Accuracy of Mean Field Approximations for Atoms and Molecules

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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

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

acting as a self-adjoint operator on $D_N := \bigwedge_{i=1}^N \tilde{\mathcal{H}} \subseteq \mathcal{H}_N := \bigwedge_{i=1}^N \mathcal{H}$, $\mathcal{H} := L^2(I\!R^3) \otimes \mathbb{C}^m$, $\tilde{\mathcal{H}} := H^2(I\!R^3) \otimes \mathbb{C}^m$. 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

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

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

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

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 $\rho \in L^1(I\!R^3)$. 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

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

self-adjointly realized on D. By general arguments $\sigma_{ess}(h_{TF}) = [0,\infty)$ and $\sigma_{disc}(h_{TF}) \subseteq (-\infty, 0)$. Moreover, if $N \ge Z$ then the chemical potential $\mu = 0$ [11] and $|\sigma_{disc}(h_{TF})| < \infty$, whereas $\mu > 0$ and $|\sigma_{disc}(h_{TF})| = \infty$ for $N < Z$. We set $P_N := \chi_{(-\infty,0)}[h_{TF}]$ in case $\mathrm{tr}_1\{\chi_{(-\infty,0)}[h_{TF}]\} \le N$. 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 $\mathrm{tr}_1\{P_N\} \le N$. For any nonnegative trace class operator $d = \sum_i \lambda_i|\chi_i\rangle\langle\chi_i|$ on $\mathcal{H}$ 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, $1 \leq j \leq K$, with fixed ratios Z_j/Z, where $Z := \sum_{j=1}^K Z_j$ and $K \geq 1$. Let $N \leq Z + cZ^{1-2/77}$. Then for any $0 < \delta < 2/231$ there exists $c_\delta > 0$ such that*

$$\begin{aligned} -c_\delta K^2 \cdot Z^{5/3-\delta} \quad &\leq \quad E_Q(N) - \Big\{ \mathrm{tr}_1\{h_{TF} P_N\} - \frac{1}{2} D(\rho_{TF}, \rho_{TF}) \\ &\qquad - c_D \int d^3x \rho_{TF}^{4/3}(x) \Big\} \\ &\leq \quad c_\delta K^2 \cdot Z^{5/3-\delta} + \frac{1}{2} D(\rho_N - \rho_{TF}, \rho_N - \rho_{TF}) \ , \end{aligned} \tag{7}$$

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

The contribution $c_D \|\rho_{TF}\|_{4/3}^{4/3}$ 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

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

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

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

from the Hartree-Fock energy $E_{HF}(N)$ of the system, disregarding exchange corrections. The question how far $E_Q(N)$ then deviates from $E_{HF}(N)$ has already been settled within the desired accuracy in [1] and we consider the present work as a continuation of [1].

In the atomic case, i.e. $K = 1$ with $N \geq Z$, 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 $\mathrm{tr}_1\{h_{TF} P_N\}$ and $D(\rho_N - \rho_{TF}, \rho_N - \rho_{TF})$ 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 $\rho' := \rho[\chi_{(-\infty,0)}(h_{TF})]$ and some $\delta > 0$ it holds

$$D(\rho' - \rho_{TF}, \rho' - \rho_{TF}) = O(Z^{5/3-\delta}) \ . \tag{10}$$

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*

$$\begin{aligned} -c_\delta K^2 \cdot Z^{5/3-\delta} &\leq \inf_N E_Q(N) - \Big\{ \mathrm{tr}_1\{[h_{TF}]_-\} - \frac{1}{2} D(\rho_{TF}, \rho_{TF}) \\ &\qquad - c_D \int d^3x \rho_{TF}^{4/3}(x) \Big\} \\ &\leq c_\delta K^2 \cdot Z^{5/3-\delta} + \frac{1}{2} D(\rho' - \rho_{TF}, \rho' - \rho_{TF}) \ , \end{aligned} \tag{11}$$

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

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 $N \geq Z + cZ^{1-9/56}$ [4, 15], and that $P_N = \chi_{(-\infty,0)}[h_{TF}]$ for $N \geq Z + cZ^{2/3}$ [7].

Moreover, Fefferman and Seco compute

$$\mathrm{tr}_1\{[h_{TF}]_-\} = E_{TF}(1,1) Z^{7/3} + \frac{m}{8} Z^2 + \frac{2}{9} c_D \|\rho_{TF}\|_{4/3}^{4/3} + O(Z^{5/3-\delta}) \tag{12}$$

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 $\frac{11}{9} c_D \|\rho_{TF}\|_{4/3}^{4/3}$, for in this case $\|\rho_{TF}\|_{4/3}^{4/3} = cZ^{5/3}$ follows from scaling and $Z \leq N \leq Z + cZ^{2/3}$ is still considered "neutral".

This paper is organized as follows. In Section 2 we reformulate the Hartree-Fock- and Mean Field approximation in terms of one-particle density matrices. In Section 3 we derive an abstract estimate on the error term in Theorem 1, which is estimated semiclassically in Section 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 Section 5. Finally, the proof of Theorem 1 is given at the end of Section 5.

