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Universality of Born-Oppenheimer curves

PhD Thesis

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Summary

In this thesis, the Born-Oppenheimer curves for diatomic molecules are investigated in the Hartree-Fock model excluding the exchange term. It is exhibited that the curves have a universal behaviour at small internuclear distances which can be understood from the simpler Thomas-Fermi theory. Notably, we show that the atomic screenings in these two theories are comparable up to a distance from the nuclei which is independent of the atomic number. This is proven iteratively, by relating to suitable Thomas-Fermi models at different length scales. We in particular study solutions to the Thomas-Fermi partial differential equation with two singularities and demonstrate that their asymptotic behaviour is universal. This thesis also contains a numerical investigation of the homonuclear Born-Oppenheimer curve in Thomas-Fermi theory which supports the analytic result.

Resumé

I denne afhandling undersøges Born-Oppenheimer-kurverne for diatomiske molekyler i Hartree-Fock-modellen eksklusiv udvekslingsleddet. Det er vist, at kurverne har en universel adfærd på små indre kerneafstande, som kan forstås fra den enklere Thomas-Fermi-teori. Især viser vi, at de atomiske screeninger i disse to teorier er sammenlignelige op til en afstand fra kernerne, der er uafhængig af atomnummeret. Dette er påvist iterativt ved at sammenligne med relevante Thomas- Fermi modeller på forskellige længdeskalaer. Vi studerer især løsninger til den Thomas-Fermi partielle differentialligning med to singulariteter og demonstrerer, at deres asymptotiske adfærd er universel. Denne afhandling indeholder også en numerisk undersøgelse af den homonukleære Born-Oppenheimer-kurve i Thomas- Fermi-teorien, der understøtter det analytiske resultat.

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This thesis is dedicated to the memory of Helena.

CHAPTER 1

Introduction

Finding an accurate description of atoms and molecules has been a driving force in physics and chemistry over the past century, leading to the development of modern quantum mechanics. Experimental data agrees to astonishing accuracy with the predictions of quantum mechanics, calculated in computational chemistry and physics. The numerical calculations are necessary since there is usually no known, explicit solution to a quantum mechanical many-body systems. This leads to the peculiar situation where although the quantitative predictions are highly accurate, it is hard to obtain *ab initio qualitative explanations* of experimental observations.

Approximate models can help us gain a better qualitative understanding. This thesis studies the *Born-Oppenheimer potential* for two such approximations, called *Thomas-Fermi* (TF) and *Hartree-Fock* (HF) model. We introduce and discuss these three concepts one by one before we state our results more precisely.

1. Born-Oppenheimer potentials

Throughout this thesis, we consider *neutral* molecules of M nuclei with nuclear charges $\mathbf{Z} = (Z_1, ..., Z_M)$ at positions $\mathbf{R} = (R_1, , ..., R_M)$. Furthermore, we assume that relativistic effects, the nuclear spin and the kinetic energy of the nuclei can be neglected. The latter is the *Born-Oppenheimer approximation* [1], a standard assumption used in computational chemistry. The nuclear charges and positions $\mathbf{Z}, \mathbf{R}$ then enter as a parameter into the remaining electronic problem. We write $E(\mathbf{Z}, \mathbf{R})$ for the energy of this system, and compare it to the energies $E(Z_i)$ of the corresponding neutral single-atom systems. This leads to the *Born-Oppenheimer potential energy surface*

$$\mathbf{R} \mapsto D(\mathbf{Z}, \mathbf{R}) = E(\mathbf{Z}, \mathbf{R}) - (E(Z_1) + ... + E(Z_M)). \tag{1.1}$$

It describes the cost or gain in energy when bringing the M atoms together to the positions $\mathbf{R}$, or breaking them completely apart. It can also be regarded as the potential for the adiabatic movement of the nuclei in the Born-Oppenheimer approximation. Its shape and the position of its local minima (if they exist) are important properties: Minima allow one to extract *bond distances* and $D(\mathbf{Z}, \mathbf{R})$ at these points equals the *dissociation energy*.

We will mainly consider *diatomic* molecules, that is $M = 2$. The energy of such a system only depends on the relative distance $R = |R_1 - R_2| > 0$ instead of the two coordinates $\mathbf{R}$ and we denote it by $E_{\mathbf{Z},R}$. The Born-Oppenheimer energy surface is then just a curve, which we denote by $D_{\mathbf{Z},R}$ and a schematic example is depicted in Figure 1.

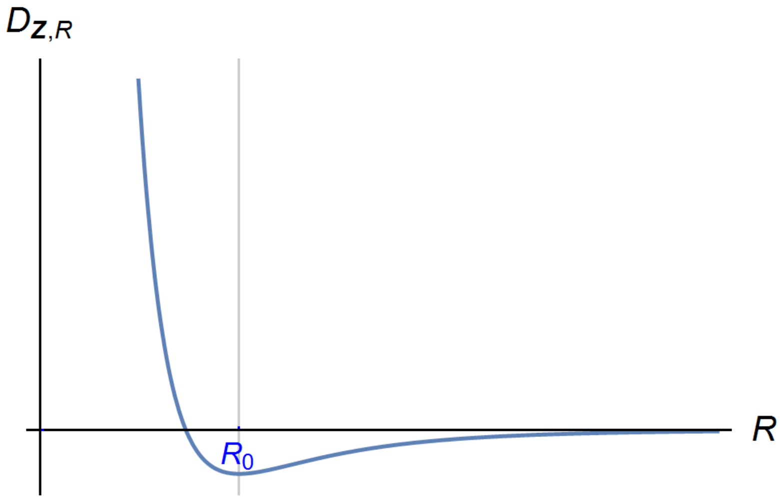


FIGURE 1. Schematic of a diatomic Born-Oppenheimer curve $D_{\mathbf{Z},R}$ with minimum at the (binding) distance R_0.

2. The Thomas-Fermi model

In 1927, L. H. Thomas and E. Fermi independently proposed [2, 3] a semi-classical statistical model to describe the distribution of non-relativistic electrons in an atom. It treats N such electrons with mass m and charge e as a gas, self-interacting via the Coulomb repulsion and subject to a nuclear potential V. Together with the semi-classical postulate that a phase-space volume of size h^3 can hold up to 2 electrons, one is lead to minimize

$$\frac{1}{2m}\int_\Omega p^2 \frac{dpdx}{h^3/2} - \int_\Omega eV(x)\frac{dpdx}{h^3/2} + \frac{1}{2}\int_\Omega\int_\Omega \frac{e^2}{|x-\tilde{x}|}\frac{dpdx}{h^3/2}\frac{d\tilde{p}d\tilde{x}}{h^3/2}$$

over all phase-space volumes $\Omega \subset \mathbb{R}^3 \times \mathbb{R}^3$ with $\int_\Omega \frac{dpdx}{h^3/2} = N$. The integration in p can be carried out explicitly and one finds that this problem is equivalent to determining the density of electrons $\rho(x) = \int \mathbb{1}_\Omega(x,p)\frac{2}{h^3}dp$ which minimizes

$$\frac{3}{5}\frac{(3\pi^2)^{\frac{2}{3}}h^2}{8\pi^2 m}\int \rho^{5/3}(x)dx - \int eV(x)\rho(x)dx + \frac{e^2}{2}\int\int \frac{\rho(x)\rho(\tilde{x})}{|x-\tilde{x}|}dxd\tilde{x} \tag{1.2}$$

under the constraint $\int \rho = N$. This model accounts for the kinetic energy (the $\rho^{5/3}$-integral), the nuclear attraction and the Coulomb self-energy of the electrons, but it neglects any 'exchange correlation'. It is understood [4, p. 624] that TF theory correctly describes the inner part of the electron density in heavy atoms, up to a distance from the nucleus of the order $Z^{\frac{-1}{3}}$. This is the critical length scale in TF theory and it in particular appears in the TF scaling relation

$$E^{\mathrm{TF}}(\mathbf{Z},\mathbf{R}) = \lambda^7 E^{\mathrm{TF}}(\lambda^{-3}\mathbf{Z},\lambda\mathbf{R}), \qquad \lambda > 0. \tag{1.3}$$

This relation has important consequences, among them that for the atomic ($M = 1$) energies, $E^{\mathrm{TF}}(Z,0) = Z^{7/3}E^{\mathrm{TF}}(1,0)$. Now Lieb and Simon showed in 1977 in their seminal work about TF theory [5] that it correctly describes the leading order of the quantum mechanical energy,

$$E^{QM}(Z,0) = Z^{7/3}E^{\mathrm{TF}}(1,0) + o(Z^{7/3}), \qquad Z \to \infty.$$

Moreover, the scaling relation (1.3) implies $D^{\mathrm{TF}}_{\mathbf{Z},R} = R^{-7}D^{\mathrm{TF}}_{R^3\mathbf{Z},1}$ and Brezis and Lieb [6] proved the existence of the limit

$$\lim_{\lambda\to\infty} D^{\mathrm{TF}}_{\lambda\mathbf{Z},R} = R^{-7}D^{\mathrm{TF}}_{\infty,1}. \tag{1.4}$$

We note that finding the value of the constant $D^{\mathrm{TF}}_{\infty,1}$ is still an open problem. It is only known to be upper bounded (in units where $h = 2\pi$ and $m = 1$) by $\pi^4 2^5 3^8 \frac{43}{35} \approx 2.51258 \times 10^7$. The exactness of TF theory as $Z \to \infty$ and the existence of limiting quantities is part of the mathematical appeal of TF theory. Nonetheless, TF theory has severe limitations which became apparent when Teller [7] proved the no-binding theorem in 1962, saying that D^{TF} is strictly positive. Or in simpler words:

There are no molecules in TF theory.

3. The Hartree-Fock model

Fock and Slater [8, 9] independently proposed in 1930 to improve Hartree's method [10] by including the antisymmetry of electronic wave functions. The resulting Hartree-Fock theory can be regarded as the restriction of the variational principle for the quantum mechanical Hamiltonian to pure wedge products, called Slater-determinants. We give a concrete description of the involved energy functional and mathematical details in Chapter 2 and continue with more general remarks here.

The HF variational problem is more complex than that of TF theory, but still accessible with modern computers.[1] The model does in particular include some 'exchange correlations' and it depends, in contrast to TF theory, not simply on the density, but on the one-particle reduced density matrix of the electronic state.

Although binding distances in HF theory have been computed numerically, a mathematical proof of binding in HF theory is still an open problem. This situation reflects our opening remarks: The better the theory and its numerical predictions, the harder it is to prove simple qualitative features.

4. Results

It has been conjectured by Solovej [11] that the Born-Oppenheimer curve of large homonuclear diatomic molecules has the universal behaviour $D_\infty^{\mathrm{TF}} R^{-7}$ for small nuclear separations R, or more precisely:

$$\limsup_{Z\to\infty} \left|D_{(Z,Z),R} - R^{-7} D_{\infty,1}^{\mathrm{TF}}\right| = o(R^{-7}), \qquad \text{as } R \to 0. \tag{1.5}$$

In view of (1.4), this can be informally rephrased as 'TF-universality of Born-Oppenheimer curves' or, with Teller's no-binding result in mind:

> Although molecules do not exist in Thomas-Fermi theory, it does describe the Born-Oppenheimer curve of large atoms for small nuclear separations.

We sought to prove this conjecture in HF theory but did *not* succeed because of the so-called exchange term in HF theory. We instead proved the conjecture for a HF model without the exchange term, which we call the *reduced* Hartree-Fock (rHF) model.[2] The main result is:

$$\boxed{\limsup_{\min\{Z_1,Z_2\}\to\infty} \left|D_{(Z_1,Z_2),R}^{\mathrm{rHF}} - R^{-7} D_{\infty,1}^{\mathrm{TF}}\right| = o(R^{-7}), \qquad \text{as } R \to 0.} \tag{1.6}$$

Our proof of (1.6) is heavily inspired by Solovej's work on the ionization conjecture in HF theory [12], where he showed that atomic screened potentials in HF and TF theory are comparable. This was known up to the TF length scale $Z^{-1/3}$, but [12] used an iteration scheme that allows to reach a length scale which is independent of Z. We use this technique and extend it to the case of a diatomic system. Moreover since this is joint work with Solovej, parts of this thesis closely follow his work.

[1] It took several decades after its invention, until the development of powerful computers, for the HF model to really shine.

[2] This is not the Hartree model, since we still require fermionic states

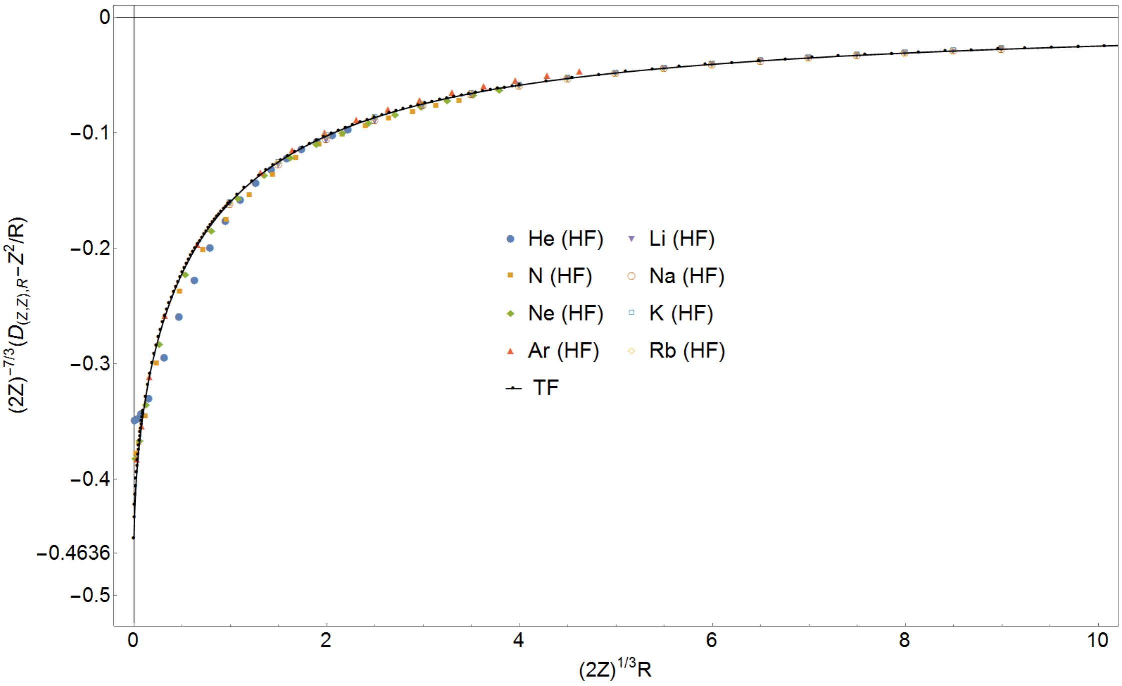


FIGURE 2. Comparison of rescaled Born-Oppenheimer curves in Thomas-Fermi (TF) and Hartree-Fock (HF) theory. TF values have been computed for this thesis, HF values are from [13]. The nuclear repulsion, a constant in this scaling, has been excluded.

Our extension to diatomic systems is in many places straightforward but overall non-trivial. It in particular involves an analysis of the diatomic TF potential in the region between the nuclei.

Solovej's conjecture is still *open*, both in HF theory and in full quantum mechanics. In Chapter 7 we provide numerical calculations which both support the conjecture for HF theory and complement our analytic result (1.6): We computed $D^{\mathrm{TF}}_{(Z,Z),R}$ and compare it to the values of $D^{\mathrm{HF}}_{(Z,Z),R}$ obtained in [13], which appear as coloured symbols in figure 2. The astonishing agreement of the curves indicates that the TF-universality of Born-Oppenheimer potentials extends to smaller atoms. In other words, the limiting behaviour (1.5) is already reached for reasonable values of Z.

5. Structure of the thesis

We now describe the structure of the thesis. After this introduction, we first give an overview of our notation and the mathematical prerequisites. It ends with Table 1 on page 12, where we collect notation which will be introduced later in this thesis.

Chapter 3 is by far the largest and starts with an overview of the basics in TF theory, followed by the bounds on atomic TF theory that we will need. It then continues with the study of *outside TF* models, which are defined for a certain class of potentials supported outside of balls centred at the nuclei. We in particular derive bounds on the Thomas-Fermi potential in outside TF models (Lemmas 3.11 and 3.12) as well as conditions under which the minimizers are neutral (Lemma 3.17). The Chapter ends with a discussion of the TF Born-Oppenheimer curve, where we in particular show in Lemma 3.22 that it can be (to leading order in $R \to 0$) determined from neutral outside TF models.

In Chapter 4, we first introduce the notion of a density matrix and give an overview of classical bounds for the negative eigenvalue of Schrödinger operators before introducing (reduced) HF theory. We then recall in Lemma 4.6 that the molecular energies in rHF and TF theory agree to leading order in $\mathbf{Z}$, since this will provide the starting point for the iteration. Finally, we study the outside part of the density in rHF theory (Lemma 4.9).

Chapter 5 presents the iterative proof of Theorem 5.1, which from a technical point of view is our main result: The screened potentials of rHF and TF theory are comparable far beyond the TF length scale $Z^{\frac{-1}{3}}$.

Then in Chapter 6 we combine results from all the previous Chapters to prove Theorem 6.1, which implies (1.6), settling Solovej's conjecture in rHF theory. We in particular derive in Lemma 6.4 that the rHF Born-Oppenheimer curve can be computed from appropriately chosen outside TF models. This ends the analytic part of the thesis.

Chapter 7 describes our numerical investigation of the Born-Oppenheimer curve in TF theory, comparing it to results from HF theory. We in particular describe how one easily obtains a highly accurate solution to the atomic Thomas-Fermi ODE. And for the diatomic case, we outline the solution process for the (nonlinear) Thomas-Fermi PDE with the finite element method, using the FEniCS platform.

Appendix A contains a short discussion of outside harmonic functions and the Kelvin transform. Straightforward but slightly technical calculations are given in appendix B and for the numerical work, the scripts and some computer output are provided in appendix C.

6. Further remarks

1) Both the HF and TF model are common starting points in computational chemistry, in the sense that a plethora of different corrections are added to overcome their shortcomings. This leads either to post-Hartree-Fock methods or density functional theory. These corrected models give better predictions but are usually based on heuristics, whereas the 'pure' models which we consider are both derived from basic principles.

2) We said that the HF model arises from a restriction of quantum mechanics to special states. We thereby implicitly considered the non-relativistic Schrödinger Hamiltonian in the Born-Oppenheimer approximation. This neglects many lower-order effects, among them the fine structure corrections, which have to be included for the mentioned accuracy of quantum mechanics. This is achieved by the use of perturbation theory and is discussed in many physics text books and to some extent also in [14, Chapter XIII.2].

3) The limit $Z \to \infty$ is of course unphysical, since atoms with $Z > 118$ have never been observed. It is more of a necessity to make a rigorous mathematical statement about an asymptotic behaviour and it stems from the fact that TF theory has a limit as $Z \to \infty$: Not only the energy and Born-Oppenheimer curve, but also the electron density converges. We can make (1.6) more precise by explicitly computing constants for the upper and lower bound, but these will be too large to be of any practical use. On the other hand, our numerical investigation (somewhat unexpectedly) indicates that this limiting behaviour is actually reached very quickly. It complements the analytic statement and suggests that the TF-universality of Born-Oppenheimer curves (at small internuclear distances) also holds for lighter atoms.

CHAPTER 2

Notation and mathematical preliminaries

We write $\mathbb{N}$ for the set of positive natural numbers and $\mathbb{R}_+$ for $(0, \infty)$. By I_q we denote the $q \times q$ identity matrix. For $a \in \mathbb{R}$, we define $[a]_+ := \max\{0, a\}$ and $[a]_- := \max\{0, -a\}$. The open ball with radius r and centre p in $\mathbb{R}^3$ will be denoted by $B(0, r)$. For any $\Omega \subset \mathbb{R}^3$, we write Ω^c for its complement and $\mathbb{1}_\Omega$ will denote the indicator function of Ω, while $|\Omega|$ denotes its Lebesgue measure (if it is Lebesgue-measurable).

For a system of M atoms at positions $\mathbf{R} = (R_1, ..., R_M) \in (\mathbb{R}^3)^M$ and with charges $\mathbf{Z} = (Z_1, ..., Z_M) \in \mathbb{R}_+^M$, we define the corresponding Coulomb-potential

$$V_{\mathbf{Z},\mathbf{R}}(x) := \sum_{j=1}^{M} \frac{Z_j}{|x - R_j|}.$$

We will focus on diatomic systems, where $M = 2$. These depend only on the relative distance

$$R := |R_1 - R_2|$$

and the nuclear charges $\mathbf{Z} = (Z_1, Z_2)$. We therefore assume without loss of generality that $R_1 = 0$ and $R_2 = R\nu$ for some $\nu \in \mathbb{S}^2$, which we assume is fixed throughout this thesis. By a slight abuse of notation we then identify $Z_0 := Z_1, Z_{R\nu} := Z_2$ so that

$$V_{\mathbf{Z},R}(x) := V_{\mathbf{Z},(0,R\nu)}(x) = \sum_{p \in \{0, R\nu\}} \frac{Z_p}{|x - p|}$$

and hope that this will not bring any confusion. For brevity, we will use the notation $m_{\mathbf{Z}} := \min\{Z_1, Z_2\}$ and $|\mathbf{Z}| := \sum_{j=1}^{M} Z_j$. Furthermore, we define the open inside and outside of two balls,

$$\mathcal{I}_r := B(0, r) \cup B(R\nu, r) \quad \text{and} \quad \mathcal{O}_r := (\overline{\mathcal{I}_r})^c.$$

We set $L^p(\Omega) = L^p(\Omega; \mathbb{R})$ and if $\Omega = \mathbb{R}^3$, we just write L^p. Whereas whenever complex-valued L^p-spaces are used, we use the explicit notation $L^p(\mathbb{R}^3; \mathbb{C}^q)$. Here q will denote the number of spin states, which is usually 2 for electrons but our analysis will be valid for any $q \in \mathbb{N}$ and we chose to keep it as a fixed free parameter throughout this thesis. We will identify $f \in L^p$ as a multiplication operator on L^p

or $L^p(\mathbb{R}^3;\mathbb{C}^q)$ that acts by $f : \varphi = (\varphi_1, ..., \varphi_q) \mapsto (f\varphi_1, ..., f\varphi_q)$.

We introduce an important quantity that will appear in the TF and rHF functional.

Definition 2.1. The **direct Coulomb energy** of two functions $f, g \in L^{6/5}(\mathbb{R}^3;\mathbb{C})$ is

$$\mathcal{D}(f,g) = \frac{1}{2}\int\int \frac{\overline{f(x)}g(y)}{|x-y|}dxdy.$$

Note that this is well-defined because of the Hardy-Littlewood-Sobolev inequality [15], [16], [17],

$$\mathcal{D}(f,g) \leq c_{\mathrm{HLS}}\|f\|_{6/5}\|g\|_{6/5}, \tag{2.1}$$

where the constant $c_{\mathrm{HLS}} = \frac{4}{3}\left(\frac{2}{\pi}\right)^{\frac{1}{3}}$ is sharp and due to Lieb [18]. We will also use the notation $\mathcal{D}(f) := \mathcal{D}(f,f)$.

A locally integrable function f is in $L^p + L^q$ with $p, q \in [0,\infty]$ iff it can be written as $f = f_p + f_q$ with $f_p \in L^p, f_q \in L^q$. And $f \in L^p + L^q_\varepsilon$ iff $f \in L^p + L^q$ and $\|f_q\|_q$ can be chosen arbitrarily small. Our main example is $V_{\mathbf{Z},\mathbf{R}} \in L^{5/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$. We define the mean of f over a bounded set Ω as $⨍_\Omega f := |\Omega|^{-1}\int f$.

As usual, the Sobolev space $H^1(\Omega)$ consists of $L^2(\Omega)$-functions with weak derivative in $L^2(\Omega)$. For $\Gamma \subset \partial\Omega$ and $g \in L^2(\Gamma)$, we define $H^1_{g,\Gamma}(\Omega)$ as the set of $H^1(\Omega)$-functions that equal g on Γ. The symbol ∂_n denotes the partial derivative in direction of the *outward* unit normal n of some boundary $\partial\Omega$ and it appears in the context of the classical formula $\int_\Omega \nabla f \nabla g = \int_{\partial\Omega} \partial_n f g - \int_\Omega \Delta f g$.

The space of smooth functions with compact support on an open subset Ω of $\mathbb{R}^n$ will be denoted by $C_c^\infty(\Omega)$. Whereas if $\Omega \subset \mathbb{R}^n$ is unbounded (and not necessarily open), we denote by $C_0(\Omega)$ the set of continuous functions f such that $\lim\limits_{|x|\to\infty} f(x) = 0$. By $T[\phi]$ we denote the action of a distribution T on a test function ϕ, then in particular $\delta_x[\phi] = \phi(x)$ for any $\phi \in C_c^\infty(\mathbb{R}^n)$.

For the Fourier transform $\mathcal{F}$ of f, we use the convention $\mathcal{F}f(k) := \int_{\mathbb{R}^3} f(x)e^{-2\pi ikx}dx$. We recall that $*$ denotes the convolution operator, that is $f * g(x) = \int f(y)g(x-y)dy$ and we frequently will use the notation $f * |x|^{-1} = \int \frac{f(y)}{|x-y|}dy$. For this we observe:

Proposition 2.2. *If $\rho \in L^1 \cap L^{5/3}$ then $\rho * |x|^{-1} \in C_0(\mathbb{R}^3)$.*

Proof. Repeating the argument from [5, Lemma II.25], we use Young's inequality $\|f * g\|_\infty \leq \|f\|_p \|g\|_q$, the fact that $|x|^{-1} \in L^{5/2} + L^q$ for any $q > 3$ and that $C_0(\mathbb{R}^3)$ is the closure of $C_c^\infty(\mathbb{R}^3)$ with respect to $\|\cdot\|_\infty$. $\square$

Let τ be a placeholder for one of the three molecular theories we will consider – either TF, rHF or HF. Then ϱ_Z^τ and $\varrho_{\mathbf{Z},R\nu}^\tau$ will denote atomic and diatomic neutral electron densities in the theory τ (see (3.4), (4.8) and (4.9) for precise definitions). Quite generally, while ρ will be some non-negative L^1-function, ϱ will denote minimizers of a functional. We define the τ-screened atomic potential at radius $r > 0$

$$\Phi_{Z,r}^\tau(x) := \frac{Z}{|x|} - \int_{B(0,r)} \frac{\varrho_Z^\tau(y)}{|x-y|} dy$$

and the τ-screened diatomic potential at radius $r > 0$

$$\Phi_{\mathbf{Z},R,r}^\tau(x) := V_{\mathbf{Z},R}(x) - \int_{\mathcal{I}_r} \frac{\varrho_{\mathbf{Z},R}^\tau(y)}{|x-y|} dy.$$

Note that in general, $\Phi_{Z_0,r}^\tau(x) + \Phi_{Z_{R\nu},r}^\tau(x - R\nu) \neq \Phi_{\mathbf{Z},R,r}^\tau(x)$.

We define the constant $c_H = \frac{h^2}{2m(2\pi)^2}$ as the one appearing in front of the kinetic part of a Hamiltonian $H = -c_H\Delta - V$. A common choice in physics are atomic units $h = 2\pi, m = 1$, whereas in operator theory, one usually considers $c_H = 1$. We keep it arbitrary but fixed. The constant c_{TF} appears in the TF functional (see Definition 3.1) and is for the purpose of the mathematical treatment of TF theory arbitrary. Only when comparing to a theory that arises from a physical Hamiltonian, one has to choose $c_{\mathrm{TF}} = c_H(6\pi^2/q)^{2/3}$, which is clear by inspection of the kinetic term in (1.2) and Definition 3.1.

Universal constants that appear in classic inequalities will be given names that refer to the name of the inequality, like in (2.1). Many other constants appear in this thesis and might depend on q and c_H but not on $\mathbf{R}, \mathbf{Z}, R, Z$ or r, unless explicitly stated. They can all be computed in principle, if not mentioned otherwise. We will sometimes just write (*cst.*) for such a constant. Some will be named after the statement they appear in, for example $c_{X.Ya}, c_{X.Yb}, ...$ if these appear in 'Lemma X.Y'. This makes it more transparent regarding which parts of a proof use earlier statements. We denote by $C, C_1, C_2, ...$ constants that are only used within a proof and whose value may therefore differ between proofs.

Symbol	Page
$\eta,\ \xi$	15
$\varrho_Z^{\mathrm{TF}},\ \varrho_{\mathbf{Z},R}^{\mathrm{TF}}$	16
$\varphi_Z^{\mathrm{TF}},\ \varphi_{\mathbf{Z},R}^{\mathrm{TF}}$	16
$E_Z^{\mathrm{TF}},\ E_{\mathbf{Z},R}^{\mathrm{TF}}$	16
a^{TF}	17
$\tilde{\eta},\ \tilde{\xi}$	18
$\mathcal{H}(\Omega)$	21
$N(V)$	21
$\mathbb{H}_p,\ \mathbb{H}_p^-,\ \mathbb{H}_p^+$	24
a, A	34
$D_{\mathbf{Z},R}^{\mathrm{TF}}$	40
$\mathcal{Q}[V_r^{(0)}, V_r^{(R\nu)}]$	42
$\gamma,\ \rho_\gamma,\ \mathcal{DM}_q$	47
H_V	48
$\mathcal{E}^{\mathrm{rHF}}$	50
$\mathcal{E}^{\mathrm{HF}}$	49
$\gamma_Z^{\mathrm{rHF}},\ \gamma_{\mathbf{Z},R}^{\mathrm{rHF}}$	50
g_ζ	51
$\{\omega_z\}, z \in \{0, R\nu, \tilde{0}, \tilde{R\nu}, \mathcal{O}\}$	56
γ_ω	56
$\mathcal{A}$	60
$V_r^{(j,p)},\ V_r^{(j)}$	69
$D_{\mathbf{Z},R}^{\mathrm{rHF}}$	69

TABLE 1. We here provide a list of symbols, which we did not introduce yet, together with the page where they are defined or explained.

CHAPTER 3

Thomas-Fermi theory

This Chapter develops the mathematical framework of Thomas-Fermi (TF) theory that we require, though there is much more that can be said about TF theory than we provide here. A very detailed analysis of the TF theory of Coulomb systems to which we refer in several places has been given by Lieb and Simon [5]. For a concise review of molecular TF theory and its extensions, we refer to Lieb's review [4] from 1981.

1. The TF functional and its Euler-Lagrange equation

We start by introducing the set of admissible TF densities with mass at most λ,

$$\mathcal{C}(\lambda) = \left\{\rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3) \middle| \rho \geq 0,\ \|\rho\|_1 \leq \lambda\right\}$$

and write $\mathcal{C} = \mathcal{C}(\infty)$ for the set of all admissible TF densities. The value of the constant $c_{\mathrm{TF}} > 0$ is arbitrary for the purpose of this Chapter.

Definition 3.1. The **Thomas-Fermi energy functional** corresponding to the potential $V \in L^{5/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$ is the map $\mathcal{E}_V^{\mathrm{TF}} : \mathcal{C} \to \mathbb{R}$ defined by

$$\mathcal{E}_V^{\mathrm{TF}}[\rho] = c_{\mathrm{TF}} \frac{3}{5} \int \rho^{\frac{5}{3}} - \int V\rho + \mathcal{D}(\rho).$$

This functional admits a simple scaling relation, which can be expressed as follows: If $V \in L^{5/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$ is such that $V(x/t) = tV(x), t > 0$, then for any $T, U \in \mathbb{R}_+$ and $\rho \in \mathcal{C}$, we have that

$$T \int \rho^{5/3} - U \int V\rho + \mathcal{D}(\rho) = U^{\frac{7}{3}} \frac{3c_{\mathrm{TF}}}{5T} \mathcal{E}_V^{\mathrm{TF}}[\tilde{\rho}] \tag{3.1}$$

with $\lambda_T^3 U^2 \tilde{\rho}(\lambda_T U^{1/3} x) = \rho(x)$ and $\lambda_T = \frac{3c_{TF}}{5T}$. This leads in particular to the mentioned scaling relation (1.3).

A proof of the following fundamental results about the TF minimization problem has been essentially given in [5].[1]

Theorem 3.2 (The TF minimization problem). *Let $V \in L^{5/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$ and $E_\lambda := \inf_{\mathcal{C}(\lambda)} \mathcal{E}_V^{\mathrm{TF}}$. Then:*

a) E_λ is finite, convex and nonincreasing in $\lambda \geq 0$ and equals

$$\inf\{\mathcal{E}_V^{\mathrm{TF}}[\rho] | \rho \in \mathcal{C}, \|\rho\|_1 = \lambda\}.$$

b) For all $\lambda \geq 0$ exists a unique $\varrho_\lambda \in \mathcal{C}(\lambda)$ such that $\mathcal{E}_V^{\mathrm{TF}}[\varrho_\lambda] = E_\lambda$.

c) For all $\lambda \geq 0$ exists a unique $\mu_\lambda \in \mathbb{R}$, called the chemical potential, such that $E_\lambda + \mu_\lambda \int \varrho_\lambda = \inf_{\rho \in \mathcal{C}} \left\{\mathcal{E}_V^{\mathrm{TF}}[\rho] + \mu_\lambda \int \rho\right\}$. Moreover, E_λ is differentiable in λ with $\frac{\partial E_\lambda}{\partial \lambda} = -\mu_\lambda$ and $\mu_\lambda \in [0, \sup V]$. If $\mu_\lambda > 0$, then $\int \varrho_\lambda = \lambda$.

