5/3}^{5/6} \ , \tag{31}$$

where $C_\varepsilon := \dfrac{1152(100\pi)^{1/3}}{3\pi 6^{1/3}} \varepsilon^{-1/2}$.

Proof. Using $X_{(r,z)} = X_{(r,z)}^{\dagger} = X_{(r,z)}^2 := \chi_{\{x \mid |x-z| \leqq r\}} \otimes 1(\sigma)$, we may decompose (see [3])

$$V = \frac{1}{\pi} \int d^3z \int_0^{\infty} \frac{dr}{r^5} (X_{(r,z)} \otimes X_{(r,z)}) \ . \tag{32}$$

An application of Lemma 3 then yields

$$\begin{aligned}
&|\mathrm{tr}_2\{VEx(a\otimes a-b\otimes b)\}|\\
&\leqq \frac{1}{\pi}\int d^3z \int_0^\infty \frac{dr}{r^5}|\mathrm{tr}_2\{(X_{(r,z)}\otimes X_{(r,z)})Ex(a\otimes a-b\otimes b)\}|\\
&\leqq \frac{1}{\pi}\int d^3z \int_0^\infty \frac{dr}{r^5}(\mathrm{tr}_1\{X_{(r,z)}(a-b)^2\})^{1/2}\\
&\quad\times \min\{(2\mathrm{tr}_1\{X_{(r,z)}(a+b)\})^{1/2},\ \mathrm{tr}_1\{X_{(r,z)}(a+b)\}\}\,. \qquad (33)
\end{aligned}$$

Observe that $\mathrm{tr}_1\{X_{(r,z)}d\}=\int_{|x-z|\leqq r}\rho[d](x)d^3x$. Denoting $\rho_-:=\rho[(a-b)^2]$ and $\rho_+:=\rho[a+b]$, the integrand on the right hand of (33) is bounded above by

$$\begin{aligned}
&\frac{1}{\pi}\int d^3z\left\{\int_0^{R(z)}\frac{dr}{r^5}\left(\int_{|x-z|\leqq r}\rho_-(x)d^3x\right)^{1/2}\left(\int_{|x-z|\leqq r}\rho_+(x)d^3x\right)\right.\\
&\left.\quad+2\int_{R(z)}^\infty\frac{dr}{r^5}\left(\int_{|x-z|\leqq r}\rho_-(x)d^3x\right)^{1/2}\left(\int_{|x-z|\leqq r}\rho_+(x)d^3x\right)^{1/2}\right\}, \qquad (34)
\end{aligned}$$

for any measurable choice of $R(z)$. We introduce the maximal function for $\rho\in L^1(\mathbb{R}^3)$ by

$$M[\rho](z):=\sup_{r>0}\left(\frac{4\pi r^3}{3}\right)^{-1}\int_{|x-z|\leqq r}\rho(x)d^3x\,. \qquad (35)$$

With the aid of the maximal functions $M_-:=M[\rho_-]$ and $M_+:=M[\rho_+]$, choosing $R(z):=4(4\pi M_+(z)/3)^{-1/3}$, we obtain the following upper bound on (34):

$$\begin{aligned}
&\left(\frac{4\pi}{3}\right)\int d^3zM_-^{1/2}(z)M_+^{1/2}(z)\left[\left(\frac{4\pi}{3}\right)^{1/2}M_+^{1/2}(z)\int_0^{R(z)}\frac{dr}{r^{1/2}}+2\int_{R(z)}^\infty\frac{dr}{r^2}\right]\\
&\leqq 3\left(\frac{4\pi}{3}\right)^{4/3}\int d^3zM_-^{1/2}(z)M_+^{5/6}(z)\\
&\leqq \frac{48}{\pi}\left(\frac{25}{2}\right)^{1/3}\varepsilon^{-1/2}\left(\int\rho_-(x)d^3x\right)^{1/2-\varepsilon}\|\rho_+\|_1^{\varepsilon}\cdot\|\rho_+\|_{5/3}^{5/6}\,. \qquad (36)
\end{aligned}$$

To get the last inequality, we applied successively the Hölder-, the maximal- and again the Hölder inequality and assumed $0<\varepsilon<1/6$. This is very similar to (88)–(91) in [1]. ∎

The form of Lemma 4 is a little inconvenient and for the cases of interest may easily be reduced to

Lemma 5. *Let* $0\leqq a,b\leqq 1$ *be two self-adjoint operators on* $\mathscr{H}$ *with* $\mathrm{tr}_1\{b\}\leqq\mathrm{tr}_1\{a\}=N<\infty$ *and* $\mathrm{tr}_1\{ha\},\mathrm{tr}_1\{hb\}<0$. *Then there exists* $C\geqq 0$ *such that for all* $0<\varepsilon<1/6$,

$$|\mathrm{tr}_2\{VEx(a\otimes a-b\otimes b)\}|\leqq\frac{C}{\varepsilon^{1/2}}\left(\frac{\mathrm{tr}_1\{a(1-b)\}}{N}\right)^{1/2-\varepsilon}N^{2/3}Z\,. \qquad (37)$$