2 One-Particle Density Matrices

We set

$$h := -\Delta - \sum_{j=1}^{K} \frac{Z_j}{|x - R_j|} \ , \quad V := \tfrac{1}{|x-y|} \ , \tag{13}$$

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

$$H_N = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i \neq j} V_{ij} \ , \tag{14}$$

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

$$\langle \phi_N | H_N \phi_N \rangle = \mathrm{tr}_1\{h\gamma_\phi\} + \frac{1}{2} \mathrm{tr}_2\{V(1 - Ex)(\gamma_\phi \otimes \gamma_\phi)\} =: \varepsilon_{HF}(\gamma_\phi) \ , \tag{15}$$

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 $\{\varphi_i\}_{i \in I\!N}$ in $\mathcal{H}$. 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 (15), may thus be rewritten as

$$E_{HF}(N) = \inf\{\varepsilon_{HF}(\gamma) | \gamma = \gamma^\dagger = \gamma^2, \ \mathrm{tr}_1\{\gamma\} = N, \ \mathrm{tr}_1\{h\gamma\} < \infty\} \ . \tag{16}$$

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

$$E_{HF}(N) = \inf\{\varepsilon_{HF}(\gamma) | 0 \le \gamma \le 1, \ \mathrm{tr}_1\{\gamma\} \le N, \ \mathrm{tr}_1\{h\gamma\} < \infty\} \ . \tag{17}$$

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

$$\begin{aligned} E_{MF}(N) &= \operatorname{tr}_1\{hP_N\} + \operatorname{tr}_2\{V(d_{TF}\otimes P_N)\} - \frac{1}{2}\operatorname{tr}_2\{V(d_{TF}\otimes d_{TF})\} \\ &\quad -c_D\int d^3x\ \rho_{TF}^{4/3}(x) \qquad (18)\\ &=: \tilde{E}_{MF}(N) - \left[c_D\int d^3x\rho_{TF}^{4/3}(x) - \frac{1}{2}\operatorname{tr}_2\{VEx(P_N\otimes P_N)\}\right]. \end{aligned}$$

This notation makes the following lemmata completely transparent

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

$$\varepsilon_{HF}(\gamma) \ge \tilde{E}_{MF}(N) - \frac{1}{2}\operatorname{tr}_2\{V\ Ex(\gamma\otimes\gamma - P_N\otimes P_N)\}\ . \qquad (19)$$

Proof:

$$\begin{aligned} &\varepsilon_{HF}(\gamma) + \frac{1}{2}\operatorname{tr}_2\{V\ Ex(\gamma\otimes\gamma)\}\\ &= \operatorname{tr}_1\{h\gamma\} + \frac{1}{2}\operatorname{tr}_2\{V(\gamma\otimes\gamma)\}\\ &\ge \operatorname{tr}_1\{h\gamma\} + \operatorname{tr}_2\{V(d_{TF}\otimes\gamma)\} - \frac{1}{2}\operatorname{tr}_2\{V(d_{TF}\otimes d_{TF})\}\\ &= \operatorname{tr}_1\{h_{TF}\gamma\} - \frac{1}{2}\operatorname{tr}_2\{V(d_{TF}\otimes d_{TF})\}\\ &\ge \tilde{E}_{MF}(N) + \frac{1}{2}\operatorname{tr}_2\{V\ Ex(P_N\otimes P_N)\}\ .\ \blacksquare \qquad (20) \end{aligned}$$

A similar estimate in the opposite direction is as follows

Lemma 2

$$E_{HF}(N) \le \tilde{E}_{MF}(N) + \frac{1}{2}D(\rho_N-\rho_{TF},\rho_N-\rho_{TF})\ . \qquad (21)$$

Proof: We estimate

$$\begin{aligned} E_{HF}(N) &\le \varepsilon_{HF}(P_N)\\ &= \operatorname{tr}_1\{hP_N\} + \frac{1}{2}\operatorname{tr}_2\{V(1-Ex)(P_N\otimes P_N)\} \qquad (22)\\ &\le \operatorname{tr}_1\{h_{TF}P_N\} + \frac{1}{2}\operatorname{tr}_2\{V[(P_N-d_{TF})\otimes(P_N-d_{TF})]\}\\ &\quad -\frac{1}{2}\operatorname{tr}_2\{V\ Ex(P_N\otimes P_N)\}\ . \end{aligned}$$

Here enters $\operatorname{tr}_1\{P_N\}\le N$. $\blacksquare$

3 Exchange Estimates

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

$$\frac{1}{2}\,\mathrm{tr}_2\{V\; Ex(\gamma\otimes\gamma - P_N\otimes P_N)\}\quad , \tag{23}$$

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

$$\frac{1}{2}\,\mathrm{tr}_2\{V\; Ex(P_N\otimes P_N)\} - c_D \int \rho_{TF}^{4/3}(x)d^3x\quad , \tag{24}$$

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

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

$$\begin{aligned} &|\mathrm{tr}_2\{(X\otimes X)Ex(a\otimes a - b\otimes b)\}| \\ &\quad\le\;\; \Big(\mathrm{tr}_1\{X(a-b)^2\}\Big)^{1/2}\cdot \min\Big\{(2\,\mathrm{tr}_1\{X(a+b)\})^{1/2}\;\;,\;\; \mathrm{tr}_1\{X(a+b)\}\Big\}\quad . \end{aligned} \tag{25}$$