*d) The minimizer ϱ_λ is the unique solution in $\mathcal{C}$ to the **TF equation***

$$c_{\mathrm{TF}} \varrho^{2/3} = [V - \varrho * |x|^{-1} - \mu_\lambda]_+ \qquad \text{in } \mathbb{R}^3,$$

*and the corresponding **TF potential** $\varphi_\lambda := V - \varrho_\lambda * |x|$ satisfies the distributional **TF differential equation***

$$\Delta \varphi_\lambda = 4\pi c_{\mathrm{TF}}^{-3/2} [\varphi_\lambda - \mu_\lambda]_+^{3/2} + \Delta V \qquad \text{in } \mathbb{R}^3.$$

The TF equation is the Euler-Lagrange equation for $\mathcal{E}_V^{\mathrm{TF}}$ and has important consequences: If the chemical potential (the Lagrange-multiplier) vanishes, then the TF equation becomes

$$\varrho(x) = c_{\mathrm{TF}}^{3/2} [\varphi(x)]_+^{3/2}. \tag{3.2}$$

This means that the minimizing density with $\mu = 0$ is completely determined by the TF potential φ, which solves the distributional partial differential equation

$$\Delta \varphi(x) = 4\pi c_{\mathrm{TF}}^{-3/2} [\varphi]_+^{3/2}(x) \qquad \forall x \in \operatorname{supp}(\Delta V)^c. \tag{3.3}$$

The prime example for this situation is the Coulomb potential $V_{\mathbf{Z},\mathbf{R}}$: It is harmonic in $\{R_1, .., R_M\}^c$ and the chemical potential for the minimization problem over $\mathcal{C}(\lambda)$ vanishes for any $\lambda \geq |\mathbf{Z}|$ due to the following result by Lieb and Simon:

Theorem 3.3. *[5, Theorems II.17 and II.18] $\mathcal{E}^{\mathrm{TF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}}$ has an absolute minimizer $\varrho^{\mathrm{TF}}_{\boldsymbol{Z},\boldsymbol{R}}$, which is neutral, that is $\int \varrho^{\mathrm{TF}}_{\boldsymbol{Z},\boldsymbol{R}} = |\boldsymbol{Z}|$.*

The study of the partial differential equation (3.3) plays a central role in this thesis, not only because it allows us to deduce properties of the TF minimizers, but in

[1] Lieb and Simon use that V is in $\cup_{q \in (\frac{5}{2}, \infty)} (L^{5/2} + L^q)$, which is a strict subset of $L^{5/2} + L^\infty_\epsilon$. If V is from the latter set, we note that $\mathcal{E}_V^{\mathrm{TF}}[\rho_n] \to \mathcal{E}_V^{\mathrm{TF}}[\rho]$ if $\rho_n \to \rho$ in $L^{5/3}$ and $\|\rho\|_1, \|\rho_n\|_1$ are uniformly bounded. This in particular replaces [5, Theorem II.2 b)] and is proven along the same lines.

particular because solutions to (3.3) have a certain universal behaviour. We give a short explanation of the underlying principle:

The only solution of the simple form $|x|^p$ is $p = -4$, but TF potentials arising from a nuclear potential have a $|x|^{-1}$-behaviour at the origin since $\varrho * |x|^{-1}$ is continuous. In this case, $|x|^{-4}$ can at most be valid for large $|x|$. This had already been noted by Sommerfeld in 1932 [19] when he studied the atomic TF problem and we speak of the *Sommerfeld asymptotic* when

$$\varphi(x) \approx c_{\mathrm{S}}|x|^{-4}, \qquad \text{as } |x| \to \infty$$

with

$$c_{\mathrm{S}} := (3/\pi)^2 c_{\mathrm{TF}}^3.$$

Looking for the next order in $|x|$, that is a function of the form $|x|^{-4}(1 + a|x|^p)$, one computes $\Delta|x|^{-4}(1 + a|x|^p) = 12|x|^{-6}(1 + a/12(12 + p^2 - 7p)|x|^p)$. Since $(|x|^{-4}(1 + a|x|^p))^{3/2} \approx |x|^{-6}(1 + \frac{3}{2}a|x|^p)$ to first order in the correction $a|x|^p$, this ansatz leads to $p^2 - 7p = 6$. We use the notation introduced by Sommerfeld and denote the solutions of this quadratic equation by η and $-\xi$, that is

$$\eta := \frac{7 + \sqrt{73}}{2} \approx 7.772, \qquad \xi := -\frac{7 - \sqrt{73}}{2} \approx 0.772.$$

Now the interesting part is the *Sommerfeld universality*: Positive solutions to (3.3) that vanish at infinity indeed satisfy the Sommerfeld asymptotic and hence have also the same correction terms $|x|^{-4-\xi}$ for large $|x|$.[2]

We note if φ is a radial solution of (3.3), then it reduces to an ordinary differential equation

$$\frac{df}{dr^2} = \frac{(f(r))^{3/2}}{\sqrt{r}}, \qquad r > 0$$

via $f(|x|) = (4\pi)^2 c_{\mathrm{TF}}^{-3}|x|\varphi(x)$. This equation has been studied, amongst others by Hille in [20]. However, since we seek to investigate the dissociation energy, which in particular involves the nonradial system of two nuclei, we need to go beyond the radial case, treating the (fully) partial differential equation. This case has already been investigated (for example in [5]) and we in particular note that the behaviour of solutions φ to (3.3) with a singularity at $p \in \mathbb{R}^3$ has been characterized by Veron [21]: Either $\lim_{x \to p} \varphi(x)|x - p|^4 = c_{\mathrm{S}}$, which is the unique 'strong' singularity, or we have a 'weak' singularity $\lim_{x \to p} \varphi(x)|x - p| = C$ for some $C > 0$. Any TF potential that corresponds to $V_{\mathbf{Z},\mathbf{R}}$ clearly falls into the latter category. Hence all $C > 0$ are

[2] compare Lemmas 3.6, 3.10 and 3.11

possible and the strong singularity can be understood as the limiting case $C \to \infty$.

The main technique for the study of the PDE (3.3) is the subharmonic comparison argument, a variation of the maximum principle for subharmonic functions.

Theorem 3.4 (Maximum principle)**.** *Let Ω be an open, bounded subset of $\mathbb{R}^n$ and assume $u \in C(\overline{\Omega})$, as a distribution, satisfies $\Delta u \geq 0$ in Ω. Then $\max_{\overline{\Omega}} u = \max_{\partial\Omega} u$.*

The maximum principle is a well-known cornerstone in harmonic analysis. For a proof of this generalization to subharmonic (continuous) distributions, see for example [22, Part 3, Chapter 3.2].

Corollary 3.5 (Subharmonic comparison)**.** *Let Ω be an open subset of $\mathbb{R}^n$ and assume $u \in C(\overline{\Omega})$ satisfies $u \leq 0$ on $\partial\Omega$ and, as a distribution, $\Delta u \geq 0$ in $\Omega \cap \{u > 0\}$. Further assume $\limsup_{x\in\Omega,\, |x|\to\infty} u(x) \leq 0$ if Ω is unbounded. Then $u(x) \leq 0$ for all $x \in \Omega$.*

Proof. Let $U_r = B(0,r) \cap \{x \in \Omega : u(x) > 0\}$ and assume there exists $\tilde{r}$ with $\tilde{x} \in U_{\tilde{r}}$. Then $0 < u(\tilde{x}) \leq \max_{\overline{U_r}} u = \max_{\partial U_r} u$ for all $r \geq \tilde{r}$. But $\limsup_{r\to\infty} \max_{\partial U_r} u \leq 0$ due to the assumptions. Hence U_r must be empty for all r. □

2. Atomic and diatomic TF theory

To discuss (neutral) atomic and diatomic TF theory, we recall that $V_{\mathbf{Z},R}(x) = \sum_{p\in\{0,R\nu\}} Z_p|x-p|^{-1}$ for some arbitrary but fixed $\nu \in \mathbb{S}^2$. Using Theorems 3.2 and 3.3 we then define the atomic and diatomic global minimizers

$$\varrho_Z^{\mathrm{TF}} := \arg\min_{\mathcal{C}} \mathcal{E}^{\mathrm{TF}}_{Z/|x|} \quad \text{and} \quad \varrho_{\mathbf{Z},R}^{\mathrm{TF}} := \arg\min_{\mathcal{C}} \mathcal{E}^{\mathrm{TF}}_{V_{\mathbf{Z},R}} \tag{3.4}$$

and denote by E_Z^{TF} and $E_{\mathbf{Z},R}^{\mathrm{TF}}$ the minimal values of the TF functional. The minimizing densities are neutral, that is $\int \varrho_Z^{\mathrm{TF}} = Z$, $\int \varrho_{\mathbf{Z},R}^{\mathrm{TF}} = |\mathbf{Z}|$ and the corresponding chemical potential vanishes. The corresponding TF potentials

$$\varphi_Z^{\mathrm{TF}}(x) := \frac{Z}{|x|} - \varrho_Z^{\mathrm{TF}} * |x|^{-1} \quad \text{and} \quad \varphi_{\mathbf{Z},R}^{\mathrm{TF}}(x) := V_{\mathbf{Z},R}(x) - \varrho_{\mathbf{Z},R}^{\mathrm{TF}} * |x|^{-1}$$

therefore satisfy the distributional differential equations

$$\Delta\varphi_Z^{\mathrm{TF}} = 4\pi c_{\mathrm{TF}}^{-3/2} (\varphi_Z^{\mathrm{TF}})^{3/2} - 4\pi Z \delta_0 \quad \text{in } \mathbb{R}^3$$

and

$$\Delta\varphi^{\mathrm{TF}}_{\mathbf{Z},R} = 4\pi c_{\mathrm{TF}}^{-3/2}(\varphi^{\mathrm{TF}}_{\mathbf{Z},R})^{3/2} - 4\pi\left(Z_0\delta_0 + Z_{R\nu}\delta_{R\nu}\right) \qquad \text{in } \mathbb{R}^3.$$

We have already announced that these equations imply the Sommerfeld asymptotic:

Lemma 3.6 (Atomic Sommerfeld bounds)**.** *Let* $Z > 0$ *and* $a^{\mathrm{TF}} := 2(44\sqrt{11}-1)\frac{c_{\mathrm{S}}^{\xi/3}}{22^{\xi}}$. *Then*

$$c_{\mathrm{S}}|x|^{-4} \geq \varphi^{\mathrm{TF}}_Z(x) \geq c_{\mathrm{S}}|x|^{-4}(1 - a^{\mathrm{TF}}Z^{-\xi/3}|x|^{-\xi}),$$

and

$$\frac{3}{\pi}c_{\mathrm{S}}|x|^{-6} \geq \varrho^{\mathrm{TF}}_Z(x) \geq \frac{3}{\pi}c_{\mathrm{S}}|x|^{-6}(1 - \tfrac{3}{2}a^{\mathrm{TF}}Z^{-\xi/3}|x|^{-\xi}).$$

Proof. It is well known that $\varphi^{\mathrm{TF}}_Z \leq c_{\mathrm{S}}|x|^{-4}$ for all $x \in \mathbb{R}^3$, see for example [12, Theorem 5.2]. A proof of the bound $\varphi^{\mathrm{TF}}_Z(x) \geq c_{\mathrm{S}}|x|^{-4}(1+aZ^{-\xi/3}|x|^{-\xi})^{-2}$, $\forall x \in \mathbb{R}^3$ with the constant $a = (44\sqrt{11}-1)c_{\mathrm{S}}^{\xi/3}22^{-\xi}$ can be found in [12, Thm 5.4].[3] From this and with $a^{\mathrm{TF}} = 2a$ we infer that for all $x \in \mathbb{R}^3$:[4]

$$c_{\mathrm{S}}^{-1}|x|^4\varphi^{\mathrm{TF}}_Z(x) \geq 1 - a^{\mathrm{TF}}Z^{-\xi/3}|x|^{-\xi}.$$

For the bound on the TF density, we use that $(c_{\mathrm{S}}/c_{\mathrm{TF}})^{3/2} = \frac{3}{\pi}c_{\mathrm{S}}$ together with the TF equation (3.2). Then the upper bound is trivial. And the lower bound also follows immediately:

$$\begin{aligned}\frac{3}{\pi}c_{\mathrm{S}}^{-1}|x|^6\varrho^{\mathrm{TF}}_Z(x) = \left(c_{\mathrm{S}}^{-1}|x|^4\varphi^{\mathrm{TF}}_Z(x)\right)^{3/2} &\geq (1 + a^{\mathrm{TF}}Z^{-\xi/3}|x|^{-\xi})^{-3}\\ &\geq 1 - 3a^{\mathrm{TF}}Z^{-\xi/3}|x|^{-\xi}.\end{aligned}$$

□

Remark: Positivity of the atomic TF potential
The lower bounds that we give in Lemma 3.6 are far from optimal, because they are just the asymptotic behaviour (for large $|x|$) of the better lower bound [12, Thm 5.4]. We note that the latter implies

$$\varphi^{\mathrm{TF}}_Z(x) > 0, \qquad \forall x \in \mathbb{R}^3.$$

The TF scaling relation (1.3), rephrased for the TF potentials, reads $\varphi^{\mathrm{TF}}_Z(x) = \lambda^4\varphi^{\mathrm{TF}}_{\lambda^3 Z}(\lambda x)$ and $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) = \lambda^4\varphi^{\mathrm{TF}}_{\lambda^3\mathbf{Z},\lambda R}(\lambda x)$ for any $\lambda > 0$. It implies that the atomic potential is, for all $Z > 0$, fully determined by one single radial function φ^{TF}_1. The diatomic potential on the other hand is already more complicated. It can only be reduced to a two-parameter family, depending on $m_{\mathbf{Z}}^3R$ and the ratio $\max(Z_1, Z_2)/m_{\mathbf{Z}}$. The same holds for the diatomic Born-Oppenheimer curve $D^{\mathrm{TF}}_{\mathbf{Z},R}$.

[3] using that $\beta_0 = c_{\mathrm{S}}^{1/3}/22$
[4] By strict convexity of $f(t) = (1+t)^{-p}$ on $(-1,\infty)$, $f(t) \geq f(0) + t\frac{df}{dt}(0) = 1 - pt$.

A classical result due to Teller [7] describes an important relation between the atomic and diatomic TF potentials. Lieb and Simon provided a rigorous proof (see [5, Thm. V.5], which contains an even sharper result not needed here). We repeat it here to showcase an application of the subharmonic comparison argument.

Lemma 3.7 (Teller)**.** *For all positive Z_1, Z_2, R and all $x \in \mathbb{R}^3$,*

$$\max\left\{\varphi^{\mathrm{TF}}_{Z_1}(x), \varphi^{\mathrm{TF}}_{Z_2}(x - R\nu)\right\} \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \leq \varphi^{\mathrm{TF}}_{Z_1}(x) + \varphi^{\mathrm{TF}}_{Z_2}(x - R\nu).$$

Proof. Note that by Proposition 2.2, $x \mapsto \varphi^{\mathrm{TF}}_{Z_1}(x) - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) + \frac{Z_2}{|x-R\nu|}$ is continuous on all of $\mathbb{R}^3$. Hence $\varphi^{\mathrm{TF}}_{Z_1} \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ on $\overline{B(R,\delta)}$ for all δ sufficiently small. We apply Corollary 3.5 with $u = \varphi^{\mathrm{TF}}_{Z_1} - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ and $\Omega = \overline{B(R,\delta)}^c$ and obtain $\varphi^{\mathrm{TF}}_{Z_1} \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ everywhere. Interchanging the roles of $\varphi^{\mathrm{TF}}_{Z_1}$ and $\varphi^{\mathrm{TF}}_{Z_2}$ in this argument proves the first inequality. While for the second inequality, we apply Corollary 3.5 with $u = \varphi^{\mathrm{TF}}_{\mathbf{Z},R} - \varphi^{\mathrm{TF}}_{Z_1} - \varphi^{\mathrm{TF}}_{Z_2}(\cdot - R\nu)$ and $\Omega = \mathbb{R}^3$. □

Combining Teller's Lemma and the atomic Sommerfeld bound gives a Sommerfeld type lower bound for $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ and an upper bound by *twice* the Sommerfeld asymptotic. A better upper bound for large $|x|$ which actually proves the Sommerfeld asymptotic for the diatomic potential will be provided later and follows from Lemma 3.10.

We improve Teller's bound close to the origin, where both $\varphi^{\mathrm{TF}}_{Z_1}(x)$ and $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)$ have the same leading term $Z_1/|x|$. We have control on the growth of their difference, independent of the value of Z_2. For this we introduce more notation, defining the constants

$$\tilde{\xi} := \frac{\xi + 4}{\eta + \xi}, \qquad \tilde{\eta} := 1 - \tilde{\xi} = \frac{\eta - 4}{\eta + \xi}.$$

Lemma 3.8. *Let $p \in \{0, R\nu\}$, assume $RZ_p^{1/3} \geq 2\left(a^{TF}\tilde{\xi}/\tilde{\eta}\right)^{1/\xi}$. Then for all $x \in \overline{B(p, R/2)}$:*

$$0 \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) - \varphi^{\mathrm{TF}}_{Z_p}(x - p) \leq c_{3.8a} c_{\mathrm{S}} R^{-4} (RZ_p^{1/3})^{-\tilde{\eta}\xi} + c_{\mathrm{S}}|x - p|^{-4}\left(\frac{2|x - p|}{R}\right)^{\eta}.$$

And for all $x \in B(p, r)^c$ with $r \in (0, R/2)$:

$$\left|(\varrho^{\mathrm{TF}}_{Z_p}(\cdot - p) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R})\mathbb{1}_{B(p,r)} * |x|^{-1}\right| \leq \frac{r}{|x|}\left(c_{3.8b} R^{-4}\left(RZ_p^{\frac{1}{3}}\right)^{-\tilde{\eta}\xi} + c_{3.8c} r^{-4}\left(\frac{2r}{R}\right)^{\eta}\right).$$

Proof. Without loss of generality we may assume $p = 0$.

Step 1 (A preliminary bound in $B(0, r)$)

Consider the function $\Psi(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + (R/r - 1)^{-4}\left(|x|/r\right)^{\eta}\right)$, which is smooth away from the origin. Since η is a solution to $\eta(\eta-7)=6$ and since $(1+\frac{3}{2}t)\leq(1+t)^{3/2}$ for $t\geq 0$, we compute for $|x|>0$:

$$\Delta\Psi(x)=12c_{\mathrm{S}}|x|^{-6}\left(1+\left(1+\tfrac{\eta(\eta-7)}{12}\right)(R/r-1)^{-4}\left(\frac{|x|}{r}\right)^{\eta}\right)\leq 12c_{\mathrm{S}}^{-1/2}\Psi(x)^{3/2}.$$

By Proposition 2.2, we have $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}-Z_1|x|^{-1}\in C(B(0,R))$. Hence there exists a $\delta>0$ such that $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}\leq\Psi$ in $\overline{B(0,\delta)}$. Let us assume for now that $r\in(0,R)$. By Lemmas 3.6 and 3.7 we find that for all $|x|=r$

$$\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)\leq c_{\mathrm{S}}r^{-4}\left(1+\frac{r^4}{|x-R\nu|^4}\right)\leq c_{\mathrm{S}}r^{-4}\left(1+\frac{r^4}{(R-r)^4}\right)\leq\Psi(x).$$

We now apply Corollary 3.5 with $u=\varphi^{\mathrm{TF}}_{\mathbf{Z},R}-\Psi$ and $\Omega=B(0,r)\setminus\overline{B(0,\delta)}$ and find

$$\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)\leq c_{\mathrm{S}}|x|^{-4}\left(1+(R/r-1)^{-4}\left(\frac{|x|}{r}\right)^{\eta}\right),\qquad\forall x\in\overline{B(0,r)}.\tag{3.5}$$

Then using Lemma 3.6 again, we conclude that for all $x\in\overline{B(0,r)}$ and $Z_1,Z_2>0$,

$$\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)-\varphi^{\mathrm{TF}}_{Z_1}(x)\leq c_{\mathrm{S}}|x|^{-4}\left(a^{\mathrm{TF}}Z_1^{-\xi/3}|x|^{-\xi}+(R/r-1)^{-4}\left(\frac{|x|}{r}\right)^{\eta}\right).\tag{3.6}$$

Step 2 (Improving the bound for small x)
For $|x|=r_0:=r\left(\frac{\tilde\xi}{\tilde\eta}a^{\mathrm{TF}}(R/r-1)^4(R/r)^{\xi}(RZ_1^{1/3})^{-\xi}\right)^{\frac{1}{\eta+\xi}}$, the right hand side of (3.6) is minimal in $|x|\in[0,r]$. So if $|x|=r_0\leq r$, which is equivalent to

$$RZ_1^{1/3}\geq C_1(r/R):=\frac{R}{r}\left(\frac{\tilde\xi}{\tilde\eta}a^{\mathrm{TF}}(R/r-1)^4\right)^{1/\xi},$$

then $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)-\varphi^{\mathrm{TF}}_{Z_1}(x)\leq c_{\mathrm{S}}a^{\mathrm{TF}}Z_1^{-\xi/3}(\eta+\xi)/(\eta-4)r_0^{-\xi-4}$. As the right hand side is a constant, we can extend the bound to all $|x|\leq r_0$ by Corollary 3.5 (with $u=\varphi^{\mathrm{TF}}_{\mathbf{Z},R}-\varphi^{\mathrm{TF}}_{Z_1}-(cst.)$ and $\Omega=B(0,r_0)$). Hence if $RZ_1^{1/3}\geq C_1(r/R)>0$, then $r_0\in(0,r]$ and we have improved (3.6) for small x:

$$\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)-\varphi^{\mathrm{TF}}_{Z_1}(x)\leq c_{\mathrm{S}}a^{\mathrm{TF}}\tfrac{\eta+\xi}{\eta-4}Z_1^{-\xi/3}r_0^{-\xi-4},\qquad\forall|x|\leq r_0.\tag{3.7}$$

We choose $r=R/2$, which fixes the constant $C_1(r/R)$. Then $r_0=(cst.)(RZ_1^{1/3})^{\frac{-\xi}{\eta+\xi}}$. Inserting this in (3.7) and combining it with (3.6), we have deduced the first bound, that if $RZ_1^{1/3}\geq C_1(1/2)=2(a^{\mathrm{TF}}\tilde\xi/\tilde\eta)^{1/\xi}$, then for all $|x|\leq R/2$:

$$\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x)-\varphi^{\mathrm{TF}}_{Z_1}(x)\leq c_{\mathrm{S}}|x|^{-4}(2|x|/R)^{\eta}+c_{\mathrm{S}}\underbrace{(a^{\mathrm{TF}})^{\tilde\eta}\left(2^{\eta}\tilde\eta/\tilde\xi\right)^{\tilde\xi}\tfrac{\eta+\xi}{\eta-4}}_{=:c_{3.8a}}R^{-4}(RZ_1^{1/3})^{-\tilde\eta\xi}.\tag{3.8}$$

Step 3 (Integrating the first bound to obtain the second)
With the TF equation and the fact that $(1+t)^{3/2}-1\leq\frac{3}{2}t+\frac{3}{2}t^{3/2}$ for any $t\geq 0$,

we have

$$\begin{aligned}c_{\mathrm{TF}}^{3/2}(\varrho_{\mathbf{Z},R}^{\mathrm{TF}}-\varrho_{Z_1}^{\mathrm{TF}}) =&(\varphi_{Z_1}^{\mathrm{TF}})^{3/2}\left((1+(\varphi_{\mathbf{Z},R}^{\mathrm{TF}}-\varphi_{Z_1}^{\mathrm{TF}})/\varphi_{Z_1}^{\mathrm{TF}})^{3/2}-1\right)\\ \leq&\frac{3}{2}\left(\varphi_{Z_1}^{\mathrm{TF}}\right)^{\frac12}\left(\varphi_{\mathbf{Z},R}^{\mathrm{TF}}-\varphi_{Z_1}^{\mathrm{TF}}\right)+\frac{3}{2}\left(\varphi_{\mathbf{Z},R}^{\mathrm{TF}}-\varphi_{Z_1}^{\mathrm{TF}}\right)^{\frac32}.\end{aligned}$$

Let $r\in(0,R/2)$. We abbreviate $C_2:=\left(2^\eta\tilde\eta/\tilde\xi\right)^{\tilde\xi}(a^{\mathrm{TF}})^{\tilde\eta}/\tilde\eta(RZ_1^{1/3})^{-\tilde\eta\xi}$ and use Lemma 3.6 with (3.8) to estimate for $x\in\overline{B(0,r)}$:

$$\begin{aligned}0\leq&c_{\mathrm{TF}}^{3/2}(\varrho_{\mathbf{Z},R}^{\mathrm{TF}}(x)-\varrho_{Z_1}^{\mathrm{TF}}(x))\\ \leq&\frac32 c_{\mathrm{S}}^{3/2}\left(|x|^{-2}R^{-4}\left(C_2+2^\eta\left[|x|/R\right]^{\eta-4}\right)+R^{-6}\left(C_2+2^\eta\left[|x|/R\right]^{\eta-4}\right)^{3/2}\right)\\ \leq&\frac32 c_{\mathrm{S}}^{3/2}\Bigg(|x|^{-2}R^{-4}C_2+2^\eta|x|^{-6}\left[|x|/R\right]^{\eta}+R^{-6}C_2^{3/2}+R^{-6}2^{\frac{3\eta}{2}}\left[|x|/R\right]^{\frac32(\eta-4)}\\ &\qquad+(2^{3/2}-2)C_2^{\frac34}2^{\frac{3\eta}{4}}\left[|x|/R\right]^{\frac34(\eta-4)}R^{-6}\Bigg).\end{aligned}$$

Here we used that $(a+b)^{3/2}\leq a^{3/2}+b^{3/2}+(2^{3/2}-2)a^{3/4}b^{3/4}$ for all $a,b\geq 0$. This bound being radial, we use Newton's theorem and obtain for $|x|\geq r\in(0,R/2)$:

$$\begin{aligned}0\leq&(\varrho_{\mathbf{Z},R}^{\mathrm{TF}}-\varrho_{Z_1}^{\mathrm{TF}})\mathbb{1}_{B(0,r)}*|x|^{-1}\\ \leq&\frac{9c_{\mathrm{S}}}{2\pi|x|}\int_{B(0,r)}\Bigg(|y|^{-2}R^{-4}C_2+2^\eta|y|^{-6}\left[|y|/R\right]^{\eta}+R^{-6}C_2^{3/2}+R^{-6}2^{\frac{3\eta}{2}}\left[|y|/R\right]^{\frac32(\eta-4)}\\ &\qquad+(2^{3/2}-2)C_2^{\frac34}2^{\frac{3\eta}{4}}\left[|y|/R\right]^{\frac34(\eta-4)}R^{-6}\Bigg)dy.\end{aligned}$$

By integration and since $ab\leq a^2/2+b^2/2$, we find that

$$\begin{aligned}&(\varrho_{\mathbf{Z},R}^{\mathrm{TF}}-\varrho_{Z_1}^{\mathrm{TF}})\mathbb{1}_{B(0,r)}*|x|^{-1}\\ &\quad\leq\frac{18c_{\mathrm{S}}r}{|x|}\Bigg(C_2R^{-4}\left[1+\frac13 C_2^{1/2}(r/R)^2+C_2^{1/2}\left(\frac{2^{\frac32}-2}{3\eta}\right)^2\right]\\ &\qquad\qquad+(2r/R)^\eta r^{-4}\left[\tfrac{1}{\eta-3}+\tfrac{1}{\frac{3\eta}{2}-3}(2r/R)^{\eta/2}+(2r/R)^{\eta/2+2}\right]\Bigg).\end{aligned}\tag{3.9}$$

Note that the assumption $RZ_1^{1/3}\geq 2(a^{\mathrm{TF}}\tilde\xi/\tilde\eta)^{1/\xi}$ is equivalent to $C_2\leq 2^4/\tilde\xi$ and that $r/R<1/2$. We use this in (3.9) and end the proof by defining

$$\begin{aligned}c_{3.8b}&:=c_{\mathrm{S}}18(a^{\mathrm{TF}})^{\tilde\eta}2^{\eta\tilde\xi}\tilde\eta^{-\tilde\eta}\tilde\xi^{-\tilde\xi}\left(1/3+\tilde\xi^{-1/2}\left(1+\frac{4(2^{3/2}-2)^2}{(3\eta)^2}\right)\right),\\ c_{3.8c}&:=c_{\mathrm{S}}18\left(\frac{1}{\eta-3}+\frac{1}{3\eta/2-3}+1\right).\end{aligned}$$

□

3. Outside TF models

The term outside Thomas-Fermi (oTF) model was used in [12] for the TF model with respect to the HF-screened atomic potential, restricted to the outside of a ball. We generalize the idea in two ways: Firstly by formulating it for a whole class of outside harmonic potentials. Secondly by showing that the same ideas apply to the diatomic case.

Before going into the details we motivate the further discussion with the simplest nontrivial outside model. It arises naturally when splitting the atomic TF energy into inside and outside energies with respect to the ball $B = B(0, r)$. By this we mean the decomposition

$$E_Z^{\mathrm{TF}} = \mathcal{E}^{\mathrm{TF}}_{Z/|x|}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_B] + \mathcal{E}^{\mathrm{TF}}_{\Phi^{\mathrm{TF}}_{Z,r}}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_{B^c}]. \tag{3.10}$$

One might object that the second summand in (3.10) does not really depend solely on the outside, since $\Phi^{\mathrm{TF}}_{Z,r}(x) = Z/|x| - \int_B \varrho_Z^{\mathrm{TF}}(y)/|x-y|dy$. However, we could also consider the restriction of this potential to the outside, $V_r = \Phi^{\mathrm{TF}}_{Z,r}\mathbb{1}_{B^c}$, and notice that $\mathcal{E}^{\mathrm{TF}}_{\Phi^{\mathrm{TF}}_{Z,r}}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_{B^c}] = \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_{B^c}]$. The minimization problem

$$\varrho_r = \arg \min_{\mathcal{C}(N_r)} \mathcal{E}^{\mathrm{TF}}_{V_r}, \qquad N_r = Z - \int_B \varrho_Z^{\mathrm{TF}}$$

is an example of an outside TF model.[5] The TF equation $c_{\mathrm{TF}}\varrho_r^{2/3} = [V_r - \varrho_r * |x|^{-1} - \mu_r]_+$ implies that the minimizing density has support outside of B. The restriction to densities with L^1-norm of at most mass $N_r = \lim_{t\to\infty} t \fint_{\partial B(0,t)} V_r$ is natural, since this is the total inside charge, seen from the outside. With this example in mind, we now present the more general framework.

Definition 3.9. Let $\Omega \subset \mathbb{R}^3$ be the complement of a compact set. Then $\mathcal{H}(\Omega)$ shall denote the space of functions $V : \mathbb{R}^3 \to \mathbb{R}$ which vanish in $\mathbb{R}^3 \setminus \overline{\Omega}$, are continuous in $\overline{\Omega}$ and satisfy $\Delta V = 0$ in Ω as well as $\lim_{|x|\to\infty} V(x) = 0$.

For any $V \in \mathcal{H}(\Omega)$, with $\Omega \subset \mathbb{R}^3$ being the complement of a compact set, we introduce the total inside charge

$$N(V) := \lim_{t\to\infty} t \fint_{\partial B(0,t)} V(\omega)d\omega.$$

[5] we use Theorem 3.2 here

This limit exists because $t \mapsto t \fint_{\partial B(0,t)} V(\omega) d\omega$ is constant for all t such that $\Omega^c \subset B(0,t)$.[6] Note that $\mathcal{H}(\Omega) \subset L^{5/3} + L^\infty_\epsilon$. Hence by Theorem 3.2, there exists

$$\varrho = \arg \min_{\mathcal{C}(N(V))} \mathcal{E}_V^{\mathrm{TF}}$$

for any $V \in \mathcal{H}(\Omega)$ and we call this minimization problem the *outside Thomas-Fermi model* corresponding to the potential V. The minimizer satisfies the TF equation, which implies that $\operatorname{supp} \varrho \subset \operatorname{supp} V \subset \overline{\Omega}$. We will treat two particular cases of oTF models,

- if $V \in \mathcal{H}(\overline{B(0,r)}^c)$, we speak of an *atomic oTF model.*
- if $V \in \mathcal{H}(\mathcal{O}_r)$, we speak of a *diatomic oTF model.*[7]

The maximum principle implies that any $V \in \mathcal{H}(\Omega)$ decays at least like the harmonic function $|x|^{-1}$. More precisely, if $V \in \mathcal{H}(\overline{B(0,r)}^c)$, then

$$|V(x)| \leq \frac{r}{|x|} \sup_{\partial B(0,r)} |V|, \qquad \forall |x| \geq r \tag{3.11}$$

and if $V \in \mathcal{H}(\mathcal{O}_r)$, then

$$|V(x)| \leq \frac{R+r}{|x|} \sup_{\partial \mathcal{O}_r} |V|, \qquad \forall |x| \geq R+r. \tag{3.12}$$

Let us have a closer look at our example $V_r = \Phi_{Z,r}^{\mathrm{TF}} \mathbb{1}_{B(0,r)^c} \in \mathcal{H}(\overline{B(0,r)}^c)$ with the minimizer $\varrho_r \in \mathcal{C}(N(V_r))$. The atomic density ϱ_Z^{TF} is (see Theorem 3.3) a global minimizer, hence by inserting the trial density $\varrho_Z^{TF} \mathbb{1}_B + \varrho_r$ in (3.10), we obtain $E_Z^{\mathrm{TF}} \leq \mathcal{E}_{Z/|x|}^{\mathrm{TF}}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_B] + \mathcal{E}_{\Phi_{Z,r}^{\mathrm{TF}}}^{\mathrm{TF}}[\varrho_r]$. On the other hand, $E_Z^{\mathrm{TF}} \geq \mathcal{E}_{Z/|x|}^{\mathrm{TF}}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_B] + \mathcal{E}_{\Phi_{Z,r}^{\mathrm{TF}}}^{\mathrm{TF}}[\varrho_r]$ by minimality of ϱ_r. Then $\mathcal{E}_{V_r}^{TF}[\varrho_Z^{\mathrm{TF}} \mathbb{1}_{B^c}] = \mathcal{E}_{V_r}^{TF}[\varrho_r]$. However, since TF minimizers are unique, $\varrho_r = \varrho_Z^{\mathrm{TF}} \mathbb{1}_{B^c}$, which is not too surprising. This implies that the corresponding chemical potential vanishes, so ϱ_r is the global minimizer of $\mathcal{E}_{V_r}^{\mathrm{TF}}$. The corresponding TF potential equals, by definition, φ_Z^{TF}, which satisfies the Sommerfeld asymptotic.

But what about other oTF models, are the minimizers global and does the corresponding TF potential satisfy the Sommerfeld asymptotic? In the following Sections, we generalize the *perturbation argument* from [12] and show that these two questions can be answered affirmatively, provided $\|V - \Phi_{Z,r}^{\mathrm{TF}} \mathbb{1}_{B(0,r)^c}\|_\infty$ (or $\|V - \Phi_{\mathbf{Z},R,r}^{\mathrm{TF}} \mathbb{1}_{\overline{\mathcal{O}_r}}\|_\infty$ in the diatomic case) is sufficiently small.

[6] See Proposition A.3 in the appendix for details.

[7] We recall that $\mathcal{O}_r = \left(\overline{B(0,r)} \cup \overline{B(R\nu, r)}\right)^c$.

Remark: Other outside models in TF theory
There exist other formulations which are quite similar to what we call oTF here. Lieb and Simon considered for example [5, Ch. VII] TF minimizers with respect to a (radial) uniform screening $Z/|x| - \int_\Lambda \rho_b/|x-y|dy,\ \rho_b \in \mathbb{R}_+$. Since V was not restricted to Λ, their potentials are not directly covered by our approach here. Another similar formulation are what Solovej in [23] calls exterior TF models: He studied (radial) atomic potentials $\overline{\nu}/|x|$ and restricted the TF minimization problem to densities supported outside of a ball. We stress that we here allow far more general potentials, which in particular are not necessarily radial, both in the atomic and diatomic case.

3.1. Sommerfeld bounds. The following result is a fairly general statement about the Sommerfeld behaviour of solutions to the TF differential equation and has been proven in [12, Theorem 4.6]:

Lemma 3.10 (atomic oTF Sommerfeld asymptotic)**.** *Let $\varphi \in C_0(\overline{B(0,r)^c})$. Assume it satisfies $\Delta\varphi = 4\pi c_{\mathrm{TF}}^{-3/2}[\varphi - \mu]_+^{3/2}$ distributionally in $\overline{B(0,r)^c}$ for some $\mu \geq 0$ as well as $\liminf_{s\searrow r} \inf_{\partial B(0,s)} \varphi > \mu$. Then*

$$\max\left\{\omega_a^-(x), \nu(\mu,r)|x|^{-1}\right\} \leq \varphi(x) \leq \omega_A^+(x) + \mu \qquad \forall x \in B(0,r)^c,$$

where $\nu(\mu,r) := \inf_{B(0,r)^c} \max\{\mu|x|, \omega_a^-(x)|x|\}$ and

$$a(r) := \liminf_{s\searrow r} \sup_{\partial B(0,s)} \left(\sqrt{c_{\mathrm{S}} s^{-4}\varphi^{-1}} - 1\right), \qquad \omega_a^-(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + a(r)(r/|x|)^\xi\right)^{-2},$$

$$A(r) := \liminf_{s\searrow r} \sup_{\partial B(0,s)} \left(c_{\mathrm{S}}^{-1} s^4(\varphi - \mu) - 1\right), \qquad \omega_A^+(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + A(r)(r/|x|)^\xi\right).$$

Remark: Sommerfeld asymptotic for $\varphi_{\mathbf{Z},R}^{\mathrm{TF}}$
The conditions of Lemma 3.10 are satisfied for the diatomic TF potential, because it is strictly positive and the corresponding chemical potential vanishes. Moreover, it is clear that we can chose any centre for the ball in Lemma 3.10. Applying it with $\varphi_{\mathbf{Z},R}^{\mathrm{TF}}$ on $B(R\nu/2, 2R)^c$, we conclude that the diatomic TF potential satisfies the Sommerfeld asymptotic.