Proof. Using a kinetic energy bound of Lieb [10] (see also [1]), we derive $\|\rho[f]\|_{5/3}^{5/3}\leqq cZ^2\mathrm{tr}_1\{f\}$ from $0\leqq f\leqq 1$ and $\mathrm{tr}_1\{hf\}\leqq 0$. We insert this,

$(x+y)^p \leqq 2^p(x^p+y^p)$ for $x, y \geqq 0$, and

$$\mathrm{tr}_1\{(a-b)^2\} = \mathrm{tr}_1\{a^2+b^2-2ab\} \leqq 2N - 2\mathrm{tr}\{ab\} = 2\mathrm{tr}_1\{a(1-b)\} \quad (38)$$

into Lemma 4 and arrive at the upper bound in (37). The lower bound is similar. ∎

4. Bounds on Truncated Particle Numbers

In the preceding section we estimated the difference of exchange terms induced by 1-pdm, a, b in terms of a *truncated particle number* $\mathrm{tr}_1\{a(1-b)\}$. For large molecules we bound these quantities in the semiclassical limit. To this end we use a coherent state method similar to Lieb [11].

For a radial, normalized $g \in L^2(\mathbb{R}^3)$ we define $f_{pq}(z) := g(z-q)\exp(ipz)$. $f_{pq} \in L^2(\mathbb{R}^3)$ is normalized and we denote $f_{pq}^\sigma := f_{pq} \otimes \delta_{\sigma,\cdot} \in \mathscr{H}$, being normalized, as well. It is easy to see [11, 8] that weakly in $H^2(\mathbb{R}^3) \otimes \mathbb{C}^m$ and for $\phi \in L^{5/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ hold

$$\sum_{\sigma=1}^m \int \frac{d^3p\,d^3q}{(2\pi)^3} |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma| = 1, \quad \sum_{\sigma=1}^m \int \frac{d^3p\,d^3q}{(2\pi)^3} p^3 |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma| = -\Delta + \|\nabla g\|_2^2,$$

$$\sum_{\sigma=1}^m \int \frac{d^3p\,d^3q}{(2\pi)^3} \phi(q) |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma| = \phi * |g|^2, \quad (39)$$

$$\langle f_{pq}^\sigma| -\Delta |f_{pq}^\sigma\rangle = p^2 + \|\nabla g\|_2^2, \quad \langle f_{pq}^\sigma|\phi f_{pq}^\sigma\rangle = [\phi * |g|^2](q),$$

$$\langle f_{pq}^\sigma \otimes f_{\tilde{p}\tilde{q}}^{\tilde{\sigma}}| V(f_{pq}^\sigma \otimes f_{\tilde{p}\tilde{q}}^{\tilde{\sigma}})\rangle \leqq \frac{1}{|q-\tilde{q}|}. \quad (40)$$

We choose $g(x) := g_\lambda(x) = \lambda^{-3/2} g_1(x/\lambda)$, $g_1(x) := \pi^{-3/4}\exp(-x^2/2)$ and define a bounded operator $0 \leqq d_\lambda \leqq 1$ on $\mathscr{H}$ by

$$d_\lambda := \sum_{\sigma=1}^m \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q) |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma|, \quad (41)$$

where $M(p,q) := \Theta[\mu - h_{\mathrm{TF}}(p,q)]$, $h_{\mathrm{TF}}(p,q) := p^2 - \phi_{\mathrm{TF}}$. Note that, via the TF-equation [11],

$$[\phi_{\mathrm{TF}}(q) - \mu]_+ = \left(\frac{6\pi^2}{m}\right)^{2/3} \rho_{\mathrm{TF}}^{2/3}(q) \quad (42)$$

away from the nuclei. Then

$$\sum_{\sigma=1}^m \int \frac{d^3p}{(2\pi)^3} M(p,q) = \rho_{\mathrm{TF}}(q) \quad (43)$$

and, thus, $\mathrm{tr}_1\{d_\lambda\} = \|\rho_{\mathrm{TF}}\|_1 = \min\{N, Z\}$. In what follows we will frequently use

$$\begin{aligned} 0 &\leqq \int d^3q \{\phi_{\mathrm{TF}}(q) - [\phi_{\mathrm{TF}} * |g_\lambda|^2](q)\}\rho(q) \\ &\leqq \int d^3q \sum_{j=1}^K \left\{\frac{Z_j}{|q-R_j|} - \int d^3x \frac{Z_j |g_\lambda(x-q)|^2}{|x-R_j|}\right\}\rho(q) \\ &\leqq cZ\lambda^{1/5}\|\rho\|_{5/3} \end{aligned} \quad (44)$$

for nonnegative $\rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$. The first two inequalities in (44) follow from a subharmonicity argument (see [11]) and the third from the Hölder- and Jensen inequality and the scaling properties of g_λ. Now, we prove the following lemma