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

$$\begin{aligned} \mathrm{tr}_2\{Ex(E\otimes F)\} &= \sum_{i,j=1}^{\infty}\langle\varphi_i\otimes\varphi_j|(E\otimes F)\varphi_j\otimes\varphi_i\rangle \\ &= \sum_{i,j=1}^{\infty}\langle\varphi_i|E|\varphi_j\rangle\langle\varphi_j|F|\varphi_i\rangle = \mathrm{tr}_1\{EF\}\quad . \end{aligned} \tag{26}$$

Hence,

$$\begin{aligned} &|\,\mathrm{tr}_2\{(X\otimes X)Ex(a\otimes a - b\otimes b)\}| \\ &= \;|\,\mathrm{tr}_1\{aXaX - bXbX\}| = |\,\mathrm{tr}_1\{(a-b)X(a+b)X\}| \\ &= \;|\,\mathrm{tr}_1\{(a-b)X[X(a+b)X]\}| \\ &\le \;\Big(\mathrm{tr}_1\{X(a-b)^2\}\Big)^{1/2}\Big(\mathrm{tr}_1\{[X(a+b)X]^2\}\Big)^{1/2}\quad . \end{aligned} \tag{27}$$

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

$$\mathrm{tr}_1\{[XFX]^2\} \le 2\,\mathrm{tr}_1\{XFX\} = 2\,\mathrm{tr}_1\{XF\}\quad . \tag{28}$$

On the other hand,

$$\mathrm{tr}_1\{[XFX]^2\} \le (\mathrm{tr}_1\{XFX\})^2\quad , \tag{29}$$

because of $0 \le XFX$. This, inserted in (27) proves the assertion. ∎

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

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

$$
\begin{aligned}
&|\mathrm{tr}_2\{V Ex(a \otimes a - b \otimes b)\}| \\
&\leq \; C_\varepsilon \left(\frac{\mathrm{tr}_1\{(a-b)^2\}}{\mathrm{tr}_1\{a+b\}} \right)^{1/2-\varepsilon} \|\rho[a+b]\|_1^{1/2} \|\rho[a+b]\|_{5/3}^{5/6} \; ,
\end{aligned}
\tag{30}
$$

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

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

$$
V = \frac{1}{\pi} \int d^3z \int_o^\infty \frac{dr}{r^5} (X_{(r,z)} \otimes X_{(r,z)}) \; . \tag{31}
$$

An application of Lemma 3 then yields

$$
\begin{aligned}
&|\mathrm{tr}_2\{V \; Ex(a \otimes a - b \otimes b)\}| \\
&\leq \; \frac{1}{\pi} \int d^3z \int_0^\infty \frac{dr}{r^5} \left| \mathrm{tr}_2\{(X_{(r,z)} \otimes X_{(r,z)}) Ex(a \otimes a - b \otimes b)\} \right| \qquad (32) \\
&\leq \; \frac{1}{\pi} \int d^3z \int_0^\infty \frac{dr}{r^5} \left(\mathrm{tr}_1\{X_{(r,z)}(a-b)^2\} \right)^{1/2} \\
&\qquad \min \left\{ \left(2\, \mathrm{tr}_1\{X_{(r,z)}(a+b)\} \right)^{1/2}, \; \mathrm{tr}_1\{X_{(r,z)}(a+b)\} \right\} \; .
\end{aligned}
$$

Observe that $\mathrm{tr}_1\{X_{(r,z)} d\} = \int_{|x-z| \leq r} \rho[d](x) d^3x$. Denoting $\rho_- := \rho[(a-b)^2]$ and $\rho_+ := \rho[a+b]$, the integrand on the right hand of (32) is bounded above by

$$
\begin{aligned}
&\frac{1}{\pi} \int d^3z \left\{ \int_0^{R(z)} \frac{dr}{r^5} \left(\int_{|x-z| \leq r} \rho_-(x) d^3x \right)^{1/2} \left(\int_{|x-z| \leq r} \rho_+(x) d^3x \right) \right. \\
&\left. \quad + 2 \int_{R(z)}^\infty \frac{dr}{r^5} \left(\int_{|x-z| \leq r} \rho_-(x) d^3x \right)^{1/2} \left(\int_{|x-z| \leq r} \rho_+(x) d^3x \right)^{1/2} \right\} \; ,
\end{aligned}
\tag{33}
$$

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

$$
M[\rho](z) := \sup_{r>0} \left(\frac{4\pi r^3}{3} \right)^{-1} \int_{|x-z| \leq r} \rho(x) d^3x \; . \tag{34}
$$

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 (33):

$$
\begin{aligned}
& \left(\frac{4\pi}{3}\right) \int d^3z M_-^{1/2}(z) M_+^{1/2}(z) \left[\left(\frac{4\pi}{3}\right)^{1/2} M_+^{1/2}(z) \int_0^{R(z)} \frac{dr}{r^{1/2}} \right. \\
& \qquad\qquad\qquad\qquad \left. + \ 2 \int_{R(z)}^{\infty} \frac{dr}{r^2} \right] \\
\leq \ & 3 \left(\frac{4\pi}{3}\right)^{4/3} \int d^3z M_-^{1/2}(z) M_+^{5/6}(z) \qquad\qquad (35) \\
\leq \ & \frac{48}{\pi} \left(\frac{25}{2}\right)^{1/3} \varepsilon^{-1/2} \left(\int \rho_-(x) d^3x \right)^{1/2-\varepsilon} \|\rho_+\|_1^{\varepsilon} \cdot \|\rho_+\|_{5/3}^{5/6} \ .
\end{aligned}
$$

