BORN-OPPENHEIMER POTENTIAL ENERGY SURFACES FOR KOHN-SHAM MODELS IN THE LOCAL DENSITY APPROXIMATION

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Abstract. We show that the Born-Oppenheimer potential energy surface in Kohn-Sham theory behaves like the corresponding one in Thomas-Fermi theory up to $o(R^{-7})$ for small nuclear separation R. We also prove that if a minimizing configuration exists, then the minimal distance of nuclei is larger than some constant which is independent of the nuclear charges.

1. Introduction

We consider a molecule with $N > 0$ electrons and K static nuclei at $R_1, \dots, R_K$ of charges $z_1, \dots, z_K > 0$. Density Functional Theory (DFT) [13, 17] tells us that the ground state energy is given by the minimization problem

$$E^{\mathrm{GS}}_{V_{\underline{R}}}(N) := \inf \left\{ F_{\mathrm{LL}}(\rho) - \int_{\mathbb{R}^3} V_{\underline{R}}(x)\rho(x)\,dx \colon \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\},$$

$$V_{\underline{R}}(x) := \sum_{j=1}^{K} \frac{z_j}{|x - R_j|}, \quad \underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}.$$

Here $F_{\mathrm{LL}}(\rho)$ is the Levy-Lieb functional defined by

$$F_{\mathrm{LL}}(\rho) := \inf_{\substack{\psi \in \bigwedge^N L^2(\mathbb{R}^3) \\ \|\psi\|_{L^2}=1 \\ \rho_\psi = \rho}} \left\{ \frac{1}{2}\sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_j \psi(\underline{X})|^2\,d\underline{X} + \sum_{1 \le i < j \le N} \int_{\mathbb{R}^{3N}} \frac{|\psi(\underline{X})|^2}{|x_i - x_j|}\,d\underline{X} \right\},$$

$$\rho_\psi(x) := N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2\,dx_2 \cdots dx_N, \quad \underline{X} = (x_1, \dots, x_N) \in \mathbb{R}^{3N},$$

where $\bigwedge^N L^2(\mathbb{R}^3)$ denotes the N-particle space of antisymmetric wave functions. Although DFT gives the exact lowest energy, we usually need suitable approximations. The Local Density Approximation (LDA) refers to an approximation such as

$$F_{\mathrm{LL}}(\rho) \approx \underbrace{\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dxdy}_{=:D(\rho)} + \underbrace{\int_{\mathbb{R}^3} f(\rho(x))\,dx}_{\text{local term}}.$$

For instance, one can obtain the Thomas-Fermi (TF) functional with $f(t) = 3/10(3\pi^2)^{2/3}t^{5/3}$. More precisely, for $V\colon \mathbb{R}^3 \to \mathbb{R}$ with $V \in L^{5/2} + L^\infty$ and $\rho \geq 0$ we define

$$\mathcal{E}_V^{\mathrm{TF}}(\rho) := \frac{3}{10}(3\pi^2)^{2/3} \int_{\mathbb{R}^3} \rho(x)^{5/3}\, dx - \int_{\mathbb{R}^3} \rho(x)V(x)\, dx + D(\rho),$$

and its energy is

$$E_V^{\mathrm{TF}}(n) := \inf \left\{ \mathcal{E}_V^{\mathrm{TF}}(\rho)\colon \rho \geq 0, \int_{\mathbb{R}^3} \rho \leq n \right\}.$$

It is well-known that the unique minimizer ρ_V^{TF} exists for any $n > 0$ (see, e.g., [16,19]). We note that the Levy-Lieb functional includes the kinetic energy and electron-electron repulsive interaction, and TF theory neglects the exchange-correlation energy. On the other hand, the kinetic energy can be written by $\mathrm{tr}[(-\Delta/2)\gamma]$ with a density-matrix $\gamma \in \mathcal{DM}$ having $\mathrm{tr}\,\gamma = N$, where

$$\mathcal{DM} := \left\{ \gamma\colon 0 \leq \gamma \leq 1, \gamma = \gamma^\dagger, \mathrm{tr}(-\Delta\gamma) < \infty \right\}.$$

For a trace operator γ, its density is $\rho_\gamma(x) := \gamma(x,x)$ with Hilbert-Schmidt kernel $\gamma(x,y) = \sum_{j\geq 1} \lambda_j \varphi_j(x)\varphi_j(y)^*$, where $\gamma\varphi_j = \lambda_j\varphi_j$. The (extended) Kohn-Sham model is given by

$$\begin{aligned} \mathcal{E}_V^{\mathrm{KS}}(\gamma) &:= \mathrm{tr}\left[\left(-\frac{1}{2}\Delta - V \right) \gamma \right] + D(\rho_\gamma) - E_{\mathrm{xc}}(\rho_\gamma), \\ E_V^{\mathrm{KS}}(n) &:= \inf \left\{ \mathcal{E}_V(\gamma)\colon \gamma \in \mathcal{DM}, \mathrm{tr}\,\gamma = n \right\}, \end{aligned}$$

where E_{xc} is the exchange-correlation energy of the form

$$-E_{\mathrm{xc}}(\rho) := \min_{\substack{\rho = \sum_j \lambda_j \rho_j \\ \sum_j \lambda_j = 1 \\ \sqrt{\rho_j} \in H^1(\mathbb{R}^3) \\ \int_{\mathbb{R}^3} \rho_j = n}} \sum_j \lambda_j F_{\mathrm{LL}}(\rho_j) - \inf_{\substack{\gamma \in \mathcal{DM} \\ \rho_\gamma = \rho \\ \mathrm{tr}\,\gamma = n}} \mathrm{tr}\left(-\frac{\Delta}{2}\gamma \right) - D(\rho).$$

Then the Kohn-Sham energy is exact, i.e., $E_{V_{\underline{R}}}^{\mathrm{GS}}(n) = E_{V_{\underline{R}}}^{\mathrm{KS}}(n)$. We use an approximate E_{xc} called the LDA exchange-correlation functional as

$$E_{\mathrm{xc}}(\rho) \approx E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho) := \int_{\mathbb{R}^3} g(\rho(x))\, dx, \tag{1.1}$$

and introduce the Kohn-Sham LDA model

$$\begin{aligned} \mathcal{E}_V(\gamma) &:= \mathrm{tr}\left[\left(-\frac{1}{2}\Delta - V \right) \gamma \right] + D(\rho_\gamma) - E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma), \\ E_V(n) &:= \inf \left\{ \mathcal{E}_V(\gamma)\colon \gamma \in \mathcal{DM}, \mathrm{tr}\,\gamma = n \right\}. \end{aligned}$$

The following assumptions will be needed throughout the paper. In (1.1), the function $g\colon \mathbb{R}_+ \to \mathbb{R}_+$ is twice differentiable and satisfies

$$\begin{aligned} g(0) &= 0, \\ g' &\geq 0, \\ \exists 0 < \beta_- \leq \beta_+ \leq \frac{2}{5} \quad & \sup_{t\in\mathbb{R}_+} \frac{|g'(t)|}{t^{\beta_-} + t^{\beta_+}} < \infty, \\ \exists 1 \leq \alpha < \frac{3}{2} \quad & \limsup_{t\to 0+} \frac{g(t)}{t^{\alpha}} > 0. \end{aligned} \tag{1.2}$$

For instance, the LDA exchange functional $g^{\mathrm{LDA}}(\rho) = (3/4)(3/\pi)^{1/3}\rho^{4/3}$ satisfies (1.2).

Mathematically, the choice $g_{\mathrm{LO}}(\rho) = 1.45\rho^{4/3}$ gives a lower bound of $E_{\mathrm{xc}}(\rho)$ [14], and it has been shown in [15] that a quantitative estimate exists between the grand canonical Levy-Lieb energy and the energy of the uniform electron gas, $\int g_{\mathrm{UEG}}(\rho(x)))\,dx$, containing the kinetic and exchange-correlation energy. The function g_{UEG} behaves like $g_{\mathrm{UEG}} \sim c_1\rho^{5/3} - c_2\rho^{4/3}$, where the first term can be interpreted as the kinetic energy. Thus the conditions (1.2) are not so restrictive.

Under the conditions, it has been shown in [1] that the Kohn-Sham energy $E_{V_{\underline{R}}}(N)$ has a minimizer (ground state) γ_0 if $N \leq Z \coloneqq \sum_{j=1}^{K} z_j$.

In this paper, we will investigate the behavior of the potential energy surface at short internuclear distance $R_{\min} \coloneqq \min_{i\neq j} |R_i - R_j| \to 0$. Let $U_{\underline{R}} \coloneqq \sum_{i<j} z_i z_j |R_i - R_j|^{-1}$ be the nucleus-nucleus interaction. Then the Born-Oppenheimer potential energy surfaces are defined as

$$D^{\mathrm{TF}}(\underline{Z}, \underline{R}) \coloneqq E^{\mathrm{TF}}_{V_{\underline{R}}}(Z) - \sum_{j=1}^{K} E^{\mathrm{TF}}_{z_j/|x-R_j|}(z_j) + U_{\underline{R}},$$

$$D(\underline{Z}, \underline{R}) \coloneqq E_{V_{\underline{R}}}(Z) - \sum_{j=1}^{K} E_{z_j/|x-R_j|}(z_j) + U_{\underline{R}}.$$

In fact, the atomic energies $E^{\mathrm{TF}}_{z_j/|x-R_j|}(z_j)$ and $E_{z_j/|x-R_j|}(z_j)$ are independent of the nuclear position R_j since translation invariance of the functionals, and thus their ground state densities are obtained by the translation of the densities, $\rho^{\mathrm{TF}}_{z_j}$ and ρ_{z_j}, for $E^{\mathrm{TF}}_{z_j/|x|}(z_j)$ and $E_{z_j/|x|}(z_j)$. In [4], Brezis and Lieb showed that $\lim_{l\to\infty} D^{\mathrm{TF}}(l^3\underline{Z}, \underline{R}) = \lim_{l\to\infty} l^7 D^{\mathrm{TF}}(\underline{Z}, l\underline{R}) \eqqcolon \Gamma(\underline{R}) > 0$ for a certain $\Gamma(\underline{R})$ which is independent of all z_j. Although [4] proved that $\Gamma(\underline{R}) = D^{\mathrm{TF}}_{\infty} R^{-7}$ for two atoms separated by $R = |R_1 - R_2|$, the exact value D^{TF}_{∞} is not known. Recently, Solovej has conjectured in [26] that for homonuclear ($z_1 = z_2 = z/2$) diatomic molecules

$$\limsup_{z\to\infty} \left| D^{\mathrm{GS}}(\underline{Z}, \underline{R}) - R^{-7} D^{\mathrm{TF}}_{\infty} \right| = o(R^{-7}), \quad \text{as } R \to 0,$$

where $D^{\mathrm{GS}}(\underline{Z}, \underline{R})$ stands for the Born-Oppenheimer potential energy surface of the ground state energy $E^{\mathrm{GS}}_{V_{\underline{R}}}(Z)$. Results on the opposite regime $R \to \infty$ are also known: for neutral atoms in the quantum theory, van der Waals interaction law $D^{\mathrm{GS}}(\underline{Z}, \underline{R}) \approx$

$-R^{-6}$ exists for large separation R [2,3,20]. Furthermore, if the influence of retardation effects is taken into account, then the long-range interaction becomes $-R^{-7}$ [5].

In reduced Hartree-Fock (rHF) theory, which is obtained by neglecting the exchange-correlation E_{xc} in the Kohn-Sham functional, Solovej's conjecture is settled by Samojlow in his Ph.D thesis [22].

Our main result is a generalization of Samojlow's result to the case of $K \geq 2$ nuclei with the LDA exchange-correlation.