Lemma 6. *Let* $0 \leqq \gamma \leqq 1$, $\mathrm{tr}_1\{h\gamma\} \leqq 0$ *be either*

(i) *the* 1-pdm $\gamma = \gamma_\psi$ *of a* $Z^{5/3}$*-approximate ground state* $\psi_N \in \mathscr{H}_N$, i.e. $\langle \psi_N | H_N \psi_N \rangle - E_Q(N) \leqq Z^{5/3}$, *or*
(ii) $\gamma = \gamma_\phi$ *for a Slater determinant* $\phi_N \in SD_N$ *and* $\varepsilon_{\mathrm{HF}}(\gamma) - E_{\mathrm{HF}}(N) \leqq Z^{5/3}$, *or*
(iii) $\gamma = P_N$.

Then

$$\mathrm{tr}_1\{h_{\mathrm{TF}}\gamma\} \leqq m \int \frac{d^3p\, d^3q}{(2\pi)^3} h_{\mathrm{TF}}(p,q) M(p,q) + c(Z^{5/3} + Z\lambda^{-2} + Z^{12/5}\lambda^{1/5}) \,. \quad (45)$$

Proof. Both in case (i) and (ii) we apply the Lieb–Oxford inequality [13]

$$\left\langle \psi_N \middle| \left(\sum_{i \neq j} \frac{1}{|x_i - x_j|} \right) \psi_N \right\rangle \geqq D(\rho[\gamma_\psi], \rho[\gamma_\psi]) - 1.68 \int d^3x\, \rho[\gamma_\psi]^{4/3}(x) \,. \quad (46)$$

This gives us

$$\begin{aligned} \mathrm{tr}_1\{h_{\mathrm{TF}}\gamma_\psi\} &\leqq \mathrm{tr}_1\{h\gamma_\psi\} + \frac{1}{2} D(\rho[\gamma_\psi], \rho[\gamma_\psi]) + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\ &\leqq \langle \psi_N | H_N \psi_N \rangle + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\ &\quad + c \, \| \rho[\gamma_\psi] \|_1^{1/2} \, \| \rho[\gamma_\psi] \|_{5/3}^{5/6} \,. \end{aligned} \quad (47)$$

For both (i) and (ii) $\mathrm{tr}_1\{h\gamma\} \leqq 0$ implies $\| \rho[\gamma] \|_{5/3}^{5/3} \leqq cZ^{7/3}$ (see [11, 1]). This yields

$$\mathrm{tr}_1\{h_{\mathrm{TF}}\gamma_\psi\} \leqq E_{\mathrm{HF}}(N) + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) + cZ^{5/3} \,. \quad (48)$$

Now, by (40) and (44)

$$\begin{aligned} &E_{\mathrm{HF}}(N) + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\ &\leqq \mathrm{tr}_1\{h d_\lambda\} + \frac{1}{2} \mathrm{tr}_2\{V(d_\lambda \otimes d_\lambda)\} + \frac{1}{2} D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\ &\leqq m \int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q) \left(p^2 + \| \nabla g_\lambda \|_2^2 - \sum_{j=1}^{K} \int d^3x \frac{Z_j |g_\lambda(x-q)|^2}{|x - R_j|} \right) \\ &\quad + D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \\ &\leqq m \int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q) (p^2 - \phi_{\mathrm{TF}}(q)) + cZ\lambda^{1/5} \| \rho_{\mathrm{TF}} \|_{5/3} \\ &\quad + N \| \nabla g_\lambda \|_2^2 \,. \end{aligned} \quad (49)$$

Inserting $\|\rho_{\mathrm{TF}}\|_{5/3} \leqq cZ^{7/5}$ and $\|\nabla g_\lambda\|_2^2 \leqq c\lambda^{-2}$ gives (45) in Case (i) and (ii). In Case (iii) we observe

$$\begin{aligned}\mathrm{tr}_1\{h_{\mathrm{TF}} P_N\} &\leqq \mathrm{tr}_1\{h_{\mathrm{TF}} d_\lambda\} \\ &\leqq m \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q)(p^2 + \|\nabla g_\lambda\|_2^2 - [\phi_{\mathrm{TF}} * |g_\lambda|^2](q)) \\ &\leqq m \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q)(p^2 - \phi_{\mathrm{TF}}(q)) \\ &\quad + cZ^{12/5}\lambda^{1/5} + cZ\lambda^{-2}\,, \end{aligned} \tag{50}$$

using (44) again. ∎

We define $F(\lambda) := Z^{5/3} + Z\lambda^{-2} + Z^{12/5}\lambda^{1/5}$. Now we derive a bound on $\mathrm{tr}_1\{d_\lambda(1-\gamma)\}$ in all the three above cases by (45).