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

$$
|\,\mathrm{tr}_2\{V\ Ex(a \otimes a - b \otimes b)\}| \leq \frac{C}{\varepsilon^{1/2}} \left(\frac{\mathrm{tr}_1\{a(1-b)\}}{N} \right)^{1/2-\varepsilon} N^{2/3} Z \ . \qquad (36)
$$

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

$$
\mathrm{tr}_1\{(a-b)^2\} = \mathrm{tr}_1\{a^2 + b^2 - 2ab\} \leq 2N - 2\,\mathrm{tr}\{ab\} = 2\,\mathrm{tr}_1\{a(1-b)\} \quad (37)
$$

into Lemma 4 and arrive at the upper bound in (36). 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 $f_{pq}^\sigma := f_{pq} \otimes \delta_{\sigma,\cdot} \in \mathcal{H}$, 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

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

$$\textstyle\sum_{\sigma=1}^m \int \frac{d^3p\, d^3q}{(2\pi)^3} \phi(q) |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma| = \phi * |g|^2 \ , \tag{38}$$

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

$$\left\langle f_{pq}^\sigma \otimes f_{\tilde{p}\tilde{q}}^{\tilde{\sigma}} \middle| V \left(f_{pq}^\sigma \otimes f_{\tilde{p}\tilde{q}}^{\tilde{\sigma}} \right) \right\rangle \le \tfrac{1}{|q-\tilde{q}|} \ . \tag{39}$$

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 $0 \le d_\lambda \le 1$ on $\mathcal{H}$ by

$$d_\lambda := \sum_{\sigma=1}^m \int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q) |f_{pq}^\sigma\rangle\langle f_{pq}^\sigma| \ , \tag{40}$$

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

$$[\phi_{TF}(q) - \mu]_+ = \left(\frac{6\pi^2}{m}\right)^{2/3} \rho_{TF}^{2/3}(q) \tag{41}$$

away from the nuclei. Then

$$\sum_{\sigma=1}^m \int \frac{d^3p}{(2\pi)^3} M(p,q) = \rho_{TF}(q) \tag{42}$$

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

$$\begin{aligned} 0 &\le \int d^3q \{\phi_{TF}(q) - [\phi_{TF} * |g_\lambda|^2](q)\} \rho(q) \\ &\le \int d^3q \sum_{j=1}^K \left\{ \frac{Z_j}{|q-R_j|} - \int d^3x \frac{Z_j |g_\lambda(x-q)|^2}{|x-R_j|} \right\} \rho(q) \\ &\le cZ\lambda^{1/5} \|\rho\|_{5/3} \end{aligned} \tag{43}$$

for nonnegative $\rho \in L^{5/3}(I\!R^3) \cap L^1(I\!R^3)$. The first two inequalities in (43) 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* $0 \le \gamma \le 1$, $\mathrm{tr}_1\{h\gamma\} \le 0$ *be either*

(i) *the 1-pdm* $\gamma = \gamma_\psi$ *of a* $Z^{5/3}$*-approximate ground state* $\psi_N \in \mathcal{H}_N$, *i.e.* $\langle\psi_N|H_N\psi_N\rangle - E_Q(N) \le Z^{5/3}$, *or*

(ii) $\gamma = \gamma_\phi$ *for a Slaterdeterminant* $\phi_N \in SD_N$ *and* $\varepsilon_{HF}(\gamma) - E_{HF}(N) \le Z^{5/3}$, *or*

(iii) $\gamma = P_N$.

Then

$$\mathrm{tr}_1\{h_{TF}\gamma\} \le m \int \frac{d^3p\, d^3q}{(2\pi)^3} h_{TF}(p,q) M(p,q) + c(Z^{5/3} + Z\lambda^{-2} + Z^{12/5}\lambda^{1/5}). \tag{44}$$

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

$$\left\langle \psi_N \middle| \left(\sum_{i\neq j} \frac{1}{|x_i - x_j|} \right) \psi_N \right\rangle \ge D(\rho[\gamma_\psi], \rho[\gamma_\psi]) - 1.68 \int d^3x \rho[\gamma_\psi]^{4/3}(x) \quad . \tag{45}$$

This gives us

$$\begin{aligned} \mathrm{tr}_1\{h_{TF}\gamma_\psi\} &\le \mathrm{tr}_1\{h\gamma_\psi\} + \frac{1}{2}D(\rho[\gamma_\psi], \rho[\gamma_\psi]) + \frac{1}{2}D(\rho_{TF}, \rho_{TF}) \\ &\le \langle\psi_N|H_N\psi_N\rangle + \frac{1}{2}D(\rho_{TF}, \rho_{TF}) \\ &\qquad + c\|\rho[\gamma_\psi]\|_1^{1/2} \|\rho[\gamma_\psi]\|_{5/3}^{5/6} \quad . \end{aligned} \tag{46}$$