Theorem 1.1. *Let* $z_{\max} = \max_{1\leq i\leq K} z_i$ *and* $z_{\min} = \min_{1\leq i\leq K} z_i$*. If* $z_{\min} \geq 1$ *and* $z_{\min} \geq \delta_0 z_{\max}$ *for some* $\delta_0 > 0$*, then there exists* $\varepsilon > 0$ *such that for any* $R_{\min} \in (0,4]$

$$\left| D(\underline{Z},\underline{R}) - D^{\mathrm{TF}}(\underline{Z},\underline{R}) \right| \leq C R_{\min}^{-7+\varepsilon}.$$

Moreover, it follows that as $R_{\min} \to 0$

$$\limsup_{\substack{z_{\min}\geq\delta_0 z_{\max}\\ z_{\min}\to\infty}} |D(\underline{Z},\underline{R}) - \Gamma(\underline{R})| = o(R_{\min}^{-7}). \tag{1.3}$$

Corollary 1.2. We assume that there is a constant δ_0 such that $z_{\min} \geq \delta_0 z_{\max}$. If there exists $\underline{R_0} = (R_0^{(1)}, \ldots, R_0^{(K)})$ such that $\inf_{\underline{R}}(E_{V_{\underline{R}}}(Z) + U_{\underline{R}}) = E_{V_{\underline{R_0}}}(Z) + U_{\underline{R_0}}$, then

$$R_{\mathrm{M}} \coloneqq \min_{i\neq j} |R_0^{(i)} - R_0^{(j)}| \geq C_0, \tag{1.4}$$

for some constant $C_0 > 0$ independently of the nuclear charges.

In [6–9], the existence of optimal $\underline{R}$ for TF-type models was settled, but we have not been able to prove that for our model. Hence, although we believe it is true, the existence of such a configuration remains open.

Remark 1.3. The assumptions (1.2) might be slightly loosened, since for a more general function $g\colon \mathbb{R}_+ \to \mathbb{R}$ (see [1, Eq. (25)–(28)]) the Kohn-Sham energy $E_{V_{\underline{R}}}(Z)$ has a minimizer. In particular, the optimal bound of β_+ in (1.2) is presumably much closer to $2/3$.

Remark 1.4. It is conjectured that $C_1 \leq R_{\min} \leq R_{\max} \coloneqq \max_{i\neq j} |R_i - R_j| \leq C_2$ for some universal constants $C_1, C_2 > 0$ if a minimizing configuration exists in the quantum theory. Hence Theorem 1.1 suggests that the energy of interaction behaves like R^{-7} if $R \lesssim r =$ the interatomic distance and $-R^{-6}$ at infinity.

Remark 1.5. An important extension is the Hartree-Fock theory which approximates the exchange-correlation by

$$E_{\mathrm{xc}}(\rho_\gamma) \approx X(\gamma) \coloneqq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma(x,y)|^2}{|x-y|}\, dxdy.$$

Unfortunately, our method does not work for Hartree-Fock theory because $X(\gamma)$ is non-local. The main difficulty is that the localization error of the energy,

$$\int_{B(R_i,r)} \int_{B(R_j,r)} \frac{|\gamma(x,y)|^2}{|x-y|}\, dxdy,$$

has to be dominated by $o(r^{-7})$ independently of the nuclear charges for small r. This problem does not arise for the LDA term $E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma)$ if r is small enough.

The proof of Theorem 1.1 follows the strategy inspired by [22]. Indeed, the main idea is to compare with TF theory, and one of the key ingredients is the Sommerfeld estimate for molecules. In the case $K = 2$, the Sommerfeld estimate was shown in [22], and the proof has been extended to the $K > 2$ case in [12]. In the present article, we generalize certain bounds [22] and [12] used on the difference between the considered theory and TF theory so that the Sommerfeld estimates can also be used in our case. From a technical point of view, the non-linearity and non-convexity of the exchange-correlation term are the main mathematical difficulties in studying the Kohn-Sham LDA model. These are also the reason why conditions (1.2) are different from the one in [1].

This article is organized as follows. In Section 2, we derive some standard properties for ground states. Besides, we study a semi-classical analysis in Kohn-Sham theory. In Section 3, we provide the comparison estimates of the screened potentials, which allows us to control the difference between a ground state density in Kohn-Sham theory with a minimizer of an outer TF functional. Due to the exchange-correlation, these analyses are always more involved than rHF theory, even in the atomic $K = 1$ case. Hence the results in Sect. 2 and Sect. 3 are also some of our contributions and novelties in this paper. The proof of Theorem 1.1 is given in Section 4 using Solovej's iterative argument introduced in [24]. In particular, we study the energy contributions of the densities away from nuclei for both Kohn-Sham and TF theories. Finally, we prove Corollary 1.2, which is a straightforward consequence of Theorem 1.1.

Conventions

We will denote by ρ^{TF}, $\rho_{z_j}^{\mathrm{TF}}$, and ρ_{z_j} the minimizers of $E_{V_{\underline{R}}}^{\mathrm{TF}}(Z)$, $E_{z_j/|x-R_j|}^{\mathrm{TF}}(z_j)$, and $E_{z_j/|x-R_j|}(z_j)$, respectively. For $N \le Z$, we denote minimizers for $E_{V_{\underline{R}}}(N)$ and $E_{V_{\underline{R}}}(Z)$ by the same γ_0 when no confusion can arise, and write its density ρ_0 for short. Then we introduce here the screened potentials defined by

$$\begin{aligned}
\Phi_r(x) &:= V_{\underline{R}}(x) - \int_{A_r^c} \frac{\rho_0(y)}{|x-y|}\,dy,\\
\Phi_r^{\mathrm{TF}}(x) &:= V_{\underline{R}}(x) - \int_{A_r^c} \frac{\rho^{\mathrm{TF}}(y)}{|x-y|}\,dy,\\
\Phi_{j,r}(x) &:= z_j|x-R_j|^{-1} - \int_{|x-R_j|<r} \frac{\rho_{z_j}(y)}{|x-y|}\,dy,\\
\Phi_{j,r}^{\mathrm{TF}}(x) &:= z_j|x-R_j|^{-1} - \int_{|x-R_j|<r} \frac{\rho_{z_j}^{\mathrm{TF}}(y)}{|x-y|}\,dy.
\end{aligned}$$

where A_r^c stands for the complement of $A_r = \{x \in \mathbb{R}^3 \colon |x - R_j| > r \text{ for all } j = 1, \ldots, K\}$. Besides, we will use the standard notation

$$D(f,g) := \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{f(x)g(y)}{|x-y|}\,dxdy.$$

Our proofs of the results in this paper also work for atomic Kohn-Sham theory with slight modifications. For instance, the quantity $R_{\min}/4$ is replaced by 1 in that case.

2. Properties of the ground state

In this section, we assume $N \leq Z$, and γ_0 denotes a minimizer for $E_{V_{\underline{R}}}(N)$. First, we show some a-priori bounds for the ground state γ_0.

Proposition 2.1. For any density matrix $\gamma \in \mathcal{DM}$ it follows that for any $\varepsilon > 0$

$$E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma) \leq \varepsilon \int \rho_\gamma^{5/3} + 2c_\varepsilon \operatorname{tr}\gamma, \tag{2.1}$$

where $c_\varepsilon = \max\{1, \varepsilon^{-3/2}\}$.

Moreover, we have

$$0 \geq E_{V_{\underline{R}}}(N) \geq \frac{1}{4}\operatorname{tr}(-\Delta\gamma_0) - C\sum_{j=1}^{K} z_j^{7/3}. \tag{2.2}$$

Proof. By our assumption, we have

$$E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma) \leq \int (\rho_\gamma^{1+\beta_+} + \rho_\gamma^{1+\beta_-}).$$

Using Hölder's inequality, we see that

$$\int \rho_\gamma^{1+\beta_\pm} \leq \left(\int \rho_\gamma^{5/3}\right)^{3\beta_\pm/2} \left(\int \rho_\gamma\right)^{1-3\beta_\pm/2}.$$

Now we use the inequality $a^\alpha b^\beta \leq \varepsilon\alpha a + \beta\varepsilon^{-\alpha\beta^{-1}} b$ for arbitrary $a, b, \varepsilon > 0$, and $0 < \alpha < 1$, $0 < \beta < 1$ such that $\alpha + \beta = 1$. This follows from inserting $x = a/b$ in the simple inequality $x^\alpha \leq \varepsilon\alpha x + (1-\alpha)\varepsilon^{-\alpha(1-\alpha)^{-1}}$. Then (2.1) follows. On the other hand, by the Lieb-Thirring inequality, we have

$$\operatorname{tr}(-\Delta\gamma_0) \geq C\int_{\mathbb{R}^3} \rho_0(x)^{5/3}\,dx.$$

In addition, we know $0 \geq E_{V_{\underline{R}}}(N)$ [1, Lem. 1]. Together with these results, we obtain

$$\begin{aligned} 0 \geq E_{V_{\underline{R}}}(N) &\geq \frac{1}{4}\operatorname{tr}(-\Delta\gamma) + C^{-1}\int \rho_0^{5/3} - \int V_{\underline{R}}\rho_0 + D(\rho_0) - CZ \\ &\geq \frac{1}{4}\operatorname{tr}(-\Delta\gamma) - C\sum_{j=1}^{K} z_j^{7/3}, \end{aligned}$$

where we have used the bound on the Thomas-Fermi energy $E_{V_{\underline{R}}}^{\mathrm{TF}}(Z) \geq -c\sum_{j=1}^{K} z_j^{7/3}$. This shows (2.2). □

The following lemma is the first step towards a proof of the universal bound of the Born-Oppenheimer energy.

Lemma 2.2 (Initial step). *It follows that*

$$E_{V_{\underline{R}}}(N) \geq \mathcal{E}^{\mathrm{TF}}_{V_{\underline{R}}}(\rho^{\mathrm{TF}}) + D(\rho_0 - \rho^{\mathrm{TF}}) - CZ^{25/11}. \tag{2.3}$$

Moreover, there is a universal constant $C_1 > 0$ such that for any $r \in (0, R_{\min}/4]$

$$\sup_{x \in \partial A_r} |\Phi^{\mathrm{TF}}_r(x) - \Phi_r(x)| \leq C_1 Z^{\frac{49}{36} - a} r^{1/12}, \tag{2.4}$$

where $a = 1/198$.

This lemma allows us to control x near the nuclei since $Z^{49/36} r^{1/12} \leq r^{-4}$ for $r \leq Z^{-1/3}$.

Proof of Lemma 2.2. We bound $\mathcal{E}(\gamma_0)$ from above and below. It is easy to see that $E_{V_{\underline{R}}}(N) \leq E^{\mathrm{rHF}}_{V_{\underline{R}}}(N) := \inf\{\mathcal{E}_{V_{\underline{R}}}(\gamma) + E^{\mathrm{LDA}}_{\mathrm{xc}}(\rho_\gamma) \colon \gamma \in \mathcal{DM}, \operatorname{tr}\gamma = N\}$, and the upper bound $E^{\mathrm{rHF}}_{V_{\underline{R}}}(N) \leq \mathcal{E}^{\mathrm{TF}}_{V_{\underline{R}}}(\rho^{\mathrm{TF}}) + CZ^{25/11}$ has been shown in [12, Eq. (5.2)].