Lemma 7. *Let* $0 \leqq \gamma \leqq 1$, $\mathrm{tr}_1\{h\gamma\} \leqq 0$, $\mathrm{tr}_1\{\gamma\} \leqq N$ *fulfill*

$$\mathrm{tr}_1\{h_{\mathrm{TF}}\gamma\} \leqq m \int \frac{d^3p\,d^3q}{(2\pi)^3} h_{\mathrm{TF}}(p,q) M(p,q) + cF(\lambda)\,. \tag{51}$$

Then

$$\mathrm{tr}_1\{d_\lambda(1-\gamma)\} \leqq cKF^{3/7}(\lambda)\,. \tag{52}$$

Proof. For any $E > 0$ we have

$$\begin{aligned}\mathrm{tr}_1\{d_\lambda(1-\gamma)\} &= \sum_{\sigma=1}^{m} \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q)\langle f_{pq}^\sigma|(1-\gamma) f_{pq}^\sigma\rangle \\ &\leqq m \int_{-\mu \geqq h_{\mathrm{TF}}(p,q) \geqq -\mu - E} \frac{d^3p\,d^3q}{(2\pi)^3} \\ &\quad + \frac{1}{E}\sum_{\sigma=1}^{m} \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q)[-h_{\mathrm{TF}}(p,q)]\langle f_{pq}^\sigma|(1-\gamma) f_{pq}^\sigma\rangle \\ &\leqq m \int_{-\mu \geqq h_{\mathrm{TF}}(p,q) \geqq -\mu - E} \frac{d^3p\,d^3q}{(2\pi)^3} \\ &\quad + \frac{1}{E}\Bigg\{\mathrm{tr}_1\{h_{\mathrm{TF}}\gamma\} - m\int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q) h_{\mathrm{TF}}(p,q) \\ &\quad + N\|\nabla g_\lambda\|_2^2 + \int d^3q(\phi_{\mathrm{TF}}(q) - [\phi_{\mathrm{TF}} * |g_\lambda|^2](q))\rho[\gamma](q)\Bigg\}\,. \end{aligned} \tag{53}$$

By (44), $\|\nabla g_\lambda\|_2^2 \leqq c\lambda^{-2}$, $\|\rho[\gamma]\|_{5/3}^{5/3} \leqq cZ^{7/3}$ and (51), this gives

$$\mathrm{tr}_1\{d_\lambda(1-\gamma)\} \leqq m \int_{-\mu \geqq h_{\mathrm{TF}}(p,q) \geqq -\mu - E} \frac{d^3p\,d^3q}{(2\pi)^3} + \frac{c}{E} F(\lambda)\,. \tag{54}$$

We distinguish $N \geqq Z$ from $N < Z$. In the former case $\mu = 0$ and it was shown in [1] that

$$m \int_{0 \geqq h_{\mathrm{TF}}(p,q) \geqq -E} \frac{d^3p\,d^3q}{(2\pi)^3} \leqq cK^{7/4}E^{3/4}\,, \tag{55}$$

which, choosing $E := K^{-1}F^{4/7}(\lambda)$, leads us to (52). Actually, (55) required $E = o(Z^{4/3})$, but if $E \geqq cZ^{4/3}$ then (55) is trivial anyway.

If $N < Z$ we emphasize $\phi_{\mathrm{TF},N}(q) := \phi_{\mathrm{TF}}(q)$, $\mu_N := \mu$ and $\rho_{\mathrm{TF},N}(q) := \rho_{\mathrm{TF}}(q)$. From TF-theory follows [11] $[\phi_{\mathrm{TF},N}(q) - \mu_N]_+ = \alpha\rho_{\mathrm{TF},N}^{2/3}(q) \leqq \alpha\rho_{\mathrm{TF},Z}^{2/3}(q) = \phi_{\mathrm{TF},Z}(q)$, with $\alpha := (6\pi^2 m^{-1})^{2/3}$. Thus

$$
\begin{aligned}
m & \int_{-\mu \geqq h_{\mathrm{TF}}(p,q) \geqq -\mu - E} \frac{d^3p\,d^3q}{(2\pi)^3} \\
&= \frac{m}{6\pi^2} \int_{\phi_{\mathrm{TF},N} \geqq \mu_N} d^3q \{[\phi_{\mathrm{TF},N}(q) - \mu_N]_+^{3/2} - [(\phi_{\mathrm{TF},N}(q) - \mu_N)_+ - E]_+^{3/2}\} \\
&\leqq \frac{m}{6\pi^2} \int d^3q \{\phi_{\mathrm{TF},Z}(q)^{3/2} - [\phi_{\mathrm{TF},Z}(q) - E]_+^{3/2}\} \\
&\leqq cK^{7/4}E^{3/4}\,, \qquad (56)
\end{aligned}
$$