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

$$\mathrm{tr}_1\{h_{TF}\gamma_\psi\} \le E_{HF}(N) + \frac{1}{2}D(\rho_{TF}, \rho_{TF}) + cZ^{5/3} \quad . \tag{47}$$

Now, by (39) and (43)

$$\begin{aligned}
&E_{HF}(N) + \frac{1}{2}D(\rho_{TF}, \rho_{TF}) \\
&\leq \; \mathrm{tr}_1\{hd_\lambda\} + \frac{1}{2}\,\mathrm{tr}_2\{V(d_\lambda \otimes d_\lambda)\} + \frac{1}{2}D(\rho_{TF}, \rho_{TF}) \qquad (48) \\
&\leq \; m\int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q)\left(p^2 + \|\nabla g_\lambda\|_2^2 - \sum_{j=1}^{K}\int d^3x \frac{Z_j|g_\lambda(x-q)|^2}{|x-R_j|}\right) \\
&\quad + D(\rho_{TF}, \rho_{TF}) \\
&\leq \; m\int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q)(p^2 - \phi_{TF}(q)) + cZ\lambda^{1/5}\|\rho_{TF}\|_{5/3} \\
&\quad + N\|\nabla g_\lambda\|_2^2 \ .
\end{aligned}$$

Inserting $\|\rho_{TF}\|_{5/3} \leq cZ^{7/5}$ and $\|\nabla g_\lambda\|_2^2 \leq c\lambda^{-2}$ gives (44) in Case (i) and (ii). In Case (iii) we observe

$$\begin{aligned}
\mathrm{tr}_1\{h_{TF}P_N\} \;&\leq\; \mathrm{tr}_1\{h_{TF}d_\lambda\} \qquad (49) \\
&\leq\; m\int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q)(p^2 + \|\nabla g_\lambda\|_2^2 - [\phi_{TF} * |g_\lambda|^2](q)) \\
&\leq\; m\int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q)(p^2 - \phi_{TF}(q)) \\
&\quad + cZ^{12/5}\lambda^{1/5} + cZ\lambda^{-2} \ ,
\end{aligned}$$

using (43) 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 (44).

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

$$\mathrm{tr}_1\{h_{TF}\gamma\} \leq m\int \frac{d^3p\, d^3q}{(2\pi)^3} h_{TF}(p,q)M(p,q) + cF(\lambda) \ . \qquad (50)$$

Then

$$\mathrm{tr}_1\{d_\lambda(1-\gamma)\} \leq cKF^{3/7}(\lambda) \ . \qquad (51)$$

Proof: For any $E > 0$ we have

$$\begin{aligned}
&\mathrm{tr}_1\{d_\lambda(1-\gamma)\} \\
&= \sum_{\sigma=1}^{m}\int \frac{d^3p\, d^3q}{(2\pi)^3} M(p,q)\langle f_{pq}^\sigma|(1-\gamma)f_{pq}^\sigma\rangle \qquad (52)
\end{aligned}$$

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

By (43), $\|\nabla g_\lambda\|_2^2\leq c\lambda^{-2}$, $\|\rho[\gamma]\|_{5/3}^{5/3}\leq cZ^{7/3}$ and (50), this gives

$$
\mathrm{tr}_1\{d_\lambda(1-\gamma)\}\leq m\int_{-\mu\geq h_{TF}(p,q)\geq-\mu-E}\frac{d^3p\,d^3q}{(2\pi)^3}+\frac{c}{E}F(\lambda)\quad. \tag{53}
$$

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

$$
m\int_{0\geq h_{TF}(p,q)\geq-E}\frac{d^3p\,d^3q}{(2\pi)^3}\leq cK^{7/4}E^{3/4}\quad, \tag{54}
$$

which, choosing $E:=K^{-1}F^{4/7}(\lambda)$, leads us to (51). Actually, (54) required $E=o(Z^{4/3})$, but if $E\geq cZ^{4/3}$ then (54) is trivial anyway.

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

$$
\begin{aligned}
&m\int_{-\mu\geq h_{TF}(p,q)\geq-\mu-E}\frac{d^3p\,d^3q}{(2\pi)^3}\\
&\quad=\;\frac{m}{6\pi^2}\int_{\phi_{TF,N}\geq\mu_N}d^3q\,\Big\{[\phi_{TF,N}(q)-\mu_N]_+^{3/2}\\
&\qquad\qquad-[(\phi_{TF,N}(q)-\mu_N)_+-E]_+^{3/2}\Big\}\\
&\quad\leq\;\frac{m}{6\pi^2}\int d^3q\,\Big\{\phi_{TF,Z}(q)^{3/2}-[\phi_{TF,Z}(q)-E]_+^{3/2}\Big\}\\
&\quad\leq\; cK^{7/4}E^{3/4}\quad,
\end{aligned}
\tag{55}
$$

again, by (54).∎

5 The Dirac Exchange Correction

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

$$d_\lambda(x,\mu|y,\nu) := \int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,q) g_\lambda(x-q) g_\lambda(y-q) e^{ip(x-y)} \delta_{\mu\nu} \ . \tag{56}$$