Inserting $\varepsilon = Z^{-8/15}$ in Proposition 2.1, we obtain

$$E^{\mathrm{LDA}}_{\mathrm{xc}}(\rho_0^{1+\beta_\pm}) \leq CZ^{\frac{9}{5}}.$$

Let $\varphi^{\mathrm{TF}} := V_{\underline{R}} - \rho^{\mathrm{TF}} \star |\cdot|^{-1}$ be the TF potential for $E^{\mathrm{TF}}_{V_{\underline{R}}}(Z)$. Then we have

$$\begin{aligned}\mathcal{E}_{V_{\underline{R}}}(\gamma_0) &\geq \operatorname{tr}\left[\left(-\frac{\Delta}{2} - V_{\underline{R}}\right)\gamma_0\right] + D(\rho_0) - CZ^{\frac{9}{5}} \\ &= \operatorname{tr}\left[\left(-\frac{\Delta}{2}(1-\varepsilon) - \varphi^{\mathrm{TF}} \star g^2\right)\gamma_0\right] + D(\rho_0 - \rho^{\mathrm{TF}}) - D(\rho^{\mathrm{TF}}) \\ &\quad + \operatorname{tr}\left[\left(-\frac{\Delta}{2}\varepsilon - (\varphi^{\mathrm{TF}} - \varphi^{\mathrm{TF}} \star g^2)\right)\gamma_0\right] - CZ^{\frac{9}{5}},\end{aligned}$$

for arbitrary $\varepsilon > 0$ and g. Now we use coherent states as in [25]. For any $s > 0$ we take the function $g \colon \mathbb{R}^3 \to \mathbb{R}$ such that $g(x) = 0$ if $|x| > s$ and $g(x) = (2\pi s)^{-1/2}|x|^{-1}\sin(\pi|x|/s)$ if $|x| \leq s$. Then it holds that

$$0 \leq g \leq 1, \quad \int g^2 = 1, \quad \int |\nabla g|^2 = \left(\frac{\pi}{s}\right)^2.$$

The coherent states associated g is given by $f_{k,y}(x) = \exp(ik \cdot x)g(x-y)$ for $k, y \in \mathbb{R}^3$. Let $\pi_{k,y}$ be the projection in $L^2(\mathbb{R}^3)$ onto $f_{k,y}$, i.e., $(\pi_{k,y}\psi)(x) = f_{k,y}\langle f_{k,y}, \psi\rangle$ for $\psi \in L^2(\mathbb{R}^3)$. Then from the resolution of the identity and representation of the kinetic energy [18, Thm. 12.8 & 12.9], we have

$$\begin{aligned}
&\mathrm{tr}\left[\left(-\frac{\Delta}{2}(1-\varepsilon)-\varphi^{\mathrm{TF}}\star g^2\right)\gamma_0\right]\\
&\quad= (2\pi)^{-3}\iint dkdy\left(\frac{k^2}{2}(1-\varepsilon)-\varphi^{\mathrm{TF}}(y)\right)\mathrm{tr}(\pi_{k,y}\gamma_0)-\pi^2(2s^2)^{-1}N\\
&\quad\geq (2\pi)^{-3}\iint_{\frac{k^2}{2}(1-\varepsilon)-\varphi^{\mathrm{TF}}(y)<0} dkdy\left(\frac{k^2}{2}(1-\varepsilon)-\varphi^{\mathrm{TF}}(y)\right)-\pi^2(2s^2)^{-1}N\\
&\quad= -2^{3/2}(15\pi^2)^{-1}(1-\varepsilon)^{-3/2}\int_{\mathbb{R}^3}\varphi^{\mathrm{TF}}(x)^{5/2}\,dx-\pi^2(2s^2)^{-1}N.
\end{aligned}$$

On the other hand, the Lieb-Thirring inequality leads to that

$$\mathrm{tr}\left[\left(-\frac{\Delta}{2}\varepsilon-(\varphi^{\mathrm{TF}}-\varphi^{\mathrm{TF}}\star g^2)\right)\gamma_0\right]\geq -C\varepsilon^{-3/2}\|[\varphi^{\mathrm{TF}}-\varphi^{\mathrm{TF}}\star g^2]_+\|_{L^{5/2}}^{5/2}.$$

Optimizing over ε, we see that

$$\begin{aligned}
&-2^{3/2}(15\pi^2)^{-1}(1-\varepsilon)^{-3/2}\int_{\mathbb{R}^3}\varphi^{\mathrm{TF}}(x)^{5/2}\,dx-C\varepsilon^{-3/2}\|[\varphi^{\mathrm{TF}}-\varphi^{\mathrm{TF}}\star g^2]_+\|_{L^{5/2}}^{5/2}\\
&\qquad\geq -2^{3/2}(15\pi^2)^{-1}\int_{\mathbb{R}^3}\varphi^{\mathrm{TF}}(x)^{5/2}\,dx-C\|\varphi^{\mathrm{TF}}\|_{L^{5/2}}\|[\varphi^{\mathrm{TF}}-\varphi^{\mathrm{TF}}\star g^2]_+\|_{L^{5/2}}^{3/2}.
\end{aligned}$$

By the TF equation $2^{-1}(3\pi^2)^{2/3}(\rho^{\mathrm{TF}})^{2/3}=\varphi^{\mathrm{TF}}$, it follows that

$$\int\varphi^{\mathrm{TF}}(x)^{5/2}\,dx\leq CZ^{7/3}$$

and

$$-2^{3/2}(15\pi^2)^{-1}\int[\varphi^{\mathrm{TF}}]_+^{5/2}-D(\rho^{\mathrm{TF}})=\mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}).$$

Next, we note that $V_{\underline{R}}-V_{\underline{R}}\star g^2\geq 0$ since $V_{\underline{R}}$ is superharmonic. Then we have

$$\|[\varphi^{\mathrm{TF}}-\varphi^{\mathrm{TF}}\star g^2]_+\|_{L^{5/2}}^{5/2}\leq\int|V_{\underline{R}}-V_{\underline{R}}\star g^2|^{5/2}\leq CZ^{5/2}s^{1/2}.$$

Here we have used

$$V_{\underline{R}}-V_{\underline{R}}\star g^2\leq\sum_{j=1}^{K}z_j(|x-R_j|^{-1}\mathbb{1}(|x-R_j|\leq s)).$$

Together with these results, we have

$$E_{V_{\underline{R}}}(N)\geq\mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}})+D(\rho_0-\rho^{\mathrm{TF}})-Cs^{-2}Z-CZ^{12/5}s^{1/5}-CZ^{\frac{9}{5}}.$$

Optimizing over $s>0$, we conclude that (2.3) and hence

$$D(\rho_0-\rho^{\mathrm{TF}})\leq CZ^{\frac{25}{11}}.$$

We use the following estimate taken from [11, Lem. 12].

Lemma 2.3 (Coulomb estimate)**.** *For any* $f \in L^{5/3} \cap L^{6/5}(\mathbb{R}^3)$ *and for any* $x \in \mathbb{R}^3$ *it follows that*

$$\left| \int_{|y|<|x|} \frac{f(y)}{|x-y|}\, dy \right| \le C\|f\|_{L^{5/3}}^{5/6}(|x|D(f))^{1/12}.$$

By harmonicity of the functional $\Phi_r^{\mathrm{TF}} - \Phi_r$, we see that for any $r \in (0, R_{\min}/4]$

$$\begin{aligned} \sup_{x\in A_r} |\Phi_r^{\mathrm{TF}} - \Phi_r| &\le \sum_{j=1}^{K} \sup_{|x-R_j|=r} \left| \int_{|y|<r} \frac{\rho_0(y+R_j) - \rho^{\mathrm{TF}}(y+R_j)}{|x-R_j-y|} \right| \\ &\le C\|\rho_0 - \rho^{\mathrm{TF}}\|_{L^{5/3}}^{5/6}(rD(\rho_0-\rho^{\mathrm{TF}}))^{1/12} \\ &\le CZ^{49/36-a}r^{1/12}, \end{aligned}$$

which is the desired conclusion. □

3. Screened potential estimates

From now on γ_0 denotes a minimizer for $E_{V_{\underline{R}}}(Z)$. we choose the smooth function $\eta_r \colon \mathbb{R}^3 \to [0,1]$ such that $\mathbb{1}_{A_r} \ge \eta_r \ge \mathbb{1}_{A_{(1+\lambda)r}}$ and partition of unity, $\eta_r^2 + \eta_+^2 + \eta_-^2 = 1$, satisfying

$$\operatorname{supp}\eta_- \subset A_r^c, \quad \operatorname{supp}\eta_+ \subset A_{(1-\lambda)r} \cap A_{(1+\lambda)r}^c,$$

where $\eta_- = 1$ in $A_{(1-\lambda)r}^c$ and

$$\sum_{\#=+,-,r} |\nabla \eta_\#|^2 \le C(\lambda r)^{-2}.$$

Now we introduce the notation

$$\mathcal{A} := \left\{ (r,\beta,\varepsilon) \colon \sup_{x\in\partial A_r} |\Phi_r^{\mathrm{TF}}(x) - \Phi_r(x)| \le \beta r^{-4+\varepsilon} \right\}. \tag{3.1}$$

Our goal in this section is to provide the following universal bound for the screened potential which is the main technical tool.

Lemma 3.1 (Screened potential estimate)**.** *If* $z_{\min} \ge \delta_0 z_{\max}$ *for some* δ_0*, then there are constants* $C_0, \varepsilon_1, \delta_1 > 0$ *such that* $(r, C_0, \varepsilon_1) \in \mathcal{A}$ *for any* $r \in (0, (R_{\min}/4)^{1+\delta_1}]$.

We will prove Lemma 3.1 by using Solovej's bootstrap argument. The strategy is based on the initial step and the following iterative step. Lemma 2.2 shows $(r, C, \varepsilon) \in \mathcal{A}$ for $r \le Z^{-1/3}$, and we can extend the range of such r up to $\mathcal{O}(1)$ by an iterative procedure.

Lemma 3.2 (Iterative step)**.** *Let* $\eta = (7+\sqrt{73})/2 \sim 7.772$ *and* $\xi = (\sqrt{7}3-7)/2 \sim 0.77$*. We put* $r \in [z_{\min}^{-1/3}, D]$ *with some* $D \in [z_{\min}^{-1/3}, R_{\min}/4]$*, and* $\tilde{r} := r^{\xi/(\xi+\eta)}(R_{\min}/4)^{\eta/(\xi+\eta)}$*. There are universal constants* $C_2, \beta_1, \delta_2, \varepsilon_2 > 0$ *such that, if* $(s, \beta_1, 0) \in \mathcal{A}$ *holds for any* $s \in (0, r]$*, then,* $(s, C_2, \varepsilon_2) \in \mathcal{A}$ *holds for any* $s \in [r^{1/(1+\delta_2)}, \min\{r^{(1-\delta_2)/(1+\delta_2)}, \tilde{r}\}]$.

Remark 3.3. The Sommerfeld asymptotic refers to $\varphi^{\mathrm{TF}}(x) \sim 3^4 2^{-3}\pi^2|x|^{-4}$ for large $|x|$, and the important thing to our purpose is the next order. The above η and ξ are the solutions of $p^2 - 7p = 6$, which comes from comparing $\Delta|x|^{-4}(1+|x|^p) = 12|x|^{-6}(1+(p^2-7p+12)|x|^p/12)$ with $(|x|^{-4}(1+|x|^p))^{3/2} \sim |x|^{-6}(1+3|x|^p/2)$. Our ξ and η are needed for large $|x|$ and for x close to ∂A_r respectively.

To prove Lemma 3.2, we collect the properties of elements in $\mathcal{A}$.

Lemma 3.4. *Let $\beta, D \in (0, R_{\min}/4]$ be some constants. We assume that $(r,\beta,0) \in \mathcal{A}$ holds for all $r \leq D$. Then for any $r \in (0, D]$ we have*

$$\sup_{A_r} |\Phi_r| \leq \frac{C}{r^4}, \tag{3.2}$$

$$\left|\int_{A_r^c} (\rho_0 - \rho^{\mathrm{TF}})\right| \leq \frac{C\beta}{r^3}, \tag{3.3}$$

$$\int_{A_r} \rho_0 \leq \frac{C}{r^3}, \tag{3.4}$$

$$\int_{A_r} \rho_0^{5/3} \leq \frac{C}{r^7}, \tag{3.5}$$

$$\mathrm{tr}(-\Delta\eta_r\gamma_0\eta_r) \leq C\left(\frac{1}{r^7} + \frac{1}{\lambda^2 r^5}\right), \quad \textit{for any } \lambda \in (0, 1/2]. \tag{3.6}$$

Proof of Lemma 3.4. We may split

$$\Phi_r(x) = \Phi_r(x) - \Phi_r^{\mathrm{TF}}(x) + \Phi_r^{\mathrm{TF}}(x).$$

From the Sommerfeld bound and the relation $\varphi^{\mathrm{TF}} \leq \sum_{j=1}^K \varphi_{z_j}^{\mathrm{TF}}$ [16, Cor. 3.6], where $\varphi_{z_j}^{\mathrm{TF}}$ is the TF potential for the density $\rho_{z_j}^{\mathrm{TF}}$, we can see that for $x \in A_r$

$$\Phi_r^{\mathrm{TF}}(x) = \varphi^{\mathrm{TF}}(x) + \int_{A_r} \frac{\rho^{\mathrm{TF}}(y)}{|x-y|}\,dy \leq Cr^{-4}.$$

Then (3.2) follows from our assumption.

Next, we use the following lemma.