We now provide the analogue of Lemma 3.10 for the diatomic case:

Lemma 3.11 (Diatomic oTF Sommerfeld asymptotic)**.** *Let $r \in (0, R/2)$ and assume that $\varphi \in C_0(\mathcal{O}_r)$ satisfies $\Delta\varphi = 4\pi c_{\mathrm{TF}}^{-3/2}[\varphi - \mu]_+^{3/2}$ distributionally in $\mathcal{O}_r$ for* *some constant $\mu \geq 0$ as well as $\liminf_{s\searrow r} \inf_{\partial\mathcal{O}_s} \varphi > \mu$. Then for all $x \in \mathcal{O}_r$ holds*

$$\max\left\{\omega_a^-(x), \omega_a^-(x - R\nu), \frac{\nu(\mu, r)}{|x|}, \frac{\nu(\mu, r)}{|x - R\nu|}\right\} \leq \varphi(x) \leq \omega_A^+(x) + \omega_A^+(x - R\nu) + \mu,$$

where $\nu(\mu, r) := \inf_{B(0,r)^c} \max\{\mu|x|, \omega_a^-(x)|x|\}$ and

$$a(r) := \liminf_{s\searrow r} \sup_{\partial\mathcal{O}_s} \left(\sqrt{c_{\mathrm{S}} s^{-4}\varphi^{-1}} - 1\right), \qquad \omega_a^-(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + a(r)(r/|x|)^{\xi}\right)^{-2},$$

$$A(r) := \liminf_{s\searrow r} \sup_{\partial\mathcal{O}_s} \left(c_{\mathrm{S}}^{-1} s^4(\varphi - \mu) - 1\right), \qquad \omega_A^+(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + A(r)(r/|x|)^{\xi}\right).$$

Notation: Half spaces
We introduce at this point some notation for the discussion of reflection symmetric functions: For $p \in \mathbb{R}^3 \setminus \{0\}$, let

$$\mathbb{H}_p := \{x \in \mathbb{R}^3 \mid (x - p) \cdot p = 0\}$$

and

$$\mathbb{H}_p^{\pm} := \{x \in \mathbb{R}^3 \mid \pm(x - p) \cdot p > 0\}$$

so that $\mathbb{R}^3$ is the disjoint union of the open half spaces $\mathbb{H}_p^+$, $\mathbb{H}_p^-$ and the plane $\mathbb{H}_p$.

Proof. **Step 1** (Reduction to continuous expressions)
By assumption on φ there exists $\tilde{r} \in (r, R/2)$ such that $\inf_{\partial\mathcal{O}_s} \varphi > \mu \geq 0$ for all $s \in (r, \tilde{r})$. This also implies that $a(s)$ is well defined for any $s \in (r, \tilde{r})$ and as φ is continuous on $\partial\mathcal{O}_s$, the suprema are actually achieved. It suffices to prove the statement with r replaced by an arbitrary $s \in (r, \tilde{r})$, since the claim then follows by taking $\liminf_{s\searrow r}$.

Step 2 (Lower bound)
We consider $f(x) = \max\left\{\omega_a^-(x), \omega_a^-(x - R\nu), \frac{\nu}{|x|}, \frac{\nu}{|x-R\nu|}\right\}$ on $\overline{\mathcal{O}_s}$. This is the maximum of the radial function $x \mapsto \max\{\omega_a^-(x), \nu|x|^{-1}\}$ and its shift to $R\nu$, hence f is reflection symmetric across the plane $\mathbb{H}_{R\nu/2}$. We also note that $a(s) > -1$ because of the assumption $\inf_{\partial\mathcal{O}_s} \varphi > \mu$. It is then easily verified that:

(a) $\omega_a^-(x)|x|$ is positive and radially decreasing for $|x| \geq s$,
(b) $\omega_a^-(x) = \inf_{\partial\mathcal{O}_s} \varphi > \mu$ for all $|x| = s$,
(c) $\Delta\omega_a^-(x) \geq 4\pi c_{\mathrm{TF}}^{-3/2}(\omega_a^-(x))^{3/2}$ for all $|x| > s$.

From (a), (b) and the fact that $\mu|x|$ is increasing, we deduce that $\nu = \mu r_0$ with r_0 being the unique radius in (s, ∞) such that $\omega_a^-(|x| = r_0) = \mu$. Moreover, for any

$x \in \overline{\mathcal{O}_s}$ we can write

$$f(x) = \begin{cases} \max\{\omega_a^-(x), \omega_a^-(x - R\nu)\} & \text{if } f(x) > \mu \\ \nu \max\{|x|^{-1}, |x - R\nu|^{-1}\} & \text{if } f(x) \leq \mu, \end{cases} \tag{3.13}$$

which together with (b) implies $f|_{\partial\mathcal{O}_s} = \inf_{\partial\mathcal{O}_s} \varphi$. To use Corollary 3.5 with $u = f - \varphi$ and $\Omega = \mathcal{O}_s$, we need to verify that $\Delta u \geq 0$ in $\mathcal{O}_s \cap \{u > 0\}$. Because $\Delta u = \Delta f - 4\pi c_{\mathrm{TF}}^{-3/2}[\varphi - \mu]_+^{3/2}$, it suffices to show $\Delta f \geq 4\pi c_{\mathrm{TF}}^{-3/2}[f - \mu]_+^{3/2}$ distributionally in $\mathcal{O}_s$. For any nonnegative $\phi \in C_c^\infty(\{x \in \mathcal{O}_s \mid f(x) > \mu\})$, we first compute (see Lemma B.1 for details)

$$\int_{\mathbb{R}^3} f\Delta\phi = \int_{\mathbb{R}^3} \Big((\Delta\omega_a^-)\mathbb{1}_{\mathbb{H}_{R\nu/2}^-} + (\Delta\omega_a^-(\cdot - R\nu))\mathbb{1}_{\mathbb{H}_{R\nu/2}^+}\Big)\phi - 2\int_{\mathbb{H}_{R\nu/2}} (\partial_\nu\omega_a^-)\phi d\sigma.$$

Due to (3.13), (c) and since $(\partial_\nu\omega_a^-) \leq 0$ on $\mathbb{H}_{R\nu/2}$, we find

$$\int_{\mathbb{R}^3} f\Delta\phi \geq 4\pi c_{\mathrm{TF}}^{-3/2}\int_{\mathbb{R}^3} f^{3/2}\phi \geq 4\pi c_{\mathrm{TF}}^{-3/2}\int_{\mathbb{R}^3} [f - \mu]_+^{3/2}\phi$$

and conclude that

$$\Delta f \geq 4\pi c_{\mathrm{TF}}^{-3/2}[f - \mu]_+^{3/2} \quad \text{in } \{f > \mu\} \cap \mathcal{O}_s. \tag{3.14}$$

Now ω_a^- is due to (c) and (a) subharmonic, while $|x|^{-1}$ is harmonic. The maximum of finitely many subharmonic functions is a subharmonic function,[8] hence f is subharmonic in $\mathcal{O}_s$, which implies[9]

$$\Delta f \geq 0 \quad \text{in } \mathcal{O}_s. \tag{3.15}$$

Now pick any nonnegative $\phi \in C_c^\infty(\mathcal{O}_s)$ and a nonnegative sequence $\xi_n \in C_c^\infty(\{f > \mu\})$ such that $\xi_n \nearrow \mathbb{1}_{\{f>\mu\}}$ pointwise in $\operatorname{supp}\phi$. Writing

$$\int f\Delta\phi = \int f\Delta(\xi_n\phi) + \int f\Delta(1 - \xi_n)\phi,$$

we then use (3.14) for the first summand and (3.15) for the second summand to deduce that $\int f\Delta\phi \geq 4\pi c_{\mathrm{TF}}^{-3/2}\int[f - \mu]_+^{3/2}(\xi_n\phi)$. By monotone convergence, $\lim_{n\to\infty}\int[f - \mu]_+^{3/2}(\xi_n\phi) = \int[f - \mu]_+^{3/2}\phi$. As outlined earlier, the lower bound now follows from Corollary 3.5.

Step 3 (upper bound)
We consider $g(x) := \omega_A^+(x) + \omega_A^+(x - R\nu) + \mu$, a continuous function on $\mathbb{R}^3 \setminus \{0, R\nu\}$.

[8] see [22, Part 3, Proposition 3.2.1]
[9] see [22, Part 3, Corollary 3.2.16]

Because $\Delta\omega_A^+ \le 4\pi c_{\mathrm{TF}}^{-3/2}(\omega_A^+)^{3/2}$ in $\overline{B(0,s)}^c$, it satisfies

$$\Delta g \le 4\pi c_{\mathrm{TF}}^{-3/2}\left((\omega_A^+)^{3/2} + (\omega_A^+(\cdot - R\nu)^{3/2}\right) \le 4\pi c_{\mathrm{TF}}^{-3/2}[g-\mu]_+^{3/2} \qquad \text{in } \mathcal{O}_s.$$

Since $\omega_A^+ \mid_{\partial B(0,s)} = \sup_{\partial\mathcal{O}_s} \varphi - \mu$, we observe that

$$g(x) \ge \omega_A^+ \mid_{\partial B(0,s)} + \mu = \sup_{\partial\mathcal{O}_s} \varphi \qquad \forall x \in \partial\mathcal{O}_s.$$

Corollary 3.5 with $u = \varphi - g$ and $\Omega = \mathcal{O}_s$ now yields the upper bound. ☐

If φ satisfies the assumptions of Lemma 3.11, then it in particular also satisfies the assumptions of Lemma 3.6 in $B(R\nu/2, R/2+r)^c$ and we see that $\varphi \approx c_{\mathrm{S}}|x|^{-4}$ for large $|x|$. Hence the lower bound of Lemma 3.11 has the correct asymptotic behaviour, whereas the upper bound is too large by a factor two, similar to how Teller's Lemma yields a bad upper bound for $\varphi_{\mathbf{Z},R}^{\mathrm{TF}}$.

The next Lemma improves the upper bound from Lemma 3.11 for x close to $\partial\mathcal{O}_r$.

Lemma 3.12. *Let $r \in (0, R/2), \mu \ge 0$ and assume that $\varphi \in C_0(\mathcal{O}_r)$ satisfies $\Delta\varphi = 4\pi c_{\mathrm{TF}}^{-3/2}[\varphi-\mu]_+^{3/2}$ distributionally in $\mathcal{O}_r$. Then*

$$\varphi(x) \le \begin{cases} \omega_{A_1,A_2}^+(x) + \mu & \text{if } x \in \overline{\mathbb{H}_{R\nu/2}^-} \cap \mathcal{O}_r \\ \omega_{A_1,A_2}^+(x - R\nu) + \mu & \text{if } x \in \mathbb{H}_{R\nu/2}^+ \cap \mathcal{O}_r \end{cases}$$

where $\omega_{A_1,A_2}^+(x) := c_{\mathrm{S}}|x|^{-4}\left(1 + A_1(r)\,(2|x|/R)^\eta + A_2(r)\,(r/|x|)^\xi\right)$, with $A_j(r) := \liminf_{s\searrow r} B_j(s), j = 1,2$ and

$$B_1(s) := \frac{4 + B_2(s)(4+\xi)(2s/R)^\xi}{\eta - 4},$$

$$B_2(s) := \left[\frac{\sup_{\partial\mathcal{O}_s}[c_S^{-1}s^4(\varphi-\mu) - 1] - \frac{4}{\eta-4}(2s/R)^\eta}{1 + \frac{4+\xi}{\eta-4}(2s/R)^{\xi+\eta}}\right]_+ .$$

Proof. We prove the upper bound with r replaced by $s \in (r, R/2)$, since $A_j(s) = B_j(s), j = 1,2$ by continuity of φ in $\mathcal{O}_r$. The claimed bound follows then by taking the $\liminf\limits_{s\searrow r}$ on both sides. We want to apply Corollary 3.5 with $\Omega = \mathcal{O}_s$ to the function

$$u(x) = \varphi(x) - \left(\omega_{B_1,B_2}^+(x)\mathbb{1}_{\overline{\mathbb{H}_{R\nu/2}^-}}(x) + \omega_{B_1,B_2}^+(x - R\nu)\mathbb{1}_{\mathbb{H}_{R\nu/2}^+}(x) + \mu\right).$$

By definition of B_1, for all $x \in \partial\mathcal{O}_s$:

$$\varphi(x) - u(x) = c_{\mathrm{S}}s^{-4}\left(1 + \frac{4}{\eta-4}(2s/R)^\eta + B_2(s)\left(1 + \tfrac{\xi+4}{\eta-4}(2s/R)^{\eta+\xi}\right)\right) + \mu.$$

Then $\varphi - u \geq \sup_{\partial \mathcal{O}_s} \varphi$ in $\partial \mathcal{O}_s$ by definition of B_2 and this implies $u \leq 0$ on $\partial \mathcal{O}_s$. It remains to show that $\Delta u \geq 0$ in $\mathcal{O}_s \cap \{u > 0\}$. We assume without loss of generality that $\nu = e_3$ to compute that, in the distributional sense in $\mathcal{O}_s$,[10]

$$\begin{aligned}\Delta u(x) =& \Delta\varphi(x) - \Delta\omega^+_{B_1,B_2}(x)\mathbb{1}_{\mathbb{H}^-_{Re_3/2}}(x) - \Delta\omega^+_{B_1,B_2}(x - R\nu)\mathbb{1}_{\mathbb{H}^+_{Re_3/2}}(x) \\ &+ 2\partial_{x_3}\omega^+_{B_1,B_2}(x_1, x_2, R/2)\delta_{R/2}(x_3).\end{aligned}$$

A simple computation shows that $\Delta\omega^+_{B_1,B_2} \leq 4\pi c_{\mathrm{TF}}^{-3/2}(\omega^+_{B_1,B_2})^{3/2}$ in $\mathbb{R}^3\backslash\{0\}$.[11] Hence $\Delta u(x) \geq 2\partial_{x_3}\omega^+_{B_1,B_2}(x_1, x_2, R/2)\delta_{R/2}(x_3)$ in $\mathcal{O}_s \cap \{u > 0\}$ and we compute that

$$\partial_{x_3}\omega^+_{B_1,B_2}(x) = x_3 c_{\mathrm{S}}|x|^{-6}\left(B_1(\eta - 4)(2|x|/R)^\eta - B_2(4 + \xi)(r/|x|)^\xi - 4\right).$$

Now observe that $\partial_{x_3}\omega^+_{B_1,B_2}(x) \geq \partial_{x_3}\omega^+_{B_1,B_2}(Re_3/2) = 0$ for all $x \in \mathbb{H}_{Re_3/2}$ by the defining relation of B_1 and because $B_2 \geq 0$. We therefore conclude $\Delta u \geq 0$ distributionally in $\mathcal{O}_s \cap \{u > 0\}$, which finishes the proof. $\square$

3.2. Controlling the chemical potential. In the same way as Lemma 3.10 allows us to control the chemical potential for atomic oTF models (see [12, Corollary 4.7]), we have that Lemma 3.11 implies control on the chemical potential for diatomic oTF models:

Lemma 3.13. *Let $V \in \mathcal{H}(\mathcal{O}_r)$ and assume the corresponding TF potential φ satisfies $\inf_{\mathcal{O}_r}\varphi > \mu$ and $\Delta\varphi = [\varphi - \mu]_+^{3/2}$ in $\mathcal{O}_r$ for some $\mu \geq 0$. Then*

$$\mu^{3/4}c_{\mathrm{S}}^{1/4}(1 + a(r))^{-1/2} \leq N(V) - \int_{\mathbb{R}^3} c_{\mathrm{TF}}^{-3/2}\varphi^{3/2},$$

with $a(r) = \sup_{\partial\mathcal{O}_r}\sqrt{c_{\mathrm{S}}s^{-4}\varphi^{-1}} - 1$.

Proof. We repeat the proof of [12, Corollary 4.7], with the only difference that we start by applying Lemma 3.11 to the function $\varphi(x) = V(x) - c_{\mathrm{TF}}^{-3/2}\varphi^{3/2} * |x|^{-1}$. Then

$$0 \leq \nu(\mu, r) \leq \liminf_{|x|\to\infty}|x|\max\left\{\omega_a^-(x), \omega_a^-(x - R\nu), \frac{\nu}{|x|}, \frac{\nu}{|x - R\nu|}\right\} \leq \liminf_{|x|\to\infty}|x|\varphi(x).$$

We bound $\nu(\mu, r) \geq \mu\inf_{B(0,r)^c}\max\{|x|, |x|^{-3}c_{\mathrm{S}}/\mu(1 + a)^{-2}\} \geq \mu^{3/4}c_{\mathrm{S}}^{1/4}(1 + a)^{-1/2}$. Next we note that φ (according to Lemma 3.11) is nonnegative so that by Fatou's Lemma

$$\liminf_{|x|\to\infty}|x|\varphi(x) \leq \liminf_{t\to\infty}\fint_{\mathbb{S}^2}\left(tV(t\omega) - tc_{\mathrm{TF}}^{-3/2}\varphi^{3/2} * |t\,\omega|^{-1}\right)d\omega.$$

[10] see Lemma B.1 in the appendix for details

[11] Here we use that both η and $-\xi$ solve $a(a - 7) = 6$ and that $(1 + \frac{3}{2}t) \leq (1 + t)^{3/2}$ for all $t \geq 0$.

The right hand side converges because $⨍_{\mathbb{S}^2} tV(t\omega)d\omega = N(V)$ for all $t > R + r$ and because $\lim_{t\to\infty} ⨍_{\mathbb{S}^2} \left(tc_{\mathrm{TF}}^{-3/2}\varphi^{3/2} * |t\,\omega|^{-1}\right) = \int c_{\mathrm{TF}}^{-3/2}\varphi^{3/2}$ due to Newton's theorem and Lebesgue's dominated convergence. □

3.3. Neutrality. We now provide sufficient conditions for oTF models to be neutral, meaning the corresponding chemical potential vanishes. The main technique is the perturbation analysis from [12, Lemma 12.3] around the screened potential $\Phi_{Z,r}^{\mathrm{TF}}$ (or $\Phi_{\mathbf{Z},R,r}^{\mathrm{TF}}$ in the diatomic case). Once neutrality has been established, Sommerfeld type bounds follow readily from our results in Chapter 3.1.

Lemma 3.14 (Atomic oTF neutrality)**.** *Let $V \in \mathcal{H}(\overline{B(0,r)}^c)$ and assume there exist $\sigma, \epsilon > 0$ such that*

$$\sup_{B(0,r)^c} \left|V - \Phi_{Z,r}^{\mathrm{TF}}\right| \le \sigma r^{-4+\epsilon}.$$

Then $N(V) \le (cst.)(1 + \sigma r^\epsilon)r^{-3}$. Moreover, if $\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{1/\xi} Z^{\frac{-1}{3}} \le r \le (c_{3.14b}/\sigma)^{1/\epsilon}$, then $\varrho_r = \arg\min_{\mathcal{C}(N(V))} \mathcal{E}_V^{\mathrm{TF}}$ satisfies $\int \varrho_r \le c_{3.14a} r^{-3}$ and the corresponding chemical potential vanishes, $\mu_r = 0$.

We do *not* give a proof because it has been proven for the special choice

$$V = \Phi_{Z,r}^{\mathrm{HF}} \mathbb{1}_{B(0,r)^c}$$

in [12] and because we present the proof for the diatomic case below. Repeating it for the atomic case largely amounts to replacing the symbol $\mathcal{O}_r$ by $\overline{B(0,r)}^c$ and changing some constants. This would needlessly overload this part of the thesis.

If $V \in \mathcal{H}(\overline{B(0,r)}^c)$, then $|N(V)| \le r\|V\|_\infty$ by (3.11). But if we use (3.12) for the diatomic case $V \in \mathcal{H}(\mathcal{O}_r)$, we find $|N(V)| \le (R + r)\|V\|_\infty$ which is a bad bound for $R \to \infty$. To improve this, we decompose the diatomic outside potential into two atomic outside potentials:

Lemma 3.15. *Assume $V \in \mathcal{H}(\mathcal{O}_r)$ with $r \in (0, R/2)$. Then there exist two unique functions $V_p \in \mathcal{H}(\overline{B(p,r)}^c)$, $p \in \{0, R\nu\}$, such that*

$$V(x) = V_0(x) + V_{R\nu}(x), \qquad \forall x \in \overline{\mathcal{O}_r}.$$

Moreover,

$$|N(V)| \le 2\left(1 + \frac{1}{R/r - 2}\right) r \sup_{\partial\mathcal{O}_r} |V|\,.$$

Proof. **Step 1** (Existence)
In the following, let $p \in \{0R\nu\}$. We set $B_p = B(p,r)$ and for $g \in C(\partial B_p)$, let $u_p[g]$

be the unique element in $\mathcal{H}(\overline{B_p}^c)$ such that $u_p[g] = g$ on ∂B_p. For any $g \in C(\partial B_0)$, we consider

$$T(g)(x) := V(x) - u_0[u_{R\nu}[V]](x) + u_0[u_{R\nu}[u_0[g]]](x), \qquad x \in \partial B_0.$$

Clearly, T maps from the Banach space $(C(\partial B_0), \|\cdot\|_\infty)$ into itself. We use (3.11) several times to estimate

$$\|T(g) - T(f)\|_\infty = \|u_0[u_{R\nu}[u_0[g-f]]]\|_\infty \leq \frac{r}{R-r}\|f-g\|_\infty.$$

Note that $r/(R-r) < 1$, hence by the Banach fixed-point theorem, there exists a unique $v \in C(\partial B_0)$ such that $T(v) = v$. We define $V_0 = u_0[v]$ and $V_{R\nu} = u_{R\nu}[V - V_0]$. Then for all $x \in \partial B_0$, $u_0[V - V_{R\nu}](x) = T(v)(x) = v(x) = V_0(x)$ and the maximum principle then implies $u_0[V - V_{R\nu}] = V_0$ in $(B_0)^c$. Overall, we have obtained $V_p \in \mathcal{H}(\overline{B_p}^c)$ which satisfy $V_0 + V_{R\nu} = V$ on $\partial\mathcal{O}_r$. Invoking the maximum principle one more time, we obtain $V_0 + V_{R\nu} = V$ in $\overline{\mathcal{O}_r}$.

Step 2 (Uniqueness)
Any decomposition $V = V_0 + V_{R\nu}$ implies $V_{R\nu} = u_{R\nu}[V - V_0]$ and $V_0 = u_0[V - V_{R\nu}]$. The restriction $v = V_0 \mid_{\partial B_0}$ must satisfy $T(v) = v$ and is unique by the previous step. Hence $V_0 = u_0[v]$ and $V_{R\nu} = V - V_0$ are unique.

Step 3 (The bound on $N(V)$)
We start with $|N(V)| = |N(V_0) + N(V_{R\nu})| \leq r\sup_{\partial B_0}|V_0| + r\sup_{\partial B_{R\nu}}|V_{R\nu}|$ and show that the right hand side can be bounded by $\sup_{\partial\mathcal{O}_r}|V|$. The triangle inequality, the maximum principle and (3.11) imply

$$\sup_{\partial B(0,r)}|V_0| \leq \sup_{\partial\mathcal{O}_r}|V| + \frac{r}{R-r}\sup_{\partial B(R\nu,r)}|V_{R\nu}|. \tag{3.16}$$

We switch the roles of V_0 and $V_{R\nu}$ in (3.16) and use the resulting inequality to bound the last summand on the right hand side of (3.16). Once more invoking (3.11), we find

$$|V_p(x)| \leq \frac{r}{|x-p|}\frac{R-r}{R-2r}\sup_{\partial\mathcal{O}_r}|V|, \qquad p \in \{0, R\nu\} \tag{3.17}$$

and use this to bound $N(V)$, which ends the proof. □

Next, we give a preliminary result, deriving some seemingly weak consequences from the perturbation assumption $\sup_{\partial\mathcal{O}_r}\left|\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r} - V(x)\right| \leq \sigma r^{-4+\epsilon}$.

Lemma 3.16. *Let* $r \le \min\left\{R/4, \sigma^{-1/\epsilon}\right\}$ *for some* $\epsilon, \sigma > 0$ *and assume* $V \in \mathcal{H}(\mathcal{O}_r)$ *satisfies* $\sup_{\partial\mathcal{O}_r}\left|\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r} - V(x)\right| \le \sigma r^{-4+\epsilon}$. *Then for* $\varrho_r = \arg\min_{\mathcal{C}(N_V)} \mathcal{E}^{\mathrm{TF}}_V$ *it holds that*

$$\varrho_r \le \left(\tfrac{\sigma r^{\varepsilon}}{c_{\mathrm{TF}}} + \tfrac{16 c_{\mathrm{S}}}{3 c_{\mathrm{TF}}}\right)^{3/2} r^{-6} \quad \text{and} \quad \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) \le c_{3.16a}\sigma r^{-7+\epsilon}. \tag{3.18}$$

Moreover, if additionally $\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{-1/3} \le r \le \sigma^{\frac{-1}{\varepsilon}} \min\left\{\left(\frac{2\xi c_{\mathrm{S}}}{(3+\xi)}\right)^{\frac{8}{3\epsilon}}, (1/3)^{\frac{8}{5\varepsilon}}\right\}$ *holds, then*

$$N(V) \ge \tfrac{2\xi c_{\mathrm{S}}}{(3+\xi)} r^{-3} \quad \text{and} \quad \mu_r \le c_{3.16b}\sqrt{\sigma r^{\epsilon}}\, r^{-4}, \tag{3.19}$$

where μ_r *is the chemical potential corresponding to* ϱ_r.

Proof. The proof is divided into five steps. The first two are of preliminary nature and deal with the simple bounds on $N(V)$ and ϱ_r. The third step develops the perturbation argument, from which the bounds on $\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r)$ and μ_r will be derived in the last two steps. We write $W := \Phi^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\overline{\mathcal{O}_r}} - V$ for the perturbation potential and note that $W \in \mathcal{H}(\mathcal{O}_r)$.

Step 1 (Nonnegativity of $N(V)$)
Applying Lemma 3.15 for W and since $r \le R/4$,

$$\int_{\mathcal{O}_r} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} = N(W) + N(V) \le 3\sigma r^{\varepsilon} r^{-3} + N(V). \tag{3.20}$$

Due to Lemma 3.7 and the lower bound from Lemma 3.6, we have $\int_{\mathcal{O}_t} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \ge \frac{1}{2}\int_{B(0,t)^c} \varrho^{\mathrm{TF}}_{Z_0} + \frac{1}{2}\int_{B(R\nu,t)^c} \varrho^{\mathrm{TF}}_{Z_{R\nu}} \ge 4 c_{\mathrm{S}} t^{-3}\left(1 - \frac{3}{2}a^{\mathrm{TF}} t^{-\xi} m_{\mathbf{Z}}^{-\xi/3}\frac{3}{3+\xi}\right)$ for any $t > 0$. Hence

$$\int_{\mathcal{O}_t} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \ge C_1 t^{-3} \quad \forall t \ge \left(\tfrac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{-1/3} \tag{3.21}$$

with $C_1 = \frac{4\xi c_{\mathrm{S}}}{(3+\xi)}$. However, if $\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{-1/3} \le r \le \sigma^{\frac{-1}{\varepsilon}} \min\left\{(C_1/2)^{\frac{8}{3\epsilon}}, (1/3)^{\frac{8}{5\varepsilon}}\right\}$, we have $3\sigma r^{\varepsilon} \le \frac{C_1}{2}$ so that (3.20) and (3.21) for $t = r$ imply

$$N(V) \ge \frac{C_1}{2} r^{-3},$$

the first bound in (3.19). On the other hand, if $N(V) < 0$ then $\mathcal{C}(N(V)) = \emptyset$ and there is nothing to prove for (3.18). We may therefore assume without loss of generality that $N(V) \ge 0$.

Step 2 (A bound on the density)
We use the TF equation (3.2) and the perturbation assumption to bound

$$c_{\mathrm{TF}}\left(\varrho_r(x)\right)^{2/3} = [V(x) - \mu_r]_+ \le \sup_{\partial\mathcal{O}_r}|V| \le r^{-4}\sigma r^{\epsilon} + \sup_{\partial\mathcal{O}_r}\left|\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}\right|.$$

Lemmas 3.7 and 3.6 imply $0 \leq \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}(x) \leq 4c_{\mathrm{S}} r^{-3}(|x|^{-1} + |x - R\nu|^{-1})$ for $x \in \mathcal{O}_r$ so that $\sup_{\partial\mathcal{O}_r} \left|\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}\right| \leq 4c_{\mathrm{S}} r^{-4}\left(1 + \frac{r}{R-r}\right) \leq 16/3 c_{\mathrm{S}} r^{-4}$. This proves the bound on the density.

Step 3 (Perturbation argument)
We will insert $\rho[r,t] := \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r\setminus\mathcal{O}_t}$ as a trial density for $\rho \mapsto \mathcal{E}^{\mathrm{TF}}_V[\rho] + \mu_r \int \rho$, which is minimal at $\rho = \varrho_r$. Since $\int \varrho_r \leq N(V)$, we know $\mu_r \neq 0 \Leftrightarrow \int \varrho_r = N(V)$, or in other words, $\mu_r \int \varrho_r = \mu_r N(V)$. Hence for any $t \geq r$,

$$0 \leq \mu_r \left(N(V) - \int \rho[r,t]\right) \leq \mathcal{E}^{\mathrm{TF}}_V[\rho[r,t]] - \mathcal{E}^{\mathrm{TF}}_V[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] + \mathcal{E}^{\mathrm{TF}}_V[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] - \mathcal{E}^{\mathrm{TF}}_V[\varrho_r]. \tag{3.22}$$

We use that

$$W(x) = \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) + \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} * |x|^{-1} - V(x), \qquad x \in \mathcal{O}_r \tag{3.23}$$

to estimate the two differences on the right hand side of (3.22). For the first,

$$\begin{aligned}
\mathcal{E}^{\mathrm{TF}}_V[\rho[r,t]] - \mathcal{E}^{\mathrm{TF}}_V[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] \overset{(3.23)}{=} & -\frac{3}{5}c_{\mathrm{TF}} \int_{\mathcal{O}_t} \left(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right)^{5/3} - \int_{\mathcal{O}_t} W \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \\
& + \int_{\mathcal{O}_t} \varphi^{\mathrm{TF}}_{\mathbf{Z},R}\varrho^{\mathrm{TF}}_{\mathbf{Z},R} + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_t}) \\
\leq & \sigma r^{-4+\epsilon} \int_{\mathcal{O}_t} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} + \frac{2}{5}\int_{\mathcal{O}_t} \varphi^{TF}_{\mathbf{Z},R}\varrho^{\mathrm{TF}}_{\mathbf{Z},R} + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_t}).
\end{aligned}$$

While for the second,

$$\begin{aligned}
&\mathcal{E}^{\mathrm{TF}}_V[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] - \mathcal{E}^{\mathrm{TF}}_V[\varrho_r] \\
&\overset{(3.23)}{=} \frac{3}{5}c_{\mathrm{TF}} \int_{\mathcal{O}_r} \left(\left(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right)^{5/3} - (\varrho_r)^{5/3}\right) + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}) - \mathcal{D}(\varrho_r) \\
&\qquad + \int_{\mathcal{O}_r} W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r) - \int_{\mathcal{O}_r} \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r) - 2\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}, \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) \\
&= \int_{\mathcal{O}_r} W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) \\
&\qquad + \int_{\mathcal{O}_r} \left(\left[\frac{3}{5}c_{\mathrm{TF}}\left(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right)^{5/3} - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right] - \left[\frac{3}{5}c_{\mathrm{TF}}(\varrho_r)^{5/3} - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}\varrho_r\right]\right) \\
&\leq \int_{\mathcal{O}_r} W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r).
\end{aligned}$$

here the last inequality is due to the fact that the function $t \mapsto \frac{3}{5}c_{\mathrm{TF}}t^{5/3} - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(y)t$ is minimal at $t = c_{\mathrm{TF}}^{-3/2}\left(\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(y)\right)^{3/2} \overset{(3.2)}{=} \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y)$, for all $y \in \mathbb{R}^3$. We use these bounds to estimate the right hand side of (3.22) and find that

$$
\begin{aligned}
0 \le \mu_r \left(N(V) - \int \rho[r,t] \right) &\le \sigma r^{-4+\epsilon} \int_{\mathcal{O}_t} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} + \frac{2}{5} \int_{\mathcal{O}_t} \varphi^{\mathrm{TF}}_{\mathbf{Z},R} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_t}) \\
&\quad + \int W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r} - \varrho_r) \\
&\le \left(\sigma r^{-4+\epsilon} + \frac{4}{5} c_{\mathrm{S}} t^{-4} + 2^{3/2} 3 c_{\mathrm{S}} t^{-4} \right) \int_{\mathcal{O}_t} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \\
&\quad + \int W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r} - \varrho_r).
\end{aligned}
$$

Here, in the last inequality, we used Lemmas 3.6 and 3.7, which imply $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \le 2c_{\mathrm{S}}|x|^{-4}$ and for $x \in \mathcal{O}_t$,

$$
\int_{\mathcal{O}_t} \frac{\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y)}{|x-y|^{-1}} dy \le \sqrt{2} \frac{3}{\pi} c_{\mathrm{S}} \int_{\mathcal{O}_t} \frac{|y|^{-6} + |y-R|^{-6}}{|x-y|} dy \le 2^{3/2} 3 c_{\mathrm{S}} t^{-4}.
$$

To control $\int W(\varrho_r - \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r})$, we proceed as in [12, p. 559] (adjusted to the case of two balls): Consider for $r \in (0, R/2)$ the cut-off function

$$
F(x) := \begin{cases} 0, & \text{for } x \in \mathcal{I}_{2r} \\ \frac{|x|-2r}{r}, & \text{for } x \in (\mathcal{I}_{3r} \setminus \mathcal{I}_{2r}) \cap \mathbb{H}^-_{R\nu/2} \\ \frac{|x-R\nu|-2r}{r}, & \text{for } x \in (\mathcal{I}_{3r} \setminus \mathcal{I}_{2r}) \cap \mathbb{H}^+_{R\nu/2} \\ 1, & \text{for } x \in \mathcal{O}_{3r}. \end{cases} \tag{3.24}
$$

and write $W = (1-F)W + FW$. We note that $F \in H^1(\mathbb{R}^3)$ with[12]

$$
\|\nabla(FW)\|_2^2 = \int |\nabla F|^2 |W|^2 \le \sup_{\mathcal{O}_r} |W|^2 |\mathcal{O}_{2r} \setminus \mathcal{O}_{3r}| r^{-2} dx \le \frac{152\pi}{3} \sigma^2 r^{-7+2\epsilon}.
$$

A crucial ingredient at this point is the Coulomb-norm estimate from [12, Lemma 9.2], saying that $|\int fg| \le \sqrt{(2\pi)^{-1}\mathcal{D}(g)} \|\nabla f\|_2$ if $f \in H^1(\mathbb{R}^3), g \in L^{6/5}$. We use it to bound

$$
\left| \int FW(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r} - \varrho_r) \right| \le \sqrt{\frac{76}{3}} \sigma r^{-7+\epsilon} \sqrt{\mathcal{D}\left(\varrho_r - \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r}\right)}.
$$

[12] see Lemma B.2 in the appendix for details

While for the other term, we use $\sup_{\mathcal{O}_r}|(1-F)W| \leq \sup_{\mathcal{O}_r}|W| \leq \sigma r^{-4+\epsilon}$ to bound

$$\left|\int(1-F)W(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r)\right| \leq \sigma r^{-4+\epsilon}\int_{\mathcal{O}_r\setminus\mathcal{O}_{3r}}(\varrho_r+\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r})$$

$$\leq \sigma r^{-4+\epsilon}\int_{\mathcal{O}_r\setminus\mathcal{O}_{3r}}\left\{\sqrt{2}\frac{3}{\pi}c_{\mathrm{S}}\left(|x|^{-6}+|x-R|^{-6}\right)+\left(\frac{\sigma r^{\epsilon}}{c_{\mathrm{TF}}}+\frac{16c_{\mathrm{S}}}{3c_{\mathrm{TF}}}\right)^{3/2}r^{-6}\right\}dx$$

$$\leq 208\left(\frac{2^{3/2}}{3^3}+\frac{\pi}{3}\left(\frac{1}{c_{\mathrm{TF}}}+\frac{16c_{\mathrm{S}}}{3c_{\mathrm{TF}}}\right)^{3/2}\right)\sigma r^{-7+\epsilon} =: C_2\sigma r^{-7+\epsilon}.$$

Collecting all the bounds that we have derived since (3.22), for any $t \geq r$:

$$0 \leq \mu_r\left(N(V)-\int\rho[r,t]\right) \leq \left(\sigma r^{-4+\epsilon}+\frac{4}{5}c_{\mathrm{S}}t^{-4}+2^{3/2}3c_{\mathrm{S}}t^{-4}\right)\int\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_t}$$
$$+C_2\sigma r^{-7+\epsilon}+\sqrt{\frac{76}{3}\mathcal{D}\left(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r\right)}\,\sigma r^{-7/2+\epsilon}$$
$$-\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r). \tag{3.25}$$

From this inequality, we will derive the bound on $\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r)$ and μ_r by appropriate choices of $t \geq r$.