The exchange term induced by d_λ reads

$$W_{ex} := \mathrm{tr}_2\{V\ Ex(d_\lambda \otimes d_\lambda)\} = \frac{m}{2}\int \frac{d^3x\,d^3y}{|x-y|} |d_\lambda(x|y)|^2 \ , \tag{57}$$

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 (57) almost explicitly. It requires a tedious integration and the result is

Lemma 8

$$\begin{aligned} &\left|\frac{1}{2}\mathrm{tr}_2\{V\ Ex(d_\lambda\otimes d_\lambda)\} - c_D\int d^3x \rho_{TF}^{4/3}(x)\right| \\ &\quad \le \ c_\nu K^2[Z\lambda^{-1} + Z^2\ln(Z)(\lambda + Z^{-1/3-\nu})] \end{aligned} \tag{58}$$

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 $p_f(q) := [\phi_{TF}(q)-\mu]_+^{1/2} = (6\pi^2 m^{-1})^{1/3}\rho_{TF}^{1/3}(q)$,

$$\begin{aligned} W_{ex} &= 2m\int \frac{d^3s\,d^3r}{|r|} e^{-r^2/\lambda^2} \left|\int \frac{d^3p\,d^3q}{(2\pi)^3} M(p,s+q) g_\lambda^2(q) e^{2i\vec{p}\cdot\vec{r}}\right|^2 \\ &= 2m\int d^3s \int \frac{d^3q\,d^3\tilde{q}}{(2\pi)^6} g_\lambda^2(q) g_\lambda^2(\tilde{q}) \int_0^{p_f(s+q)} p^2dp \int_0^{p_f(s+\tilde{q})} \tilde{p}^2 d\tilde{p} \\ &\quad \int_0^\infty r e^{-r^2/\lambda^2} dr \int d\Omega_p d\Omega_{\tilde{p}} 2\pi \int_{-1}^1 dx \exp(2i|\vec{p}-\vec{\tilde{p}}|rx) \ . \end{aligned} \tag{59}$$

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

$$\int d\Omega_p d\Omega_{\tilde{p}} 2\pi \int_{-1}^1 dx \exp(2i|\vec{p}-\vec{\tilde{p}}|rx) = \frac{2(2\pi)^3}{p\tilde{p}r^2}\sin(2rp)\sin(2r\tilde{p}) \ . \tag{60}$$

This yields

$$W_{ex} = \frac{4m}{(2\pi)^3} \int d^3 s \int_0^\infty dr \frac{e^{-r^2/\lambda^2}}{r} \left(\int d^3 q g_\lambda^2(q) \int_0^{p_f(s+q)} p \sin(2rp) dp \right)^2 . \tag{61}$$

Defining

$$\begin{aligned} \varepsilon_1 \quad &:= \quad \frac{4m}{(2\pi)^3} \int d^3 s \int_0^\infty dr \frac{e^{-r^2/\lambda^2}}{r} \int d^3 q g_\lambda^2(q) \, d^3 \tilde{q} g_\lambda^2(\tilde{q}) \\ & \qquad \left(\int_0^{p_f(s+q)} p \sin(2rp) dp - \int_0^{p_f(s+\tilde{q})} p \sin(2rp) dp \right)^2 \end{aligned} \tag{62}$$

and

$$\begin{aligned} \varepsilon_2 \quad &:= \quad \frac{4m}{(2\pi)^3} \int d^3 s \, p_f^{4/3}(s) \int_0^\infty \frac{[\sin(r) - r\cos(r)]^2 dr}{r^5} \\ & \qquad \left[1 - \exp\left(- \frac{r^2}{2 p_f^2(s) \lambda^2} \right) \right] \quad , \end{aligned} \tag{63}$$

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

$$\begin{aligned} W_{ex} \quad &= \quad \frac{4m}{(2\pi)^3} \left(\int_0^\infty \frac{[\sin(r) - r\cos(r)]^2}{r^5} dr \right) \int p_f^4(s) d^3 s - \varepsilon_1 - \varepsilon_2 \\ &= \quad c_D \int \rho_{TF}^{4/3}(x) d^3 x \; - \varepsilon_1 - \varepsilon_2 \quad . \end{aligned} \tag{64}$$

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

$$\int_0^\infty f(x)(1 - e^{-x^2/a^2}) dx \leq \frac{1}{a^2} \left(\int_0^\infty \frac{f(x)\, dx}{x} \right)^{1/2} \left(\int_0^\infty x e^{-x^2/a^2} dx \right)^{1/2} \leq \frac{c}{a}. \tag{65}$$

This, inserted in (63), yields

$$\varepsilon_2 \leq \frac{c}{\lambda} \int p_f^3(s) d^3 s \leq \frac{cZ}{\lambda} \quad . \tag{66}$$

The estimate on ε_1 is more delicate. We use

$$\left(\int_{2rp_f}^{2r\tilde{p}_f} p \sin(p) dp \right)^2 \leq \frac{64 r^6}{9} \left(p_f^3 - \tilde{p}_f^3 \right)^2 \tag{67}$$

for small $r > 0$ and

$$[\sin(2rp_f) - 2rp_f\cos(2rp_f) - \sin(2r\tilde{p}_f) + 2r\tilde{p}_f\cos(2r\tilde{p}_f)]^2 \leq cr^2[p_f + \tilde{p}_f]^2 \tag{68}$$