Lemma 3.5. *Let f_j be a continuous harmonic function on $B(R_j, r)^c$ vanishing at infinity and $f := \sum_{j=1}^K f_j$. Then we have for any $x \in A_r$ with $r \in (0, R_{\min}/4]$*

$$|f(x)| \leq \frac{4}{3} r \sup_{\partial A_r} |f| \sum_{j=1}^K |x - R_j|^{-1}.$$

Proof of Lemma 3.5. We note that $|x - R_j||f_j(x)| \leq r\sup_{\partial B(R_j,r)} |f_j|$ for any $x \in B(R_j, r)^c$ by the maximum principle (see [10, Lem. 6.5]). Then we have for any fixed j and $x \in A_r$

$$\left|\sum_{i\neq j} f_i(x)\right| \leq \sup_{\partial A_r} |f| + \frac{r}{R_{\min} - r} \sup_{\partial B(R_j,r)} |f_j|.$$

Since $f_j = f - \sum_{i\neq j} f_i$, we see that $\sup_{\partial B(R_j,r)} |f_j| \leq (4/3)\sup_{\partial A_r} |f|$ and thus for any $x \in A_r$

$$|f(x)| \leq \sum_{j=1}^{K} \frac{r}{|x-R_j|} \sup_{\partial B(R_j,r)} |f_j| \leq \sup_{\partial A_r} |f| \sum_{j=1}^{K} \frac{4r}{3|x-R_j|}, \quad \forall x \in A_r,$$

which shows the lemma □

Using Lemma 3.5 with $f = \Phi_r - \Phi_r^{\mathrm{TF}}$, we have

$$\left|\int_{A_r^c} (\rho_0 - \rho^{\mathrm{TF}})\right| = \lim_{|x|\to\infty} |x| \left|\Phi_r^{\mathrm{TF}}(x) - \Phi_r(x)\right| \leq \frac{4}{3}\beta K r^{-3}.$$

This shows (3.3). Then (3.4) follows from the Sommerfeld bound $\int_{A_r} \rho^{\mathrm{TF}} \leq Cr^{-3}$ and splitting

$$\int_{A_r} \rho_0 = \int_{A_r} \rho^{\mathrm{TF}} + \int_{A_r^c} (\rho^{\mathrm{TF}} - \rho_0) \leq Cr^{-3},$$

where we have used (3.3).

Now we introduce the exterior reduced Hartree-Fock model

$$\mathcal{E}_r^{\mathrm{rHF}}(\gamma) := \mathcal{E}_{\Phi_r}^{\mathrm{rHF}}(\gamma) = \mathrm{tr}\left[\left(-\frac{\Delta}{2} - \Phi_r\right)\gamma\right] + D(\rho_\gamma).$$

Then we can split outsides from insides as follows.

Lemma 3.6. *For any $r \in (0, R_{\min}/4], \lambda \in (0, 1/2]$ and for any $0 \leq \gamma \leq 1$ satisfying*

$$\mathrm{supp}\,\rho_\gamma \subset A_r, \quad \mathrm{tr}\,\gamma \leq \int_{A_r} \rho_0,$$

it holds that

$$\mathcal{E}_{V_{\underline{R}}}(\eta_-\gamma_0\eta_-) + \mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) - \mathcal{R} \leq \mathcal{E}_{V_{\underline{R}}}(\gamma_0) \leq \mathcal{E}_{V_{\underline{R}}}(\eta_-\gamma_0\eta_-) + \mathcal{E}_r^{\mathrm{rHF}}(\gamma),$$

where

$$\begin{aligned}\mathcal{R} \leq C(1 + (\lambda r)^{-2}) &\int_{A_{(1-\lambda)r} \cap A^c_{(1+\lambda)r}} \rho_0 + C\lambda r^3 \sup_{A_{(1-\lambda)r}} [\Phi_{(1-\lambda)r}]_+^{5/2} \\ &+ C\left(\mathrm{tr}(-\Delta\eta_r\gamma_0\eta_r)\right)^{1/2} \left(\int \eta_r\rho_0\right)^{1/2}\end{aligned} \tag{3.7}$$

Proof of Lemma 3.6. First, we note that $N \mapsto E_{V_{\underline{R}}}(N)$ is non-increasing by [1, Lem. 1]. Since η_- and ρ_γ have disjoint supports, we obtain

$$\begin{aligned}\mathcal{E}_{V_{\underline{R}}}(\gamma_0) &\leq \mathcal{E}_{V_{\underline{R}}}(\gamma + \eta_-\gamma_0\eta_-) \\ &= \mathcal{E}_{V_{\underline{R}}}(\eta_-\gamma_0\eta_-) + \mathcal{E}_{V_{\underline{R}}}(\gamma) + 2D(\eta_-^2\rho_0, \rho_\gamma) \\ &\leq \mathcal{E}_{V_{\underline{R}}}(\eta_-\gamma_0\eta_-) + \mathcal{E}_r^{\mathrm{rHF}}(\gamma),\end{aligned}$$

which is the desired upper bound.

Second, by the IMS formula we see that

$$\begin{aligned}\mathcal{E}_{V_{\underline{R}}}(\gamma_0) = &\sum_{\#=+,-,r}\left(\mathcal{E}_{V_{\underline{R}}}(\eta_\#\gamma_0\eta_\#) - \int |\nabla\eta_\#|^2\rho_0\right)\\ &+ 2D(\eta_r^2\rho_0, (\eta_+^2+\eta_-^2)\rho_0) + 2D(\eta_-^2\rho_0, \eta_+^2\rho_0)\\ &- \int\left(g(\rho_0) - \sum_{\#=+,-,r} g(\eta_\#^2\rho_0)\right).\end{aligned}$$

For the error terms, we have

$$\sum_{\#=+,-,r}\int |\nabla\eta_\#|^2\rho_0 \le C(\lambda r)^{-2}\int_{A_{(1-\lambda)r}\cap A^c_{(1+\lambda)r}}\rho_0.$$

Next, a simple computation shows that

$$\begin{aligned}&\mathcal{E}_{V_{\underline{R}}}(\eta_r\gamma_0\eta_r) + 2D(\eta_r^2\rho_0, (\eta_+^2+\eta_-^2)\rho_0)\\ &\quad\ge \mathcal{E}_{V_{\underline{R}}}(\eta_r\gamma_0\eta_r) + 2D(\eta_r^2\rho_0, \mathbb{1}_{A_r^c}\rho_0)\\ &\quad= \mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) - E_{\mathrm{xc}}^{\mathrm{LDA}}(\eta_r^2\rho_0),\end{aligned}$$

and

$$\begin{aligned}&\mathcal{E}_{V_{\underline{R}}}(\eta_+\gamma_0\eta_+) + 2D(\eta_+^2\rho_0, \eta_-^2\rho_0)\\ &\quad\ge \mathcal{E}_{V_{\underline{R}}}(\eta_+\gamma_0\eta_+) + 2D(\eta_+^2\rho_0, \mathbb{1}_{A^c_{(1-\lambda)r}}\rho_0)\\ &\quad= \mathcal{E}_{(1-\lambda)r}^{\mathrm{rHF}}(\eta_+\gamma_0\eta_+) - E_{\mathrm{xc}}^{\mathrm{LDA}}(\eta_+^2\rho_0).\end{aligned}$$

We note that

$$g(\rho_0) - g(\eta_-^2\rho_0) \le C(\rho_0^{\beta_-} + \rho_0^{\beta_+})(\eta_+^2 + \eta_r^2)\rho_0,$$

and, by Hölder's inequality and the Lieb-Thirring inequality, for any $\beta \le 2/5$ and $0 \le \chi \le 1$

$$\begin{aligned}\int_{A_{(1-\lambda)r}}\rho_0^{1+\beta}\chi^2 &\le \left(\int (\chi^2\rho_0)^{5/3}\right)^{3\beta/2}\left(\int_{A_{(1-\lambda)r}}\rho_0\right)^{1-3\beta/2}\\ &\le C\left(\mathrm{tr}(-\Delta\chi\gamma_0\chi)\right)^{3\beta/2}\left(\int_{A_{(1-\lambda)r}}\rho_0\right)^{1-3\beta/2}\\ &\le \frac{1}{8}\mathrm{tr}(-\Delta\chi\gamma_0\chi) + C\int_{A_{(1-\lambda)r}}\rho_0.\end{aligned}$$

In the last inequality, we have used the simple inequality $a^\alpha b^\beta \le \varepsilon\alpha a + \beta\varepsilon^{-\alpha\beta^{-1}}b$ for arbitrary $a, b, \varepsilon > 0$, and $0 < \alpha < 1$, $0 < \beta < 1$ such that $\alpha + \beta = 1$ (recall the proof of Proposition 2.1). The Lieb-Thirring inequality with $V = \Phi_{(1-\lambda)r}\mathbb{1}_{\mathrm{supp}\eta_+}$ implies that

$$\mathrm{tr}\left[\left(-\frac{\Delta}{4} - \Phi_{(1-\lambda)r}\right)\eta_+\gamma_0\eta_+\right] \ge -C\int [V]_+^{5/2} \ge -C\lambda r^3 \sup_{A_{(1-\lambda)r}}[\Phi_{(1-\lambda)r}]_+^{5/2}.$$

Together with these estimates, we have the lemma. □

Applying Lemma 3.6, we can obtain the kinetic energy estimate.

Lemma 3.7. *For all $r \in (0, R_{\min}/4]$ and all $\lambda \in (0, 1/2]$ it holds that*

$$\operatorname{tr}(-\Delta\eta_r\gamma_0\eta_r) \le C(1 + (\lambda r)^{-2}) \int_{A_{(1-\lambda)r}} \rho_0 + C\lambda r^3 \sup_{A_{(1-\lambda)r}} [\Phi_{(1-\lambda)r}]_+^{5/2} + C \sup_{\partial A_r} |r\Phi_r|^{7/3}.$$

Proof of Lemma 3.7. We use Lemma 3.6 with $\gamma = 0$ and obtain $\mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) \le \mathcal{R}$. On the other hand, by the Lieb-Thirring inequality and property of the ground state energy of TF theory, we have

$$\begin{aligned}\mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) &\ge \operatorname{tr}\left(-\frac{\Delta}{4}\eta_r\gamma_0\eta_r\right) + C^{-1}\int (\eta_r^2\rho_0)^{5/3} \\ &\quad - C\sup_{\partial A_r}|r\Phi_r| \sum_{j=1}^K \int \eta_r^2 \frac{\rho_0(x)}{|x - R_j|}\, dx + D(\eta_r^2\rho_0) \\ &\ge \operatorname{tr}\left(-\frac{\Delta}{4}\eta_r\gamma_0\eta_r\right) - C\sup_{\partial A_r}|r\Phi_r|^{7/3},\end{aligned}$$

where we have used Lemma 3.5. This completes the proof. □

Combining this with (3.4), we deduce from $(1-\lambda)r > r/3$ that

$$\operatorname{tr}(-\Delta\eta_r\gamma_0\eta_r) \le C\left(\lambda^{-2}r^{-5} + r^{-7}\right),$$

which shows (3.6) Replacing r by $r/3$, we learn

$$\int_{A_r} \rho_0^{5/3} \le \int (\eta_{r/3}^2\rho_0)^{5/3} \le C\operatorname{tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \le C\left(\lambda^{-2}r^{-5} + r^{-7}\right),$$

where we have used the Lieb-Thirring inequality. Choosing $\lambda = 1/2$, we have (3.5). □

With $V_r(x) = \mathbb{1}_{A_r}\Phi_r(x)$, we denote the exterior Thomas-Fermi functional $\mathcal{E}_{V_r}^{\mathrm{TF}}(\rho)$ briefly by $\mathcal{E}_r^{\mathrm{TF}}(\rho)$. The following lemmata are very similar to that of [12, Lem. 6.4, 6.6, 6.8], but we provide their proofs for the reader's convenience.