again, by (55). ∎

5. The Dirac Exchange Correction

In this section we link the exchange term induced by d_λ with the Dirac exchange correction $c_D \|\rho_{\mathrm{TF}}\|_{4/3}^{4/3}$ (see [2, 14]). Recall from the last section we may represent the 1-pdm d_λ by its integral kernel

$$
d_\lambda(x, \mu | y, \nu) := \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p, q) g_\lambda(x - q) g_\lambda(y - q) e^{ip(x-y)} \delta_{\mu\nu}\,. \qquad (57)
$$

The exchange term induced by d_λ reads

$$
W_{ex} := \mathrm{tr}_2\{V Ex(d_\lambda \otimes d_\lambda)\} = \frac{m}{2} \int \frac{d^3x\,d^3y}{|x - y|} |d_\lambda(x|y)|^2\,, \qquad (58)
$$

where $d_\lambda(x|y) := d_\lambda(x, \mu|y, \mu)$. Our specific choice of g_λ allows us to compute the right hand of (58) almost explicitly. It requires a tedious integration and the result is

Lemma 8.

$$
\begin{aligned}
&\left|\frac{1}{2}\mathrm{tr}_2\{V Ex(d_\lambda \otimes d_\lambda)\} - c_D \int d^3x\, \rho_{\mathrm{TF}}^{4/3}(x)\right| \\
&\qquad \leqq c_\nu K^2 [Z\lambda^{-1} + Z^2 \ln(Z)(\lambda + Z^{-1/3-\nu})] \qquad (59)
\end{aligned}
$$

for any $\nu > 0$.

Proof. We start with a change of variables $2s := x + y$, $2r := x - y$. Moreover, we observe $g_\lambda(z + r) g_\lambda(z - r) = g_\lambda^2(z) \cdot \exp(-r^2/\lambda^2)$. Hence, abbreviating $p_f(q) := [\phi_{\mathrm{TF}}(q) - \mu]_+^{1/2} = (6\pi^2 m^{-1})^{1/3} \rho_{\mathrm{TF}}^{1/3}(q)$,

$$
\begin{aligned}
W_{ex} &= 2m \int \frac{d^3s\,d^3r}{|r|} e^{-r^2/\lambda^2} \left| \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p, s + q) g_\lambda^2(q) e^{2i\vec{p}\cdot\vec{r}} \right|^2 \\
&= 2m \int d^3s \int \frac{d^3q\,d^3\tilde{q}}{(2\pi)^6} g_\lambda^2(q) g_\lambda^2(\tilde{q}) \int_0^{p_f(s+q)} p^2\,dp \int_0^{p_f(s+\tilde{q})} \tilde{p}^2\,d\tilde{p} \\
&\quad \times \int_0^\infty r e^{-r^2/\lambda^2}\,dr \int d\Omega_p\,d\Omega_{\tilde{p}}\, 2\pi \int_{-1}^{1} dx \exp(2i|\vec{p} - \vec{\tilde{p}}|rx)\,. \qquad (60)
\end{aligned}
$$

Here, we wrote $\vec{x}$ whenever necessary to distinguish it from $|\vec{x}|$. We observe

$$\int d\Omega_p d\Omega_{\tilde{p}} 2\pi \int_{-1}^{1} dx \exp(2i|\vec{p} - \vec{\tilde{p}}|rx) = \frac{2(2\pi)^3}{p\tilde{p}r^2} \sin(2rp)\sin(2r\tilde{p}) . \tag{61}$$

This yields

$$W_{ex} = \frac{4m}{(2\pi)^3} \int d^3 s \int_0^\infty dr \frac{e^{-r^2/\lambda^2}}{r} \left(\int d^3 q\, g_\lambda^2(q) \int_0^{p_f(s+q)} p \sin(2rp) dp \right)^2 . \tag{62}$$

Defining

$$\varepsilon_1 := \frac{4m}{(2\pi)^3} \int d^3 s \int_0^\infty dr \frac{e^{-r^2/\lambda^2}}{r} \int d^3 q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q})$$

$$\left(\int_0^{p_f(s+q)} p \sin(2rp) dp - \int_0^{p_f(s+\tilde{q})} p \sin(2rp) dp \right)^2 \tag{63}$$

and

$$\varepsilon_2 := \frac{4m}{(2\pi)^3} \int d^3 s\, p_f^{4/3}(s) \int_0^\infty \frac{[\sin(r) - r\cos(r)]^2 dr}{r^5} \left[1 - \exp\left(- \frac{r^2}{2p_f^2(s)\lambda^2} \right) \right], \tag{64}$$

we can extract the leading part from W_{ex};

$$W_{ex} = \frac{4m}{(2\pi)^3} \left(\int_0^\infty \frac{[\sin(r) - r\cos(r)]^2}{r^5} dr \right) \int p_f^4(s) d^3 s - \varepsilon_1 - \varepsilon_2$$

$$= c_D \int \rho_{\mathrm{TF}}^{4/3}(x) d^3 x - \varepsilon_1 - \varepsilon_2 . \tag{65}$$