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 $R = R(s, q, \tilde{q})$,

$$\varepsilon_1 \leq c\int d^3s \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) \left[(p_f^3 - \tilde{p}_f^3)R^2 + \frac{(p_f + \tilde{p}_f)^2}{R^2}\right] \quad . \tag{69}$$

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

$$\varepsilon_1 \leq c\int d^3s \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q})|p_f^4 - \tilde{p}_f^4| \quad . \tag{70}$$

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

$$|p_f^4(s+q) - p_f^4(s+\tilde{q})| \leq \int_q^{\tilde{q}} |\nabla p_f^4(s+s')|ds' \quad , \tag{71}$$

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

$$\begin{aligned}
\varepsilon_1 &\leq c\int d^3s \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} |\nabla p_f^4(s+s')|ds' \\
&\leq c\int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} \left(\int d^3s |\nabla p_f^4(s+s')|\right) ds' \\
&\leq c\left(\int |\nabla p_f^4(s)| d^3s\right) \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q})|q - \tilde{q}| \\
&\leq c\|\nabla p_f^4\|_1 \cdot \lambda \quad .
\end{aligned} \tag{72}$$

The trouble with this estimate is that $|\nabla p_f^4| \notin L^1(I\!R^3)$, 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 $p_0 > 0$:

$$|p_f^4 - \tilde{p}_f^4| \leq \Theta[p_0 - p_f]\Theta[p_0 - \tilde{p}_f] \cdot |p_f^4 - \tilde{p}_f^4| + 2\Theta[p_f - p_0]\cdot p_f^4 + 2\Theta[\tilde{p}_f - p_0]\cdot \tilde{p}_f^4 \quad . \tag{73}$$

Hence

$$\begin{aligned}
\varepsilon_1 &\leq c\int d^3s \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q})\Theta[p_0 - p_f]\Theta[p_0 - \tilde{p}_f]\; |p_f^4 - \tilde{p}_f^4| \\
&\quad + c\int d^3s \int d^3q g_\lambda^2(q)\Theta[p_f - p_0]p_f^4 \quad .
\end{aligned} \tag{74}$$

Now, we estimate

$$|p_f^4(s+q) - p_f^4(s+\tilde{q})| \leq \int_q^{\tilde{q}} |\nabla p_f^4(s+s')| ds' \quad , \tag{75}$$

where we assume the path $s + s' \notin A := \{x \in I\!R^3 | p_f(x) > p_0\}$ 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 $p_f^2(x) \leq c \sum_{j=1}^K Z_j |x - R_j|^{-1}$. It follows

$$\int_q^{\tilde{q}} ds' \leq |q - \tilde{q}| + KZ^{-1/3-\nu} \quad . \tag{76}$$

We obtain

$$\begin{aligned}
\varepsilon_1 \quad &\leq \quad c \int d^3s \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} |\nabla p_f^4(s+s')| \chi_{I\!R^3 \setminus A}(s+s') ds' \\
&\quad + c \int_A p_f^4(s) d^3s \\
&\leq \quad c \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) \int_q^{\tilde{q}} \left(\int d^3s |\nabla p_f^4(s+s')| \chi_{I\!R^3 \setminus A}(s+s') \right) ds' \\
&\quad + cKZ^2 \int_{|x| \leq Z^{-1/3-\nu}} \frac{d^3x}{|x|^2} \\
&\leq \quad c \left(\int_{I\!R^3 \setminus A} |\nabla p_f^4(s)| d^3s \right) \left(KZ^{-1/3-\nu} + \int d^3q g_\lambda^2(q)\, d^3\tilde{q} g_\lambda^2(\tilde{q}) |q - \tilde{q}| \right) \\
&\qquad + cKZ^{5/3-\nu} \\
&\leq \quad c \|\chi_{I\!R^3 \setminus A} \nabla p_f^4\|_1 (KZ^{-1/3-\nu} + \lambda) + cKZ^{5/3-\nu} \quad .
\end{aligned} \tag{77}$$

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

$$\begin{aligned}
&\|\chi_{I\!R^3 \setminus A} \nabla p_f^4\|_1 \\
&\quad \leq \quad cKZ^2 \int_{(I\!R^3 \setminus A) \cap A'} \sum_{j=1}^K \frac{d^3x}{|x - R_j|^3} + c \int_{A'} Z^{8/3} |\nabla p_{f,1}(Z^{1/3}x)| d^3x \\
&\quad \leq \quad c_\nu K^2 Z^2 \ln(Z) + cZ^2 \quad ,
\end{aligned} \tag{78}$$

and we finally arrive at

$$\varepsilon_1 + \varepsilon_2 \leq c_\nu K^2 [Z\lambda^{-1} + Z^2 \ln(Z)(\lambda + Z^{-1/3-\nu})] \quad . \blacksquare \tag{79}$$