Lemma 3.8. *The exterior TF energy $E_r^{\mathrm{TF}}(\operatorname{tr}(\mathbb{1}_{A_r}\gamma_0\mathbb{1}_{A_r}))$ has a unique minimizer ρ_r^{TF}, which is supported on A_r and satisfies the TF equation*

$$\frac{1}{2}(3\pi^2)^{2/3}\rho_r^{\mathrm{TF}}(x)^{2/3} = [\varphi_r^{\mathrm{TF}}(x) - \mu_r]_+$$

with $\varphi_r^{\mathrm{TF}}(x) = V_r(x) - \rho_r^{\mathrm{TF}} \star |x|^{-1}$ and a constant $\mu_r \ge 0$. Moreover,

(i) *If $\mu_r > 0$, then*

$$\int \rho_r^{\mathrm{TF}} = \int_{A_r} \rho_0.$$

(ii) *If* $(r,\beta,0)\in\mathcal{A}$ *holds true for some* β *and any* $r\in(0,D]$ *with* $D\in(0,R_{\min}/4]$, *then*

$$\int(\rho_r^{\rm TF})^{5/3}\le Cr^{-7},\quad \textit{for any } r\in(0,D].$$

Proof. By $\varphi_r^{\rm TF}\le V_r$ and the TF equation, $\operatorname{supp}\rho_r^{\rm TF}\subset A_r$ follows. From the fact that $\inf_{\rho\ge0}\mathcal{E}^{\rm TF}_{V_{\underline{R}}}(\rho)\ge -C\sum_j z_j^{7/3}$ and Lemma 3.5, we can see

$$\begin{aligned}0\ge\mathcal{E}^{\rm TF}_{V_r}(\rho_r^{\rm TF})&\ge\frac{3}{10}(3\pi^2)^{2/3}\int(\rho_r^{\rm TF})^{5/3}-Cr^{-3}\sum_{j=1}^{K}\int\rho_r^{\rm TF}(x)|x-R_j|^{-1}\,dx+D(\rho_r^{\rm TF})\\&\ge\frac{3}{5}(3\pi^2)^{2/3}\int(\rho_r^{\rm TF})^{5/3}-Cr^{-7},\end{aligned}$$

which shows (ii). The rest of the proof was shown in [19]. □

Lemma 3.9. *Let* $D\in[z_{\min}^{-1/3},R_{\min}/4]$. *We can choose a universal constant* $\beta>0$ *small enough such that, if* $(r,\beta,0)\in\mathcal{A}$ *holds for any* $r\in[z_{\min}^{-1/3},D]$, *then* $\mu_r=0$ *and for any* $s\in[r,\tilde r]$ *with* $\tilde r=r^{\frac{\xi}{\xi+\eta}}(R_{\min}/4)^{\frac{\eta}{\xi+\eta}}$ *it follows that*

$$\sup_{x\in\partial A_s}|\varphi_r^{\rm TF}(x)-\varphi^{\rm TF}(x)|\le C(r/s)^{\xi}s^{-4},\tag{3.8}$$

$$\sup_{x\in\partial A_s}|\rho_r^{\rm TF}(x)-\rho^{\rm TF}(x)|\le C(r/s)^{\xi}s^{-6}.\tag{3.9}$$

Proof. **(Step 1)**: First, we show that $\mu_r\le C\beta^{1/2}r^{-4}$ and

$$D(\rho_r^{\rm TF}-\rho^{\rm TF}\mathbb{1}_{A_r})\le C\beta r^{-7+\varepsilon}.\tag{3.10}$$

Let $\rho_{r,t}:=\rho^{\rm TF}\mathbb{1}_{A_r\cap A_t^c}$ and $W(x)=\Phi_r^{\rm TF}(x)-\Phi_r(x)$. Then for any $t\ge r$

$$\mathcal{E}_r^{\rm TF}(\rho_{r,t})+\mu_r\int\rho_{r,t}\ge\mathcal{E}_r^{\rm TF}(\rho_r^{\rm TF})+\mu_r\int\rho_r^{\rm TF},$$

where we have used the fact that $\mu_r\int\rho_r^{\rm TF}=\mu_r\int_{A_r}\rho_0$. By the same method as in the proof of Lemma 3.8, we can see that

$$\begin{aligned}\mathcal{E}_r^{\rm TF}(\rho_{r,t})-\mathcal{E}_r^{\rm TF}(\rho^{\rm TF}\mathbb{1}_{A_r})&=-\mathcal{E}_W^{\rm TF}(\rho^{\rm TF}\mathbb{1}_{A_t})+\int_{A_t}\Phi_t^{\rm TF}\rho^{\rm TF}\\&\le C\beta r^{-7+\varepsilon}+Ct^{-7}.\end{aligned}$$

Since $t\mapsto(3/10)c_{\rm TF}t^{5/3}-\varphi^{\rm TF}t$ takes its minimum at $t=\rho^{\rm TF}$, we learn

$$\begin{aligned}\mathcal{E}_r^{\rm TF}(\rho^{\rm TF}\mathbb{1}_{A_r})-\mathcal{E}_r^{\rm TF}(\rho_r^{\rm TF})&=\int_{A_r}W\left(\rho^{\rm TF}-\rho_r^{\rm TF}\right)-D(\rho_r^{\rm TF}-\rho^{\rm TF}\mathbb{1}_{A_r})\\&\quad+\int_{A_r}\left(\frac{3}{10}c_{\rm TF}(\rho^{\rm TF})^{5/3}-\frac{3}{10}c_{\rm TF}(\rho_r^{\rm TF})^{5/3}-\varphi^{\rm TF}\rho^{\rm TF}+\varphi^{\rm TF}\rho_r^{\rm TF}\right)\\&\le C\beta r^{-7+\varepsilon}-D(\rho_r^{\rm TF}-\rho^{\rm TF}\mathbb{1}_{A_r}).\end{aligned}$$

Combining these estimates, we arrive at

$$0 \le \mu_r \left(\int_{A_r} \rho_0 - \int \rho_{r,t} \right) \le \mathcal{E}_r^{\mathrm{TF}}(\rho_{r,t}) - \mathcal{E}_r^{\mathrm{TF}}(\rho^{\mathrm{TF}} \mathbb{1}_{A_r}) + \mathcal{E}_r^{\mathrm{TF}}(\rho^{\mathrm{TF}} \mathbb{1}_{A_r}) - \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}})$$
$$\le C(\beta r^{-7+\varepsilon} + \beta r^{-7+\varepsilon} + t^{-7}) - D(\rho_r^{\mathrm{TF}} - \rho^{\mathrm{TF}} \mathbb{1}_{A_r}).$$

Choosing $t = \beta^{-1/7} r^{1-\varepsilon}$, we have (3.10).

Since $\varphi^{\mathrm{TF}} \ge \max_j \varphi_{z_j}^{\mathrm{TF}}$ [16, Thm. 3.4] and the Sommerfeld bound [25, Thm. 5.4], we see $\int_{A_s} \rho^{\mathrm{TF}} \ge C^{-1} s^{-3}$ for any $s \ge z_{\min}^{-1/3}$. We note that

$$\int_{A_r} (\rho^{\mathrm{TF}} - \rho_0) = \int_{A_r^c} (\rho_0 - \rho^{\mathrm{TF}}) \le \beta r^{-3} \le C\beta \int_{A_r} \rho^{\mathrm{TF}}.$$

Hence it holds that for $t = \beta^{-1/6} r$

$$\int_{A_r} \rho_0 - \int \rho_{r,t} \ge \int_{A_t} \rho^{\mathrm{TF}} - C\beta \int_{A_r} \rho^{\mathrm{TF}} \ge C^{-1} \beta^{1/2} r^{-3} - C\beta r^{-3}.$$

Then the conclusion $\mu_r \le C\beta^{1/2} r^{-4}$ follows for β sufficiently small.

(Step 2): We turn to prove $\mu_r = 0$. By the Sommerfeld bound and our assumption, we see

$$\inf_{\partial A_r} \varphi_r^{\mathrm{TF}} = \inf_{\partial A_r} \left(\varphi^{\mathrm{TF}} - [\Phi_r^{\mathrm{TF}} - \Phi_r] + (\rho^{\mathrm{TF}} \mathbb{1}_{A_r} - \rho_r^{\mathrm{TF}}) \star |x|^{-1} \right)$$
$$\ge C^{-1} r^{-4} - \beta r^{-4+\varepsilon} - \sup_{\partial A_r} |(\rho^{\mathrm{TF}} \mathbb{1}_{A_r} - \rho_r^{\mathrm{TF}}) \star |x|^{-1}|.$$

By Step 1 and the Coulomb estimate $f \star |x|^{-1} \le C \|f\|_{L^{5/3}}^{5/7} D[f]^{1/7}$ [10, Lem. 6.4], we find

$$\sup_{\partial A_r} |(\rho^{\mathrm{TF}} \mathbb{1}_{A_r} - \rho_r^{\mathrm{TF}}) \star |x|^{-1}| \le C \|\rho^{\mathrm{TF}} \mathbb{1}_{A_r} - \rho_r^{\mathrm{TF}}\|_{L^{5/3}}^{5/7} D[\rho^{\mathrm{TF}} \mathbb{1}_{A_r} - \rho_r^{\mathrm{TF}}]^{1/7}$$
$$\le C\beta^{1/7} r^{-4+\varepsilon}.$$

Hence if $\beta > 0$ is small enough then we deduce from Step 1 that

$$\inf_{\partial A_r} \varphi_r^{\mathrm{TF}} > C^{-1} r^{-4} \ge \mu_r.$$

Then by the Sommerfeld estimate for molecules [12, Lem. 4.1] we see

$$C^{-1} \mu_r^{3/4} (1 + a(r))^{-1/2} \le \lim_{|x| \to \infty} |x| \varphi_r^{\mathrm{TF}}(x) = \int_{A_r} \rho_0 - \int \rho_r^{\mathrm{TF}},$$

where $a(r) \coloneqq \sup_{\partial A_r} (\sqrt{c_{\mathrm{S}} (\varphi_r^{\mathrm{TF}})^{-1} r^{-4}} - 1)$. This shows $\mu_r = 0$ by Lemma 3.8.

(Step 3): Let $D_j \coloneqq \min_{i \ne j} |R_i - R_j|/2$. Using the Sommerfeld bound for molecules [12, Lem. 4.1 & Lem. 4.2], we have for any $x \in A_r \cap \Gamma_j$

$$|\varphi^{\mathrm{TF}}(x) - \varphi_r^{\mathrm{TF}}(x)| \le C|x - R_j|^{-4} \left(\left(\frac{|x - R_j|}{D_j} \right)^{\eta} + \left(\frac{r}{|x - R_j|} \right)^{\xi} \right),$$

where $\xi = (-7+\sqrt{73})/2$ and $\eta = (7+\sqrt{73})/2$. Since $s \le \tilde{r}$ implies $(s/D_j)^\eta \le C(r/s)^\xi$, we have (3.8). Then (3.9) follows from $(1+a)^{3/2} \le 1 + a((1+b)^{3/2}-1)/b$ for any $a \in [0,b]$. □

Lemma 3.10. *Let $\beta > 0$ be as in Lemma 3.9 and $D \in [z_{\min}^{-1/3}, R_{\min}/4]$. We assume that $(r,\beta,0) \in \mathcal{A}$ for any $r \in (0,D]$. Then, if $r \in [z_{\min}^{-1/3}, D]$, we have*

$$\mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + D(\eta_r^2\rho_0 - \rho_r^{\mathrm{TF}}) - Cr^{-7+1/3} \le \mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) \le \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + Cr^{-7+1/3}, \quad (3.11)$$

and

$$D(\rho_r^{\mathrm{TF}} - \mathbb{1}_{A_r}\rho) \le Cr^{-7+1/3}.$$

Proof. Upper Bound. We will prove that

$$\mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) \le \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + Cr^{-7}(r^{2/3} + \lambda^{-2}r^2 + \lambda).$$

Let $s \le r$ be a constant to be chosen later. We take the function g and projection $\pi_{k,y}$ as in Lemma 2.2, and define

$$\widetilde{\gamma} := (2\pi)^{-3} \iint_{\frac{k^2}{2} - V_r'(y) \le 0} \pi_{k,y}\, dy dk,$$

with $V_r' := \mathbb{1}_{A_{r+s}}\varphi_r^{\mathrm{TF}}$. Since $\mu_r = 0$ by Lemma 3.9 and the TF equation in Lemma 3.8, we can see

$$\rho_{\widetilde{\gamma}} = (\mathbb{1}_{A_{r+s}}\rho_r^{\mathrm{TF}}) \star g^2.$$

Since $\rho_{\widetilde{\gamma}}$ is supported in A_r and

$$\mathrm{tr}\,\widetilde{\gamma} = \int \rho_{\widetilde{\gamma}} = \int_{A_{r+s}} \rho_r^{\mathrm{TF}} \le \int \rho_r^{\mathrm{TF}} \le \int_{A_r} \rho_0,$$

we may apply Lemma 3.6 and obtain $\mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) \le \mathcal{E}_r^{\mathrm{rHF}}(\widetilde{\gamma}) + \mathcal{R}$. By simple computation

$$\mathrm{tr}\left(-\frac{\Delta}{2}\widetilde{\gamma}\right) = 2^{3/2}(5\pi^2)^{-1}\int [V_r']_+^{5/2} + 2^{1/2}(3s^2)^{-1}\int [V_r']_+^{3/2},$$

we have

$$\begin{aligned}\mathcal{E}_r^{\mathrm{rHF}}(\widetilde{\gamma}) \le \frac{3}{10}(3\pi^2)^{2/3}\int (\rho_r^{\mathrm{TF}})^{5/3} - \int_{A_r}\Phi_r\rho_r^{\mathrm{TF}} + D(\rho_r^{\mathrm{TF}}) \\ + Cs^{-2}\int \rho_r^{\mathrm{TF}} + \int_{A_{r+s}}(\Phi_r - \Phi_r \star g^2)\rho_r^{\mathrm{TF}} + \int_{A_r\cap A_{r+s}^c}\Phi_r\rho_r^{\mathrm{TF}} \\ = \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + Cs^{-2}\int \rho_r^{\mathrm{TF}} + \int_{A_r\cap A_{r+s}^c}\Phi_r\rho_r^{\mathrm{TF}},\end{aligned}$$

where we have used $\Phi_r - \Phi_r \star g^2 = 0$ on A_{r+s}. This fact follows from the mean value property. Using Lemma 3.5 and Lemma 3.9, we have

$$\int_{A_r\cap A_{r+s}^c}\Phi_r\rho_r^{\mathrm{TF}} \le Csr^{-8}.$$

We choose $s = r^{5/3}$ and get

$$\mathcal{E}_r^{\mathrm{rHF}}(\widetilde{\gamma}) \leq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + Cr^{-7+2/3}.$$

Finally, since $\lambda \leq 1/2$, we have

$$\mathcal{R} \leq C(\lambda^{-2} r^{-5} + \lambda r^{-7}),$$

which shows the desired upper bound.