It remains to estimate $\varepsilon_1, \varepsilon_2 \geqq 0$. We start with ε_2. Using $1 - e^{-\alpha^2} \leqq \alpha^2 e^{-\alpha^2}$, we get for $f(x) \geqq 0$,

$$\int_0^\infty f(x)(1 - e^{-x^2/a^2}) dx \leqq \frac{1}{a^2} \left(\int_0^\infty \frac{f(x)\,dx}{x} \right)^{1/2} \left(\int_0^\infty x e^{-x^2/a^2} dx \right)^{1/2}$$

$$\leqq \frac{c}{a} \left(\int_0^\infty \frac{f(x)\,dx}{x} \right)^{1/2} . \tag{66}$$

This, inserted in (64), yields

$$\varepsilon_2 \leqq \frac{c}{\lambda} \int p_f^3(s) d^3 s \leqq \frac{cZ}{\lambda} . \tag{67}$$

The estimate on ε_1 is more delicate. We use

$$\left(\int_{2rp_f}^{2r\tilde{p}_f} p \sin(p) dp \right)^2 \leqq \frac{64 r^6}{9} (p_f^3 - \tilde{p}_f^3)^2 \tag{68}$$

for small $r > 0$ and

$$[\sin(2rp_f) - 2rp_f \cos(2rp_f) - \sin(2r\tilde{p}_f) + 2r\tilde{p}_f \cos(2r\tilde{p}_f)]^2 \leqq cr^2 [p_f + \tilde{p}_f]^2 \tag{69}$$

for large $r > 0$, denoting $p_f := p_f(s + q)$, $\tilde{p}_f := p_f(s + \tilde{q})$. Therefore, for any measurable choice of $R = R(s, q, \tilde{q})$,

$$\varepsilon_1 \leqq c \int d^3 s \int d^3 q\, g_\lambda^2(q)\, d^3 \tilde{q}\, g_\lambda^2(\tilde{q}) \left[(p_f^3 - \tilde{p}_f^3) R^2 + \frac{(p_f + \tilde{p}_f)^2}{R^2} \right] . \tag{70}$$

We optimize by choosing $R := (p_f + \tilde{p}_f)|p_f^3 - \tilde{p}_f^3|^{-1}$. Furthermore, we apply $(a + b)|a^3 - b^3| \leqq 2|a^4 - b^4|$ which holds for $a, b \geqq 0$ and obtain

$$\varepsilon_1 \leqq c \int d^3s \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) |p_f^4 - \tilde{p}_f^4| \,. \tag{71}$$

We pause to motivate the next step. We would like to estimate

$$|p_f^4(s + q) - p_f^4(s + \tilde{q})| \leqq \int_q^{\tilde{q}} |\nabla p_f^4(s + s')| ds' \,, \tag{72}$$

where s' is on the straight line between q and $\tilde{q}$. Then

$$\begin{aligned}
\varepsilon_1 &\leqq c \int d^3s \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} |\nabla p_f^4(s + s')| ds' \\
&\leqq c \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} \left(\int d^3s |\nabla p_f^4(s + s')| \right) ds' \\
&\leqq c \left(\int |\nabla p_f^4(s)| d^3s \right) \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) |q - \tilde{q}| \\
&\leqq c \|\nabla p_f^4\|_1 \cdot \lambda \,.
\end{aligned} \tag{73}$$

The trouble with this estimate is that $|\nabla p_f^4| \notin L^1(\mathbb{R}^3)$, due to singularities at R_j. To overcome this difficulty we have to cut out the region around the nuclei.

To this end, we introduce a cut-off $p_0 > 0$:

$$\begin{aligned}
|p_f^4 - \tilde{p}_f^4| \leqq\; & \Theta[p_0 - p_f]\Theta[p_0 - \tilde{p}_f] \cdot |p_f^4 - \tilde{p}_f^4| + 2\Theta[p_f - p_0] \cdot p_f^4 \\
& + 2\Theta[\tilde{p}_f - p_0] \cdot \tilde{p}_f^4 \,.
\end{aligned} \tag{74}$$

Hence

$$\begin{aligned}
\varepsilon_1 \leqq\; & c \int d^3s \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) \Theta[p_0 - p_f]\Theta[p_0 - \tilde{p}_f] |p_f^4 - \tilde{p}_f^4| \\
& + c \int d^3s \int d^3q\, g_\lambda^2(q) \Theta[p_f - p_0] p_f^4 \,.
\end{aligned} \tag{75}$$