Step 4 We choose $t_1(r) := \sup\{t>0 \mid \int\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r\setminus\mathcal{O}_t} \leq N(V)\}$. Since $N(V)\geq 0$, we have $t_1 \geq r$ and with (3.20),

$$\int\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_{t_1}} = \left[\int\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-N(V)\right]_+ \leq 3\sigma r^{-3+\epsilon}. \tag{3.26}$$

Hence we obtain from (3.25) with $t=t_1$ that

$$\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r) \leq C_3\sigma r^{-7+\epsilon}+\left(\frac{76}{3}\right)^{1/2}\sqrt{\sigma r^{-7+\epsilon}}\sqrt{\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r)}$$

where $C_3 = 3\left(1+\frac{4c_{\mathrm{S}}}{5}+2^{3/2}3c_{\mathrm{S}}\right)+C_2$. This implies[13]

$$\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}-\varrho_r) \leq c_{3.16a}\sigma r^{-7+\epsilon}$$

with $c_{3.16a} = \left(\sqrt{C_3+\frac{19}{3}}+\sqrt{\frac{19}{3}}\right)^2$.

Step 5 We choose $t_2(r) := \left(\frac{C_1}{2}\right)^{\frac{1}{3}}(\sigma r^{\epsilon})^{-1/8}r$ and assume for the remaining proof that also

$$\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}}m_{\mathbf{Z}}^{-1/3} \leq r \leq \sigma^{\frac{-1}{\epsilon}}\min\left\{(C_1/2)^{\frac{8}{3\epsilon}},(1/3)^{8/5}\right\}.$$

[13]Note that for a,b,x positive, $\mathcal{D} \leq ax^2+2bx\sqrt{\mathcal{D}} \Leftrightarrow (\sqrt{\mathcal{D}}-bx)^2 \leq (a+b^2)x^2$ which implies $\sqrt{\mathcal{D}}-bx \leq \sqrt{(a+b^2)}x$.

Then $t_2 \geq r$ and we may apply (3.21) with $t = t_2$, so that

$$\int_{\mathcal{O}_{t_2}} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \geq C_1 t_2^{-3} = 2r^{-3}(\sigma r^{\varepsilon})^{\frac{3}{8}}. \tag{3.27}$$

Since $(\sigma r^{\varepsilon})^{\frac{-5}{8}} \geq 3$ we deduce with (3.26) that $\int_{\mathcal{O}_{t_2}} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \geq 2\int_{\mathcal{O}_{t_1}} \varrho^{\mathrm{TF}}_{\mathbf{Z},R}$. Hence, $N(V) \geq \int \rho[r,t_1] \geq \int \rho[r,t_2] + \frac{1}{2}\int \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_{t_2}}$. We use this in (3.25) for $t = t_2$ and find that

$$\begin{aligned}
0 \leq \mu_r \frac{1}{2}\int \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_{t_2}} \leq & \left(\sqrt{\sigma r^{\epsilon}} + \tfrac{4}{5}c_{\mathrm{S}}\left(\tfrac{2}{C_1}\right)^{\frac{4}{3}} + 2^{3/2}3c_{\mathrm{S}}\left(\tfrac{2}{C_1}\right)^{\frac{4}{3}}\right) r^{-4}\sqrt{\sigma r^{\epsilon}}\int \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_{t_2}} \\
& + C_2\sigma r^{-7+\epsilon} + \sqrt{\frac{76}{3}}\sqrt{\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r)}\sigma r^{-7/2+\epsilon} \\
\leq & r^{-4}\sqrt{\sigma r^{\epsilon}}\frac{c_{3.16b}}{2}\int \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_{t_2}},
\end{aligned} \tag{3.28}$$

where the last inequality is due to (3.27) and

$$c_{3.16b} = 2\left(3^{-4/5} + \frac{4}{5}c_{\mathrm{S}}\left(\frac{2}{C_1}\right)^{4/3} + 2^{3/2}3c_{\mathrm{S}}\left(\frac{2}{C_1}\right)^{4/3}\right) + C_2 3^{-1/5} + \sqrt{\frac{76c_{3.16a}}{3^3}}.$$

According to (3.27), we may divide by $\int_{\mathcal{O}_{t_2}} \varrho^{\mathrm{TF}}_{\mathbf{Z},R}$ in (3.28) to end the proof. □

Lemma 3.16 says that the perturbation assumption implies that ϱ_r and $\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}$ are close in Coulomb norm $\|\cdot\| = \sqrt{\mathcal{D}(\cdot)}$. Surprisingly, this is sufficient to obtain the crucial condition $\mu_r < \liminf_{s\searrow r} \inf_{\partial\mathcal{O}_s} \varphi_r$, provided r is sufficiently small. It immediately implies the neutrality and Sommerfeld type bounds, as we will see now.

Lemma 3.17 (Diatomic oTF neutrality)**.** *Let $V \in \mathcal{H}(\mathcal{O}_r)$ and $\epsilon, \sigma > 0$ such that*

$$\sup_{\mathcal{O}_r}\left|V - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}\right| \leq \sigma r^{-4+\epsilon}$$

and

$$\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{\frac{-1}{3}} \leq r \leq \min\left\{(c_{3.17}/\sigma)^{\frac{1}{\epsilon}}, R/4\right\}.$$

Consider $\varrho_r = \arg\min_{\mathcal{C}(N_V)} \mathcal{E}^{\mathrm{TF}}_V$ with corresponding chemical potential μ_r and TF potential φ_r. Then $\mu_r = 0$, and there exist constants $A = \frac{c_{3.17}}{c_{\mathrm{S}}} + \frac{13}{3} > 0$ and $a = \sqrt{\frac{c_{\mathrm{S}}}{\sqrt{c_{3.17}c_{3.16b}}}} - 1 > -1$ such that $\int \varrho_r \leq 2^{7/2}(1+A)^{3/2}c_{\mathrm{S}}r^{-3}$ and for all $x \in \mathcal{O}_r$:

$$\begin{aligned}
\max\left\{\frac{c_{\mathrm{S}}|x|^{-4}}{(1+a|x/r|^{-\xi})^2}, \frac{c_{\mathrm{S}}|x-R\nu|^{-4}}{(1+a|(x-R\nu)/r|^{-\xi})^2}\right\} &\leq \varphi_r(x) \\
&\leq c_{\mathrm{S}}|x|^{-4}(1+A|x/r|^{-\xi}) + c_{\mathrm{S}}|x-R\nu|^{-4}(1+A|(x-R\nu)/r|^{-\xi}).
\end{aligned}$$

Proof. The proof is divided into three steps. First we show that

$$\liminf_{s\searrow r}\inf_{\partial\mathcal{O}_s}\varphi_r > \mu_r.$$

Then we can apply Lemma 3.13 to deduce neutrality. Last, we use Lemma 3.11 to deduce the claimed bounds and estimate the constants $a(r), A(r)$. With C_2 given below in (3.30) we define

$$c_{3.17} = \min\left\{3^{-8/5}, \left(\frac{2\xi c_{\mathrm{S}}}{(3+\xi)}\right)^{\frac{8}{3}}, \tfrac{1}{2}\max\left\{t>0 \mid C_2(t)\geq \sqrt{t}c_{3.16b}\right\}\right\}$$

and may therefore apply Lemma 3.16.

Step 1 Since $\varphi_r \in C(\overline{\mathcal{O}_r})$, we have $\liminf_{s\searrow r}\inf_{\partial\mathcal{O}_s}\varphi_r = \inf_{\partial\mathcal{O}_r}\varphi_r$. Moreover,

$$\begin{aligned}\inf_{\partial\mathcal{O}_r}\varphi_r =& \inf_{\partial\mathcal{O}_r}\left(\varphi^{\mathrm{TF}}_{\mathbf{Z},R} - [V_{\mathbf{Z},R} - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{I}_r} * |x|^{-1} - V] + (\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) * |x|^{-1}\right)\\ \geq& \frac{c_{\mathrm{S}}}{3}r^{-4} - \sigma r^{-4+\epsilon} - \sup_{\partial\mathcal{O}_r}\left|(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) * |x|^{-1}\right|.\end{aligned}$$

where we have used Lemma 3.6 and $r^{-\xi}m_{\mathbf{Z}}^{-\xi/3} \leq \frac{2}{3a^{\mathrm{TF}}}$ to estimate $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ on $\partial\mathcal{O}_r$. For the last summand, we use [12, Cor. 9.3], so that with Lemma 3.16 and $t\in(0,\infty)$:

$$\begin{aligned}\left|(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) * |x|^{-1}\right| \leq& t^{1/5}\left(\frac{5\pi^2}{4}\right)^{2/5}\|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r\|_{L^{5/3}(B(x,t))}\\ &+ t^{-1/2}\sqrt{2\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r)}\\ \leq& t^{1/5}\left(\frac{5\pi^2}{4}\right)^{2/5}\max\left\{\|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}\|_{L^{5/3}(B(x,t))}, \|\varrho_r\|_{L^{5/3}(B(x,t))}\right\}\\ &+ t^{-1/2}\sqrt{2c_{3.16a}\sigma r^{-7+\epsilon}}.\end{aligned} \tag{3.29}$$

We infer from Lemma 3.7 and Lemma 3.6 that

$$\|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}\|_{L^{5/3}(B(x,t))} \leq \left(2\frac{c_{\mathrm{S}}}{c_{\mathrm{TF}}}r^{-4}\right)^{3/2}|B(x,t)|^{3/5} = r^{-6}t^{9/5}2^{3/2}\frac{3}{\pi}c_{\mathrm{S}}\left(\frac{4\pi}{3}\right)^{3/5}.$$

Similar, using (3.18), $\|\varrho_r\|_{L^{5/3}(B(x,t))} \leq r^{-6}t^{9/5}\left(\frac{c_{3.17}}{c_{\mathrm{TF}}} + \frac{16c_{\mathrm{S}}}{3c_{\mathrm{TF}}}\right)^{3/2}\left(\frac{4\pi}{3}\right)^{3/5}$. We first insert these bounds in (3.29) and then optimize over $t\in(0,\infty)$, so that

$$\left|(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) * |x|^{-1}\right| \leq \sigma^{\frac{2}{5}}r^{-4+\frac{2}{5}\epsilon}C_1$$

with $C_1 = \frac{5^{27/25}\pi^{7/25}c_{3.16a}^{2/5}}{2^{28/25}3^{3/25}}\left(\frac{c_{3.17}}{c_{\mathrm{TF}}} + \frac{16c_{\mathrm{S}}}{3c_{\mathrm{TF}}}\right)^{3/10}$. We then collect the bounds we have derived so far and obtain

$$r^4\inf_{\partial\mathcal{O}_r}\varphi_r \geq \left(\frac{c_{\mathrm{S}}}{3} - \sigma r^{\epsilon} - (\sigma r^{\epsilon})^{2/5}C_1\right) =: C_2(\sigma r^{\epsilon}). \tag{3.30}$$

Recall that $\sigma r^\epsilon \le c_{3.17} < \max\{t > 0 \mid C_2(t) \ge \sqrt{t} c_{3.16b}\}$ and note that C_2 is strictly decreasing, hence

$$\inf_{\partial\mathcal{O}_r} \varphi_r \ge r^{-4} C_2(c_{3.17}) > r^{-4}\sqrt{c_{3.17}} c_{3.16b} \ge \mu_r \tag{3.31}$$

where we have used Lemma 3.16.

Step 2 (Neutrality)
We have just verified that we may use Lemma 3.13 so that

$$(\mu_r)^{3/4} c_{\mathrm{S}}^{1/2} (1 + a(r) r^{-\xi})^{-1/2} \le N(V) - \int \varrho_r. \tag{3.32}$$

Note that $\inf_{\partial\mathcal{O}_r} \varphi_r > \mu_r$ and thus $1 + a(r) > 0$ by definition of $a(r)$. Now, *if we had* $\mu_r > 0$, then $\int \varrho_r = N(V)$ (compare Theorem 3.2) and the right hand side of (3.32) were zero, while the left hand side is positive. Thus $\mu_r = 0$.

Step 3 (Sommerfeld bounds)
We apply Lemma 3.11 for a vanishing chemical potential. To obtain the claimed inequalities, it remains to bound the constants $A(r)$ and $a(r)$ by expressions that are uniform in $r \in \left[(3/2a^{\mathrm{TF}})^{1/\xi} m_{\mathbf{Z}}^{-1/3}, (c_{3.17}/\sigma)^{\frac{1}{\epsilon}}\right]$. With (3.18),

$$A(r) = r^4 \sup_{\partial\mathcal{O}_r} \frac{c_{\mathrm{TF}}}{c_{\mathrm{S}}} \varrho_r^{2/3} - 1 \le \frac{\sigma r^\varepsilon}{c_{\mathrm{S}}} + \frac{16}{3} - 1 \le \frac{c_{3.17}}{c_{\mathrm{S}}} + \frac{13}{3} =: A.$$

We use (3.31) to deduce

$$a(r) = \sqrt{\frac{c_{\mathrm{S}}}{r^4 \inf_{\partial\mathcal{O}_r} \varphi_r}} - 1 \le \sqrt{\frac{c_{\mathrm{S}}}{\sqrt{c_{3.17}} c_{3.16b}}} - 1 =: a.$$

Last, we use the upper bound from Lemma 3.11 together with the TF equation (3.2) to bound

$$\int \varrho_r \le \frac{3}{\pi} c_{\mathrm{S}} (1 + A)^{3/2} \int_{\mathcal{O}_r} \sqrt{2}(|x|^6 + |x - R\nu|^{-6}) dx \le 2^{7/2} c_{\mathrm{S}} (1 + A)^{3/2} r^{-3}.$$

□

Next, we show how the Sommerfeld bounds allow us to compare the diatomic TF potential and density to diatomic oTF potentials and densities.

Lemma 3.18. *Assume* $V \in \mathcal{H}(\mathcal{O}_r)$ *satisfies* $\sup_{\mathcal{O}_r} \left|\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r} - V\right| \le \sigma r^{-4+\epsilon}$ *for some* $\epsilon, \sigma > 0$ *and*

$$\left(\frac{3}{2} a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{\frac{-1}{3}} \le r \le \min\left\{(c_{3.17}/\sigma)^{\frac{1}{\epsilon}}, c_{3.18b} R/2\right\}.$$

Let $\tilde r = c_{3.18a} r^{\frac{\xi}{\xi+\eta}} (R/2)^{\frac{\eta}{\xi+\eta}}$ *and consider* $\varrho_r = \arg \min_{\mathcal{C}(N_V)} \mathcal{E}_V^{\mathrm{TF}}$ *with corresponding TF potential* φ_r*. Then* $\tilde r \in (r, R/2)$ *and for all* $s \in [r, \tilde r]$*:*

$$\sup_{\partial\mathcal{O}_s} |\varphi^{\mathrm{TF}}_{\mathbf{Z},R} - \varphi_r| \le c_{\mathrm{S}} s^{-4} c_{3.18c} \left(\frac{r}{s}\right)^{\xi} \tag{3.33}$$

and

$$\sup_{\partial\mathcal{O}_s} \left|(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r)\mathbb{1}_{\mathcal{O}_s} * |x|^{-1}\right| \le c_{\mathrm{S}} s^{-4} c_{3.18d} \left(\frac{r}{s}\right)^{\xi}. \tag{3.34}$$

Proof. The proof is divided into four steps. We start with (3.33), a straightforward consequence of the Sommerfeld type bounds and neutrality of the TF potentials. In the second (and third) step we bound the densities in $\mathcal{I}_{R/2}$ (and $\mathcal{O}_{\tilde r}$) sufficiently well to derive (3.34) by integration in the last step.

Step 1 (Proof of (3.33)) Let r be as in the Lemma and $c_{3.18b} \le 1/2$, so Lemma 3.17 applies. We combine it with Lemma 3.12 and note that $A_2(r) \le A$ and $A_1(r) \le \frac{4}{\eta-4} + A\frac{4+\xi}{\eta-4}$.[14] Hence if $|x| \in [r, R/2]$, then

$$\varphi_r(x) \le c_{\mathrm{S}}|x|^{-4}\left(1 + A(r/|x|)^{\xi} + \frac{4 + A(\xi+4)}{\eta-4}(2|x|/R)^{\eta}\right).$$

As $a^{\mathrm{TF}} Z_1^{-\xi/3} \le r^{\xi} 2/3$, we infer that $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \ge c_{\mathrm{S}}|x|^{-4}(1 - 2/3(r/|x|)^{\xi})$ from Lemma 3.6 and obtain for $|x| \in [r, R/2]$:

$$\varphi_r(x) - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \le c_{\mathrm{S}}|x|^{-4}\left((2/3 + A)\left(\frac{r}{|x|}\right)^{\xi} + \frac{4 + A(\xi+4)}{\eta-4}\left(\frac{2s}{R}\right)^{\eta}\right). \tag{3.35}$$

On the other hand, we know (by using (3.5) with $r = R/2$) that $\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \le c_{\mathrm{S}}|x|^{-4}(1 + (2|x|/R)^{\eta})$ for any $x \in B(0, R/2)$ and according to Lemma 3.17 also $\varphi_r(x) \ge c_{\mathrm{S}}|x|^{-4}(1 + a(r/|x|)^{\xi})^{-2} \ge c_{\mathrm{S}}|x|^{-4}(1 - 2a(r/|x|)^{\xi})$ if $|x| \in [r, R/2]$. All together, we obtain for all $|x| \in [r, R/2]$:

$$|\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) - \varphi_r(x)| \le c_{\mathrm{S}}|x|^{-4}\left(\tfrac{4+A(\xi+4)}{\eta-4}\left(\frac{2|x|}{R}\right)^{\eta} + \max\left\{\tfrac{2}{3} + A, 2a\right\}\left(\frac{r}{|x|}\right)^{\xi}\right).$$

The same arguments apply if $|x - R\nu| \in [r, R/2]$ and since $s \le \tilde r$ is equivalent to $(2s/R)^{\eta} \le c_{3.18a}^{\eta+\xi}(r/s)^{\xi}$, we conclude (3.33) with

$$c_{3.18c} = \left(c_{3.18a}^{\eta+\xi}\tfrac{4+A(\xi+4)}{\eta-4} + \max\left\{\tfrac{2}{3} + A, 2a\right\}\right).$$

Step 2 (A bound on the densities in $\mathcal{O}_r \cap \mathcal{I}_{R/2}$)
We use the TF equation for $\varphi_r, \varphi^{\mathrm{TF}}_{\mathbf{Z},R}$ and repeat the arguments that led to (3.35)

[14] see Lemmas 3.12 and 3.17 for the definition of A, A_1, A_2.

to deduce that for all $|x| \in [r, R/2]$:[15]

$$\varrho_r(x) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x) \leq \frac{3}{\pi} c_{\mathrm{S}} |x|^{-6} \left((AC_1 + 1) \left(\frac{r}{|x|} \right)^{\xi} + C_1 \frac{4 + A(\xi + 4)}{\eta - 4} \left(\frac{2|x|}{R} \right)^{\eta} \right)$$

with a constant $C_1 = \frac{\eta - 4}{4 + A(\xi+4)} \left(\left(1 + A + \frac{4 + A(\xi+4)}{\eta - 4} \right)^{3/2} - 1 \right)$, as well as

$$\varrho_r(x) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x) \geq -\frac{3}{\pi} c_{\mathrm{S}} |x|^{-6} \left(3a \left(\frac{r}{|x|} \right)^{\xi} + (2^{3/2} - 1) \left(\frac{2|x|}{R} \right)^{\eta} \right).$$

All together we find

$$|\varrho_r(x) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x)| \leq \frac{3}{\pi} c_{\mathrm{S}} |x|^{-6} \left(C_2 \left(\frac{r}{|x|} \right)^{\xi} + C_3 \left(\frac{2|x|}{R} \right)^{\eta} \right), \qquad \forall |x| \in [r, R/2] \tag{3.36}$$

where $C_2 = \max\{3a, AC_1 + 1\}$ and $C_3 = \max\left\{ (2^{3/2} - 1), C_1 \frac{4 + A(\xi+4)}{\eta - 4} \right\}$ and the analogous bound holds for $|x - R\nu| \in [r, R/2]$.

Step 3 (A bound on the densities in $\mathcal{O}_{\tilde{r}}$)
Let $r, \tilde{r}$ be as in the statement, then $a^{\mathrm{TF}} Z_1^{-\xi/3} |x|^{-\xi} \leq \frac{2}{3} (r/|x|)^{\xi}$. According to the proof of Lemma 3.6 or [12, Theorem 5.4], $\varphi^{\mathrm{TF}}_Z \geq c_{\mathrm{S}} |x|^{-4} (1 + \frac{a^{\mathrm{TF}}}{2} Z^{-\xi/3} |x|^{-\xi})^{-2}$. Hence we then find with Lemma 3.7 that $c_{\mathrm{S}} |x|^{-4} \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \left(1 + 7/9 (r/|x|)^{\xi} \right)$ for all $|x| \geq r$. This, together with $\mu_r = 0$, Lemma 3.17 and Lemma 3.12 implies

$$\varphi_r(x) \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \left[1 + C_8 (2|x|/R)^{\eta} + C_9 (r/|x|)^{\xi} \right] \forall x \in B(0,r)^c \cap \mathbb{H}^-_{R/2}, \tag{3.37}$$

where $C_8 := \frac{16}{9} \frac{4 + A(\xi+4)}{\eta - 4}$ and $C_9 := [16A/9 + 7/9]$. The term in square brackets in (3.37) is minimal in $|x|$ at $r_0 := \left(\frac{\xi C_9}{\eta C_8} \right)^{\frac{1}{\eta+\xi}} r^{\frac{\xi}{\eta+\xi}} (R/2)^{\frac{\eta}{\eta+\xi}}$ where it equals $\underbrace{C_8^{\frac{\xi}{\eta+\xi}} C_9^{\frac{\eta}{\eta+\xi}} (\eta+\xi) \xi^{\frac{-\xi}{\eta+\xi}} \eta^{\frac{-\eta}{\eta+\xi}}}_{=:C_4} (2r/R)^{\frac{\xi\eta}{\eta+\xi}}$. Note that to ensure $\partial B(0, r_0) \subset B(0,r)^c \cap \overline{\mathbb{H}^-_{R/2}}$, it is sufficient to require $r_0 \in [r, R/2]$ which is equivalent to $2r/R \leq \min\left\{ \left(\frac{\eta C_8}{\xi C_9} \right)^{\frac{1}{\xi}}, \left(\frac{\xi C_9}{\eta C_8} \right)^{\frac{1}{\eta}} \right\} = C_5$. Repeating these steps for $x \in B(R, r)^c \cap \mathbb{H}^+_{R/2}$, we obtain (with r_0 defined above) that if $2r/R \leq \min\{C_5, 1/2\}$, then

$$\varphi_r(x) \leq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \left(1 + C_4 (2r/R)^{\frac{\xi\eta}{\eta+\xi}} \right) \tag{3.38}$$

for all $x \in \partial \mathcal{O}_{r_0}$. We infer from Corollary 3.5, with $u = \varphi_r - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(1 + (cst.))$ and $\Omega = \mathcal{O}_{r_0}$, that (3.38) is true for all $x \in \mathcal{O}_{r_0}$. Next, we prove a corresponding lower bound. Combining (3.5) for $r = R/2$ with the lower bound from Lemma 3.11 we

[15] We use that $(1+t)^{3/2} \leq 1 + t \frac{(1+T)^{3/2} - 1}{T}$ for all $t \in [0, T]$ by convexity.

find

$$\varphi_r(x) \geq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}\left(1 - (2|x|/R)^\eta - 2a(r/|x|)^\xi\right) \qquad \forall x \in B(0,r)^c \cap B(0,R/2).$$

We proceed as before, minimizing $(2|x|/R)^\eta + 2a(r/|x|)^\xi$ in $|x| \in (r, R/2)$ to obtain a bound on the sphere $|x| = r_1 := (2a\xi/\eta)^{\frac{1}{\eta+\xi}} r^{\frac{\xi}{\eta+\xi}} (R/2)^{\frac{\eta}{\eta+\xi}}$, provided $r_1 \in [r, R/2]$. Repeating the argument for $x \in \mathbb{H}^+_{R/2}$, we deduce that $u = \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(1-(cst.)) - \varphi_r \leq 0$ on $\partial\mathcal{O}_{r_1}$. We then extend this bound to $\mathcal{O}_{r_1}$ by applying Corollary 3.5 again, this time with $\Omega = \mathcal{O}_{r_1}$. The conclusion is that

$$\varphi_r(x) \geq \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) \left(1 - \underbrace{(2a)^{\frac{\xi}{\xi+\eta}}(\eta+\xi)\xi^{\frac{-\xi}{\eta+\xi}}\eta^{\frac{-\eta}{\eta+\xi}}}_{=C_6}(2r/R)^{\frac{\xi\eta}{\eta+\xi}}\right), \qquad \forall x \in \mathcal{O}_{r_1}, \quad (3.39)$$

as long as $r_1 \in [r, R/2]$, which is equivalent to $2r/R \leq \min\{(\frac{\eta}{2\xi a})^{1/\xi}, (\frac{2\xi a}{\eta})^{1/\eta}\}$. We chose $\tilde{r} = \max(r_0, r_1)$, which means $c_{3.18a} := (\xi/\eta \max\{2a, C_9/C_8\})^{\frac{1}{\xi+\eta}}$, and set $c_{3.18b} := \min\left\{\frac{1}{2}, (\frac{\eta}{2\xi a})^{1/\xi}, (\frac{2\xi a}{\eta})^{1/\eta}, (\frac{\eta C_8}{\xi C_9})^{1/\xi}, (\frac{\xi C_9}{\eta C_8})^{1/\eta}\right\}$. Then it is a straightforward consequence of the TF equation, (3.38) and (3.39) that

$$|\varrho_r(x) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x)| \leq \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x) C_7 \,(2r/R)^{\frac{\xi\eta}{\eta+\xi}}$$

for all $x \in \mathcal{O}_{\tilde{r}}$, with $C_7 := \max\left\{\frac{3}{2}C_6, c_{3.18b}^{-\xi\eta/(\eta+\xi)}\left[\left(1 + C_4 c_{3.18b}^{\xi\eta/(\eta+\xi)}\right)^{3/2} - 1\right]\right\}$.[16] Hence with Lemmas 3.6 and 3.7:

$$|\varrho_r(x) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(x)| \leq \sqrt{2}\frac{3}{\pi}c_{\mathrm{S}} C_7 \left(\frac{2r}{R}\right)^{\frac{\xi\eta}{\eta+\xi}} \left(|x|^{-6} + |x - R\nu|^{-6}\right), \qquad \forall x \in \mathcal{O}_{\tilde{r}}. \quad (3.40)$$

Step 4 (Proof of (3.34))

Let $s, r, \tilde{r}$ be as in the statement and $|x| = s$, then

$$\left|(\varrho^{\mathrm{TF}}_{\mathbf{Z},R} - \varrho_r)\mathbb{1}_{\mathcal{O}_s} * |x|^{-1}\right| \leq \sum_{p \in \{0, R\nu\}} \int\limits_{B(p,\tilde{r})\setminus B(p,s)} \frac{|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho_r(y)|}{|x-y|} dy + \int_{\mathcal{O}_{\tilde{r}}} \frac{|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho_r(y)|}{|x-y|} dy.$$

We use (3.36), (3.40) and Newton's theorem to bound the integrands on the right hand side: For the first two,

$$\int\limits_{B(p,\tilde{r})\setminus B(p,s)} \frac{|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho_r(y)|}{|x-y|} dy \leq \frac{3}{\pi}c_{\mathrm{S}} \int\limits_{B(0,\tilde{r})\setminus B(0,s)} \frac{C_2(r/|y|)^\xi + C_3(2|y|/R)^\eta}{|y|^7} dy$$
$$\leq 12 c_{\mathrm{S}} \left(\frac{C_2}{4+\xi} s^{-4}\left(\frac{r}{s}\right)^\xi + \frac{C_3}{\eta - 4}\tilde{r}^{-4}\left(\frac{2\tilde{r}}{R}\right)^\eta\right),$$

[16] Here we use the bound $(1+t)^{3/2} \leq 1 + t\frac{(1+T)^{3/2}-1}{T}$ for all $t \in [0,T]$ and $2r/R \leq c_{3.18b}^{\xi\eta/(\eta+\xi)}$.

while for the last integral,

$$\int_{\mathcal{O}_{\tilde r}} \frac{|\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y)-\varrho_r(y)|}{|x-y|}dy \leq \frac{2^{5/2}3}{\pi} c_{\mathrm{S}} C_7 \left(\frac{2r}{R}\right)^{\frac{\xi\eta}{\eta+\xi}} \int\limits_{B(0,\tilde r)^c\cap \mathbb{H}^-_{R\nu/2}} |y|^{-7}dy$$
$$\leq 2^{5/2}3 c_{\mathrm{S}} C_7 \left(\frac{2r}{R}\right)^{\frac{\xi\eta}{\eta+\xi}} \tilde r^{-4}.$$

Finally note that $(2\tilde r/R)^\eta = c^{\eta}_{3.18a}(2r/R)^{\frac{\xi\eta}{\eta+\xi}}$ and $s\leq \tilde r \Leftrightarrow (2r/R)^{\frac{\xi\eta}{\eta+\xi}} \leq c^{\xi}_{3.18a}(r/s)^\xi$ so that we have proven (3.34) with $c_{3.18d} = 12\left(\frac{C_2}{4+\xi} + \frac{C_3 c^{\eta+\xi}_{3.18a}}{\eta-4} + 2^{1/2}C_7 c^{\xi}_{3.18a}\right)$. $\square$

4. The Born-Oppenheimer curve

The diatomic TF energy $E^{\mathrm{TF}}_{\mathbf{Z},R}$ describes only the electronic part of the energy in the Born-Oppenheimer approximation and does not include the repulsion between the nuclei. The diatomic Born-Oppenheimer potential (1.1) in TF theory therefore equals

$$D^{\mathrm{TF}}_{\mathbf{Z},R} = E^{\mathrm{TF}}_{\mathbf{Z},R} - E^{\mathrm{TF}}_{Z_1} - E^{\mathrm{TF}}_{Z_2} + \frac{Z_1Z_2}{R}.$$

We collect several properties of this function:

(1) $D^{\mathrm{TF}}_{\mathbf{Z},R} > 0$ for all $\mathbf{Z}, R$, due to Teller's no-binding result.
(2) $\partial_{Z_p} D^{\mathrm{TF}}_{\mathbf{Z},R} = \lim_{x\to p}\left(\varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) - \varphi^{\mathrm{TF}}_{Z_p}(x-p)\right) > 0$ for $p\in\{0,R\nu\}$.[17]
(3) $D^{\mathrm{TF}}_{\mathbf{Z},R} = R^{-7}D^{\mathrm{TF}}_{R^3\mathbf{Z},1}$ by the usual TF scaling relation.
(4) $D^{\mathrm{TF}}_{\mathbf{Z},R} \leq c^6_{\mathrm{TF}}\frac{2^{11}3^4 43}{\pi^4 35}R^{-7}$ was shown by Brezis and Lieb in [6]. This, together with (2) and (3), allows them to conclude the existence of the limit

$$\lim_{m_{\mathbf{Z}}\to\infty} D^{\mathrm{TF}}_{\mathbf{Z},R} = D^{\mathrm{TF}}_{\infty,1}R^{-7}. \tag{3.41}$$

Remark: The value of the constant
The exact value of $D^{\mathrm{TF}}_{\infty,1}$ is not known and the only bound on it that we are aware of is the one from [6] mentioned previously. The TF equation and the identity $(\varphi^{\mathrm{TF}}_{(Z,Z),R} - \varphi^{\mathrm{TF}}_{Z})(0) = \int(\varrho^{\mathrm{TF}}_Z(y) - \varrho^{\mathrm{TF}}_{(Z,Z),R}(y))|y|^{-1}dy + \frac{Z}{R}$ imply

$$D^{\mathrm{TF}}_{(Z,Z),R} = \frac{1}{10c^{3/2}_{\mathrm{TF}}}\int\left(\left(\varphi^{\mathrm{TF}}_{Z,R}\right)^{\frac52} - 2\left(\varphi^{\mathrm{TF}}_{Z}\right)^{\frac52}\right) + Z\left(\varphi^{\mathrm{TF}}_{(Z,Z),R} - \varphi^{\mathrm{TF}}_Z\right)(0). \tag{3.42}$$

We have used this formula to compute $D^{\mathrm{TF}}_{(Z,Z),R}$ numerically for relatively small values of Z,R (see Chapter 7) but it was not possible to obtain a meaningful extrapolation of the Born-Oppenheimer potential for large ZR^3 or a guess for the value $D^{\mathrm{TF}}_{\infty,1}$. We also note that by an argument due to Laurent Bétermin,[18]

[17] see [5, Theorem V.6.b)]
[18] unpublished, private communications, January 2018

$Z\left(\varphi^{\mathrm{TF}}_{(Z,Z),R}-\varphi^{\mathrm{TF}}_{Z}\right)(0)\xrightarrow[Z\to\infty]{}0$. Hence

$$D^{\mathrm{TF}}_{\infty,1}=\frac{1}{10c_{\mathrm{TF}}^{3/2}}\lim_{Z\to\infty}\int\left(\left(\varphi^{\mathrm{TF}}_{(Z,Z),1}\right)^{\frac{5}{2}}-2\left(\varphi^{\mathrm{TF}}_{Z}\right)^{\frac{5}{2}}\right) \tag{3.43}$$

and it is tempting to compute $D^{\mathrm{TF}}_{\infty,1}$ from this identity. For the atomic TF potential, we have the pointwise convergence $\varphi^{\mathrm{TF}}_{Z}(x)\xrightarrow[Z\to\infty]{}c_{\mathrm{S}}|x|^{-4}$. Unfortunately, we do not have an exact expression for the limiting function in the diatomic case.