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 $E_{HF}(N)$. This was done in [1] and we quote Theorem 2 therein:

$$|E_Q(N) - E_{HF}(N)| \le \frac{c}{\varepsilon^{1/3}} \left(\operatorname{tr}_1\{\gamma_\psi - \gamma_\psi^2\}\right)^{1/3-\varepsilon} Z^{4/3+\varepsilon} \tag{80}$$

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

$$\begin{aligned}
&-\frac{1}{2}\operatorname{tr}_2\{V\ Ex(\gamma_{HF}\otimes\gamma_{HF} - P_N \otimes P_N)\} - Z^{4/3} \\
&\le\ E_{HF}(N) - \operatorname{tr}_1\{h_{TF}P_N\} + \frac{1}{2}D(\rho_{TF},\rho_{TF}) - \frac{1}{2}\operatorname{tr}_2\{V\ Ex(P_N\otimes P_N)\} \\
&\le\ \frac{1}{2}D(\rho_N - \rho_{TF}, \rho_N - \rho_{TF})
\end{aligned} \tag{81}$$

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

$$\begin{aligned}
&|\operatorname{tr}_2\{V\ Ex(\gamma_{HF}\otimes\gamma_{HF} - P_N\otimes P_N)\}| \\
&\le\ \frac{c}{\varepsilon^{1/2}}\left(\operatorname{tr}_1\{\gamma_{HF}(1-d_\lambda)\} + \operatorname{tr}_1\{P_N(1-d_\lambda)\}\right)^{1/2-\varepsilon} Z^{7/6+\varepsilon}\ . \qquad (82) \\
&\le\ \frac{c}{\varepsilon^{1/2}}\left(\operatorname{tr}_1\{d_\lambda(1-\gamma_{HF})\} + \operatorname{tr}_1\{d_\lambda(1-P_N)\} + Z^{1-2/77}\right)^{1/2-\varepsilon} Z^{7/6+\varepsilon}\ .
\end{aligned}$$

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

$$\operatorname{tr}_1\{\gamma_\psi - \gamma_\psi^2\} \le \operatorname{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \operatorname{tr}_1\{(1-d_\lambda)\gamma_\psi\} = 2\operatorname{tr}_1\{d_\lambda(1-\gamma_\psi)\}\ . \tag{83}$$

We insert (80), (82) and (83) into (81) and obtain for any $0 < \varepsilon < 1/12$

$$\begin{aligned}
&\frac{c}{\varepsilon^{1/3}}\Big(\operatorname{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \operatorname{tr}_1\{d_\lambda(1-\gamma_{HF})\} \\
&\qquad\qquad + \operatorname{tr}_1\{d_\lambda(1-P_N)\} + Z^{1-2/77}\Big)^{1/3-\varepsilon} Z^{4/3+\varepsilon} \\
&\le\ E_Q(N) - \operatorname{tr}_1\{h_{TF}P_N\} + \frac{1}{2}D(\rho_{TF},\rho_{TF}) - \frac{1}{2}\operatorname{tr}_2\{V\ Ex(d_\lambda\otimes d_\lambda)\} \\
&\le\ \frac{c}{\varepsilon^{1/3}}\Big(\operatorname{tr}_1\{d_\lambda(1-\gamma_\psi)\} + \operatorname{tr}_1\{d_\lambda(1-\gamma_{HF})\} + Z^{1-2/77} \qquad (84) \\
&\qquad + \operatorname{tr}_1\{d_\lambda(1-P_N)\}\Big)^{1/3-\varepsilon} Z^{4/3+\varepsilon} \ + \frac{1}{2}D(\rho_N-\rho_{TF},\rho_N-\rho_{TF}).
\end{aligned}$$

In (84) exactly the three cases treated in Lemma 6 occur, which, therefore, fulfill the assumptions in Lemma 7 and imply the bound

$$
\begin{aligned}
& \frac{c}{\varepsilon^{1/3}} K^{1/3} [Z^{7/3-2/33} + Z\lambda^2 + Z^{12/5}\lambda^{1/5}]^{1/7-\varepsilon} Z^{4/3+\varepsilon} \\
\leq \quad & E_Q(N) - \mathrm{tr}_1\{h_{TF} P_N\} + \frac{1}{2} D(\rho_{TF}, \rho_{TF}) - \frac{1}{2}\,\mathrm{tr}_2\{V\, Ex(d_\lambda \otimes d_\lambda)\} \\
\leq \quad & \frac{1}{2} D(\rho_N - \rho_{TF}, \rho_N - \rho_{TF}) \\
& + \frac{c}{\varepsilon^{1/3}} K^{1/3} [Z^{7/3-2/33} + Z\lambda^2 + Z^{12/5}\lambda^{1/5}]^{1/7-\varepsilon} Z^{4/3+\varepsilon} \quad . \qquad (85)
\end{aligned}
$$

The error term we pick up when replacing $\frac{1}{2}\,\mathrm{tr}_2\{V\, Ex(d_\lambda \otimes d_\lambda)\}$ by $c_D \int \rho_{TF}^{4/3}$ is estimated in Lemma 8 and turns out to be small compared to the λ-dependent error term in (85). More precisely, Theorem 1 follows now from Lemma 8 and the choice $\lambda := Z^{-21/33}$ and $\nu := 10/33$.∎

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