Now, we estimate

$$|p_f^4(s + q) - p_f^4(s + \tilde{q})| \leqq \int_q^{\tilde{q}} |\nabla p_f^4(s + s')| ds' \,, \tag{76}$$

where we assume the path $s + s' \notin A := \{x \in \mathbb{R}^3 | p_f(x) > p_0\}$ and to be of shortest possible length. We choose $p_0^2 := cZ^{4/3+\nu}$ for some $\nu > 0$ to be picked later. Then $A \subseteq \bigcup_{j=1}^K B_{Z^{-1/3-\nu}}(R_j)$, because $p_f^2(x) \leqq c\sum_{j=1}^K Z_j |x - R_j|^{-1}$. It follows

$$\int_q^{\tilde{q}} ds' \leqq |q - \tilde{q}| + KZ^{-1/3-\nu} \,. \tag{77}$$

We obtain

$$\begin{aligned}
\varepsilon_1 \leqq\; & c \int d^3s \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} |\nabla p_f^4(s + s')| \chi_{\mathbb{R}^3 \setminus A}(s + s') ds' + c \int_A p_f^4(s) d^3s \\
\leqq\; & c \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} \left(\int d^3s |\nabla p_f^4(s + s')| \chi_{\mathbb{R}^3 \setminus A}(s + s') \right) ds' \\
& + cKZ^2 \int_{|x| \leqq Z^{-1/3-\nu}} \frac{d^3x}{|x|^2}
\end{aligned}$$

$$\leqq c\left(\int_{\mathbb{R}^3\setminus A} |\nabla p_f^4(s)|\,d^3s\right)\left(KZ^{-1/3-\nu} + \int d^3q\, g_\lambda^2(q)\, d^3\tilde{q}\, g_\lambda^2(\tilde{q})|q-\tilde{q}|\right) + cKZ^{5/3-\nu}$$

$$\leqq c\,\|\chi_{\mathbb{R}^3\setminus A}\nabla p_f^4\|_1 (KZ^{-1/3-\nu} + \lambda) + cKZ^{5/3-\nu}\,. \tag{78}$$

We split up the remaining integral by means of $A' := \bigcup_{j=1}^K B_{Z^{-1/3}}(R_j)$;

$$\|\chi_{\mathbb{R}^3\setminus A}\nabla p_f^4\|_1 \leqq cKZ^2 \int_{(\mathbb{R}^3\setminus A)\cap A'} \sum_{j=1}^K \frac{d^3x}{|x-R_j|^3} + c\int_{A'} Z^{8/3}|\nabla p_{f,1}(Z^{1/3}x)|\,d^3x$$

$$\leqq c_\nu K^2 Z^2 \ln(Z) + cZ^2\,, \tag{79}$$

and we finally arrive at

$$\varepsilon_1 + \varepsilon_2 \leqq c_\nu K^2[Z\lambda^{-1} + Z^2\ln(Z)(\lambda + Z^{-1/3-\nu})]\,. \quad \blacksquare \tag{80}$$

Proof of Theorem 1. The first step of the proof consists in linking the quantum mechanical ground state energy $E_Q(N)$ with the Hartree–Fock energy $E_{\mathrm{HF}}(N)$. We invoke Theorem 2:

$$|E_Q(N) - E_{\mathrm{HF}}(N)| \leqq \frac{c}{\varepsilon^{1/3}}(\mathrm{tr}_1\{\gamma_\psi - \gamma_\psi^2\})^{1/3-\varepsilon} Z^{4/3+\varepsilon} \tag{81}$$

for $0 < \varepsilon < 1/12$ and γ_ψ being the 1-pdm of a $Z^{4/3}$-approximate ground state $\psi_N \in \mathscr{H}_N$ of H_N. From Lemma 1 and 2 we derive

$$-\frac{1}{2}\mathrm{tr}_2\{VEx(\gamma_{\mathrm{HF}}\otimes\gamma_{\mathrm{HF}} - P_N\otimes P_N)\} - Z^{4/3}$$

$$\leqq E_{\mathrm{HF}}(N) - \mathrm{tr}_1\{h_{\mathrm{TF}}P_N\} + \frac{1}{2}D(\rho_{\mathrm{TF}},\rho_{\mathrm{TF}}) - \frac{1}{2}\mathrm{tr}_2\{VEx(P_N\otimes P_N)\}$$

$$\leqq \frac{1}{2}D(\rho_N - \rho_{\mathrm{TF}}, P_N - \rho_{\mathrm{TF}}) \tag{82}$$