The main goal of the present work is to show that (3.41) is, to leading order as $R\to 0$, also the correct description for $D^{\mathrm{rHF}}_{\mathbf{Z},R}$. An important ingredient in our proof is that $D^{\mathrm{TF}}_{\mathbf{Z},R}$ can be determined from outside TF models,[19] if they are appropriately chosen. Before making this statement rigorous, we need to introduce more notation.

For $\rho_1,\rho_2\in\mathcal{C}$, we will abuse notation and denote by $2\mathcal{D}\left(Z_1\delta_0-\rho_1,Z_2\delta_{R\nu}-\rho_2\right)$ the expression

$$\frac{Z_1Z_2}{R}-Z_1\int\frac{\rho_2(x)}{|x|}dx-Z_2\int\frac{\rho_1(x)}{|x-R\nu|}dx+2\mathcal{D}(\rho_1,\rho_2) \tag{3.44}$$

because it is shorter to write and because it emphasizes that this is the Coulomb interaction of two screened charge distributions. If these charge distributions have disjoint and compact supports, then (3.44) can be computed solely from their potentials, evaluated outside of the supports:

Proposition 3.19. *Let $r<R/2$ and assume $\rho_p\in\mathcal{C}$ with $p\in\{0,R\nu\}$ satisfy* $\operatorname{supp}\rho_p\subset B(p,r)$. *With $\Phi_p(x):=\frac{Z_p}{|x-p|}-\int\frac{\rho_p(y)}{|x-y|}dy$, we then have*

$$2\mathcal{D}(Z_0\delta_0-\rho_0,Z_{R\nu}\delta_{R\nu}-\rho_{R\nu})=\frac{1}{4\pi}\int_{\partial\Omega}\left(\partial_n\Phi_0\Phi_{R\nu}-\Phi_0\partial_n\Phi_{R\nu}\right)$$

for any $\Omega\subset B(R,r)^c$ such that $B(0,r)\subset\Omega$.

Proof. Note that $\Phi_p\in L^1_{loc}(\mathbb{R}^3)$. The distribution $-\Delta\Phi_0=4\pi(Z_0\delta_0-\rho_0)$ has support in $B(0,r)$, where $\Phi_{R\nu}$ is smooth. Hence

$$-(4\pi)^{-1}\Delta\Phi_0[\Phi_{R\nu}]=2\mathcal{D}(Z_0\delta_0-\rho_0,Z_{R\nu}\delta_{R\nu}-\rho_{R\nu}),$$

where the right hand side is to be read in the sense of (3.44). Assume for now that $\operatorname{dist}(\Omega,B(R\nu,r))>0$ and pick $\chi\in C_c^\infty(\overline{B(R\nu,r)}^c)$ with $\chi=1$ in Ω, where

[19] to the relevant order $o(R^{-7})$ as $R\to 0$

$-\Delta\Phi_{R\nu} = 0$. Then, by definition of the distributional derivative,

$$-\Delta\Phi_0[\Phi_{R\nu}] = -\Delta\Phi_0[\chi\Phi_{R\nu}] = \int \Phi_0(-\Delta\chi\Phi_{R\nu}) = \int\limits_{(B(R\nu)\cup\Omega)^c} \Phi_0(-\Delta\chi\Phi_{R\nu}). \quad (3.45)$$

Both Φ_0 and $\Phi_{R\nu}$ are harmonic in $\mathcal{O}_r \supset (\overline{B(R\nu, r)} \cup \Omega)^c$. We integrate by parts twice on the right hand side of (3.45) and find (using the properties of χ) that it equals $\int_{\partial\Omega} (\partial_n\Phi_0\Phi_{R\nu} - \Phi_0\partial_n\Phi_{R\nu})$. The case $\operatorname{dist}(\Omega, B(R\nu, r)) = 0$ is easily obtained as a limit of what we have proved. $\square$

Green's identity, $\int_\Omega(\Delta u\, v - u\, \Delta v) = \int_{\partial\Omega}(\partial_n u\, v - u\, \partial_n v)$, ensures that the following definition does indeed not depend on the exact choice of Ω:

Definition 3.20. The **Coulomb interaction energy** corresponding to two potentials $V_r^{(p)} \in \mathcal{H}(B(p,r)^c), p \in \{0, R\nu\}$ with $r < R/2$ is

$$\mathcal{Q}[V_r^{(0)}, V_r^{(R\nu)}] = \frac{1}{4\pi} \int\limits_{\partial\Omega} \left(V_r^{(0)}\partial_n V_r^{(R\nu)} - \partial_n V_r^{(0)} V_r^{(R\nu)}\right)$$

with Ω such that $B(0,r) \subset \Omega \subset \overline{B(R,r)}^c$.

Lemma 3.21. *Let $r < R/2$ and $V_r^{(p)} \in \mathcal{H}(B(p,r)^c), p \in \{0, R\nu\}$. Then*

$$\mathcal{Q}[V_r^{(0)}, V_r^{(R\nu)}] \le \frac{5\pi}{4\sqrt{1-(2r/R)^2}} \sup_{\partial B(0,r)} |V_r^{(0)}| \sup_{\partial B(R\nu,r)} |V_r^{(R\nu)}| \frac{r^2}{R}.$$

Proof. We consider $P_r(x,\xi) = \frac{1}{4\pi}\frac{r^2-|x|^2}{|x-\xi|^3}$, the Poisson kernel for the ball of radius r and write $P_r^c(x,\xi) = -P_r(x,\xi)$. Then[20]

$$V_r^{(p)}(x) = \int_{\partial B(p,r)} P_r^c(x-p, \xi-p) V_r^{(p)}(\xi) d\xi \qquad \forall |x-p| > r.$$

We infer from $\nabla P_r(x,\xi) = P_r(x,\xi)\left(\frac{2x}{|x|^2-r^2} - \frac{3(x-\xi)}{|x-\xi|^2}\right)$, together with a standard application of the mean value theorem and Lebesgue's dominated convergence, that if $|x-p| > r$,

$$\begin{aligned} \left|\nabla V_r^{(p)}(x)\right| =& \left| \int\limits_{\partial B(p,r)} V_r^{(p)}(\xi) P_r^c(x-p,\xi-p) \left(\frac{2(x-p)}{|x-p|^2-r^2} - \frac{3(x-\xi)}{|x-\xi|^2}\right)\right| \\ \le& \frac{2|(x-p)V_r^{(p)}(x)|}{|x-p|^2-r^2} + \sup_{\partial B(p,r)} |V_r^{(p)}| \int\limits_{\partial B(p,r)} \frac{3P_r^c(x-p,\xi-p)}{|x-\xi|} d\xi. \end{aligned}$$

For the last summand, we note that $\int_{\partial B(0,r)} P_r^c(x,\xi)|x-\xi|^{-1} d\xi = f_x(x)$, where f_y (with $|y| > r$) solves $\Delta f_y = 0$ in $\overline{B(0,r)}^c$, vanishes at infinity and equals $g_y(x) =$

[20] For details, see Lemma A.2 and the examples thereafter.

$|y-x|^{-1}$ on the sphere $\partial B(0,r)$. Since g_y is harmonic in $B(0,r)$, we may conclude that f_y is the Kelvin transform of g_y with respect to $\partial B(0,r)$, that is $f_y(x) = \frac{r}{|x|} g_y(x\frac{r^2}{|x|}) = \frac{r}{|x||y-x\frac{r^2}{|x|^2}|}$. (See Definition A.1 and Lemma A.2 in the appendix.) Hence $\int_{\partial B(0,r)} P_r(x,\xi)|x-\xi|^{-1}d\xi = \frac{r}{|x|^2-r^2}$ and since $V_r^{(p)}(x) \le \frac{r}{|x-p|} \sup_{\partial B(p,r)} |V_r^{(p)}|$, we find

$$|\nabla V_r^{(p)}(x)| \le \sup_{\partial B(p,r)} |V_r^{(p)}| \frac{5r}{|x-p|^2 - r^2} \qquad \forall |x-p| > r. \tag{3.46}$$

Together with the choice $\Omega = \mathbb{H}_{R\nu/2}$ in Definition 3.20, this bound implies

$$4\pi \mathcal{Q}[V_r^{(0)}, V_r^{(R\nu)}] \le r^2 \sup_{\partial B(0,r)} |V_r^{(0)}| \sup_{\partial B(R,r)} |V_r^{(R\nu)}| \int_{\mathbb{H}_{R\nu/2}} I_{r,R\nu}(x)dx$$

where $I_{r,R\nu}(x) := \left(\frac{5}{(|x|^2-r^2)|x-R\nu|} + \frac{5}{(|x-R\nu|^2-r^2)|x|}\right)$ and we easily compute

$$\int_{\mathbb{H}_{R\nu/2}} I_{r,R\nu}(x)dx = \frac{5\pi^2}{R\sqrt{1-(2r/R)^2}}$$

to obtain the result. $\square$

We now make our previous remark, that $D^{\mathrm{TF}}_{\mathbf{Z},R}$ is to leading order (in small R) determined by oTF models, more precise.

Lemma 3.22. *Let $V^{(p)} \in \mathcal{H}(\overline{B(0,r)}^c)$ with $p \in \{0, R\nu\}$ and $V = (V^{(0)} + V^{R\nu})\mathbb{1}_{\overline{\mathcal{O}_r}}$. Assume there exist positive $\epsilon, \epsilon^*, \sigma, \sigma^*$ such that $\sup_{\mathcal{O}_r} |V - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}| \le \sigma r^{-4+\epsilon}$ and $\sup_{B(p,r)^c} |V^{(p)} - \Phi^{\mathrm{TF}}_{Z_p,r}| \le \sigma^* r^{-4+\epsilon^*}$ for $p \in \{0, R\nu\}$. Furthermore assume that*

$$(3/2a^{\mathrm{TF}})^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}} \le r \le \min\{R/4, (c_{3.14b}/\sigma^*)^{1/\epsilon^*}, (c_{3.17}/\sigma)^{1/\epsilon}\}.$$

Then with $E^{\mathrm{TF}}_V = \min_{\mathcal{C}(N(V))} \mathcal{E}^{\mathrm{TF}}_V$ and $E^{\mathrm{TF}}_{V^{(p)}} = \min_{\mathcal{C}(N(V^{(p)}))} \mathcal{E}^{\mathrm{TF}}_{V^{(p)}}$,

$$E^{\mathrm{TF}}_V - E^{\mathrm{TF}}_{V^{(0)}} - E^{\mathrm{TF}}_{V^{(R\nu)}} + \mathcal{Q}[V^{(0)}, V^{(R\nu)}] - D^{\mathrm{TF}}_{\mathbf{Z},R} \le c_{3.22a} r^{-7} \sigma^* r^{\epsilon^*} \tag{3.47}$$

and

$$E^{\mathrm{TF}}_V - E^{\mathrm{TF}}_{V^{(0)}} - E^{\mathrm{TF}}_{V^{(R\nu)}} + \mathcal{Q}[V^{(0)}, V^{(R\nu)}] - D^{\mathrm{TF}}_{\boldsymbol{Z},R} \ge -c_{3.22b} r^{-7} \sigma r^{\epsilon}. \tag{3.48}$$

Proof. **Step 1** (Preliminary bounds)
We recall that both $\sup_{B(0,r)^c} |\Phi^{\mathrm{TF}}_{Z,r}|$ and $\sup_{\mathcal{O}_r} |\Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}|$ are bounded by $(cst.)r^{-4}$. The assumptions therefore imply $\|V^{(p)}\|_\infty \le (cst.)r^{-4}$ and $\|V\|_\infty \le (cst.)r^{-4}$. They also allow us to use Lemmas 3.14 and 3.17 to infer that the minimizers $\varrho_r = \arg\min_{\mathcal{C}(N(V))} \mathcal{E}^{\mathrm{TF}}_V$ and $\varrho_r^{(p)} = \arg\min_{\mathcal{C}(N(V^{(p)}))} \mathcal{E}^{\mathrm{TF}}_{V^{(p)}}$ are neutral and their L^1-norm is bounded by $(cst.)r^{-3}$. The L^1-norm of $\varrho^{\mathrm{TF}}_{Z_p} \mathbb{1}_{B(0,r)^c}$ and $\varrho^{\mathrm{TF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r}$ is (due to Lemmas 3.7 and 3.6) also bounded by $(cst.)r^{-3}$. We will use all these bounds freely in the upper and lower bound we are about to derive next. For this we start with two

identities: For any $\rho \in \mathcal{C}$, $\tilde{V} \in L^{5/2}(\mathbb{R}^3)$ it holds that

$$\begin{aligned}\mathcal{E}^{\mathrm{TF}}_{Z/|x|}[\rho] =& \mathcal{E}^{\mathrm{TF}}_{Z/|x|}[\rho \mathbb{1}_{B(0,r)}] + \mathcal{E}^{\mathrm{TF}}_{\tilde{V}}[\rho \mathbb{1}_{B(0,r)^c}] \\ &+ \int_{B(0,r)^c} \rho \left(\tilde{V} - Z|x|^{-1} + \rho \mathbb{1}_{B(0,r)} * |x|^{-1}\right),\end{aligned} \tag{3.49}$$

and

$$\begin{aligned}\mathcal{E}^{\mathrm{TF}}_{V_{\mathbf{Z},R}}[\rho] + Z_1 Z_2/R =& \mathcal{E}^{\mathrm{TF}}_{Z_1/|x|}[\rho \mathbb{1}_{B(0,r)}] + \mathcal{E}^{\mathrm{TF}}_{Z_2/|x-R\nu|}[\rho \mathbb{1}_{B(R\nu,r)}] + \mathcal{E}^{\mathrm{TF}}_{\tilde{V}}[\rho \mathbb{1}_{\mathcal{O}_r}] \\ &+ \int_{\mathcal{O}_r} \rho \left(\tilde{V} - V_{\mathbf{Z},R} + \rho \mathbb{1}_{\mathcal{I}_r} * |x|^{-1}\right) \\ &+ 2\mathcal{D}\left(Z_1\delta_0 - \rho \mathbb{1}_{B(0,r)}, Z_2 \delta_R - \rho \mathbb{1}_{B(R\nu,r)}\right).\end{aligned} \tag{3.50}$$

Step 2 (Proof of (3.48))
We insert $\rho = \varrho^{\mathrm{TF}}_{Z_0} \mathbb{1}_{B(0,r)} + \varrho^{\mathrm{TF}}_{Z_{R\nu}}(\cdot - R\nu)\mathbb{1}_{B(R\nu,r)} + \varrho_r$, $\tilde{V} = V$ in (3.50) and $\rho = \varrho^{\mathrm{TF}}_{Z_p}(\cdot - p)$, $\tilde{V} = V^{(p)}$ in (3.49). Then

$$\begin{aligned}D^{\mathrm{TF}}_{\mathbf{Z},R} \le& E^{\mathrm{TF}}_V - \mathcal{E}^{\mathrm{TF}}_{V^{(0)}}[\varrho^{\mathrm{TF}}_{Z_0} \mathbb{1}_{B(0,r)^c}] - \mathcal{E}^{\mathrm{TF}}_{V^{(R\nu)}}[\varrho^{\mathrm{TF}}_{Z_{R\nu}}(\cdot - R\nu)\mathbb{1}_{B(R\nu,r)^c}] \\ &+ \sup_{\mathcal{O}_r} \left|V - \Phi^{\mathrm{TF}}_{Z_0,r} - \Phi^{\mathrm{TF}}_{Z_{R\nu},r}(\cdot - R\nu)\right| \int \varrho_r \\ &+ \sum_{p\in\{0,R\nu\}} \sup_{B(p,r)^c} \left|V^{(p)} - \Phi^{\mathrm{TF}}_{Z_p,r}(\cdot - p)\right| \int_{B(p,r)^c} \varrho^{\mathrm{TF}}_{Z_p} \\ &+ 2\mathcal{D}(Z_0\delta_0 - \varrho^{\mathrm{TF}}_{Z_0}\mathbb{1}_{B(0,r)}, Z_{R\nu}\delta_{R\nu} - \varrho^{\mathrm{TF}}_{Z_{R\nu}}(\cdot - R\nu)\mathbb{1}_{B(R\nu,r)}).\end{aligned} \tag{3.51}$$

By neutrality, $\mathcal{E}^{\mathrm{TF}}_{V^{(p)}}[\varrho^{\mathrm{TF}}_{Z_p}\mathbb{1}_{B(p,r)^c}] \ge E^{\mathrm{TF}}_{V^{(p)}}$. Due to the maximum principle, we have the bound

$$\sup_{\mathcal{O}_r} \left|V - \Phi^{\mathrm{TF}}_{Z_0,r} - \Phi^{\mathrm{TF}}_{Z_{R\nu},r}(\cdot - R\nu)\right| \le \sum_{p\in\{0,R\nu\}} \sup_{B(p,r)^c} \left|V^{(p)} - \Phi^{\mathrm{TF}}_{Z_p}\right| \le 2\sigma r^{-4+\epsilon}$$

in the second line of (3.51). Using Proposition 3.19, we observe that last line of (3.51) equals $\mathcal{Q}[\Phi^{\mathrm{TF}}_{Z_0,r}, \Phi^{\mathrm{TF}}_{Z_{R\nu},r}(\cdot - R\nu)]$. We rewrite it and use Lemma 3.21 together with the assumptions to estimate

$$\begin{aligned}&\mathcal{Q}[\Phi^{\mathrm{TF}}_{Z_0,r}, \Phi^{\mathrm{TF}}_{Z_{R\nu},r}(\cdot - R\nu)] - \mathcal{Q}[V^{(0)}, V^{(R\nu)}] \\ &= \mathcal{Q}[\Phi^{\mathrm{TF}}_{Z_0,r}, \Phi^{\mathrm{TF}}_{Z_{R\nu},r}(\cdot - R\nu) - V^{(R\nu)}] + \mathcal{Q}[\Phi^{\mathrm{TF}}_{Z_0,r} - V^{(0)}, V^{(R\nu)}] \\ &\le (cst.)\sigma r^{-7+\epsilon}.\end{aligned} \tag{3.52}$$

The claimed upper bound on $D^{\mathrm{TF}}_{\mathbf{Z},R}$ follows from our preliminary bounds and the assumptions. We can choose

$$c_{3.22b} = 2^3 c_{\mathrm{S}} \left((2(1+A))^{3/2} + 1 + \frac{20}{\sqrt{3}}\left(1 + \frac{c_{3.14b}}{2^3 c_{\mathrm{S}}}\right)\right).$$

Step 3 (Proof of (3.47))
We insert $\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(p,r)} + \varrho_r^{(p)}$, $\tilde{V} = V^{(p)}$ into (3.49) and $\rho = \varrho^{\mathrm{TF}}_{\mathbf{Z},R}$, $\tilde{V} = V$ in (3.50). Then

$$\begin{aligned} D^{\mathrm{TF}}_{\mathbf{Z},R} \geq & \mathcal{E}_V^{\mathrm{TF}}[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] - E^{\mathrm{TF}}_{V^{(0)}} - E^{\mathrm{TF}}_{V^{(R\nu)}} - \sup_{\mathcal{O}_r} \left|V - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}\right| \int_{\mathcal{O}_r} \varrho^{\mathrm{TF}}_{\mathbf{Z},R} \\ & - \sum_{p\in\{0,R\nu\}} \sup_{B(p,r)^c} \left| V^{(p)} - Z/|x-p| + \int_{B(p,r)} \varrho^{\mathrm{TF}}_{\mathbf{Z},R}/|x-y| \right| \int_{B(p,r)^c} \varrho_r^{(p)} \\ & + 2\mathcal{D}(Z_0\delta_0 - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(0,r)}, Z_{R\nu}\delta_{R\nu} - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(R\nu,r)}). \end{aligned}$$

Again, by neutrality, $\mathcal{E}_V^{\mathrm{TF}}[\varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}] \geq E_V^{\mathrm{TF}}$. We apply (3.17) with

$$V_p(x) := (V^{(p)}(x) - Z_p/|x-p| + \int_{B(p,r)} \varrho^{\mathrm{TF}}_{\mathbf{Z},R}/|x-y|)\mathbb{1}_{B(p,r)^c}(x).$$

Then $\sup_{B(p,r)^c} |V_p| \leq 3\sigma^* r^{-4+\epsilon^*}$ (since $r \leq R/4$) and via the triangle inequality,

$$\sup_{B(p,r)^c} |Z_p/|x-p| - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(p,r)} * |x|^{-1}| \leq \sup_{B(p,r)^c} |V^{(p)}| + 3\sigma^* r^{-4+\epsilon^*}, \qquad p \in \{0, R\nu\}.$$

We use these bounds together with Proposition 3.19 and Lemma 3.21 to deduce (with the same arguments as for (3.52)) that

$$2\mathcal{D}(Z_0\delta_0 - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(0,r)}, Z_{R\nu}\delta_{R\nu} - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\mathbb{1}_{B(R\nu,r)}) - \mathcal{Q}[V^{(0)}, V^{(R\nu)}] \geq -(cst.)\sigma^* r^{-7+\epsilon^*}.$$

This proves, together with the preliminary bounds and the assumptions, the lower bound on $D^{\mathrm{TF}}_{\mathbf{Z},R}$ and we choose

$$c_{3.22a} = 2^{7/2}c_{\mathrm{S}} + 6c_{3.14a} + \frac{40}{\sqrt{3}}\left(8c_{\mathrm{S}} + 2c_{3.14b} + 3c_{3.17}\right).$$

□

CHAPTER 4

Reduced Hartree-Fock theory

Before we discuss the (reduced) Hartree-Fock functional, we need to introduce the notion of a density matrix[1] and collect some classical inequalities about density matrices and eigenvalues of Schrödinger operators.

1. Density matrices and classical inequalities

Definition 4.1. An operator $\gamma : L^2(\mathbb{R}^3; \mathbb{C}^q) \to L^2(\mathbb{R}^3; \mathbb{C}^q)$ is a **density matrix** iff it satisfies $0 \leq \gamma \leq \mathbb{1}$ and has finite trace.

We will denote by $\mathcal{DM}_q$ the set of density matrices on $L^2(\mathbb{R}^3; \mathbb{C}^q)$. Note that any $\gamma \in \mathcal{DM}_q$ is in particular a compact, self-adjoint operator and therefore has a spectral decomposition: There exist orthonormal eigenvectors u_j with corresponding eigenvalues $\lambda_j \in [0,1]$, which converge to zero, and such that

$$\gamma = \sum_{j=1}^{\infty} \lambda_j \langle u_j, \cdot \rangle u_j. \tag{4.1}$$

Moreover, any trace-class operator is Hilbert-Schmidt and thus $\gamma \in \mathcal{DM}_q$ can be rewritten as an integral operator. By a slight abuse of notation, we write $\gamma(x,y)$ for its integral kernel, which is a $q \times q$-matrix at each point (x,y). With the spectral decomposition (4.1) of $\gamma \in \mathcal{DM}_q$ we define the corresponding density $\rho_\gamma \in L^1(\mathbb{R}^3)$ by[2]

$$\rho_\gamma(x) := \sum_{j=1}^{\infty} \lambda_j |u_j(x)|^2,$$

and the (possibly infinite) value

$$\operatorname{tr}[-\Delta\gamma] := \sum_{\lambda_j > 0}^{\infty} \lambda_j \int (2\pi p)^2 |\mathcal{F} u_j(p)|^2 dp.$$

Here, abusing notation, we *defined* the left hand side by the right hand side. If $\operatorname{tr}[-\Delta\gamma] < \infty$, as will be the case for the concrete density matrices we consider later, then all eigenfunctions that correspond to non-zero eigenvalues are in $H^1(\mathbb{R}^3)$

[1] Another frequently used (and more accurate) name would be *one-particle reduced density matrix.*
[2] This is well-defined since two decompositions of the form (4.1) can only differ for eigenvectors corresponding to the eigenvalue $\lambda_j = 0$.

and then

$$\mathrm{tr}[-\Delta\gamma] = \sum_{\lambda_j>0}^{\infty} \lambda_j \|\nabla u_j\|_2^2.$$

If the eigenfunctions are in $H^2(\mathbb{R}^3)$, then this is actually an identity where the left hand side has the usual meaning. Furthermore, if $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, then

$$\mathrm{tr}[V\gamma] = \sum_{j=1}^{\infty} \lambda_j \int V|u_j|^2 = \int V\rho_\gamma < \infty.$$

We will consider one-particle, spin-diagonal Schrödinger operators,

$$H_V = (-c_H\Delta - V) \otimes I_q \quad \text{on} \quad L^2(\mathbb{R}^3; \mathbb{C}^q)$$

for potentials $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. Then H_V is bounded from below and therefore realized via the Friedrich's extension.[3]

The min-max principle implies that if $\gamma \in \mathcal{DM}_q$ with $\mathrm{tr}[\gamma] \le N$, then $\mathrm{tr}[-(c_H\Delta - V)\gamma]$ is bounded from below by the sum of the N lowest nonpositive eigenvalues of H_V.[4] The *Lieb-Thirring inequality* [25] bounds the sum of all such eigenvalues if $[V]_+ \in L^{5/2}(\mathbb{R}^3)$,

$$\sum_{\substack{e\le 0 \text{ eigenvalue} \\ \text{of } H_V}} |e| \le c_H^{-3/2} q L_1 \int [V]_+^{5/2}. \tag{4.2}$$

Here the best-known constant is $L_1 = \frac{\pi}{\sqrt{3}} L^{sc}$ (see [26]) and $L^{sc} = \frac{1}{15\pi^2}$ is the corresponding semiclassical value.[5] The Lieb-Thirring inequality is dual to the *kinetic energy inequality* (see for example [27]), which is the statement

$$\mathrm{tr}[-\Delta\gamma] \ge q^{-2/3} K_1 \int \rho_\psi^{5/3}, \qquad \forall \gamma \in \mathcal{DM}_q. \tag{4.3}$$

Here $K_1 = \frac{3}{5}\left(\frac{2}{5L_1}\right)^{2/3}$ is the best constant if and only if L_1 is the best known for (4.2). Note that this bound, together with the Hardy-Littlewood-Sobolev bound (2.1) implies

$$\mathcal{D}(\rho_\gamma) < \infty, \qquad \forall\gamma \in \mathcal{DM}_q \ \text{ with } \ \mathrm{tr}[-\Delta\gamma] < \infty. \tag{4.4}$$

[3]For the Friedrich's extension, see for example [24, Theorem X.23].
[4]For the min-max principle, see for example [14, Theorem XIII.I].
[5]L^{sc} is obtained by summing the classical Hamiltonian function $H_{cl}(x,p) = p^2/(2m) - V(x)$ over the phase space region with negative energy and postulating that a phase-space volume of size h^3 can only hold q states: $\int\int [H_{cl}(x,p)]_- \frac{dpdx}{h^3/q} = -(\sqrt{2m}/\hbar)^3 \frac{q}{15\pi^2} \int [V(x)]_+^{5/2} dx$. Note that $c_H = \hbar^2/(2m)$.

The *CLR inequality* (derived independently by Cwikel [28], Lieb[29], and Rozenblum [30], [31]) bounds $N(H_V)$, the number of nonpositive eigenvalues of H_V, by

$$N(H_V) \leq c_H^{-3/2} q L_0 \int [V]_+^{3/2}. \tag{4.5}$$

The best known constant, $L_0 \leq 0.116$, is due to Lieb [29].

The *Lieb-Oxford inequality* [32] gives a lower bound on the *indirect part* of the Coulomb energy. That is for any normalized N-particle wave function Ψ with density ρ_Ψ,

$$\sum_{1\leq k<l\leq N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(x_1,...,x_N)|^2}{|x_k - x_l|} dx_1...dx_N - \mathcal{D}(\rho_\Psi) \geq -c_{\mathrm{LO}} \int_{\mathbb{R}^3} \rho_\Psi^{4/3}. \tag{4.6}$$

The best-known constant is $c_{\mathrm{LO}} = 1.64$, due to Chan and Handy [33]. Also note that this bound holds for any $q \geq 1$.

2. The reduced Hartree Fock minimization problem

We will primarily consider the reduced Hartree-Fock (rHF) theory, a simplification of Hartree-Fock (HF) theory. The latter is more natural since it arises as the restriction of Schrödinger quantum mechanics to pure wedge products: Consider the Hamiltonian $H_{V,N}^{QM}$ of N electrons interacting with a single-particle potential V, that is

$$H_{V,N}^{QM} = \left(\sum_{j=1}^{N} (-c_H \Delta_j - V(x_j)) + \sum_{1\leq k<l\leq N} \frac{1}{|x_k - x_l|} \right) \otimes I_{q^N}.$$

One computes that the indirect part of the Coulomb energy (the left hand side in (4.6)) of a N-particle Slater determinant $\Psi_S = u_1 \wedge ... \wedge u_N$ only depends on the corresponding density matrix γ_{S} (the orthogonal projection onto the subspace spanned by $u_1, ..., u_N$). It is called the *exchange term* of γ_S and equals

$$\mathcal{X}[\gamma_S] := \frac{1}{2} \int\int \frac{\mathrm{tr}_{\mathbb{C}^q}[|\gamma_S(x,y)|^2]}{|x-y|}]dxdy \tag{4.7}$$

where $\mathrm{tr}_{\mathbb{C}^q}[|\gamma(x,y)|^2] = \sum_{k,l} |[\gamma(x,y)]_{kl}|^2$. Hence, by restricting the min-max principle for $H_{V,N}^{QM}$ to normalized N-particle Slater determinants $\Psi_S = u_1 \wedge ... \wedge u_N$, we find that the energy only depends on γ_{S}. This defines the Hartree-Fock functional $\mathcal{E}_V^{\mathrm{HF}}$ by

$$\langle \Psi_S, H_{V,N}^{QM} \Psi_S \rangle = \mathrm{tr}[(-c_H \Delta - V)\gamma_{\mathrm{S}}] + \mathcal{D}(\rho_{\gamma_{\mathrm{S}}}) - \mathcal{X}[\gamma_S] =: \mathcal{E}_V^{\mathrm{HF}}[\gamma_S].$$

This definition, and in particular (4.7), extends to any $\gamma \in \mathcal{DM}_q$ and due to a result by Lieb [34], this extension does not lower the infimum for Coulomb-potentials $V(x) = V_{\mathbf{Z},\mathbf{R}}(x)$. In particular, molecular HF minimizers under the constraint $\mathrm{tr}[\gamma] \leq |\mathbf{Z}|$ exist (see [35]) and are orthogonal projections.

There is much more that can be said about HF theory but for this we refer to the mentioned literature and make just one more remark: The exchange-energy $\mathcal{X}$ is quite challenging, it for example causes the HF functional to be non-convex. It is also the reason why we did not prove Theorems 5.1 and 6.1 for (full) HF theory. Hence we consider reduced Hartree-Fock theory, which is basically HF theory *without* the exchange term:

Definition 4.2. The **reduced Hartree-Fock functional** corresponding to a potential $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ is the map $\mathcal{E}_V^{\mathrm{rHF}} : \mathcal{DM}_q \to \mathbb{R}$ defined by

$$\mathcal{E}_V^{\mathrm{rHF}}[\gamma] := \mathrm{tr}[(-c_H\Delta - V)\gamma] + \mathcal{D}(\rho_\gamma).$$

Theorem 4.3 (The rHF minimization problem)**.** *Let $\boldsymbol{Z} \in \mathbb{R}_+^M$, $\boldsymbol{R} \in (\mathbb{R}^3)^M$. Then for all $N > 0$ there exists a $\gamma \in \mathcal{DM}_q$ such that*

$$\mathcal{E}_{V_{\boldsymbol{Z},\boldsymbol{R}}}^{\mathrm{rHF}}[\gamma] = \inf_{\substack{\gamma \in \mathcal{DM}_q \\ \mathrm{tr}[\gamma] \leq N}} \mathcal{E}_{V_{\boldsymbol{Z},\boldsymbol{R}}}^{\mathrm{rHF}}[\gamma] \qquad \textit{and} \qquad \mathrm{tr}[\gamma] \leq N.$$

Moreover, there exists $N_c(\boldsymbol{Z}) \geq |\boldsymbol{Z}|$ such that for all $N \leq N_c$, $\mathrm{tr}[\gamma] = N$.

Proof. The minimization problem for the atomic case (which is $M = 1$) was studied in [23] via the *direct method*.[6] Radial symmetry of the minimizing candidate, which obviously does not hold for $M > 1$, was used to prove that its direct Coulomb energy is finite. But we can replace this argument by (4.4). Hence the same proof applies in the general case $M \geq 1$. $\square$

Note that the minimizer in Theorem 4.3 need not be unique. We therefore denote by γ_Z^{rHF} an arbitrary neutral atomic minimizer, that is

$$\mathcal{E}_{Z/|x|}^{\mathrm{rHF}}[\gamma_Z^{\mathrm{rHF}}] = \min_{\substack{\gamma \in \mathcal{DM}_q \\ \mathrm{tr}[\gamma] \leq Z}} \mathcal{E}_{Z/|x|}^{\mathrm{rHF}}[\gamma] \quad \text{and let} \quad \varrho_Z^{\mathrm{rHF}} = \rho_{\gamma_Z^{\mathrm{rHF}}}. \tag{4.8}$$

Similar, we denote by γ_Z^{rHF} an arbitrary diatomic neutral minimizer, meaning

$$\mathcal{E}_{\mathbf{Z},R}^{\mathrm{rHF}}[\gamma_{\mathbf{Z},R}^{\mathrm{rHF}}] = \min_{\substack{\gamma \in \mathcal{DM}_q \\ \mathrm{tr}[\gamma] \leq |\mathbf{Z}|}} \mathcal{E}_{V_{\mathbf{Z},R}}^{\mathrm{rHF}}[\gamma] \quad \text{and let} \quad \varrho_{\mathbf{Z},R}^{\mathrm{rHF}} = \rho_{\gamma_{\mathbf{Z},R}^{\mathrm{rHF}}}. \tag{4.9}$$

[6] Developed around 1900 and refined later, a modern and detailed discussion can be found in [36].

They both depend on the number of spin states q, which we suppress in the notation, since it as a fixed parameter. We denote by E_Z^{rHF} and $E_{\mathbf{Z},R}^{\mathrm{rHF}}$ the corresponding minima and note that the latter does not contain the nuclear repulsion $\frac{Z_1 Z_2}{R}$. If $|\mathbf{Z}| \in \mathbb{N}$, then we use a similar notation for atomic and diatomic HF minimizers $\gamma_Z^{\mathrm{HF}}, \gamma_{\mathbf{Z},R}^{\mathrm{HF}}$ and energies E_Z^{HF}, $E_{\mathbf{Z},R}^{\mathrm{HF}}$.

3. Relation to TF theory

The purpose of this Chapter is twofold: We introduce Lemma 4.4 which will be very useful in the remainder of this thesis when comparing TF and HF type models. We immediately demonstrate its use by comparing the molecular rHF energy to the molecular TF energy, showing that they agree to leading order in $|\mathbf{Z}| \to \infty$. Neither the results nor the proofs that we present in this Section are new.