Lower bound We will prove

$$\mathcal{E}_r^{\mathrm{rHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\mathrm{TF}}) - Cr^{-7+1/3}.$$

As in the proof of Lemma 2.2, we see

$$\begin{aligned}\mathcal{E}_r^{\mathrm{rHF}}(\eta_r \gamma_0 \eta_r) &= \mathrm{tr}\left[\left(-\frac{\Delta}{2} - \varphi_r^{\mathrm{TF}}\right)\eta_r \gamma_0 \eta_r\right] + D(\eta_r^2 \rho_0 - \rho_r^{\mathrm{TF}}) - D(\rho_r^{\mathrm{TF}}) \\ &\geq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\mathrm{TF}}) - Cs^{-2}\int \eta_r^2 \rho_0 \\ &\quad - C\left(\int [\varphi_r^{\mathrm{TF}}]_+^{5/2}\right)^{3/5}\left(\int [\varphi_r^{\mathrm{TF}} - \varphi_r^{\mathrm{TF}} \star g^2]_+^{5/2}\right)^{2/5}.\end{aligned}$$

We note that $|x|^{-1} - |x|^{-1} \star g^2 \geq 0$ and thus $\rho_r^{\mathrm{TF}} \star (|x|^{-1} - |x|^{-1} \star g^2) \geq 0$. Since the TF equation, we have

$$\varphi_r^{\mathrm{TF}} - \varphi_r^{\mathrm{TF}} \star g^2 \leq \mathbb{1}_{A_r}\Phi_r - \mathbb{1}_{A_r}\Phi_r \star g^2 =: f.$$

By the mean value property, we infer that $\mathrm{supp} f \subset A_{r-s} \cap A_{r+s}^c$ and thus

$$[\varphi_r^{\mathrm{TF}} - \varphi_r^{\mathrm{TF}} \star g^2]_+ \leq Cr^{-4}\mathbb{1}_{A_{r-s}\cap A_{r+s}^c}.$$

Together with these facts, we conclude that

$$\mathcal{E}_r^{\mathrm{rHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\mathrm{TF}}) - C(s^{-2} r^{-3} + r^{-37/5} s^{2/5}).$$

Then we choose $s = r^{11/6}$ and arrive at the desired lower bound. After choosing $\lambda = r^{1/3}/2$, the estimate (3.11) follows.

Conclusion Combining the upper and lower bound, we learn

$$D(\eta_r^2 \rho_0 - \rho_r^{\mathrm{TF}}) \leq Cr^{-7}(r^{1/3} + \lambda^{-2} r^2 + \lambda).$$

Using the Hardy-Littlewood-Sobolev inequality, we have

$$\begin{aligned}D(\chi_r^+ \rho_0 - \eta_r^2 \rho_0) &\leq C\|\mathbb{1}_{A_r \cap A_{(1+\lambda)r}^c}\rho_0\|_{L^{6/5}}^2 \\ &\leq C\left(\int_{A_r} \rho_0^{5/3}\right)^{6/5}\left(\sum_{j=1}^K \int_{r \leq |x-R_j| \leq (1+\lambda)r} dx\right)^{7/15} \\ &= C\lambda^{7/15} r^{-7}.\end{aligned}$$

By convexity of the Coulomb term $D(\cdot)$, we see

$$\begin{aligned} D(\chi_r^+\rho_0 - \rho_r^{\mathrm{TF}}) &\le 2D(\chi_r^+\rho_0 - \eta_r^2\rho_0) + 2D(\eta_r^2\rho_0 - \rho_r^{\mathrm{TF}}) \\ &\le Cr^{-7}(\lambda^{7/15} + r^{1/3} + \lambda^{-2}r^2), \end{aligned}$$

for any $\lambda \in (0, 1/2]$. Choosing $\lambda = r^{30/37}/2$, we have the upper bound. □

Proof of Lemma 3.2. Let $\delta > 0$ be a constant sufficiently small and $s \in [r^{1/(1+\delta)}, \min\{r^{\frac{1-\delta}{1+\delta}}, \tilde{r}\}]$ with $\tilde{r} = r^{\frac{\xi}{\xi+\eta}}(R_{\min}/4)^{\frac{\eta}{\xi+\eta}}$. We split

$$\begin{aligned} \Phi_s(x) - \Phi_s^{\mathrm{TF}}(x) = \varphi_r^{\mathrm{TF}}(x) - \varphi^{\mathrm{TF}}(x) + \int_{A_s} \frac{\rho_r^{\mathrm{TF}}(y) - \rho^{\mathrm{TF}}(y)}{|x-y|}\,dy \\ + \sum_{j=1}^{K} \int_{|y-R_j|<s} \frac{\rho_r^{\mathrm{TF}}(y) - \mathbb{1}_{A_r}(y)\rho_0(y)}{|x-y|}\,dy. \end{aligned}$$

Using Lemma 3.9, we have

$$\sup_{\partial A_s} |\varphi_r^{\mathrm{TF}}(x) - \varphi^{\mathrm{TF}}(x)| + \sup_{\partial A_s} \left|\mathbb{1}_{A_s}(\rho_r^{\mathrm{TF}} - \rho^{\mathrm{TF}}) \star |x|^{-1}\right| \le C\left(\frac{r}{s}\right)^{\xi} s^{-4}.$$

The Coulomb estimate [10, Lem. 6.4] and Lemma 3.10 lead to that for any $x \in \partial B(R_j, s)^c$

$$\begin{aligned} \left|\mathbb{1}_{B(R_j,s)}(\rho_r^{\mathrm{TF}} - \mathbb{1}_{A_r}\rho_0) \star |x|^{-1}\right| &\le C\|\rho_r^{\mathrm{TF}} - \mathbb{1}_{A_r}\rho_0\|_{L^{5/3}}^{5/6} \left(sD\left[\mathbb{1}_{A_r}\rho_0 - \rho_r^{\mathrm{TF}}\right]\right)^{1/12} \\ &\le Cs^{-4}\left(\frac{s}{r}\right)^4 r^{\varepsilon/12}. \end{aligned}$$

Since $s^{2\delta/(1-\delta)} \le r/s \le s^{\delta}$, we have the lemma. □

Proof of Lemma 3.1. The following proof is the same as in [12, Thm. 7.1] and [22, Thm. 5.1]. By Lemma 2.2, there are constants $C_3 > 0$ and $\varepsilon > 0$ such that $(r, C_3, \varepsilon) \in \mathcal{A}$ for any $r \le z_{\min}^{-1/3}$. Let $\delta > 0$ be a constant small enough, $\sigma = \max\{C_2, C_3\}$ and $D_0 = z_{\min}^{-1/3}$, where C_2 is defined in Lemma 3.2. Now we define for $\varepsilon_0 > 0$ sufficiently small

$$M := \sup\left\{r \in \mathbb{R}\colon \sup_{x\in\partial A_s} \left|\Phi_s(x) - \Phi_s^{\mathrm{TF}}(x)\right| \le \sigma s^{-4+\varepsilon_0},\ \text{for any } s \le r^{\frac{1}{1+\delta}}\right\}.$$

Next, we suppose that (1) $M < R_{\min}/4$, and (2) $(M^{\frac{1}{1+\delta}}, \min\{M^{\frac{1-\delta}{1+\delta}}, \tilde{M}\}) \neq \emptyset$, where $\tilde{M} := M^{\xi/(\xi+\eta)}(R_{\min}/4)^{\eta/(\xi+\eta)}$. If $D_0 < M$, then there is a sequence such that $D_n \to M$ and $D_0 \le D_n \le M$ for large n. From this and Lemma 3.2, we see

$$\sup_{x\in\partial A_r} \left|\Phi_r(x) - \Phi_r^{\mathrm{TF}}(x)\right| \le \sigma r^{-4+\varepsilon_0}, \quad \text{for any } r \in \left[D_n^{\frac{1}{1+\delta}}, \min\left\{D_n^{\frac{1-\delta}{1+\delta}}, \tilde{D}_n\right\}\right],$$

where $\tilde{D}_n := D_n^{\xi/(\xi+\eta)}(R_{\min}/4)^{\eta/(\xi+\eta)}$. From (2), we have

$$M^{\frac{1}{1+\delta}} \in \left(D_n^{\frac{1}{1+\delta}}, \min\left\{D_n^{\frac{1-\delta}{1+\delta}}, \tilde{D}_n\right\}\right) \neq \emptyset$$

for large n. This contradicts the definition of M. If $D_0 = M$, then $D_0 \le R_{\min}/4$ and $(r, \sigma, \varepsilon_0) \in \mathcal{A}$ for any $r \le \min\{M^{\frac{1-\delta}{1+\delta}}, \tilde{M}\}$, which also contradicts the definition of M. Finally, if $D_0 > M$ then we can choose $M' \in (M, D_0)$. This contradicts $(r, \sigma, \varepsilon_0) \in \mathcal{A}$ for any $r \le D_0$. Hence at least one of (1) and (2) cannot hold. If (1) is true, then $M \ge R_{\min}^{\frac{\eta(1+\delta)}{\eta-\delta\xi}}$. Hence the lemma follows. □

4. Proof of Theorem 1.1

The following lemma allows us to control the outside models.

Lemma 4.1. *We assume that $z_{\min} \ge \delta_0 z_{\max}$ for some δ_0, and for $\varepsilon_3, \delta_3 > 0$ sufficiently small $4 \ge R_{\min} \ge \delta_3^{-1} z_{\min}^{-1/3+\alpha}$ with some $\alpha < 2/231$, and $r = \delta_3 R_{\min}^{1+\varepsilon_3}$. Then for any $s \le r$ and $j = 1, \dots, K$ we have*

(1) $\sup_{B(R_j,s)^c} \left| (\rho_{z_j}^{\mathrm{TF}} - \rho^{\mathrm{TF}}) \mathbb{1}_{B(R_j,s)} \star |x|^{-1} \right| \le C s^{-4+\varepsilon_4}$,
(2) $\sup_{B(R_j,s)^c} \left| (\rho_0 - \rho^{\mathrm{TF}}) \mathbb{1}_{B(R_j,s)} \star |x|^{-1} \right| \le C s^{-4+\varepsilon_4}$,
(3) $\left| \int_{B(R_j,s)} (\rho_{z_j}^{\mathrm{TF}} - \rho^{\mathrm{TF}}) \right| \le C s^{-4+\varepsilon_4}$,
(4) $\left| \int_{B(R_j,s)} (\rho_0 - \rho^{\mathrm{TF}}) \right| \le C s^{-4+\varepsilon_4}$,

where $\varepsilon_4 > 0$ is some constant.