for any orthogonal projection $\gamma_{\mathrm{HF}} = \gamma_{\mathrm{HF}}^\dagger = \gamma_{\mathrm{HF}}^2$, $\mathrm{tr}_1\{\gamma_{\mathrm{HF}}\} = N$, with $\varepsilon_{\mathrm{HF}}(\gamma_{\mathrm{HF}}) - E_{\mathrm{HF}}(N) \leqq Z^{4/3}$. Now, we use Lemma 5 combined with the triangle inequality and find for any $\varepsilon \leqq 0$,

$$|\mathrm{tr}_2\{VEx(\gamma_{\mathrm{HF}}\otimes\gamma_{\mathrm{HF}} - P_N\otimes P_N)\}|$$

$$\leqq \frac{c}{\varepsilon^{1/2}}(\mathrm{tr}_1\{\gamma_{\mathrm{HF}}(1-d_\lambda)\} + \mathrm{tr}_1\{P_N(1-d_\lambda)\})^{1/2-\varepsilon} Z^{7/6+\varepsilon}$$

$$\leqq \frac{c}{\varepsilon^{1/2}}(\mathrm{tr}_1\{d_\lambda(1-\gamma_{\mathrm{HF}})\} + \mathrm{tr}_1\{d_\lambda(1-P_N)\} + Z^{1-2/77})^{1/2-\varepsilon} Z^{7/6+\varepsilon}\,. \tag{83}$$

Note that in the second inequality we used $N \leqq Z + Z^{1-2/77}$ and $\mathrm{tr}_1\{d_\lambda\} = \min\{N, Z\}$. Of course, this estimate holds for $|\mathrm{tr}_2\{VEx(d_\lambda\otimes d_\lambda - P_N\otimes P_N)\}|$, as well. Moreover, notice that

$$\mathrm{tr}_1\{\gamma_\psi - \gamma_\psi^2\} \leqq \mathrm{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \mathrm{tr}_1\{(1-d_\lambda)\gamma_\psi\} = 2\mathrm{tr}_1\{d_\lambda(1-\gamma_\psi)\}\,. \tag{84}$$

We insert (81), (83) and (84) into (82) and obtain for any $0 < \varepsilon < 1/12$,

$$\begin{aligned}
&\frac{c}{\varepsilon^{1/3}}(\mathrm{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \mathrm{tr}_1\{d_\lambda(1-\gamma_{\mathrm{HF}})\} \\
&\qquad + \mathrm{tr}_1\{d_\lambda(1-P_N)\} + Z^{1-2/77})^{1/3-\varepsilon} Z^{4/3+\varepsilon} \\
&\qquad \leqq E_Q(N) - \mathrm{tr}_1\{h_{\mathrm{TF}}P_N\} + \frac{1}{2}D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \frac{1}{2}\mathrm{tr}_2\{V Ex(d_\lambda \otimes d_\lambda)\} \\
&\qquad \leqq \frac{c}{\varepsilon^{1/3}}(\mathrm{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \mathrm{tr}_1\{d_\lambda(1-\gamma_{\mathrm{HF}})\} + Z^{1-2/77} \\
&\qquad\quad + \mathrm{tr}_1\{d_\lambda(1-P_N)\}\}^{1/3-\varepsilon} Z^{4/3+\varepsilon} \\
&\qquad\quad + \frac{1}{2}D(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}})\,.
\end{aligned} \tag{85}$$

In (85) exactly the three cases treated in Lemma 6 occur, which, therefore, fulfill the assumptions in Lemma 7 and imply the bound

$$\begin{aligned}
&\frac{c}{\varepsilon^{1/3}}K^{1/3}[Z^{7/3-2/33} + Z\lambda^2 + Z^{12/5}\lambda^{1/5}]^{1/7-\varepsilon}Z^{4/3+\varepsilon} \\
&\qquad \leqq E_Q(N) - \mathrm{tr}_1\{h_{\mathrm{TF}}P_N\} + \frac{1}{2}D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \frac{1}{2}\mathrm{tr}_2\{V Ex(d_\lambda \otimes d_\lambda)\} \\
&\qquad \leqq \frac{1}{2}D(\rho_N - \rho_{\mathrm{TF}}, \rho_N - \rho_{\mathrm{TF}}) \\
&\qquad\quad + \frac{c}{\varepsilon^{1/3}}K^{1/3}[Z^{7/3-2/33} + Z\lambda^2 + Z^{12/5}\lambda^{1/5}]^{1/7-\varepsilon}Z^{4/3+\varepsilon}\,.
\end{aligned} \tag{86}$$

The error term we pick up when replacing $\frac{1}{2}\mathrm{tr}_2\{V Ex(d_\lambda \otimes d_\lambda)\}$ by $c_D \int \rho_{\mathrm{TF}}^{4/3}$ is estimated in Lemma 8 and turns out to be small compared to the λ-dependent error term in (86). More precisely, Theorem 1 follows now from Lemma 8 and the choice $\lambda := Z^{-21/23}$ and $v := 10/33$. ∎

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