Since we will compare TF theory to rHF theory, we need to fix the TF constant c_{TF} according to the chosen physical units (compare (1.2)). From here until the end of Chapter 6, we set

$$c_{\mathrm{TF}} = c_H (6\pi/q)^{2/3}.$$

For $\zeta \in (0,\infty)$, we define

$$g_\zeta(x) = \begin{cases} \frac{\sin(\pi|x|/\zeta)}{\sqrt{2\pi\zeta}\,|x|}, & \text{if } |x| < \zeta \\ 0, & \text{if } |x| \geq 0. \end{cases}$$

In other words, g_ζ is the normalized eigenvector of the Dirichlet-Laplacian on $B(0,\zeta)$, corresponding to the lowest eigenvalue $\|\nabla g_\zeta\|^2 = \pi^2/\zeta^2$ and vanishing on the complement of $B(0,\zeta)$.

Lemma 4.4 ([12, Thm. 8.2])**.** *Let $\zeta \in (0,\infty)$. Assume $[V]_+, [V * g_\zeta]_+ \in L^{5/2}(\mathbb{R}^3)$ and $\delta \in (0,1)$. Then the sum of the N lowest negative eigenvalues of H_V is bounded from below by*

$$-\frac{2}{5} c_{\mathrm{TF}}^{-3/2} (1-\delta)^{-3/2} \int [V]_+^{5/2} - c_H (1-\delta) \frac{\pi^2}{\zeta^2} N - (c_H \delta)^{-3/2} q L_1 \| [V - V * g_\zeta^2]_+ \|_{5/2}^{5/2}. \tag{4.10}$$

Moreover, if also $[V]_+ \in L^{3/2}(\mathbb{R}^3)$, then there exists a $\gamma \in \mathcal{DM}_q$ such that $\rho_\gamma = c_{\mathrm{TF}}^{-3/2} [V]_+^{3/2} * g_\zeta^2$ and

$$\mathrm{tr}[-c_H \Delta \gamma] = \frac{3}{5} c_{\mathrm{TF}}^{-3/2} \int [V]_+^{5/2} + c_H c_{\mathrm{TF}}^{-3/2} \frac{\pi^2}{\zeta^2} \int [V]_+^{3/2}. \tag{4.11}$$

For a proof, see [12, Thm. 8.2] and note that the operator H_V we consider here has a q-fold degenerate spectrum and that Solovej defines the Lieb-Thirring constant

L_1 for $-\frac{1}{2}\Delta - V$. The only real difference is the term $c_H(1-\delta)\frac{\pi^2}{\zeta^2}N$ which is due to a hardly relevant mistake in [12, Thm. 8.2].

Lemma 4.5 ([12, Lemma 11.1])**.** *Let $\boldsymbol{Z} \in \mathbb{R}_+^M, \boldsymbol{R} \in (\mathbb{R}^3)^M$ and assume $\rho \in \mathcal{C}$ satisfies $\alpha \int \rho^{5/3} \leq \int V_{\boldsymbol{Z},\boldsymbol{R}}\rho$ for some $\alpha > 0$. Then*

$$\int \rho^{5/3} \leq \frac{c_{4.5}}{\alpha^2}\left(\int \rho\right)^{1/3} \sum_{j=1}^{M} Z_j^2.$$

Proof. The proof is a part of [12, Lemma 11.1] and we repeat it here for convenience: First we use that $ab \leq \frac{3}{5}(\delta a)^{5/3} + \frac{2}{5}(b/\delta)^{5/2}$ for any $\delta > 0$ to estimate that

$$\begin{aligned} Z_j \int_{\mathbb{R}^3} \frac{\rho(x)dx}{|x-R_j|}dx =& Z_j \int_{B(R_j,r)} \frac{\rho(x)dx}{|x-R_j|} + Z_j \int_{B(R_j,r)^c} \frac{\rho(x)dx}{|x-R_j|} \\ \leq& \frac{3}{5}\int_{B(R_j,r)} (\delta\rho(x))^{5/3}dx + \frac{2}{5}\int_{B(R_j,r)} (Z_j|x-R_j|^{-1}/\delta)^{5/2}dx \\ & \qquad + r^{-1}Z_j \int \rho \\ =& 3/5\delta^{5/3}\int \rho^{5/3} + 16/5\pi r^{1/2} Z_j^{5/2}\delta^{-5/2} + r^{-1}Z_j\int\rho. \end{aligned}$$

We use this bound on the right hand side of the assumption $\alpha \int \rho^{5/3} \leq \int V_{\mathbf{Z},\mathbf{R}}\rho$ and minimize over $r \in (0,\infty)$. Then we solve for $\int \rho^{5/3}$ and find for $0 < M\frac{3}{5}\delta^{5/3} < \alpha$, that

$$\int \rho^{5/3} \leq \left(\int\rho\right)^{1/3}\left(\sum_{j=1}^{M} Z_j^2\right)(\delta^{5/3}(\alpha - M\tfrac{3}{5}\delta^{5/3}))^{-1}(2^{1/3}+2^{-2/3})(\tfrac{16\pi}{5})^{2/3}.$$

We conclude the Lemma with $c_{4.5} = \frac{12M}{5}\left(\frac{16\pi}{5}\right)^{2/3}\left(2^{1/3}+2^{-2/3}\right)$ and the optimal choice, $M\frac{3}{5}\delta^{5/3} = \alpha/2$. □

Remark: Since $\min_{\mathcal{C}} \mathcal{E}^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} < 0$, the assumptions of Lemma 4.5 are satisfied for the minimizing TF density with $\alpha = \frac{3}{5}c_{\mathrm{TF}}$. By nonpositivity of the HF and rHF energies and due to (4.3), they are also satisfied for densities corresponding to minimizers of $\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}}$ and $\mathcal{E}^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}}$ over $\mathcal{DM}_q \cap \{\mathrm{tr}[\gamma] \leq |\mathbf{Z}|\}$, with $\alpha = c_H q^{-2/3}K_1 = (\sqrt{3}/\pi)^{\frac{2}{3}}\frac{3}{5}c_{\mathrm{TF}}$.[7]

Lemma 4.6. *Let $\boldsymbol{R} \in (\mathbb{R}^3)^M$ and $\boldsymbol{Z} \in \mathbb{R}_+^M$ with $|\boldsymbol{Z}| \geq 1$. Then*

$$\mathcal{D}(\varrho^{\mathrm{TF}}_{\boldsymbol{Z},\boldsymbol{R}} - \varrho^{\mathrm{rHF}}_{\boldsymbol{Z},\boldsymbol{R}}) + E^{\mathrm{TF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}} - c_{4.6a}|\boldsymbol{Z}|^{\frac{7}{3}-\frac{2}{33}} \leq E^{\mathrm{rHF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}} \leq E^{\mathrm{TF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}} + c_{4.6b}|\boldsymbol{Z}|^{\frac{7}{3}-\frac{2}{33}}$$

[7] In the HF case, we implicitly assume here that $|\mathbf{Z}| \in \mathbb{N}$.

and if $|\boldsymbol{Z}| \in \mathbb{N}$,

$$\mathcal{D}(\varrho^{\mathrm{TF}}_{\boldsymbol{Z},\boldsymbol{R}} - \varrho^{\mathrm{HF}}_{\boldsymbol{Z},\boldsymbol{R}}) + E^{\mathrm{TF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}} - c_{4.6c}|\boldsymbol{Z}|^{\frac{7}{3}-\frac{2}{33}} \le E^{\mathrm{HF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}} \le E^{\mathrm{rHF}}_{V_{\boldsymbol{Z},\boldsymbol{R}}}.$$

Proof. **Step 1** (Preliminaries)
The existence of minimizers is known (see [35] and Theorems 3.3 and 4.3). If $|\mathbf{Z}| \in \mathbb{N}$, then $E^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}} \le \mathcal{E}^{\mathrm{HF}}[\gamma^{\mathrm{rHF}}] = \mathcal{E}^{\mathrm{rHF}}[\gamma^{\mathrm{rHF}}] - \mathcal{X}[\gamma^{\mathrm{rHF}}_{\mathbf{Z},\mathbf{R}}] \le E^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}}$. To derive the other bounds, we use Lemma 4.4 with $V = \varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}$ and begin with a check that the assumptions are satisfied: Since g_ζ is radial, we have that for all $x \in \mathbb{R}^3$ and all $\zeta \in (0,\infty)$,

$$G_\zeta(x) = |x|^{-1} - g_\zeta^2 * |x|^{-1} = \int_{B(0,|x|)^c} g_\zeta^2(y) \left(|x|^{-1} - |y|^{-1}\right) dy \ge 0$$

due to Newton's theorem. This implies that $[V(x) - V * g_\zeta^2(x)]_+ \le \sum_{j=1}^M Z_j G(x - R_j)$. Using Jensen's inequality, we find with $c_g = \int (G_1(x))^{5/2} dx$ that

$$\int \left[V(x) - V * g_\zeta^2(x)\right]_+^{5/2} dx \le |\mathbf{Z}|^{5/2} \int (G_\zeta(x))^{5/2} = |\mathbf{Z}|^{5/2} \sqrt{\zeta} c_g < \infty. \tag{4.12}$$

Finally, (3.2) implies $V = \varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} = c_{\mathrm{TF}} \left(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}\right)^{2/3} \in L^{5/2}(\mathbb{R}^3)$.

Step 2 (The upper bound)
According to Lemma 4.4, there exists a $\gamma \in \mathcal{DM}_q$ with $\rho_\gamma = c_{\mathrm{TF}}^{-3/2}[V]_+^{3/2} * g_\zeta^2 = \varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2$, so that $\mathrm{tr}[\gamma] \le \int \rho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} = |\mathbf{Z}|$ and $E^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}} \le \mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}}[\gamma]$. Using (4.11), we obtain

$$\begin{aligned} E^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}} \le & \frac{3}{5} c_{\mathrm{TF}} \int \left(\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}}\right)^{5/3} + c_H \frac{\pi^2}{\zeta^2}|\mathbf{Z}| - \int (\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2) V_{\mathbf{Z},\mathbf{R}} + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2) \\ \le & E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + c_H \frac{\pi^2}{\zeta^2}|\mathbf{Z}| + \int (\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} - \varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2) V_{\mathbf{Z},\mathbf{R}}. \end{aligned} \tag{4.13}$$

Here we once more used the TF equation and that $\mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2) \le \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}})$.[8] We use Hölder's inequality to bound

$$\int (\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} - \varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} * g_\zeta^2) V_{\mathbf{Z},\mathbf{R}} = \sum_{j=1}^M Z_j \int \varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}(x) G_\zeta(x - R_j) dx \le |\mathbf{Z}| \|\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}\|_{5/3} \zeta^{1/5} c_g^{2/5},$$

plug this back into (4.13) and optimize in $\zeta \in (0,\infty)$, so that

$$E^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}} \le E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + |\mathbf{Z}| \|\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}\|_{\frac{5}{3}}^{\frac{10}{11}} c_g^{\frac{4}{11}} c_H^{\frac{1}{11}} \pi^{\frac{2}{11}} 11 \cdot (10)^{\frac{-10}{11}}.$$

[8]see Proposition B.3 in the appendix for details

Using Lemma 4.5 with $\alpha = \frac{3}{5}c_{\mathrm{TF}}$, we obtain the claimed upper bound

$$E^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}} \leq E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + |\mathbf{Z}|^{\frac{7}{3}-\frac{2}{33}} \underbrace{c_g^{\frac{4}{11}} c_H^{\frac{1}{11}} \pi^{\frac{2}{11}} c_{4.5}^{\frac{6}{11}} (\tfrac{3}{5}c_{\mathrm{TF}})^{-\frac{12}{11}} 11 \cdot 10^{-\frac{10}{11}}}_{=:c_{4.6b}}.$$

Step 3 (The HF-lower bound)
We begin with

$$E^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}} = \mathrm{tr}[H_{\varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}} \gamma^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}] + \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} - \varrho^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}) - \mathcal{D}(\varrho^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}) - \mathcal{X}(\gamma^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}). \tag{4.14}$$

Since $\gamma^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}$ is a projection onto a $|\mathbf{Z}|$-dimensional space, $\mathrm{tr}[H_{\varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}} \gamma^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}]$ is, according to the min-max principle, bounded from below by the sum of the $|\mathbf{Z}|$ lowest negative eigenvalues of $H_{\varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}}$. We may therefore use (4.10) together with (4.12) in (4.14) and optimize over $\zeta \in (0,\infty)$ to find that for all $\delta \in (0,1)$:

$$\begin{aligned} E^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}} \geq & E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + \mathcal{D}(\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} - \varrho^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}}) - \mathcal{X}(\gamma^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}}) \\ & - \left((1-\delta)^{\frac{-3}{2}} - 1\right) \frac{2}{5} c_{\mathrm{TF}} \int \left(\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}}\right)^{5/3} \\ & - |\mathbf{Z}|^{\frac{11}{5}} \delta^{-6/5} (1-\delta)^{1/5} \underbrace{c_H^{-1} (c_g q L_1)^{4/5} \pi^{2/5} (4^{1/5} + 4^{-4/5})}_{=:C_1}. \end{aligned}$$

Lemma 4.5 with $c = \frac{3}{5}c_{\mathrm{TF}}$ bounds the $L^{5/3}$-norm of $\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}}$. With the Lieb-Oxford and Hölder inequalities and Lemma 4.5 for $c = (3/\pi^2)^{1/3} \frac{3}{5} c_{\mathrm{TF}}$,

$$\mathcal{X}(\gamma^{\mathrm{HF}}) \leq c_{\mathrm{LO}} \| \left(\varrho^{\mathrm{HF}}\right)^{1/2} \|_2 \| \left(\varrho^{\mathrm{HF}}\right)^{5/6} \|_2 \leq \underbrace{\frac{5\pi^{2/3} c_{\mathrm{LO}} \sqrt{c_{4.5}}}{c_{TF} 3^{4/3}}}_{=C_3} |\mathbf{Z}|^{5/3}.$$

So far we have for all $\delta \in (0,1)$ the lower bound

$$\begin{aligned} E^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}} \geq & E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + \mathcal{D}(\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} - \varrho^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}}) - C_3 |\mathbf{Z}|^{5/3} \\ & - |\mathbf{Z}|^{7/3} \left((1-\delta)^{\frac{-3}{2}} - 1\right) \frac{10 c_{4.5}}{9 c_{\mathrm{TF}}} - |\mathbf{Z}|^{\frac{11}{5}} \delta^{-6/5} C_1. \end{aligned}$$

We choose $\delta = \alpha |\mathbf{Z}|^p$ with $\alpha \in (0,1)$. Because $|\mathbf{Z}| \geq 1$, we indeed have $\delta \in (0,1)$ for any $p < 0$. Then $(1-\delta)^{-3/2} \leq 1 + |\mathbf{Z}|^p \left((1-\alpha)^{-3/2} - 1\right)$ by convexity and $p = -\frac{2}{33}$ is optimal for large $|\mathbf{Z}|$. Thus, for all $\alpha \in (0,1)$,

$$E^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}} \geq E^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} + \mathcal{D}(\varrho^{\mathrm{TF}}_{V_{\mathbf{Z},\mathbf{R}}} - \varrho^{\mathrm{HF}}_{V_{\mathbf{Z},\mathbf{R}}}) - C_3 |\mathbf{Z}|^{5/3} - C_2(\alpha) |\mathbf{Z}|^{\frac{7}{3}-\frac{2}{33}}$$

with $C_2(\alpha) = ((1-\alpha)^{-3/2} - 1) \frac{10 c_{4.5}}{9 c_{\mathrm{TF}}} + C_1/\alpha^{6/5}$. Now choose $c_{4.6c} = C_3 + \min_{\alpha \in (0,1)} C_2(\alpha)$.

Step 4 (The rHF-lower bound)
The proof of the lower bound on the rHF energy is nearly the same, up to two modifications: First, the exchange term is not present, which simplifies the proof.

Second, $\gamma^{\mathrm{rHF}}_{V_{\mathbf{Z},\mathbf{R}}}$ is not necessarily an orthogonal projection and thus we may only bound $\mathrm{tr}[H_{\varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}}\gamma^{\mathrm{rHF}}_{\mathbf{Z},\mathbf{R}}]$ from below by the sum of *all* its negative eigenvalues. Fortunately, (4.5) allows us to bound the number of these by $qL_0c_H^{-3/2}\int[\varphi^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}}]_+^{3/2} = qL_0(c_{\mathrm{TF}}/c_H)^{3/2}|\mathbf{Z}|$. From here, the proof remains the same, up to a change in the constants so that

$$c_{4.6a} = \min_{\alpha\in(0,1)}\left(\left((1-\alpha)^{-3/2}-1\right)\frac{10c_{4.5}}{9c_{\mathrm{TF}}} + \alpha^{-6/5}\frac{q(c_gL_1)^{4/5}\pi^{2/5}L_0^{1/5}c_{\mathrm{TF}}^{3/10}}{c_H^{13/10}}\right).$$

□

Remark (The large-Z limit of Quantum Mechanics)
Consider the Hamiltonian of N electrons subject to a nuclear potential $V_{\mathbf{Z},\mathbf{R}}$ in the Born-Oppenheimer approximation, $H^{QM}_{V_{\mathbf{Z},\mathbf{R}},N} = \sum_{j=1}^N\left(-c_H\Delta_j - V_{\mathbf{Z},\mathbf{R}}(x_j)\right) + \sum\limits_{1\le i<j\le N}|x_i-x_j|^{-1}$. Then for any normalized N-electron wave function Ψ, we have

$$\langle\Psi, H^{QM}_{V_{\mathbf{Z},\mathbf{R}},N}\Psi\rangle \ge \mathrm{tr}[H_{V_{\mathbf{Z},\mathbf{R}}}\gamma_\Psi] + \mathcal{D}(\rho_\Psi) - c_{\mathrm{LO}}\int\rho_\Psi^{4/3}$$

due to the Lieb-Oxford inequality (4.6).[9] Similar to the proof of the lower bound in Lemma 4.6, one can therefore show (see [35, Theorem 5.1]) that for $|\mathbf{Z}|\in\mathbb{N}$,

$$E^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} - (cst.)|\mathbf{Z}|^{\frac{7}{3}-\frac{1}{30}} \le E^{QM}_{\mathbf{Z},\mathbf{R}} \le E^{\mathrm{HF}}_{\mathbf{Z},\mathbf{R}}.$$

Together with the TF scaling (1.3), one concludes that TF, rHF and HF theory agree with the quantum mechanical energy to leading order in $|\mathbf{Z}|\to\infty$ and the leading order term is given by Thomas-Fermi theory.

Also the next-order term, called Scott-correction, is known [37]: $E^{QM}_{\mathbf{Z},\mathbf{R}} = E^{\mathrm{TF}}_{\mathbf{Z},\mathbf{R}} + \frac{1}{2}\sum_{j=1}Z_j^2 + o(|\mathbf{Z}|^2)$ as $|\mathbf{Z}|\to\infty$. For atoms, even the $Z^{5/3}$-correction has been proven in [38]. These expansions in Z and their predictions have a large history and literature which we do not cover here. Both of the two mentioned results contain an overview of these.

4. The outside in rHF theory

We extend the results of [12, Chapter 6] to the diatomic case, studying the rHF density on the outside $\mathcal{O}_r$ by splitting the rHF energy into an inside and an outside part. We begin with the well-known IMS-formula, which achieves such a splitting for the Laplace operator.

[9] Here γ_Ψ is the density matrix obtained by tracing out $|\Psi\rangle\langle\Psi|$ and ρ_Ψ the corresponding density.

Lemma 4.7 (IMS - formula). *If $\{\omega_j\}_{j=1}^n \subset C^1(\mathbb{R}^3,[0,1])$ with bounded gradients and $\sum_{j=1}^n \omega_j(x) = 1$, then for all $\gamma \in \mathcal{DM}_q$ with $\operatorname{tr}[-\Delta\gamma] < \infty$:*

$$\operatorname{tr}[-\Delta\gamma] = \sum_{j=1}^n \operatorname{tr}[-\Delta(\omega_j\gamma\omega_j)] - \sum_{j=1}^n \operatorname{tr}[|\nabla\omega_j|^2\gamma].$$

The proof is a straightforward computation, see for example [12, Lemma 2.4]. It can also be found in [39, Chapter 3.1], together with references of its origin. A set $\{\omega_j\}_j^n$ satisfying the hypothesis of Lemma 4.7 is called a *quadratic partition of unity*. We will use a special choice of such a partition with $n = 5$:

Definition 4.8. Let $\delta, r > 0$. A family of functions $\{\omega_z\} \subset C^1(\mathbb{R}^3,[0,1])$ indexed by $z \in \{0, R\nu, \tilde{0}, \tilde{R\nu}, \mathcal{O}\}$ is a **δ-partition at radius** r iff

(1) $|\nabla\omega_z| \le \frac{\pi}{2\delta}$ for all z, $\sum_z \omega_z^2(x) = 1$ for all x,
(2) $\operatorname{supp}\omega_z \subset B(z,r)$ and $\omega_z|_{B(z,r-\delta)} = 1$ for $z \in \{0, R\nu\}$,
(3) $\operatorname{supp}\omega_{\mathcal{O}} \subset \mathcal{O}_r$ and $\omega_{\mathcal{O}}|_{\mathcal{O}_{r+\delta}} = 1$.

Note that $\tilde{0}, \tilde{R\nu}$ and $\mathcal{O}$ are only labels, whereas 0 and $R\nu$ also denote points in $\mathbb{R}^3$. A δ-partition at radius r exists for any $\delta \in (0, \min\{r, \frac{R}{2} - r\})$, see for example [12, p. 532].

Let $\omega \in L^\infty(\mathbb{R}^3)$, then ω is a bounded operator on $L^2(\mathbb{R}^3;\mathbb{C}^q)$ and for any $\gamma \in \mathcal{DM}_q$, we define

$$\gamma_\omega := \omega\gamma\omega$$

which is also a density matrix if $\|\omega\|_\infty \le 1$. Using the cyclicity of the trace, we find $\int \rho_{\gamma_\omega}\phi = \operatorname{tr}[\gamma_\omega\phi] = \operatorname{tr}[\gamma(\omega\phi\omega)] = \int \rho_\gamma\omega^2\phi$ for any $\phi \in C_c^\infty(\mathbb{R}^3)$. This implies that

$$\rho_{\gamma_\omega} = \rho_\gamma\omega^2 \quad \text{ a.e. in } \mathbb{R}^3.$$

Now comes the the main result of this section: $\gamma_{\omega_{\mathcal{O}}}^{\mathrm{rHF}}$ almost minimizes $\mathcal{E}^{rHF}_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}$ over density matrices supported in $\mathcal{O}_r$ and with trace bounded by the trace of $\omega_{\mathcal{O}}\gamma^{\mathrm{rHF}}\omega_{\mathcal{O}}$. This then implies a bound on $\int \left(\varrho^{\mathrm{rHF}}\omega_{\mathcal{O}}^2\right)^{5/3}$.

Lemma 4.9. *Assume $\delta \in (0, \min\{r, \frac{R}{2} - r\})$, let γ^{rHF} be a neutral minimizer of $\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}$ and $\{\omega_z\}$ a δ-partition at radius $r < R/2$. Then*

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}] \ge{}& \mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}_{\omega_0} + \gamma^{\mathrm{rHF}}_{\omega_{R\nu}}] + \operatorname{tr}\left[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}\right] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega_{\mathcal{O}}^2) \\ & - c_H^{-3/2} q L_1 \int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} [\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r-\delta}]_+^{5/2} - c_H\frac{\pi^2}{2\delta^2} \int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} \varrho^{\mathrm{rHF}}\end{aligned} \qquad (4.15)$$

and for any $\tilde{\gamma} \in \mathcal{DM}_q$ *with* $\mathrm{tr}[-\Delta\tilde{\gamma}] < \infty, \mathrm{tr}[\tilde{\gamma}] \leq \int_{\mathcal{O}_r} \varrho^{\mathrm{rHF}}$ *and* $\mathrm{supp}\, \rho_{\tilde{\gamma}} \subset \mathcal{O}_r$*:*

$$\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}] \leq \mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}_{\omega_0} + \gamma^{\mathrm{rHF}}_{\omega_{R\nu}}] + \mathrm{tr}\left[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\tilde{\gamma}\right] + \mathcal{D}(\rho_{\tilde{\gamma}}). \tag{4.16}$$

Moreover, with K_1 *defined in* (4.3)*,*

$$\begin{aligned}\int \left(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}\right)^{5/3} \leq & \frac{4q^{2/3}\pi^{2/3}\left|E^{\mathrm{TF}}_1\right|}{3^{1/3}c_H K_1}\left[r \sup_{\partial\mathcal{O}_r} \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}\right]^{7/3}_{+} \\ & + \frac{\pi^2 q^{2/3}}{\delta^2 K_1}\int_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} \varrho^{\mathrm{rHF}} + \frac{2L_1 q^{5/3}}{K_1 c_H^{5/2}}\int_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} [\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r-\delta}]^{5/2}_{+}.\end{aligned} \tag{4.17}$$

Proof. All we do is rewrite the proof of [12, Theorem 6.2] and [12, Corollary 6.3] for the diatomic case. For the upper bound, we take the trial state $\gamma = \gamma^{\mathrm{rHF}}_{\omega_0} + \gamma^{\mathrm{rHF}}_{\omega_{R\nu}} + \tilde{\gamma}$. Then $\gamma^{\mathrm{rHF}}_{\omega_0}\tilde{\gamma} = 0 = \gamma^{\mathrm{rHF}}_{\omega_0}\gamma^{\mathrm{rHF}}_{\omega_{R\nu}}$ by the support properties of the δ-partition. Hence $\gamma^2 = \gamma$ and in particular $\gamma \in \mathcal{DM}_q$. Moreover,

$$\mathrm{tr}[\gamma] \leq \int \varrho^{\mathrm{rHF}}(\omega_0^2 + \omega^2_{R\nu} + \mathbb{1}_{\mathcal{O}_r}) \leq |\mathbf{Z}|,$$

so γ is a trial density matrix for the diatomic rHF minimization problem and we obtain

$$\begin{aligned}E^{\mathrm{rHF}}_{V_{\mathbf{Z},R}} \leq \mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma] =& \mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}_{\omega_0} + \gamma^{\mathrm{rHF}}_{\omega_{R\nu}}] + \mathrm{tr}\left[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\tilde{\gamma}\right] + \mathcal{D}(\rho_{\tilde{\gamma}}) \\ & + 2\mathcal{D}(\rho_{\tilde{\gamma}}, \varrho^{\mathrm{rHF}}(\omega_0^2 + \omega^2_{R\nu} - \mathbb{1}_{\mathcal{I}_r})).\end{aligned}$$

Here, the last term is clearly nonpositive. We simply drop it to obtain (4.16). For the lower bound, we first use the IMS-formula (Lemma 4.7) and properties of the δ-partition to deduce that

$$\mathrm{tr}[-c_H\Delta\gamma^{\mathrm{rHF}}] \geq \sum_z \mathrm{tr}[-c_H\Delta\gamma^{\mathrm{rHF}}_{\omega_z}] - c_H\frac{\pi^2}{2\delta^2}\int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} \varrho^{\mathrm{rHF}}.$$

Next, we use that $(\omega_0^2 + \omega^2_{R\nu} + \omega_{\tilde{0}}^2 + \omega^2_{\tilde{R\nu}}) \geq \mathbb{1}_{\mathcal{I}_r}$ and $(\omega_0^2 + \omega^2_{R\nu}) \geq \mathbb{1}_{\mathcal{I}_{r-\delta}}$ to bound

$$\begin{aligned}\mathcal{D}(\varrho^{\mathrm{rHF}}) =& \sum_{z,z'} \mathcal{D}\left(\varrho^{\mathrm{rHF}}\omega_z^2, \varrho^{\mathrm{rHF}}\omega^2_{z'}\right) \\ \geq& \mathcal{D}(\varrho^{\mathrm{rHF}}(\omega_0^2 + \omega^2_{R\nu})) + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}) \\ & + 2\mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{I}_r}, \varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}) + 2\mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{I}_{r-\delta}}, \varrho^{\mathrm{rHF}}(\omega_{\tilde{0}}^2 + \omega^2_{\tilde{R\nu}})).\end{aligned}$$

Since $\operatorname{tr}\left[V_{\mathbf{Z},R}\gamma^{\mathrm{rHF}}\right] = \sum_z \operatorname{tr}\left[V_{\mathbf{Z},R}\gamma^{\mathrm{rHF}}_{\omega_z}\right]$ we find, by collecting the bounds we deduced so far, that

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}] \geq &\mathcal{E}^{\mathrm{rHF}}_{V_{\mathbf{Z},R}}[\gamma^{\mathrm{rHF}}_{\omega_0} + \gamma^{\mathrm{rHF}}_{\omega_{R\nu}}] + \operatorname{tr}\left[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}\right] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}})\\ &+ \operatorname{tr}\left[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r-\delta}}(\gamma^{\mathrm{rHF}}_{\omega_{\tilde{0}}} + \gamma^{\mathrm{rHF}}_{\omega_{\tilde{R\nu}}})\right] - c_H\frac{\pi^2}{2\delta^2}\int_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} \varrho^{\mathrm{rHF}}.\end{aligned}$$

Applying the Lieb-Thirring inequality (4.2) with $V = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r-\delta}\mathbb{1}_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}}$ now yields (4.15).

Finally, we prove (4.17). We use that $\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}(x) \leq \frac{r}{|x|}\sup\limits_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}$ for all $x \in \mathcal{O}_r$ together with the kinetic energy-inequality (4.3):

$$\begin{aligned}&\operatorname{tr}[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}) \geq\\ &c_H q^{-2/3}K_1\int\left(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}\right)^{5/3} - [r\sup_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}]_+\int\frac{\varrho^{\mathrm{rHF}}(x)\omega^2_{\mathcal{O}}(x)}{|x|}dx + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}).\end{aligned}$$

This is lower bounded by the atomic TF energy, with $[r\sup_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}]_+$ as the nuclear charge and constant $c_H q^{-2/3}K_1 = (\sqrt{3}/\pi)^{2/3}\frac{3}{5}c_{\mathrm{TF}}$ instead of $\frac{3}{5}c_{\mathrm{TF}}$ in front of the kinetic term. We take only half the kinetic term (which is optimal, since $1/2$ is the minimum of $1/[\epsilon(1-\epsilon)]$) and use the scaling relation (3.1) with $U = [r\sup_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}]_+$ and $T = \frac{1}{2}c_H q^{-2/3}K_1$. Then

$$\begin{aligned}&\operatorname{tr}[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}})\\ &\qquad\geq \frac{c_H K_1}{2q^{2/3}}\int\left(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}}\right)^{5/3} - [r\sup_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}]_+^{7/3}2\left(\pi^2/3\right)^{1/3}|E^{\mathrm{TF}}_1|.\end{aligned}$$

On the other hand, (4.15) and (4.16) for $\tilde{\gamma} = 0$ imply that

$$\begin{aligned}&\operatorname{tr}[H_{\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}})\\ &\qquad\leq\frac{qL_1}{c_H^{3/2}}\int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}}[\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r-\delta}]_+^{5/2} + c_H\frac{\pi^2}{2\delta^2}\int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}}\varrho^{\mathrm{rHF}}.\end{aligned}$$

Combining the last two inequalities and multiplying by $\frac{2q^{2/3}}{c_H K_1}$ proves (4.17). $\square$

CHAPTER 5

Comparing screened potentials

The screened potentials for a homonuclear diatomic system in Thomas-Fermi and reduced Hartree-Fock theory are (independently of $Z_1, Z_2 > 0$) comparable. The precise statement and our main result (from a technical point of view) is

Theorem 5.1. *There exist constants $\delta_{5.1}, c_{5.1a}, c_{5.1b} > 0$ such that for all $R > 0$, $\delta \in (0, \delta_{5.1}]$ and all $\boldsymbol{Z} \in \mathbb{R}^2_+$ with $|\boldsymbol{Z}| \geq 1$: If $r \leq c_{5.1b} \min\left\{1, (R/2)^{1+\frac{\delta\xi}{\eta-\delta\xi}}\right\}$, then*

$$\sup_{x \in \partial\mathcal{O}_r} \left| \int_{\mathcal{I}_r} \frac{\varrho^{\mathrm{TF}}_{\boldsymbol{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\boldsymbol{Z},R}(y)}{|x-y|} dy \right| \leq c_{5.1a} r^{-4+\delta\xi}.$$

We give the proof on page 62. The corresponding result for atomic rHF theory is:

Theorem 5.2. *There exist constants $\varepsilon_{5.2}, c_{5.2a}, c_{5.2b} > 0$ such that for all $|x| \leq c_{5.2b}$ and all $Z \geq 1$:*

$$\left| \int_{B(0,|x|)} \frac{\varrho^{\mathrm{TF}}_Z(y) - \varrho^{\mathrm{rHF}}_Z(y)}{|x-y|} dy \right| \leq c_{5.2a} |x|^{-4+\varepsilon_{5.2}}.$$

We do not give a proof of Theorem 5.2, since Solovej proved it for the 'full' HF case in [12]. The same proof applies for the rHF model, with minor modifications: The lack of the exchange term makes the proof easier and it is not important that a minimizing density is an orthogonal projection. These modifications can also be observed by comparison to our proof of Theorem 5.1, because we adapt the proof from [12] to the diatomic rHF model. Moreover, another proof of Theorem 5.2 has essentially been given in [23], where it is shown that for any $\delta > 0$ there exist $\alpha, D > 0$ such that $|\int_{B(0,r)^c} \varrho^{\mathrm{rHF}}_Z - 4c_{\mathrm{S}} r^{-3}| \leq \delta r^{-3}$ for any $r \in [\alpha Z^{-1/3}, D]$.[1]

1. The iterative proof

The proof in [23] proposed an astute iteration scheme but it relied on spherical symmetry and can therefore not be generalized to the diatomic case. Going beyond

[1]According to Lemma 3.6, we have $\int_{B(0,r)^c} \varrho^{\mathrm{TF}}_Z \approx 4c_S r^{-3}$, hence with Newton's theorem and the choice $\delta = (cst.) r^{\varepsilon}$, one easily deduces the claimed bound for $(cst.) Z^{-1/3} \leq r \leq D$. The case $r \leq (cst.) Z^{1/3}$ follows from Lemma 4.6 by the same arguments as we provide in Lemma 5.3.

the spherical case in [12] was a major improvement and is the main reason that we can treat the diatomic case. We will prove Theorem 5.1 by iteration of the statement

$$\mathcal{A}(r,\varepsilon,\sigma) :\Leftrightarrow \left| \int_{\mathcal{I}_r} \frac{\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|} dy \right| \le (\sigma r^{\varepsilon})\, r^{-4},\ \forall x \in \mathcal{O}_r.$$

Remarks

- A priori, the statement $\mathcal{A}(r,\varepsilon,\sigma)$ does depend on $\mathbf{Z}$ and R. The strong claim behind Theorem 5.1 is that if r and $2r/R^{1+\frac{\epsilon}{\eta-\epsilon}}$ are sufficiently small, then $\mathcal{A}(r,\varepsilon,\sigma)$ holds for all $\mathbf{Z}$ and R.
- It is no coincidence that if $\mathcal{A}$, then $V = \Phi^{\mathrm{rHF}}_{Z,R,r}\mathbb{1}_{\overline{\mathcal{O}_r}}$ satisfies the perturbation assumption of Lemmas 3.16, 3.17 and 3.18: The universality of the Sommerfeld asymptotic, or more precisely the fact that any neutral oTF potential has the second order term $(cst.)|x|^{-4-\xi}$ for large $|x|$, with a universal $\xi \approx 0.77$, is the heart of the iterative technique we will develop in Lemma 5.4.
- When we consider the Born-Oppenheimer curve in Chapter 6, it will be important that Theorem 5.1 holds up to r of order $R^{1+\frac{\delta\xi}{\eta-\delta\xi}}$, because it implies that $r^{-7+\delta\xi} = R^{-7} r^{\delta\xi}(r/R)^{-7} \approx R^{-7} R^{\frac{\delta\xi(\eta-7)}{\eta-\delta\xi}} << R^{-7}$ for small R.
- Note that

  $$\int_{\mathcal{I}_r} \frac{\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|} dy = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}(x) - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}(x)$$

  and due to Lemmas 3.7 and 3.6,

  $$c_{\mathrm{S}} r^{-4}(1 - a^{\mathrm{TF}}(r\, m_{\mathbf{Z}}^{1/3})^{-\xi}) \le \sup_{\mathcal{O}_r} \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r} \le 2^3 c_{\mathrm{S}} r^{-4}.$$

  Hence $\mathcal{A}(r,\varepsilon,\sigma)$ implies that $\sup_{\mathcal{O}_r} |\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}| \le (cst.) r^{-4}(1+\sigma r^{\varepsilon})$ and Theorem 5.1 therefore says that the diatomic screening in rHF theory is, for fixed $\mathbf{Z}$, to leading order in r the same as in TF theory.