Proof. Let $D_j := \min_{i \ne j} |R_i - R_j|/2$ and $\varepsilon > 0$ be a small constant. First, we note that $(s/D_j)^\eta \le C s^\varepsilon$, $s^{1+\varepsilon} \le R_{\min}/4$ by $s \le r$, and $r \ge z_{\min}^{-1/3}$. Using the Sommerfeld estimate [12, Thm. 4.1 & 4.2], we see that for any $x \in \partial B(R_j, s)$

$$\begin{aligned} \varphi^{\mathrm{TF}}(x) - \varphi_{z_j}^{\mathrm{TF}}(x) &\le c_{\mathrm{S}} s^{-4} \left(c_1 \left(\frac{s}{D_j} \right)^\eta + c_2 \left(\frac{s^{1+\varepsilon}}{|x - R_j|} \right)^\xi \right) \\ &=: \varphi_M(x), \end{aligned}$$

where $c_1, c_2 > 0$ are some constants. We recall $\varphi^{\mathrm{TF}} \le \sum_{j=1}^K \varphi_{z_j}^{\mathrm{TF}}$ [16, Cor. 3.6]. Hence for $\delta > 0$ sufficiently small we have $\varphi^{\mathrm{TF}} - \varphi_{z_j}^{\mathrm{TF}} \le \varphi_M$ in $\overline{B(R_j, \delta)}$. Then the maximum principle implies that $\varphi^{\mathrm{TF}} - \varphi_{z_j}^{\mathrm{TF}} \le \varphi_M$ in $\overline{B(R_j, s)}$. Since $(1+t)^{3/2} - 1 \le 3t/2 + 3t^{3/2}/2$ for $t \ge 0$, we obtain

$$\begin{aligned} \rho^{\mathrm{TF}} - \rho_{z_j}^{\mathrm{TF}} &= c (\varphi_{z_j}^{\mathrm{TF}})^{3/2} \left(\left(1 + \left(\varphi^{\mathrm{TF}} - \varphi_{z_j}^{\mathrm{TF}} \right) / \varphi_{z_j}^{\mathrm{TF}} \right)^{3/2} - 1 \right) \\ &\le C \left(\varphi_{z_j}^{\mathrm{TF}} \right)^{1/2} \left(\varphi^{\mathrm{TF}} - \varphi_{z_j}^{\mathrm{TF}} \right) + C \left(\varphi^{\mathrm{TF}} - \varphi_{z_j}^{\mathrm{TF}} \right)^{3/2}. \end{aligned}$$

Using Newton's theorem, we have for $|x - R_j| = s$

$$\int_{|y - R_j| < s} \frac{\rho^{\mathrm{TF}}(y) - \rho_{z_j}^{\mathrm{TF}}(y)}{|x - y|} \, dy \le C s^{-4+\varepsilon},$$

which proves (1).

Next, we split

$$u_j(x) \coloneqq (\rho_0 - \rho^{\mathrm{TF}})\mathbb{1}_{B(R_j,s)} \star |x|^{-1}$$
$$= \underbrace{(\rho_0 - \rho^{\mathrm{TF}})\mathbb{1}_{A_s^c} \star |x|^{-1}}_{=:u_s(x)} - \underbrace{\sum_{i\neq j}(\rho_0 - \rho^{\mathrm{TF}})\mathbb{1}_{B(R_i,s)} \star |x|^{-1}}_{=:u_0(x)}.$$

We note that u_j is harmonic on $B(R_j, s)^c$ and thus $|x - R_j||u_j(x)| \le s \sup_{\partial B(R_j,s)} |u_j|$ for any $x \in B(R_j, s)^c$ by the maximum principle. Hence we see that for all j

$$\sup_{\partial A_s} |u_0| \le \sup_{\partial A_s} |u_s| + \frac{s}{R_{\min} - s} \sup_{B(R_j,s)^c} |u_j|.$$

Then we obtain by Lemma 3.1

$$\sup_{B(R_j,s)^c} |u_j| \le C \sup_{\partial A_s} |u_s| \le C s^{-4+\varepsilon},$$

which shows (2). Moreover, (3) and (4) are easy consequences of the estimates such as

$$\lim_{|x|\to\infty} |x| \left| \int_{|y-R_j|<s} \frac{\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{TF}}_{z_j}(y)}{|x-y|}\, dy \right| \le C s^{-4+\varepsilon}.$$

This completes the proof. □

Let $N_j \coloneqq z_j - \int_{B(R_j,r)} \rho_{z_j}$ and $V_j \coloneqq \mathbb{1}_{B(R_j,r)^c}\Phi_{j,r}$. We note that

$$-\Delta\Phi^{\mathrm{TF}}_{j,r} = 4\pi(z_j\delta_j - \rho^{\mathrm{TF}}_{z_j}\mathbb{1}_{B(R_j,r)}),$$

where δ_j is the Dirac measure at R_j, and thus

$$\begin{aligned}\frac{1}{4\pi}\int_{\mathbb{R}^3} \Phi^{\mathrm{TF}}_{j,r}(-\Delta\Phi^{\mathrm{TF}}_{i,r}) &= \frac{z_i z_j}{|R_i - R_j|} - \int_{|x-R_i|<r} \frac{z_j \rho^{\mathrm{TF}}_{z_i}(x)}{|x-R_j|}\, dx - \int_{|x-R_j|<r} \frac{z_i \rho^{\mathrm{TF}}_{z_j}(x)}{|x-R_i|}\, dx \\ &\quad + \iint \frac{(\mathbb{1}_{B(R_j,r)}\rho^{\mathrm{TF}}_{z_j})(x)(\mathbb{1}_{B(R_i,r)}\rho^{\mathrm{TF}}_{z_i})(y)}{|x-y|}\, dxdy \\ &= 2D(z_i\delta_i - \rho^{\mathrm{TF}}_{z_i}\mathbb{1}_{B(R_i,r)}, z_j\delta_j - \rho^{\mathrm{TF}}_{z_j}\mathbb{1}_{B(R_j,r)}) \\ &=: \mathcal{Q}^{\mathrm{TF}}_{ij}.\end{aligned}$$

Then we can see that D^{TF} is determined by the outside TF models as follows.

Lemma 4.2. *Under the same assumptions as in Lemma 4.1, there is a constant* ε_5 *such that*

$$\left| D^{\mathrm{TF}}(\underline{Z}, \underline{R}) - \left(\mathcal{E}^{\mathrm{TF}}_r(\rho^{\mathrm{TF}}_r) - \sum_{j=1}^K E^{\mathrm{TF}}_{V_j}(N_j) \right) \right| \le C r^{-7+\varepsilon_5}.$$

Proof. Lower bound. Let $\rho_r^{(j)}$ be a minimizer for the TF problem $E_{V_j}^{\mathrm{TF}}(N_j)$. We note that for any ρ

$$\begin{aligned}\mathcal{E}_{V_{\underline{R}}}^{\mathrm{TF}}(\rho) = &\sum_{j=1}^{K} \mathcal{E}_{z_j|x-R_j|^{-1}}^{\mathrm{TF}}(\mathbb{1}_{B(R_j,r)}\rho) + \mathcal{E}_r^{\mathrm{TF}}(\mathbb{1}_{A_r}\rho) \\ &+ \int_{A_r} \rho(x)(\rho-\rho_0)\mathbb{1}_{A_r^c} \star |x|^{-1}\,dx + \sum_{i<j} 2D(\rho\mathbb{1}_{B(R_i,r)}, \rho\mathbb{1}_{B(R_j,r)^c}) \\ &- \sum_{i\neq j}\int_{|x-R_j|<r} z_i|x-R_i|^{-1}\rho(x)\,dx.\end{aligned} \tag{4.1}$$

and

$$\begin{aligned}\mathcal{E}_{z_j/|x-R_j|}^{\mathrm{TF}}(\rho) = &\,\mathcal{E}_{z_j/|x-R_j|}^{\mathrm{TF}}(\rho\mathbb{1}_{B(R_j,r)}) + \mathcal{E}_{V_j}^{\mathrm{TF}}(\rho\mathbb{1}_{B(R_j,r)^c}) \\ &+ 2D(\rho\mathbb{1}_{B(R_j,r)^c}, (\rho-\rho_{z_j})\mathbb{1}_{B(R_j,r)}).\end{aligned} \tag{4.2}$$

We use (4.1) with $\rho = \rho^{\mathrm{TF}}$ and insert $\rho = \rho^{\mathrm{TF}}\mathbb{1}_{B(R_j,r)} + \rho_r^{(j)}$ into (4.2). Then since Lemma 3.1 and Lemma 4.1 we see

$$D^{\mathrm{TF}}(\underline{Z},\underline{R}) \geq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) - \sum_{j=1}^{K} E_{V_j}^{\mathrm{TF}}(N_j) + \sum_{i<j} \mathcal{Q}_{ij}^{\mathrm{TF}} - Cr^{-7+\varepsilon_5}.$$

Upper bound. Inserting $\rho = \sum_{j=1}^{K} \rho_{z_j}^{\mathrm{TF}}\mathbb{1}_{B(R_j,r)} + \rho_r^{\mathrm{TF}}$ into (4.1) and $\rho = \rho_{z_j}^{\mathrm{TF}}$ in (4.2), we have

$$D^{\mathrm{TF}}(\underline{Z},\underline{R}) \leq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) - \sum_{j=1}^{K} E_{V_j}^{\mathrm{TF}}(N_j) + \sum_{i<j} \mathcal{Q}_{ij}^{\mathrm{TF}} + Cr^{-7+\varepsilon_5},$$

where we have used Lemma 3.1 and Lemma 4.1.

Finally, we will show that

$$\left|\mathcal{Q}_{ij}^{\mathrm{TF}}\right| \leq Cr^{-7+\varepsilon_5}. \tag{4.3}$$

Let Ω_j be a set satisfying $B(R_j, R_{\min}/4) \subset \Omega_j$ and $\Omega_j \subset B(R_i, R_{\min}/4)^c$ for $i \neq j$. Now we pick a smooth function $\chi \in C_c^\infty(\overline{B(R_i, R_{\min}/4)^c})$ with $\chi = 1$ in Ω_j. Then, since integration by parts (or equivalently, Green's theorem), we have

$$\mathcal{Q}_{ij}^{\mathrm{TF}} = \int_{\Omega_j} \Phi_{j,r}^{\mathrm{TF}}(-\Delta\chi\Phi_i^{\mathrm{TF}}) = \int_{\partial\Omega_j} \left(\Phi_{j,r}^{\mathrm{TF}}\hat{n}_j\cdot\nabla\Phi_{i,r}^{\mathrm{TF}} - \Phi_{i,r}^{\mathrm{TF}}\hat{n}_j\cdot\nabla\Phi_{j,r}^{\mathrm{TF}}\right),$$

where $\hat{n}_j$ is the outward normal to $\partial\Omega_j$. We introduce the Poisson kernel $p_r(x,\xi)$ by

$$p_r(x,\xi) := \frac{1}{4\pi r}\frac{|x|^2 - r^2}{|x-\xi|^3}.$$

By harmonicity (see, e.g., [23, Prob. 3.11]), it holds that for $|x - R_i| > r$

$$\Phi_{i,r}^{\mathrm{TF}}(x) = \int_{\partial B(R_i,r)} p_r(x-R_i, \xi-R_i)\Phi_{i,r}^{\mathrm{TF}}(\xi)\,d\omega(\xi).$$

By direct computation, we see that

$$\nabla_x p_r(x,\xi) = p_r(x,\xi)\left(\frac{3(x-\xi)}{|x-\xi|^2} - \frac{2x}{|x|^2-r^2}\right),$$

and therefore, in $B(R_j,r)^c$,

$$\begin{aligned}\left|\nabla\Phi_{i,r}^{\mathrm{TF}}(x)\right| &\le \frac{2|x-R_i|\left|\Phi_{i,r}^{\mathrm{TF}}(x)\right|}{|x-R_i|^2-r^2} + \sup_{\partial B(R_i,r)}\left|\Phi_{i,r}^{\mathrm{TF}}\right|\int_{\partial B(R_i,r)}\frac{3p_r(x-R_i,\xi-R_i)}{|x-\xi|}\,d\omega(\xi)\\ &\le \frac{Cr}{R_{\min}^2}\sup_{\partial B(R_i,r)}\left|\Phi_{i,r}^{\mathrm{TF}}\right|,\end{aligned}$$

where we have used $|x-R_i||\Phi_{i,r}^{\mathrm{TF}}(x)| \le r\sup_{\partial B(R_i,r)}\left|\Phi_{i,r}^{\mathrm{TF}}\right|$ for any $|x-R_i|\ge r$ (see [10, Lem. 6.5]) and a simple estimate, followed by $|x-\xi|\ge|x-R_i|-r$ on $|x-R_i|=\xi$,

$$\int_{\partial B(R_i,r)}\frac{p_r(x-R_i,\xi-R_i)}{|x-\xi|}\,d\omega(\xi) \le \frac{Cr}{R_{\min}^2}.$$