Any iteration needs to start from somewhere.

Lemma 5.3 (The first step)**.** *Let $\boldsymbol{Z} \in \mathbb{R}^2_+$ with $|\boldsymbol{Z}| \ge 1$ Then*

$$\mathcal{A}\left(r, \frac{1}{66}, c_{5.3}\beta^{4+\frac{3}{44}}\right), \qquad \forall r \le \beta |\boldsymbol{Z}|^{-\frac{1}{3}}.$$

Proof. Let $f_p(y) = \left(\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)\right) \mathbb{1}_{B(p,r)}(y)$ and note that by (3.11),

$$\sup_{\partial\mathcal{O}_r} |(f_0 + f_{R\nu}) * |x|^{-1}| \le \sup_{\partial B(0,r)} |f_0 * |x|^{-1}| + \sup_{\partial B(R\nu,r)} |f_{R\nu} * |x|^{-1}|.$$

We minimize [12, (83)] over $\kappa > 0$ and apply it to f_p, so that

$$\sup_{\partial B(p,r)} |f_p * |x|^{-1}| \leq r^{\frac{1}{12}} 2^{\frac{29}{12}} 5^{\frac{-5}{6}} 3\pi^{\frac{1}{3}} \max\left\{\|[-f_p]_+\|_{5/3}^{\frac{5}{6}}, \|[f_p]_+\|_{5/3}^{\frac{5}{6}}\right\} (\mathcal{D}(f_p))^{\frac{1}{12}}.$$

We use Lemma 4.6 and Lemma 4.5 (it applies with $\alpha = (3/\pi^2)^{1/3} \frac{3}{5} c_{\mathrm{TF}}$) to bound the right hand side and conclude with

$$c_{5.3} := 2^{41/12} 3^{-1/3} 5^{1/6} \pi c_{\mathrm{TF}}^{-1} (c_{4.5})^{1/2} (c_{4.6a} + c_{4.6b})^{1/12}.$$

□

Next we present the iterative step, which allows us to boot strap the result of Lemma 5.3 to even larger values of r which are independent of $\mathbf{Z}$.

Lemma 5.4 (The iteration step). *There exists a universal constant $\delta_{5.4} > 0$ such that for all $\delta \in (0, \delta_{5.4}]$: If $\mathcal{A}(s, \varepsilon, \sigma)$ for some $\sigma, \varepsilon > 0$ and all $s \in (0, r]$ with*

$$\left(\tfrac{3}{2} a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}} \leq r \leq D(\sigma, \varepsilon, R) := \min\left\{1/2, c_{3.18b} R/2, (c_{3.17}/\sigma)^{\frac{1}{\varepsilon}}\right\}$$

then $\mathcal{A}(s, \delta\xi, c_{5.4})$ for all $s \in [r^{\frac{1}{1+\delta}}, \min\{r^{\frac{1-\delta}{1+\delta}}, \tilde{r}\}]$, with $\tilde{r} := c_{3.18a} r^{\frac{\xi}{\xi+\eta}} (R/2)^{\frac{\eta}{\eta+\xi}}$ and a universal constant $c_{5.4} > 0$.

Proof. Analogously to [12, Lemma 10.3], we consider the outside TF model with respect to the potential $V_r(x) = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r} \mathbb{1}_{\overline{\mathcal{O}_r}}(x)$. Let $\varrho_r = \arg\min_{\mathcal{C}(N(V_r))} \mathcal{E}^{\mathrm{TF}}_{V_r}$ and denote by $\varphi_r(x)$ the corresponding TF potential. We then write for $x \in \partial\mathcal{O}_s$ with $s \geq r$:

$$\begin{aligned}\int_{\mathcal{I}_s} \frac{\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|} dy =& \varphi_r(x) - \varphi^{\mathrm{TF}}_{\mathbf{Z},R}(x) + \int_{\mathcal{O}_s} \frac{\varrho_r(y) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y)}{|x-y|} dy \\ &+ \int_{\mathcal{I}_s \setminus \mathcal{I}_r} \frac{\varrho_r(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|} dy.\end{aligned}$$

The assumptions on r are such that we may apply Lemma 3.18 and Corollary 5.7. We therefore deduce that

$$\left| \int_{\mathcal{I}_s} \frac{\varrho^{\mathrm{TF}}_{\mathbf{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|} dy \right| \leq s^{-4} \left(c_{\mathrm{S}} c_{3.18c} \left(\frac{r}{s}\right)^{\xi} + c_{\mathrm{S}} c_{3.18d} \left(\frac{r}{s}\right)^{\xi} + c_{5.7} s^{\frac{1}{36}} \left(\frac{s}{r}\right)^{4+\frac{2}{36}} \right),$$

for all $x \in \partial\mathcal{O}_s$ and $s \in [r, \tilde{r}]$. Note that $s \in \left[r^{\frac{1}{1+\delta}}, r^{\frac{1-\delta}{1+\delta}}\right]$ is equivalent to $s^{\frac{2\delta}{1-\delta}} \leq r/s \leq s^{\delta}$ and that $r \leq r^{\frac{1}{1-\delta}}$ because $D(\sigma, \varepsilon, R) \leq 1$. Hence with

$$\tilde{\varepsilon}(\delta) := \min\left\{\delta\xi, \frac{1}{36} - \frac{2\delta}{1-\delta}\left(4 + \frac{2}{36}\right)\right\}$$

and $c_{5.4} := c_{\mathrm{S}}(c_{3.18c} + c_{3.18d}) + c_{5.7}$ we conclude

$$\mathcal{A}(s, \tilde{\varepsilon}(\delta), c_{5.4}), \qquad \forall s \in \left[r^{\frac{1}{1+\delta}}, \min\left\{r^{\frac{1-\delta}{1+\delta}}, \tilde{r}\right\}\right].$$

Choosing $\delta_{5.4} := \max\{\delta \mid \tilde{\varepsilon}(\delta) = \delta\xi\}$ finishes the proof. □

We are now in a position to prove Theorem 5.1.

Proof. The proof combines Lemma 5.3 and Lemma 5.4. It is divided in three steps. Note that Lemma 5.4 assumes $\mathcal{A}$ for $s \leq r$ and concludes $\mathcal{A}$ for $s \in \left[r^{\frac{1}{1+\delta}}, \min\{\tilde{r}, r^{\frac{1-\delta}{1+\delta}}\}\right]$, but it does not tell us whether $\mathcal{A}$ is true for $s \in (r, r^{\frac{1}{1+\delta}})$. Hence we reformulate Lemma 5.3, the starting point of the iteration procedure in the first step, such that $\mathcal{A}$ holds up to s of order $Z^{\frac{-1}{3(1+\delta)}}$. Only then can we use Lemma 5.4 to successfully iterate the statement in the second step, where one also observes that there are two conditions which limit how far we can iterate. In the last step, we define the constants and conclude.

Step 1 (Reformulating the first step)
Let $R > 0$ and (later to be fixed) $\delta > 0$. We define $\beta_{\mathbf{Z}} := (\frac{3}{2}a^{\mathrm{TF}})^{\frac{1}{\xi(1+\delta)}} m_{\mathbf{Z}}^{\frac{\delta}{3(1+\delta)}}$ which is chosen such that $r_{\mathbf{Z}} := (\beta_{\mathbf{Z}} m_{\mathbf{Z}}^{-1/3})^{1+\delta} = (\frac{3}{2}a^{\mathrm{TF}})^{\frac{1}{\xi}} m_{\mathbf{Z}}^{\frac{-1}{3}}$. Lemma 5.3 then implies $\mathcal{A}\left(r, 1/66, c_{5.3}\beta_{\mathbf{Z}}^{49/12-1/66}\right)$ for all $r \leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$. Further observe that if $\varepsilon_0 \in (0, 1/66]$ and $r \leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$:

$$\begin{aligned}
r^{-4+1/66} c_{5.3} \beta_{\mathbf{Z}}^{\frac{49}{12}-\frac{1}{66}} \leq& r^{-4+\varepsilon_0} c_{5.3} \beta_{\mathbf{Z}}^{\frac{49}{12}-\frac{1}{66}} \left(\beta_{\mathbf{Z}} m_{\mathbf{Z}}^{\frac{-1}{3}}\right)^{\frac{1}{66}-\varepsilon_0} \\
=& r^{-4+\varepsilon_0} c_{5.3} \left(\tfrac{3}{2}a^{\mathrm{TF}}\right)^{\frac{\frac{49}{12}-\varepsilon_0}{\xi(1+\delta)}} m_{\mathbf{Z}}^{\frac{1}{3}\left(\frac{\delta(\frac{49}{12}-\varepsilon_0)}{1+\delta} - (\frac{1}{66}-\varepsilon_0)\right)}.
\end{aligned}$$

To cancel the $m_{\mathbf{Z}}$-factor, we choose $\varepsilon_0(\delta) := \frac{1}{66} - \delta(\frac{49}{12} - \frac{1}{66})$ and assume from now on that $\delta < 2/537$, which is equivalent to $\varepsilon_0(\delta) > 0$. Hence $\mathcal{A}(r, \varepsilon_0(\delta), \sigma_0(\delta))$ for all $r \leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$ with $\sigma_0(\delta) := c_{5.3}\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{49/12-\varepsilon_0}{\xi(1+\delta)}}$. To ensure that the conclusion of Lemma 5.4 implies its assumptions (so that we may actually iterate), we define $\varepsilon_1(\delta) := \min\{\varepsilon_0(\delta), \delta\xi\}$ and fix $\sigma_1 := \max_{\delta \in [0, 2/537]}\{\sigma_0(\delta), c_{5.4}\}$. Hence $\sigma_0(\delta) r^{\varepsilon_0(\delta)} \leq \sigma_1 r^{\varepsilon_1(\delta)}$ for all $r \leq 1$ and

$$\forall \delta \in (0, 2/537),\ \forall \mathbf{Z} \in \mathbb{R}_+^2: \qquad \mathcal{A}\left(r, \varepsilon_1(\delta), \sigma_1\right) \forall r \leq \min\left\{1, r_{\mathbf{Z}}^{\frac{1}{1+\delta}}\right\}. \tag{5.1}$$

Step 2 (Iteration)
We define for any $R > 0$, $\mathbf{Z} \in \mathbb{R}_+^2$ and $\delta \in (0, \frac{2}{537}) \cap (0, \delta_{5.4}]$

$$M(R, \mathbf{Z}, \delta) := \sup\left\{r \in \mathbb{R}: \ \mathcal{A}(s, \varepsilon_1(\delta), \sigma_1),\ \forall s \leq r^{\frac{1}{1+\delta}}\right\}$$

and assume (for a contradiction) the existence of a triple $R, \mathbf{Z}, \delta$ (for which M is defined) and such that *both*

(A) $M < D(\sigma_1, \varepsilon_1, R)$, with D from Lemma 5.4, *and*
(B) $(M^{\frac{1}{1+\delta}}, \min\{M^{\frac{1-\delta}{1+\delta}}, \tilde{M}\}) \neq \emptyset$, with $\tilde{M} = c_{3.18a} M^{\frac{\xi}{\xi+\eta}} (R/2)^{\frac{\eta}{\eta+\xi}}$.

If $r_{\mathbf{Z}} < M$, we may take $r_n \nearrow M$ and notice that by (A), $r_{\mathbf{Z}} \leq r_n \leq D$ for n large enough. This implies $\mathcal{A}(s, \varepsilon_1, \sigma_1)$, $\forall s \in \left[r_n^{\frac{1}{1+\delta}}, \min\left\{ r_n^{\frac{1-\delta}{1+\delta}}, \tilde{r_n} \right\} \right]$ by Lemma 5.4. However, for large n, (B) implies

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

and this contradicts M being the supremum. If $r_{\mathbf{Z}} = M$, then $r_{\mathbf{Z}} \leq D \leq 1/2$ by (A) and according to (5.1), we may apply Lemma 5.4 with $r = r_{\mathbf{Z}}$ so that $\mathcal{A}(s, \varepsilon_1, \sigma_1)$, $\forall s \leq \min\{M^{\frac{1-\delta}{1+\delta}}, \tilde{M}\}$. This together with (B) again contradicts M being the supremum. Finally, if $r_{\mathbf{Z}} > M$, then we find $M' \in (M, \min\{1, r_{\mathbf{Z}}\})$ since $M < 1$ due to (A). Now (5.1) yields a contradiction. We therefore conclude that for any triple of $R, \mathbf{Z}, \delta$ for which we defined M, at least one of the two properties (A) and (B) can not hold. If (A) is true, then $M < 1$ and (B) is equivalent to $M^{\frac{1}{1+\delta}} < \tilde{M} = c_{3.18a} M^{\frac{\xi}{\eta+\xi}} (R/2)^{\frac{\eta}{\eta+\xi}}$. We therefore deduce that

$$\inf_{\mathbf{Z} \in \mathbb{R}^2_+} M(R, \mathbf{Z}, \delta) \geq \min\left\{ 1/2, (c_{3.17}/\sigma_1)^{\frac{1}{\varepsilon_1}}, c_{3.18b} R/2, c_{3.18a}^{\frac{(\eta+\xi)(1+\delta)}{\eta-\delta\xi}} (R/2)^{\frac{\eta(1+\delta)}{\eta-\delta\xi}} \right\}. \quad (5.2)$$

Step 3 (Conclusion)
Since $\delta \leq (537/2 + 66\xi)^{-1} \Leftrightarrow \varepsilon_0(\delta) \geq \delta\xi$, we choose $\delta_{5.1} := \min\{\delta_{5.4}, (537/2 + 66\xi)^{-1}\}$ so that $\varepsilon_1(\delta) = \delta\xi$ for any $\delta \in (0, \delta_{5.1}]$. Also note that as a function of $R/2$, the right hand side in (5.2) is constant for $R/2 > (cst.)$ or equals $(cst.)(R/2)^{\frac{\eta(1+\delta)}{\eta-\delta\xi}}$ for $R/2 < (cst.)$. More precisely, we infer from (5.2) that for all $R > 0$ and $\delta \in (0, \delta_{5.1}]$:[2]

$$\left(\inf_{\mathbf{Z} \in \mathbb{R}^2_+} M(R, \mathbf{Z}, \delta) \right)^{\frac{1}{1+\delta}}$$
$$\geq \min\left\{ 1/2, \left(\frac{c_{3.17}}{\sigma_1} \right)^{\frac{1}{\delta\xi(1+\delta)}}, (c_{3.18b})^{\frac{1}{1+\delta}}, c_{3.18a}^{\frac{(\eta+\xi)}{\eta-\delta\xi}} \right\} \min\left\{ 1, (R/2)^{\frac{\eta}{\eta-\delta\xi}} \right\}.$$

We now define $c_{5.1b} := \min_{\delta \in [0, \delta_{5.1}]} \left\{ 1/2, (c_{3.17}/\sigma_1)^{\frac{1}{\delta\xi(1+\delta)}}, (c_{3.18b})^{\frac{1}{1+\delta}}, c_{3.18a}^{\frac{(\eta+\xi)}{\eta-\delta\xi}} \right\} > 0$, and note that this, by definition of M, ends the proof. ☐

[2]We use that if $a, b, c, x > 0$ then $\min\{a x^{\frac{1}{1+\delta}}, b x^{\frac{1}{1-\delta\xi/\eta}}, c\} \geq \min\{a, b, c\} \min\{1, x^{\frac{1}{1-\delta\xi/\eta}}\}$. Note that this is not optimal.

2. Comparing rHF to its oTF model

Before comparing the outside part of the rHF density to the density of the outside TF model corresponding to the rHF-screened diatomic potential, we collect some simple bounds.

Lemma 5.5. *Let either $\Omega_s = \overline{B(0,s)}^c$ or $\Omega_s = \mathcal{O}_s$. Assume $V \in \mathcal{H}(\Omega_r)$ satisfies $\|V\|_\infty \le C_V r^{-4}$ and consider $\varrho_r = \arg\min_{\mathcal{C}(N(V_r))} \mathcal{E}^{\mathrm{TF}}_{V_r}$. Then, for any $\delta, \zeta > 0$, it holds that:*

a) $\int_{\Omega_r \setminus \Omega_{r+\delta}} [V_r]_+^{5/2} \le |\Omega_1^c| C_V^{5/2}((1+\delta/r)^3 - 1) r^{-7}$,

b) $\int_{\Omega_{r-\delta} \setminus \Omega_{r+\delta}} \varrho_r * g_\zeta^2 \le |\Omega_1^c| \frac{C_V^{3/2}}{c_{\mathrm{TF}}^{3/2}}((1+\delta/r)^3 - (1-\delta/r)^3) r^{-3}$,

c) $\int \varrho_r (V_r - V_r * g_\zeta^2) \le 2|\Omega_1^c| C_V^{5/2} c_{\mathrm{TF}}^{-3/2}((1+\zeta/r)^3 - 1) r^{-7}$,

d) $\int \left[\varphi_r - \varphi_r * g_\zeta^2\right]_+^{5/2} \le |\Omega_1^c| (2C_V)^{5/2}((1+\zeta/r)^3 - (1-\zeta/r)^3) r^{-7}$.

Proof. For each bound, we use $\int_\Omega f \le \|f\|_\infty |\Omega|$ and note that $|\Omega_r^c| = r^3 |\Omega_1^c|$. Then a) follows immediately from the assumptions. For b), we note that $\varrho_r * g_\zeta(x) \le \varrho_r(x)$ and by the TF equation (3.2), $\varrho_r(x) \le c_{\mathrm{TF}}^{-3/2} |V_r(x)|^{3/2} \le (C_V/c_{\mathrm{TF}})^{3/2} r^{-6}$. To prove c) and d), we first note that $V_r - V_r * g_\zeta^2$ vanishes in $(\Omega_{r-\zeta})^c$. Next, if $x \in \Omega_{r+\zeta}$, then $B(x,\zeta) \subset \Omega_r$ and the mean value property applied to $V_r(\cdot + x)$, together with g_ζ being radial and normalized, implies

$$V_r * g_\zeta^2(x) = \int_0^\zeta g_\zeta^2(t) t^2 \int_{\mathbb{S}^2} V_r(t\omega + x) d\omega dt = V_r(x).$$

Hence we conclude that $V_r - V_r * g_\zeta^2$ has support in $\overline{\Omega_{r-\zeta}} \setminus \Omega_{r+\zeta}$ and is bounded by $2C_V r^{-4}$. This, together with the TF equation, proves c). We also use this argument for d), where we in particular note that $\left[\varphi_r - \varphi_r * g_\zeta^2\right]_+ \le \left[V_r - V_r * g_\zeta^2\right]_+$ because $|x|^{-1} * g_\zeta^2 - |x|^{-1} \le 0$. $\square$

Lemma 5.6. *Let $V_r = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r} \mathbb{1}_{\overline{\mathcal{O}_r}}$ and $\varrho_r = \arg\min_{\mathcal{C}(N(V_r))} \mathcal{E}^{\mathrm{TF}}_{V_r}$. There exist constants $c_{5.6a}, c_{5.6b} > 0$ such that if*

$$\left(\frac{3}{2} a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\mathbf{Z}}^{\frac{-1}{3}} \le r \le \min\left\{\frac{1}{2}, (c_{3.17}/\sigma)^{\frac{1}{\varepsilon}}, R/4\right\}$$

and if $\mathcal{A}(t, \sigma, \varepsilon)$ for all $t \le r$, then

$$\mathcal{D}(\varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R} \mathbb{1}_{\mathcal{O}_r}) \le c_{5.6a} r^{-7+\frac{1}{3}} \tag{5.3}$$

and

$$\int_{\mathcal{O}_r} \left(\varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\right)^{5/3} \le c_{5.6b} r^{-7}. \tag{5.4}$$

Moreover, if $\omega_{\mathcal{O}}$ is from a δ-partition at radius r with $\delta \leq r^{\frac{12}{7}}$, then

$$\mathcal{E}^{\mathrm{rHF}}_{V_r}[\omega_{\mathcal{O}}\gamma^{\mathrm{rHF}}_{\mathbf{Z},R}\omega_{\mathcal{O}}] \geq \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] - c_{5.6c} r^{-7+\frac{1}{3}}. \tag{5.5}$$

Proof. All we do is rewrite the proof of [12, Lemma 12.6] for the diatomic case. Note that $\mu_r = 0$ by Lemma 3.17 and that $V_r = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}$ on the support of any $\omega_{\mathcal{O}}$. We drop the subscripts $\mathbf{Z}, R$ in this proof to simplify the notation.

Step 1 (An upper bound)

We use the second part of Lemma 4.4 with $V(x) = \varphi_r(x)$ to obtain a density matrix $\tilde{\gamma}$ with $\rho_{\tilde{\gamma}} = \varrho_r * g_\zeta^2$ and such that by (4.11),

$$\mathrm{tr}[H_{V_r}\tilde{\gamma}] + \mathcal{D}(\rho_{\tilde{\gamma}}) = \frac{3}{5}c_{\mathrm{TF}} \int \varrho_r^{5/3} - \int V_r(\varrho_r * g_\zeta^2) + \mathcal{D}(\varrho_r * g_\zeta^2) + \frac{c_H \pi^2}{\zeta^2} \int \varrho_r.$$

Newton's theorem for the radial, normalized function g_ζ implies $\mathcal{D}(\varrho_r * g_\zeta^2) \leq \mathcal{D}(\varrho_r)$, hence

$$\mathrm{tr}[H_{V_r}\tilde{\gamma}] + \mathcal{D}(\rho_{\tilde{\gamma}}) \leq \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] + \frac{c_H \pi^2}{\zeta^2} \int \varrho_r + \int \varrho_r (V_r - V_r * g_\zeta^2).$$

To bound the left hand side, we would like to use Lemma 4.9, but $\tilde{\gamma}$ is not necessarily supported on $\mathcal{O}_r$. We therefore pick a δ-partition $\{\omega_z\}$ at radius r with $\delta \in (0, r)$ and consider $\tilde{\gamma}_{\omega_{\mathcal{O}}} = \omega_{\mathcal{O}}\tilde{\gamma}\omega_{\mathcal{O}}$ which has support in $\mathcal{O}_r$. Moreover, $\mathrm{tr}[\tilde{\gamma}_{\omega_{\mathcal{O}}}] \leq \int \varrho_r \leq N(V_r) = \int_{\mathcal{O}_r} \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}$, hence $\tilde{\gamma}_{\omega_{\mathcal{O}}}$ satisfies the assumptions of Lemma 4.9. Since $\varrho_{\tilde{\gamma}} \geq \varrho_{\tilde{\gamma}_{\omega_{\mathcal{O}}}} = \varrho_{\tilde{\gamma}}\omega_{\mathcal{O}}^2$ pointwise, we have $\mathcal{D}(\varrho_{\tilde{\gamma}}) \geq \mathcal{D}(\varrho_{\tilde{\gamma}_{\omega_{\mathcal{O}}}})$. The IMS-formula (Lemma 4.7) together with the Lieb-Thirring inequality (4.2) then implies

$$\mathrm{tr}[H_{V_r}\tilde{\gamma}] \geq \mathrm{tr}[H_{V_r}\tilde{\gamma}_{\omega_{\mathcal{O}}}] - c_H^{-3/2} q L_1 \int\limits_{\mathcal{I}_{r+\delta}} [V_r]_+^{5/2} - \frac{c_H \pi^2}{2\delta^2} \int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r+\delta}} (\varrho_r * g_\zeta^2).$$

We use Lemma 4.9 and collect all the bounds we have derived so far. Then, for any $\delta \in (0, \min\{r, R/2\})$ and $\zeta \in (0, \infty)$,

$$\begin{aligned} \mathrm{tr}\left[H_{V_r}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}\right] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega_{\mathcal{O}}^2) \leq& \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] + \frac{c_H \pi^2}{\zeta^2} \int \varrho_r + \int \varrho_r (V_r - V_r * g_\zeta^2) \\ &+ c_H^{-3/2} q L_1 \int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} [V_{r-\delta}]_+^{5/2} + c_H \frac{\pi^2}{2\delta^2} \int\limits_{\mathcal{I}_{r+\delta}\setminus\mathcal{I}_{r-\delta}} \varrho^{\mathrm{rHF}} \\ &+ c_H^{-3/2} q L_1 \int\limits_{\mathcal{I}_{r+\delta}} [V_r]_+^{5/2} + \frac{c_H \pi^2}{2\delta^2} \int\limits_{\mathcal{I}_{r-\delta}\setminus\mathcal{I}_{r+\delta}} (\varrho_r * g_\zeta^2). \end{aligned} \tag{5.6}$$

Step 2 (The lower bound)

To prove a lower bound on the left hand side of (5.6), we write

$$\mathrm{tr}[H_{V_r}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega_{\mathcal{O}}^2) = \mathrm{tr}[H_{\varphi_r}\gamma^{\mathrm{rHF}}_{\omega_{\mathcal{O}}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega_{\mathcal{O}}^2 - \varrho_r) - \mathcal{D}(\varrho_r).$$

The first part of Lemma 4.4, applied to the potential $V = \varphi_r$, together with the CLR-bound (4.5) on the number of nonpositive eigenvalues of H_{φ_r} and the TF equation tell us that for any $\delta' \in (0,1), \zeta \in (0,\infty)$ and $\delta \in (0,r)$:

$$\begin{aligned}\operatorname{tr}[H_{\varphi_r}\gamma^{\mathrm{rHF}}_{\omega_\mathcal{O}}] \geq &-(1-\delta')^{-3/2}\frac{2}{5}c_{\mathrm{TF}}\int \varrho_r^{5/3} - \frac{c_{\mathrm{TF}}^{3/2}}{\sqrt{c_H}}(1-\delta')\frac{\pi^2}{\zeta^2}qL_0\int \varrho_r \\ &- (c_H\delta')^{-3/2}qL_1\left\|\left[\varphi_r - \varphi_r * g_\zeta^2\right]_+\right\|_{5/2}^{5/2}.\end{aligned}$$

And $\mathcal{D}(\varrho^{\mathrm{rHF}}\omega_\mathcal{O}^2 - \varrho_r) \geq \mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{rHF}}(\omega_\mathcal{O}^2 - \mathbb{1}_{\mathcal{O}_r}))$ simply because $\mathcal{D}(\varrho_r, \varrho^{\mathrm{rHF}}(\mathbb{1}_{\mathcal{O}_r} - \omega_\mathcal{O}^2)) \geq 0$. Moreover, $-\frac{2}{5}c_{\mathrm{TF}}\int \varrho_r^{5/3} - \mathcal{D}(\varrho_r) = \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r]$, so that for any $\delta' \in (0,1), \zeta \in (0,\infty)$ and $\delta \in (0,r)$:

$$\begin{aligned}\operatorname{tr}[H_{V_r}\gamma^{\mathrm{rHF}}_{\omega_\mathcal{O}}] + \mathcal{D}(\varrho^{\mathrm{rHF}}\omega_\mathcal{O}^2) \geq &\mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] + \mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) \\ &- \left((1-\delta')^{-3/2} - 1\right)\frac{2}{5}c_{\mathrm{TF}}\int \varrho_r^{5/3} \\ &- \frac{c_{\mathrm{TF}}}{\sqrt{c_H}}(1-\delta')\frac{\pi^2}{\zeta^2}qL_0\int \varrho_r \\ &- (c_H\delta')^{-3/2}qL_1\|[\varphi_r - \varphi_r * g_\zeta^2]_+\|_{5/2}^{5/2} \\ &- \mathcal{D}(\varrho^{\mathrm{rHF}}(\omega_\mathcal{O}^2 - \mathbb{1}_{\mathcal{O}_r})).\end{aligned} \tag{5.7}$$

Step 3 (Bounds on the error terms)
We now bound all terms on the right hand sides of (5.6) and (5.7), except for $\mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r]$ and $\mathcal{D}(\varrho^{\mathrm{rHF}}\omega_\mathcal{O}^2 - \varrho_r)$. Using that $r \leq R/4$, we have $\sup_{\mathcal{O}_t}\Phi^{\mathrm{TF}}_{\mathbf{Z},R,t} \leq 4c_{\mathrm{S}}(1 + \frac{1}{R/t-1})t^{-4} \leq \frac{16}{3}c_{\mathrm{S}}t^{-4}$ for all $t \leq r$. Hence

$$\|V_t\|_\infty \leq \left(c_{3.17} + \frac{16}{3}c_{\mathrm{S}}\right)t^{-4} =: C_1 t^{-4}, \qquad \forall t \leq r, \tag{5.8}$$

and we may use the bounds from Lemma 5.5 for $\Omega_s = \mathcal{O}_t, V = V_t$ and any $t \leq r$. Due to neutrality, Lemma 3.15 and the assumptions, we have

$$\int \varrho_t = \int_{\mathcal{O}_t}\varrho^{\mathrm{rHF}} = N(\Phi^{\mathrm{TF}}_{\mathbf{Z},R,t}) + N(V_t - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,t}) \leq (8c_{\mathrm{S}} + 3c_{3.17})\,t^{-3}, \qquad \forall t \leq r. \tag{5.9}$$

Since $\mu_r = 0$, we infer from the TF equation and Lemma 3.17 that

$$\int \varrho_r^{5/3} \leq \left(\frac{c_{\mathrm{S}}}{c_{\mathrm{TF}}}(1+A)\right)^{5/2}\frac{2^{9/2}\pi}{7}r^{-7}. \tag{5.10}$$

Let $\omega_\mathcal{O}$ be from a δ-partition at $\tilde{r} := r - \delta$, then $\int_{\mathcal{O}_r}(\varrho^{\mathrm{rHF}})^{5/3} \leq \int(\varrho^{\mathrm{rHF}}\omega_\mathcal{O}^2)^{5/3}$. To bound the right hand side, we use (4.17) for $\delta = \lambda r^2$ and $\lambda \in (0,1)$ to be chosen later. Note that indeed $\delta < \min\{\tilde{r}, R/2 - \tilde{r}\}$. Together with (5.8), (5.9) and Lemma 5.5 a) we obtain

$$\begin{aligned}
\int_{\mathcal{O}_r} \left(\varrho^{\mathrm{rHF}}\right)^{5/3} \leq & \frac{4q^{2/3}\pi^{2/3}\left|E_1^{\mathrm{TF}}\right|}{3^{1/3}c_H K_1}\left[\tilde{r}\sup_{\partial\mathcal{O}_{\tilde{r}}}\Phi^{\mathrm{rHF}}_{0+R,\tilde{r}}\right]_+^{7/3} \\
& + \frac{\pi^2 q^{2/3}}{\delta^2 K_1}\int_{\mathcal{I}_{\tilde{r}+\delta}\setminus\mathcal{I}_{\tilde{r}-\delta}}\varrho^{\mathrm{rHF}} + \frac{2L_1 q^{5/3}}{K_1 c_H^{5/2}}\int_{\mathcal{I}_{\tilde{r}+\delta}\setminus\mathcal{I}_{\tilde{r}-\delta}}[\Phi^{\mathrm{rHF}}_{0+R,\tilde{r}-\delta}]_+^{5/2} \\
\leq & \frac{4q^{2/3}\pi^{2/3}\left|E_1^{\mathrm{TF}}\right|}{3^{1/3}c_H K_1}C_1^{7/3}\left(\frac{2}{2-\lambda}\right)^7 r^{-7} \\
& + \frac{\pi^2 q^{2/3}}{K_1}\left(8c_{\mathrm{S}} + 3c_{3.17}\right)\frac{1}{\lambda^2(1-\lambda)^3}r^{-7} \\
& + \frac{2L_1 q^{5/3}}{K_1 c_H^{5/2}}\frac{2^3\pi}{3}C_1^{5/2}(1-\lambda)^{-7}\left((1-\lambda)^{-3}-1\right)r^{-7} \\
=: & C_2(\lambda) r^{-7}.
\end{aligned}$$

This proves (5.4) with $c_{5.6b} := \min\{C_2(\lambda)|0 < \lambda < 1\}$. We combine it with the Hardy-Littlewood-Sobolev and Hölder inequalities to deduce that for any $\delta \in (0, r)$:

$$\begin{aligned}
\mathcal{D}(\varrho^{\mathrm{rHF}}(\omega_{\mathcal{O}}^2 - \mathbb{1}_{\mathcal{O}_r})) \leq & c_{\mathrm{HLS}}\|\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r\setminus\mathcal{O}_{r+\delta}}\|_{6/5}^2 \\
\leq & c_{\mathrm{HLS}}\|\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r}\|_{5/3}^2|\mathcal{O}_r\setminus\mathcal{O}_{r+\delta}|^{7/15} \\
\leq & c_{\mathrm{HLS}}c_{5.6b}^{6/5}\left(\frac{8\pi}{3}\right)^{7/15}\left((1+\delta/r)^3-1\right)^{7/15} r^{-7}. \qquad (5.11)
\end{aligned}$$

Step 4 (Conclusion)
Let $\delta = r^{1+d}, \zeta = r^{1+s}$ and $\delta' = r^p$ for some $d, s \in (0,1)$ and $p \in (0,\infty)$. Note that since $r \leq 1/2$, we have $\delta, \zeta \in (0, r)$ and $\delta' \in (0,1)$. We use this choice of δ, ζ, δ' in (5.6) and (5.7), together with (5.8) - (5.11) and Lemma 5.5. Since $((1+t^a)^3-1) \leq 2^a((1+2^{-a})^3-1)t^a$ for any $t \in [0,1/2], a > 0$, we obtain the lower bound

$$\begin{aligned}
&\mathcal{E}^{\mathrm{rHF}}_{V_r}[\omega_{\mathcal{O}}\gamma^{\mathrm{rHF}}_{\mathbf{Z},R}\omega_{\mathcal{O}}] \geq \\
&\qquad \mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) + \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] - C_2(p,s,d)r^{-7}\left(r^p + r^{2(1-s)} + r^{s-\frac{3}{2}p} + r^{\frac{7}{15}d}\right)
\end{aligned}$$

and the upper bound

$$\mathcal{E}^{\mathrm{rHF}}_{V_r}[\omega_{\mathcal{O}}\gamma^{\mathrm{rHF}}_{\mathbf{Z},R}\omega_{\mathcal{O}}] \leq \mathcal{E}^{\mathrm{TF}}_{V_r}[\varrho_r] + C_3(s,d)r^{-7}\left(r^d + r^s + r^{2(1-s)} + r^{2(1-d)}\right).$$

Note that the left hand side in both bounds depends on d via the smooth cutoff $\omega_{\mathcal{O}}$. Optimizing these bounds in $d, s \in (0,1)$ and $p \in (0,\infty)$ proves (5.3) and (5.5).
□

Corollary 5.7. *Let* $V_r = \Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}\mathbb{1}_{\overline{\mathcal{O}_r}}$ *and* $\varrho_r = \arg\min_{\mathcal{C}(N(V_r))} \mathcal{E}^{\mathrm{TF}}_{V_r}$*. There exists a constant* $c_{5.7} > 0$ *such that if*

$$\left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}} \leq r \leq \min\left\{\frac{1}{2}, (c_{3.17}/\sigma)^{\frac{1}{\varepsilon}}, R/4\right\}$$

and if $\mathcal{A}(t,\sigma,\varepsilon)$ *for all* $t \leq r$*, then for any* $s \in [r, R/2)$ *:*

$$\sup_{x\in\partial\mathcal{O}_s}\left|\int_{\mathcal{I}_s\setminus\mathcal{I}_r} \frac{\varrho_r(y)-\varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|}dy\right| \leq c_{5.7} r^{-4+\frac{1}{36}}\left(\frac{s}{r}\right)^{1/12}.$$

Proof. We assume that $|x| = s$ and apply [12, Cor. 9.3] twice, first with $f = \varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}$ and then with $f = \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r} - \varrho_r$. After optimizing in the free parameter κ of [12, Cor. 9.3], we obtain

$$|\varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}|\mathbb{1}_{B(0,s)} * |x|^{-1} \leq 2^{29/12}5^{-5/6}3\pi^{1/3}s^{1/12}m^{5/6}\left(\mathcal{D}(\varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r})\right)^{1/12}$$

with $m = \max\{\|\varrho_r\|_{5/3}, \|\varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}\|_{5/3}\}$. According to (5.10) and (5.4), we have

$$m^{5/6} \leq \max\left\{\sqrt{c_{5.6b}}, \frac{2^{9/4}\pi^{1/2}}{\sqrt{7}}\left(\frac{c_{\mathrm{S}}}{c_{\mathrm{TF}}}(1+A)\right)^{5/4}\right\} r^{-7/2} =: C_1 r^{-7/2}.$$

With this bound and (5.3) we find $|\varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}|\mathbb{1}_{B(0,s)} * |x|^{-1} \leq \frac{1}{2}c_{5.7}r^{-4+\frac{1}{36}}\left(\frac{s}{r}\right)^{1/12}$ for any $|x| = s$ and $c_{5.7} := 2^{\frac{41}{12}}5^{-5/6}3\pi^{\frac{1}{3}}C_1 c_{5.6a}^{\frac{1}{12}}$. The same proof applies for $|x - R\nu| = s$. Since

$$\sup_{\partial\mathcal{O}_s}\left|\int_{\mathcal{I}_s\setminus\mathcal{I}_r} \frac{\varrho_r(y)-\varrho^{\mathrm{rHF}}_{\mathbf{Z},R}(y)}{|x-y|}dy\right| \leq \sum_{p\in\{0,R\nu\}} \sup_{\partial B(p,s)} |\varrho_r - \varrho^{\mathrm{rHF}}_{\mathbf{Z},R}\mathbb{1}_{\mathcal{O}_r}|\mathbb{1}_{B(p,s)} * |x|^{-1},$$

this completes the proof. $\square$

CHAPTER 6

The Born-Oppenheimer curve in rHF theory

We now turn our attention to our main result about the asymptotic of

$$D_{\mathbf{Z},R}^{\mathrm{rHF}} := E_{\mathbf{Z},R}^{\mathrm{rHF}} - E_{Z_1}^{\mathrm{rHF}} - E_{Z_2}^{\mathrm{rHF}} + \frac{Z_1 Z_2}{R},$$

the Born-Oppenheimer curve in reduced Hartree-Fock theory.