Consequently, we obtain

$$\begin{aligned}|\mathcal{Q}_{ij}^{\mathrm{TF}}| &\le Cr\sup_{\partial B(R_i,r)}\left|\Phi_{i,r}^{\mathrm{TF}}\right|\sup_{\partial B(R_j,r)}\left|\Phi_{j,r}^{\mathrm{TF}}\right|\\ &\le Cr^{-7+\varepsilon_6},\end{aligned}$$

which shows (4.3). This finishes the proof. □

As in the TF case, we define

$$\mathcal{Q}_{ij} \coloneqq 2D(z_i\delta_i - \rho_0(\eta_-^{(i)})^2, z_j\delta_j - \rho_0(\eta_-^{(j)})^2).$$

Lemma 4.3. *Under the same assumptions as in Lemma 4.1, there exists $\varepsilon_6>0$ such that*

$$\left|D(\underline{Z},\underline{R}) - \left(\mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) - \sum_{j=1}^K E_{V_j}^{\mathrm{TF}}(N_j)\right)\right| \le Cr^{-7+\varepsilon_6}.$$

Proof. Lower bound. We recall Lemma 3.6. By construction, $\eta_-^{(j)} \coloneqq \mathbb{1}_{B(R_j,r)}\eta_-$ is smooth for all $j=1,\dots,K$, and thus we have

$$\mathcal{E}(\eta_-\gamma_0\eta_-) = \sum_{j=1}^K\mathcal{E}(\eta_-^{(j)}\gamma_0\eta_-^{(j)}) + \sum_{i<j}2D((\eta_-^{(j)})^2\rho_0,(\eta_-^{(i)})^2\rho_0).$$

We note from Lemma 3.1 that inequalities (3.2)–(3.6) hold true. Applying Lemma 3.6 and Lemma 3.10, we see

$$\begin{aligned}\mathcal{E}(\gamma_0) &\ge \mathcal{E}(\eta_-\gamma_0\eta_-) + \mathcal{E}_r^{\mathrm{rHF}}(\eta_r\gamma_0\eta_r) - \mathcal{R}\\ &\ge \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + \sum_{j=1}^K\mathcal{E}_{z_j/|x-R_j|}(\eta_-^{(j)}\gamma_0\eta_-^{(j)}) + \sum_{i<j}2D((\eta_-^{(j)})^2\rho_0,(\eta_-^{(i)})^2\rho_0)\\ &\quad - \sum_{i\ne j}\int z_j|x-R_j|^{-1}(\eta_-^{(i)})^2\rho_0 - C\lambda^{-2}r^{-5} - Cr^{-7+1/3}.\end{aligned}$$

We note that $\mathrm{tr}(\eta_-^{(j)}\gamma_0\eta_-^{(j)}) < z_j$ for all $j = 1, \dots, K$. To see this, we use the atomic Sommerfeld bound [25, Thm. 5.4], namely, there is a constant $C > 0$ such that

$$\int_{|x-R_j|>r} \rho_{z_j}^{\mathrm{TF}}(x)\, dx \geq C^{-1} r^{-3}.$$

Combining this with Lemma 4.1, we see that

$$\begin{aligned} z_j - \mathrm{tr}(\eta_-^{(j)}\gamma_0\eta_-^{(j)}) &\geq \int_{|x-R_j|>r} \rho_{z_j}^{\mathrm{TF}}(x)\, dx + \int_{|x-R_j|<r} \Big(\rho_{z_j}^{\mathrm{TF}}(x) - \rho_0(x)\Big)\, dx \\ &\geq C^{-1} r^{-3} - C r^{-3+\varepsilon_4} \\ &> 0. \end{aligned}$$

Then as in the case of the molecules, we have

$$\begin{aligned} E_{z_j/|x-R_j|}(z_j) &\leq \mathcal{E}_{z_j/|x-R_j|}\left(\eta_-^{(j)}\gamma_0\eta_-^{(j)} + \eta_r^{(j)}\gamma_{z_j}\eta_r^{(j)}\right) \\ &\leq \mathcal{E}_{z_j/|x-R_j|}\left(\eta_-^{(j)}\gamma_0\eta_-^{(j)}\right) + \mathcal{E}_{V_j}^{\mathrm{rHF}}\left(\eta_r^{(j)}\gamma_{z_j}\eta_r^{(j)}\right) + C r^{-7+\varepsilon_6}, \end{aligned}$$

where we have used Lemma 4.1 in the last inequality. Using Lemma 3.10, we see

$$\mathcal{E}_{V_j}^{\mathrm{rHF}}\left(\eta_r^{(j)}\gamma_{z_j}\eta_r^{(j)}\right) \leq \mathcal{E}_{V_j}^{\mathrm{TF}}(\rho_r^{(j)}) + C r^{-7+1/3}.$$

Then we obtain

$$\begin{aligned} \mathcal{E}(\gamma_0) + U_{\underline{R}} \geq \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) &+ \sum_{j=1}^K \left(E_{z_j/|x-R_j|}(z_j) - \mathcal{E}_{V_j}^{\mathrm{TF}}(\rho_r^{(j)})\right) \\ &+ \sum_{i<j} \mathcal{Q}_{ij} - C r^{-7+1/3}, \end{aligned} \tag{4.4}$$

which shows the lower bound.

<u>Upper bound.</u> Since Lemma 3.6 and Lemma 3.10–4.1, we see

$$\begin{aligned} E_{V_{\underline{R}}}(Z) + U_{\underline{R}} &\leq \mathcal{E}_{V_{\underline{R}}}\left(\sum_{j=1}^K \eta_-^{(j)}\gamma_{z_j}\eta_-^{(j)} + \eta_r\gamma_0\eta_r\right) + U_{\underline{R}} \\ &\leq \sum_{j=1}^K \mathcal{E}_{z_j/|x-R_j|}\left(\eta_-^{(j)}\gamma_{z_j}\eta_-^{(j)}\right) + \mathcal{E}_r(\eta_r\gamma_0\eta_r) + \sum_{i<j}\mathcal{Q}_{ij} + C r^{-7+\varepsilon_6} \\ &\leq \sum_{j=1}^K \left(E_{z_j/|x-R_j|}(z_j) - E_{V_j}^{\mathrm{TF}}(N_j)\right) + \mathcal{E}_r^{\mathrm{TF}}(\rho_r^{\mathrm{TF}}) + \sum_{i<j}\mathcal{Q}_{ij} + C r^{-7+\varepsilon_6}. \end{aligned}$$

By copying the proof of (4.3), we can see $|\mathcal{Q}_{ij}| \leq C r^{-7+\varepsilon_6}$. Then the proof is complete. □

Proof of Theorem 1.1. First, we assume that $4 \geq R_{\min} \geq \delta_3^{-1} z_{\min}^{-1/3+\alpha}$ and $r = \delta_3 R_{\min}^{1+\varepsilon_3}$ as in Lemma 4.1. Combining Lemma 4.3 and Lemma 4.2, we have the desired conclusion in this case. Moreover, we obtain (1.3).

Next, we consider the case $R_{\min} \le Z^{-1/3}$. By (2.3) we know $|E_{V_{\underline{R}}}(Z) - E^{\rm TF}_{V_{\underline{R}}}(Z)| \le CZ^{7/3-2/33}$ and $|E_{z_j/|x-R_j|}(z_j) - E^{\rm TF}_{z_j/|x-R_j|}(z_j)| \le Cz_j^{7/3-2/33}$ for all $j = 1, \ldots, K$. Let $C_{\underline{Z}} := z_{\max}/z_{\min}$. Then it follows that there is a $\varepsilon > 0$ so that

$$\left|D(\underline{Z}, \underline{R}) - D^{\rm TF}(\underline{Z}, \underline{R})\right| \le C\left(1 + C_{\underline{Z}}^{7/3-2/33}\right) R_{\min}^{-7+\varepsilon},$$

which shows the conclusion.

Similarly, we deduce from $z_{\min}^{-1} = C_{\underline{Z}} z_{\max}^{-1}$ that the desired result for $Z^{-1/3} \le R_{\min} \le \delta_3^{-1} z_{\min}^{-1/3+\alpha}$. □

Proof of Corollary 1.2. Let $E_{\rm mol}(\underline{Z}) := \inf_{\underline{R}}(E_{V_{\underline{R}}}(Z) + U_{\underline{R}})$ be the Born-Oppenheimer ground state energy in Kohn-Sham theory. The following lemma is an elementary property of this energy.

Lemma 4.4. *For any configurations $\underline{Z}_1 = (z_{\pi(1)}, \ldots, z_{\pi(p)})$ and $\underline{Z}_2 = (z_{\pi(p+1)}, \ldots, z_{\pi(K)})$ with $1 \le p \le K-1$ and π permutation of $\{1, \ldots, K\}$, we have*

$$E_{\rm mol}(\underline{Z}) \le E_{\rm mol}(\underline{Z}_1) + E_{\rm mol}(\underline{Z}_2).$$

Proof of Lemma 4.4. Let $\varepsilon > 0$. We can take $\gamma_n^{(i)}$ and $\underline{R}_n^{(i)}$ such that $\operatorname{tr}\gamma_n^{(i)} = |\underline{Z}_i|$, each $\operatorname{supp}\rho_{\gamma_n^{(i)}}$ is in a ball of radius $r > 0$, and

$$\mathcal{E}_{V_{\underline{R}_n}^{(i)}}(\gamma_n^{(i)}) + U_{\underline{R}_n^{(i)}} \le E_{\rm mol}(\underline{Z}_i) + 1/n.$$

For $r_n \in \mathbb{R}^3$ we define $\gamma_n^{(3)} := \tau_{-r_n}\gamma_n^{(2)}\tau_{r_n}$ with τ being the translation operator, and $\gamma_n := \gamma_n^{(1)} + \gamma_n^{(3)}$. Then we see that $0 \le \gamma_n \le 1$, $\operatorname{tr}\gamma_n = Z$, and $\operatorname{supp}\rho_{\gamma_n^{(1)}} \cap \operatorname{supp}\rho_{\gamma_n^{(3)}} = \emptyset$ for large $|r_n| > 0$. Let $\underline{R}_n := (R_n^{(\pi(1))}, \ldots, R_n^{(\pi(p))}, R_n^{(\pi(p+1))} + r_n, R_n^{(\pi(p+2))} + r_n, \ldots, R_n^{(\pi(K))} + r_n)$ with $|r_n| > n$. By simple computation, we have

$$2D(\rho_{\gamma_n^{(1)}}, \rho_{\gamma_n^{(3)}}) \le \frac{Z^2}{n - 2r},$$

and hence

$$\begin{aligned} E_{\rm mol}(\underline{Z}) &\le \mathcal{E}_{V_{\underline{R}_n}}(\gamma_n) + U_{\underline{R}_n} \\ &\le E_{\rm mol}(\underline{Z}_1) + E_{\rm mol}(\underline{Z}_2) + \varepsilon \end{aligned}$$

for large n. □

Now we assume that there exists $\underline{R_0}$ such that $E_{\rm mol}(\underline{Z}) = E_{V_{\underline{R_0}}}(Z) + U_{\underline{R_0}}$. Let $R_{\rm M} := \min_{i \ne j}|R_0^{(i)} - R_0^{(j)}|$. With Lemma 2.2 and Lemma 4.4, it follows that

$$0 \ge E_{V_{\underline{R_0}}}(Z) + U_{\underline{R_0}} \ge -C_3 Z^{7/3} + \frac{Z^2}{C_3 R_{\rm M}},$$

and thus $R_{\rm M} \ge C_3^{-2} Z^{-1/3}$. Then we have $D^{\rm TF}(\underline{Z}, \underline{R_0}) \ge C_4 R_{\rm M}^{-7}$ (see the proof of [21, Thm. 8]). Without loss of generality we can assume $z_{\min} \ge 1$. Using Theorem 1.1 and Lemma 4.4, we have

$$0 \ge D(\underline{Z}, \underline{R_0}) \ge C_5^{-1} R_{\rm M}^{-7} - C_5 R_{\rm M}^{-7+\varepsilon}.$$

This completes the proof. □

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