Theorem 6.1. *There exists $\varepsilon_{6.1} > 0$ and an increasing $\theta : \mathbb{R}_+ \to \mathbb{R}_+$ such that for all $R \in (0,2]$ and all $\boldsymbol{Z} \in \mathbb{R}_+^2$ with $|\boldsymbol{Z}| \geq 1$:*

$$\left| D_{\boldsymbol{Z},R}^{\mathrm{TF}} - D_{\boldsymbol{Z},R}^{\mathrm{rHF}} \right| \leq \theta\left(\frac{\max\{Z_1, Z_2\}}{m_{\boldsymbol{Z}}} \right) R^{-7+\varepsilon_{6.1}}.$$

We give the proof on page 75. It is by upper and lower bounds, choosing appropriate trial states for the atomic and diatomic rHF energies. Since $D_{\mathbf{Z},R}^{\mathrm{TF}}$ can be determined from oTF models (Lemma 3.22), we compare $D_{\mathbf{Z},R}^{\mathrm{rHF}}$ to such oTF models. 'Appropriate' therefore means we try to cancel those terms in the rHF functional, that correspond to the regions close to the nuclei (the inside $\mathcal{I}_r$ for some r). This approach leads to rHF functionals with respect to four different screened potentials.

Definition 6.2 (The rHF screenings)**.** For $p \in \{0, R\nu\}$ and $r > 0$ we define

$$V_r^{(1,p)}(x) := \left(\frac{Z_p}{|x-p|} - \int_{B(p,r)} \frac{\varrho_{\mathbf{Z},R}^{\mathrm{rHF}}(y)}{|x-y|} dy \right) \mathbb{1}_{B(p,r)^c}(x)$$

and

$$V_r^{(2,p)}(x) := \left(\frac{Z_p}{|x-p|} - \int_{B(p,r)} \frac{\varrho_{Z_p}^{\mathrm{rHF}}(y-p)}{|x-y|} dy \right) \mathbb{1}_{B(p,r)^c}(x).$$

For $r \in (0, R/2)$ we define

$$V_r^{(3)}(x) := \left(V_r^{(1,0)}(x) + V_r^{(1,R\nu)}(x) \right) \mathbb{1}_{\overline{\mathcal{O}_r}}(x)$$

and

$$V_r^{(4)}(x) := \left(V_r^{(2,0)}(x) + V_r^{(2,R\nu)}(x) \right) \mathbb{1}_{\overline{\mathcal{O}_r}}(x).$$

By construction, we have $V_r^{(1,p)}, V_r^{(2,p)} \in \mathcal{H}(\overline{B(p,r)}^c)$ and $V_r^{(3)}, V_r^{(4)} \in \mathcal{H}(\mathcal{O}_r)$. We use Theorem 3.2 to define the corresponding TF minimizers

$$\varrho_r^{(j,p)} := \arg \min_{\mathcal{C}(V_r^{(j,p)})} \mathcal{E}^{\mathrm{TF}}_{V_r^{(j,p)}}, \qquad j \in \{1,2\},\ p \in \{0, R\nu\},$$

and

$$\varrho_r^{(j)} := \arg \min_{\mathcal{C}(V_r^{(j)})} \mathcal{E}^{\mathrm{TF}}_{V_r^{(j)}}, \qquad j \in \{3,4\}.$$

Furthermore, let $E_r^{(j,p)}, E_r^{(j)}$ denote the minimum values; $\varphi_r^{(j,p)}, \varphi_r^{(j)}$ the TF potentials and $\mu_r^{(j,p)}, \mu_r^{(j)}$ the chemical potentials of the corresponding minimization problems. With the tools developed in Chapter 3, we find that the latter actually vanish, provided r is chosen sufficiently small:

Lemma 6.3. *(Controlling the outside models) Let $\boldsymbol{Z} \in \mathbb{N}^2$ with $|\boldsymbol{Z}| \geq 1$. Assume that $2 \geq R \geq 2\left(a^{\mathrm{TF}}\tilde{\xi}/\tilde{\eta}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ and $r := c_{6.3b}(R/2)^{1+\frac{\varepsilon}{\eta-\varepsilon}} \geq \left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ with $\varepsilon \in (0, \delta_{5.1}\xi]$. Then for all $s \leq r$ and $p \in \{0, R\nu\}$:*

i) $\sup_{B(p,s)^c} \left| \left(\varrho^{\mathrm{rHF}}_{\mathbf{Z},R} - \varrho^{\mathrm{TF}}_{Z_p}(\cdot - p)\right) \mathbb{1}_{B(p,s)} * |x|^{-1} \right| \leq c_{6.3a} s^{-4+\varepsilon\frac{4}{\eta}} + \frac{3}{2} c_{5.1a} s^{-4+\varepsilon}$

ii) $\sup_{B(0,s)^c} \left| \left(\varrho^{\mathrm{rHF}}_{Z_p} - \varrho^{\mathrm{TF}}_{Z_p}\right) \mathbb{1}_{B(0,s)} * |x|^{-1} \right| \leq c_{5.2a} s^{-4+\varepsilon_{5.2}}$

iii) $\sup_{\mathcal{O}_s} \left| \left(\varrho^{\mathrm{rHF}}_{\mathbf{Z},R} - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right) \mathbb{1}_{\mathcal{I}_s} * |x|^{-1} \right| \leq c_{5.1a} s^{-4+\varepsilon}$

iv) $\sup_{\mathcal{O}_s} \left| \sum_p \left(\varrho^{\mathrm{rHF}}_{Z_p}(\cdot - p) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right) \mathbb{1}_{B(p,s)} * |x|^{-1} \right| \leq 2c_{6.3a} s^{-4+4\frac{\varepsilon}{\eta}} + 2c_{5.2a} s^{-4+\varepsilon_{5.2}}.$

Furthermore (under the same assumptions),

v) $\mu_r^{(j,p)} = 0$ *and* $\int \varrho_r^{(j,p)} \leq c_{3.14a} r^{-3}$ *for* $j \in \{1,2\},\ p \in \{0, R\nu\}$,

vi) $\mu_r^{(j)} = 0$ *and* $\int \varrho_r^{(j)} \leq 2^{7/2}(1+A)^{3/2} c_{\mathrm{S}} r^{-3}$ *for* $j \in \{3,4\}$.

Proof. We will choose $c_{6.3b} \leq \min\{c_{5.1b}, c_{5.2b}\}$ and recall that $c_{5.1b} \leq 1/2$. Then ii) and iii) follow from Theorem 5.1 and Theorem 5.2. For i) and iv), we first note that since $s \leq r \Leftrightarrow (2s/R)^\eta \leq c_{6.3b}^{\eta-\varepsilon} s^\varepsilon$, Lemma 3.8 implies

$$\sup_{B(p,s)^c} \left| \left(\varrho^{\mathrm{TF}}_{Z_p}(\cdot - p) - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right) \mathbb{1}_{B(p,s)} * |x|^{-1} \right| \leq c_{6.3a} s^{-4+\varepsilon 4/\eta},\ p \in \{0, R\nu\}, \tag{6.1}$$

where $c_{6.3a} := \min_{\varepsilon \in (0,\delta_{5.1}\xi)} \left(c_{3.8b} \left(\frac{\tilde{\eta}}{2^\xi a^{\mathrm{TF}} \tilde{\xi}}\right)^{\tilde{\eta}} \left(c_{6.3b}^{1-\varepsilon/\eta}/2\right)^4 + c_{3.8c} c_{6.3b}^{\eta+1-\varepsilon(1+4/\eta)} \right)$. Next, we combine Lemma 3.15 for $u_p(x) = \left(\varrho^{\mathrm{rHF}}_{\mathbf{Z},R} - \varrho^{\mathrm{TF}}_{\mathbf{Z},R}\right) \mathbb{1}_{B(p,s)} * |x|^{-1}$ together with iii):

$$\sup_{B(p,s)^c} |u_p| \leq \frac{R-s}{R-2s} c_{5.1a} s^{-4+\varepsilon} \leq \frac{3}{2} c_{5.1a} s^{-4+\varepsilon}. \tag{6.2}$$

The triangle inequality, (6.1) and (6.2) prove i). Statement iv) follows by the triangle inequality from (6.1) and ii). Let us further choose[1]

$$c_{6.3b} \leq \min \left\{ 1, \left(\frac{c_{3.14b}}{c_{6.3a} + 3/2 c_{5.1a}} \right)^{\frac{\eta}{4\delta_{5.1}\xi}}, \left(\frac{c_{3.14b}}{c_{5.2a}} \right)^{\frac{1}{\varepsilon_{5.2}}} \right\}. \tag{6.3}$$

This means that due to i) and ii), the assumptions of Lemma 3.14 are satisfied for $V_r^{(1,p)}$ and $V_r^{(2,p)}$, which proves v). Similar, we also choose

$$c_{6.3b} \leq \min \left\{ 1, \left(\frac{c_{3.17}}{c_{5.1a}} \right)^{\frac{1}{\delta_{5.1}\xi}}, \left(\frac{c_{3.17}}{2c_{6.3a} + 2c_{5.2a}} \right)^{\max\{\frac{\eta}{4\delta_{5.1}\xi}, \frac{1}{\varepsilon_{5.2}}\}} \right\} \tag{6.4}$$

so vi) is a consequence of iii), iv) and Lemma 3.17 for the potentials $V_r^{(3)}$ and $V_r^{(4)}$. □

Lemma 6.3 tells us that the assumptions of Lemma 3.22 are satisfied for the potentials of Definition 6.2. The next result establishes the analogue of Lemma 3.22 for the Born-Oppenheimer potential in rHF theory.

Lemma 6.4 ($D_{\mathbf{Z},R}^{\mathrm{rHF}}$ is determined by oTF models)**.** *Let $\boldsymbol{Z} \in \mathbb{N}^2$ with $|\boldsymbol{Z}| \geq 1$. Assume that $2 \geq R \geq 2 \left(a^{\mathrm{TF}} \tilde{\xi} / \tilde{\eta} \right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ and $r = c_{6.3b} (R/2)^{1+\frac{\varepsilon}{\eta - \varepsilon}} \geq \left(\frac{3}{2} a^{\mathrm{TF}} \right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ with $\varepsilon \in (0, \delta_{5.1}\xi]$. Then*

$$E_r^{(3)} - E_r^{(1,0)} - E_r^{(1,R\nu)} + \mathcal{Q}[V_r^{(1,0)}, V_r^{(1,R\nu)}] - (cst.) r^{-7+\frac{1}{3}} \leq D_{\mathbf{Z},R}^{\mathrm{rHF}} \tag{6.5}$$

and

$$E_r^{(4)} - E_r^{(2,0)} - E_r^{(2,R\nu)} + \mathcal{Q}[V_r^{(2,0)}, V_r^{(2,R\nu)}] + (cst.) r^{-7+\frac{1}{3}} \geq D_{\mathbf{Z},R}^{\mathrm{rHF}}. \tag{6.6}$$

Proof. **Step 1** (Proof of (6.5))
Let $\{\omega_z\}$ be a δ-partition at $r < R/2$ with $\delta \in (0, \min\{r, R/2 - r\})$. We consider, for $p \in \{0, R\nu\}$, any $\tilde{\gamma}_p \in \mathcal{DM}_q$ with $\mathrm{tr}[\tilde{\gamma}_p] \leq Z_p - \int_{B(p,r)} \varrho_{\mathbf{Z},R}^{\mathrm{rHF}} = N(V_r^{(1,p)})$ and $\mathrm{supp}\, \rho_{\tilde{\gamma}_p} \subset B(p,r)^c$. Then $\omega_p \gamma_{\mathbf{Z},R}^{\mathrm{rHF}} \omega_p + \tilde{\gamma}_p$ is a trial state for the rHF minimization problem with potential $Z_p/|x-p|$. Together with Lemma 4.9 we find

$$\begin{aligned} D_{\mathbf{Z},R}^{\mathrm{rHF}} \geq & \mathcal{E}_{V_r^{(3)}}^{\mathrm{rHF}} [\omega_{\mathcal{O}} \gamma_{\mathbf{Z},R}^{\mathrm{rHF}} \omega_{\mathcal{O}}] - \sum_{p \in \{0, R\nu\}} \mathcal{E}_{V_r^{(1,p)}}^{\mathrm{rHF}} [\tilde{\gamma}_p] + \mathcal{Q}[V_r^{(1,0)}, V_r^{(1,R\nu)}] \\ & - c_H^{-3/2} q L_1 \int\limits_{\mathcal{I}_{r+\delta}} \left[V_{r-\delta}^{(3)} \right]_+^{5/2} - c_H \frac{\pi^2}{2\delta^2} \int\limits_{\mathcal{I}_{r+\delta} \setminus \mathcal{I}_{r-\delta}} \varrho_{\mathbf{Z},R}^{\mathrm{rHF}}. \end{aligned} \tag{6.7}$$

Note that $V_r^{(3)}$ equals V_r from Lemma 5.6. We pick $\delta = r^{4/3}$ in (6.7), and use (5.9), Lemma 5.5 a) and $r \leq 1/2$ to bound the last line in (6.7) by $(cst.) r^{-7+1/3}$. Since

[1] This is not optimal, we could use $r \leq c_{6.3b}$ instead of $r \leq 1$.

$r^{4/3} \le r^{12/7}$, we may apply (5.5) to bound $\mathcal{E}^{\mathrm{rHF}}_{V_r^{(3)}}[\omega_{\mathcal{O}}\gamma^{\mathrm{rHF}}_{\mathbf{Z},R}\omega_{\mathcal{O}}]$ from below and arrive at:

$$D^{\mathrm{rHF}}_{\mathbf{Z},R} \ge E_r^{(3)} - \sum_{p\in\{0,R\nu\}} \mathcal{E}^{\mathrm{rHF}}_{V_r^{(1,p)}}[\tilde{\gamma}_p] + \mathcal{Q}[V_r^{(1,0)}, V_r^{(1,R\nu)}] - (cst.)r^{-7+1/3}, \tag{6.8}$$

for *any* $\tilde{\gamma}_p \in \mathcal{DM}_q$ with support in $B(p,r)^c$ and such that $\mathrm{tr}[\tilde{\gamma}_p] \le N(V_r^{(1,p)})$. We now construct appropriate $\tilde{\gamma}_p$ to bound $\mathcal{E}^{\mathrm{rHF}}_{V_r^{(1,p)}}[\tilde{\gamma}_p]$ from above by $E_r^{(1,p)}$. Without loss of generality, we only give the details for $p = 0$. With $\zeta \in (0,\infty)$, let γ be given by Lemma 4.4 for $V = \varphi_r^{(1,0)}$ and let ω_z be a δ-partition at radius r. We set $\omega_{\bar{0}} := \sqrt{1-\omega_0^2-\omega_{\tilde{0}}^2}$ and choose $\tilde{\gamma}_0 := \omega_{\bar{0}}\gamma\omega_{\bar{0}}$ as a trial state in $\mathcal{E}^{\mathrm{rHF}}_{V_r^{(1,0)}}$. We then combine the IMS-formula (Lemma 4.7) with (4.11), so that

$$\begin{aligned}\mathrm{tr}[-c_H\Delta\tilde{\gamma}_0] \le \mathrm{tr}\left[c_H\Delta\sqrt{\omega_0^2+\omega_{\tilde{0}}^2}\gamma\sqrt{\omega_0^2+\omega_{\tilde{0}}^2}\right] + c_H\frac{\pi^2}{2\delta^2}\,\mathrm{tr}[\gamma] \\ +\frac{3}{5}c_{\mathrm{TF}}\int(\varrho_r^{(1,0)})^{5/3} + c_H\frac{\pi^2}{\zeta^2}\int \varrho_r^{(1,0)}.\end{aligned}$$

We use the Lieb-Thirring inequality (4.2) with $V = \left[V_r^{(1,0)}\right]_+ \mathbb{1}_{B(0,r+\delta)}$ to bound

$$\begin{aligned}\mathrm{tr}\left[c_H\Delta\sqrt{\omega_0^2+\omega_{\tilde{0}}^2}\gamma\sqrt{\omega_0^2+\omega_{\tilde{0}}^2}\right] \le & c_H^{-3/2}qL_1\int_{B(0,r+\delta)}\left[V_r^{(1,0)}\right]_+^{5/2} \\ & - \int_{B(0,r+\delta)}\left[V_r^{(1,0)}\right]_+\rho_\gamma(1-\omega_{\tilde{0}}^2).\end{aligned}$$

Further note that $\rho_{\tilde{\gamma}_0} \le \rho_\gamma = (\varrho_r^{(1,0)} * g_\zeta^2)$, hence $\mathcal{D}(\rho_{\tilde{\gamma}_0}) \le \mathcal{D}(\varrho_r^{(1,0)})$ by Newton's Theorem and $\mathrm{tr}[\tilde{\gamma}_0] \le \mathrm{tr}[\gamma] = \int \varrho_r^{(1,0)} = N(V_r^{(1,p)})$. Here the last equality is due to $\mu_r^{(1,0)} = 0$. All together, we arrive at

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}_{V_r^{(1,0)}}[\tilde{\gamma}_0] \le & E_r^{(1,0)} + \left(\frac{c_H\pi^2}{2\delta^2} + \frac{c_H\pi^2}{\zeta^2}\right)\int\varrho_r^{(1,0)} \\ & + c_H^{-3/2}qL_1\int_{B(0,r+\delta)}\left[V_r^{(1,0)}\right]_+^{5/2} \\ & + \int V_r^{(1,0)}\left(\varrho_r^{(1,0)} - \varrho_r^{(1,0)} * g_\zeta^2\right),\end{aligned} \tag{6.9}$$

for any $\zeta \in (0,\infty)$, $\delta \in (0, \min\{r, R/2-r\})$. Since $\|\Phi^{\mathrm{TF}}_{Z_p,t}\mathbb{1}_{B(0,t)^c}\|_\infty \le 4c_{\mathrm{S}}t^{-4}$ for all $t > 0$, Lemma 6.3 i) implies

$$\|V_t^{(1,p)}\|_\infty \le (cst.)t^{-4}, \qquad \forall t \le r \tag{6.10}$$

We may therefore use Lemma 5.5 for $V = V_t^{(1,0)}$ to bound the terms on the right hand side of (6.9). We also use Lemma 6.3 v) in the first line of (6.9) and choose

$\delta = \zeta = r^{4/3}$, so that $\mathcal{E}^{\mathrm{rHF}}_{V_r^{(1,0)}}[\tilde{\gamma}_0] \leq E_r^{(1,0)} - (cst.) r^{-7+\frac{1}{3}}$. Repeating these arguments for $p = R\nu$ and revisiting (6.8) proves (6.5).

Step 2 (Proof of (6.6))

We begin with a lower bound on the atomic rHF energies. Let $\{\omega_z\}$ be any δ-partition at radius r (with $\delta \in (0, \min\{r, R/2 - r\})$) and $\omega_{\overline{0}} = \sqrt{1 - \omega_0^2 - \omega_{\tilde{0}}^2}$. The support properties of $\{\omega_z\}$ and $\mathcal{D}$ being nonnegative imply

$$\begin{aligned}\mathcal{D}(\varrho_{Z_0}) \geq & \mathcal{D}(\varrho^{\mathrm{rHF}}_{Z_0}\omega_0^2) + \mathcal{D}(\varrho^{\mathrm{rHF}}_{Z_0}\omega_{\overline{0}}^2) + \int \varrho^{\mathrm{rHF}}_{Z_0}\omega_{\overline{0}}^2(x) \int_{B(0,r)} \frac{\varrho^{\mathrm{rHF}}_{Z_0}(y)}{|x-y|} dy dx \\ & + \int \varrho^{\mathrm{rHF}}_{Z_0}\omega_{\tilde{0}}^2(x) \int_{B(0,r-\delta)} \frac{\varrho^{\mathrm{rHF}}_{Z_0}(y)}{|x-y|} dy dx.\end{aligned}$$

From this bound and the IMS-formula (Lemma 4.7) we infer

$$\begin{aligned}E^{\mathrm{rHF}}_{Z_0} \geq & \mathcal{E}^{\mathrm{rHF}}_{Z_0/|x|}[\omega_0\gamma^{\mathrm{rHF}}_{Z_0}\omega_0] + \mathcal{E}^{\mathrm{rHF}}_{V_r^{(2,p)}}[\omega_{\overline{0}}\gamma^{\mathrm{rHF}}_{Z_0}\omega_{\overline{0}}] - c_H\frac{\pi^2}{2\delta^2}\int_{B(0,r+\delta)\setminus B(0,r-\delta)} \varrho^{\mathrm{rHF}}_{Z_0} \\ & + \mathrm{tr}[-c_H\Delta\omega_{\tilde{0}}\gamma^{\mathrm{rHF}}_{Z_0}\omega_{\tilde{0}}] - \int \varrho^{\mathrm{rHF}}_{Z_0}\omega_{\tilde{0}}^2 V^{(2,0)}_{r-\delta},\end{aligned}$$

where the last line is bounded from below by $-c_H^{3/2} q L_1 \int_{B(0,r+\delta)} [V^{(2,0)}_{r-\delta}]_+^{5/2}$ due to the Lieb-Thirring inequality (4.2) and as usual, we have an analogous lower bound on $E^{\mathrm{rHF}}_{Z_{R\nu}}$. For an upper bound on the diatomic rHF energy, we consider the trial state $\omega_0\gamma^{\mathrm{rHF}}_{Z_0}\omega_0 + \omega_{R\nu}\gamma^{\mathrm{rHF}}_{Z_{R\nu}}\omega_{R\nu} + \tilde{\gamma}$. Here $\tilde{\gamma} \in \mathcal{DM}_q$ has to satisfy $\mathrm{tr}[\tilde{\gamma}] \leq \int_{B(0,r)^c} \left(\varrho^{\mathrm{rHF}}_{Z_0} + \varrho^{\mathrm{rHF}}_{Z_{R\nu}}\right) = N(V_r^{(4)})$ and $\mathrm{supp}\,\rho_{\tilde{\gamma}} \subset \mathcal{O}_r$. All together we obtain

$$\begin{aligned}D^{\mathrm{rHF}}_{\mathbf{Z},R} \leq & \mathcal{E}^{\mathrm{rHF}}_{V_r^{(4)}}[\tilde{\gamma}] - \sum_{p\in\{0,R\nu\}} \mathcal{E}^{\mathrm{rHF}}_{V_r^{(2,p)}}[\omega_{\overline{p}}\gamma^{\mathrm{rHF}}_{Z_p}\omega_{\overline{p}}] + \mathcal{Q}[V_r^{(2,0)}, V_r^{(2,R\nu)}] \\ & + \sum_{p\in\{0,R\nu\}} c_H^{-3/2} q L_1 \int_{B(p,r+\delta)} \left[V^{(2,p)}_{r-\delta}\right]_+^{5/2} + \frac{c_H\pi^2}{2\delta^2}\int_{B(0,r+\delta)\setminus B(0,r-\delta)} \left(\varrho^{\mathrm{rHF}}_{Z_0} + \varrho^{\mathrm{rHF}}_{Z_{R\nu}}\right),\end{aligned} \tag{6.11}$$

We bound $\mathcal{E}^{\mathrm{rHF}}_{V_r^{(2,p)}}[\omega_{\overline{p}}\gamma^{\mathrm{rHF}}_{Z_p}\omega_{\overline{p}}]$ (uniformly in δ) from below. For any $\gamma \in \mathcal{DM}_q$ with $\mathrm{supp}\,\rho_\gamma \subset B(p,r)^c$, we write

$$\mathcal{E}^{\mathrm{rHF}}_{V_r^{(2,p)}}[\gamma] = \mathrm{tr}[(-c_H\Delta - \varphi_r^{(2,p)})\gamma] - 2\mathcal{D}(\varrho_r^{(2,p)}, \rho_\gamma) + \mathcal{D}(\rho_\gamma).$$

The CLR-bound (4.5), (4.10) for $V = \varphi_r^{(2,p)}$ and the TF equation for $\varphi_r^{(2,p)}$ then imply that for any $\delta' \in (0,1), \zeta \in (0,\infty)$,

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}_{V_r^{(2,p)}}[\gamma] \geq & E_r^{(2,p)} + \mathcal{D}(\varrho_r^{(2,p)} - \rho_\gamma) \\ & - c_H^{-1/2}(1-\delta')\frac{\pi^2}{\zeta^2} q L_0 c_{\mathrm{TF}}^{3/2} \int \varrho_r^{(2,p)} \\ & - (c_H \delta')^{-3/2} q L_1 \left\| \left[\varphi_r^{(2,p)} - \varphi_r^{(2,p)} * g_\zeta^2\right]_+ \right\|_{5/2}^{5/2} \\ & - ((1-\delta')^{-3/2} - 1)\frac{2}{5} c_{\mathrm{TF}} \int (\varrho_r^{(2,p)})^{5/3}. \end{aligned} \tag{6.12}$$

Next, we bound last three lines in (6.12) and the last line in (6.11). As before we note that $\|\Phi^{\mathrm{TF}}_{Z_0,t} \mathbb{1}_{B(0,t)^c}\|_\infty \leq 4 c_{\mathrm{S}} t^{-4}$ together with Lemma 6.3 ii) implies

$$\|V_t^{(2,p)}\|_\infty \leq (cst.) t^{-4}, \qquad \forall t \leq r, \tag{6.13}$$

so that we may use Lemma 5.5 for $V = V_t^{(2,p)}$. Moreover, (6.13) and $r \leq 1/2$ imply $\int_{B(0,r+\delta)} [V_{r-\delta}^{(2,p)}]_+^{5/2} \leq (cst.) r^{-7}(\delta/r)$ as well as $c_{\mathrm{TF}} \int (\varrho_r^{(2,p)})^{5/3} \leq \int \varrho_r^{(2,p)} V_r^{(2,p)} \leq (cst.) r^{-7}$, where we used the TF equation and Lemma 6.3 v). We combine Lemma 6.3 ii) and Lemma 3.14 to deduce that

$$\int\limits_{B(0,r+\delta)\setminus B(0,r-\delta)} \varrho^{\mathrm{rHF}}_{Z_p} \leq \int\limits_{B(0,r-\delta)^c} \varrho^{\mathrm{rHF}}_{Z_p} = N(V_{r-\delta}^{(2,p)}) \leq (cst.)(r-\delta)^{-3}.$$

All together, we choose $\delta = r^{5/3}$, $\zeta = r^{11/6}$, $\delta' = r^{1/3}$ and conclude the last two terms in (6.11) are bounded by $(cst.) r^{-7+\frac{2}{3}}$ whereas the last three terms of (6.12) are bounded from below by $-(cst.) r^{-7+\frac{1}{3}}$. We have therefore derived that

$$D^{\mathrm{rHF}}_{\mathbf{Z},R} \leq \mathcal{E}^{\mathrm{rHF}}_{V_r^{(4)}}[\tilde{\gamma}] - \sum_{p \in \{0, R\nu\}} E_r^{(2,p)} + \mathcal{Q}[V_r^{(2,0)}, V_r^{(2,R\nu)}] + (cst.) r^{-7+\frac{1}{3}} \tag{6.14}$$

for any $\tilde{\gamma} \in \mathcal{DM}_q$ with $\operatorname{supp} \rho_{\tilde{\gamma}} \in \mathcal{O}_r$ and $\operatorname{tr}[\tilde{\gamma}] \leq N(V_r^{(4)})$. Let $\{\omega_z\}$ be a δ-partition at radius r (as usual, $\delta \in (0, \min\{r, R/2 - r\})$ but may possibly be different than before) and let γ be the density matrix from Lemma 4.4 for the potential $V = \varphi_r^{(4)}$, i.e. such that $\rho_\gamma = \varrho_r^{(4)} * g_\zeta^2$, with $\zeta \in (0,\infty)$ and also (4.11) holds. We now choose $\tilde{\gamma} = \omega_{\mathcal{O}} \gamma \omega_{\mathcal{O}}$ in (6.14) and proceed as usual: Combining the Thomas-Fermi equation for $\varphi_r^{(4)}$, the IMS-formula, the Lieb-Thirring inequality and (4.11) we derive the upper bound

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}_{V_r^{(4)}}[\tilde{\gamma}] \leq & E_r^{(4)} + \int \varrho_r^{(4)} \left(V_r^{(4)} - V_r^{(4)} * g_\zeta^2\right) + c_H^{-3/2} q L_1 \int_{\mathcal{I}_{r+\delta}} \left[V_r^{(4)}\right]_+^{5/2} \\ & + c_H \frac{\pi^2}{\zeta^2} \int \varrho_r^{(4)} + c_H \frac{\pi^2}{2\delta^2} \int_{\mathcal{I}_{r+\delta} \setminus \mathcal{I}_{r-\delta}} \varrho_r^{(4)} * g_\zeta^2. \end{aligned} \tag{6.15}$$

According to (6.13), $\|V_r^{(4)}\|_\infty \leq (cst.)t^{-4}, \forall t \leq r$. Lemma 5.5 for $V = V_t^{(4)}$ and Lemma 6.3 vi), together with the choice $\delta = \zeta = r^{5/3}$, then imply that the terms on the right hand side of (6.15) can be bounded such that

$$\mathcal{E}^{\mathrm{rHF}}_{V_r^{(4)}}[\tilde{\gamma}] \leq E_r^{(4)} + (cst.)r^{-7+\frac{2}{3}}.$$

Plugging this bound into (6.14) proves (6.6). □

We are now ready to prove Theorem 5.1 by a combination of Lemma 6.3, Lemma 6.4 and Lemma 3.22.

Proof of Theorem 6.1.

Let $\varepsilon_0 := \min\left\{\varepsilon_{5.2}, \delta_{5.1}\xi, \frac{1}{3}\right\}$. We choose $r = c_{6.3b}(R/2)^{1+\frac{\varepsilon_0}{\eta-\varepsilon_0}}$ and assume that $2 \geq R \geq Cm_{\mathbf{Z}}^{-\frac{1}{3}}$ with $C = 2\max\left\{(a^{\mathrm{TF}}\tilde{\xi}/\tilde{\eta})^{\frac{1}{\xi}}, ((a^{\mathrm{TF}}3/2)^{\frac{1}{\xi}}c_{6.3b})^{\frac{\eta-\varepsilon_0}{\eta}}\right\}$. This implies $r \geq (3/2a^{\mathrm{TF}})^{\frac{1}{\xi}}m_{\mathbf{Z}}^{-\frac{1}{3}}$ and $Rm_{\mathbf{Z}}^{\frac{1}{3}} \geq 2(\tilde{\eta}/\tilde{\xi}a^{\mathrm{TF}})^{\frac{1}{\xi}}$ so that the assumptions of Lemma 6.3 and 6.4 are satisfied. This means that both (6.3) and (6.4) hold. Hence we see that the assumptions of Lemma 3.22 are (using Lemma 6.3 i), iii)) satisfied for $V^{(p)} = V_r^{(1,p)}$, as well as (using Lemma 6.3 ii), iv)) for $V^{(p)} = V_r^{(2,p)}$. Combining (3.47) with (6.6) and (3.48) with (6.5), we thus find

$$R^7\left|D^{\mathrm{rHF}}_{\mathbf{Z},R} - D^{\mathrm{TF}}_{\mathbf{Z},R}\right| \leq (cst.)R^{\varepsilon_0\frac{\eta-7}{\eta-\varepsilon_0}}, \qquad \forall R \in [Cm_{\mathbf{Z}}^{-\frac{1}{3}}, 2]. \tag{6.16}$$

Let us now consider the case $R \leq Cm_{\mathbf{Z}}^{-\frac{1}{3}}$. If we choose $V_C(x) = V_{\mathbf{Z},R}(x)$ in Lemma 4.6, then $|E^{\mathrm{TF}}_{\mathbf{Z},R} - E^{\mathrm{rHF}}_{\mathbf{Z},R}| \leq \max\{c_{4.6a}, c_{4.6b}\}|\mathbf{Z}|^{\frac{7}{3}-\frac{2}{33}}$, and if $V_C(x) = Z|x|^{-1}$, then $|E^{\mathrm{TF}}_Z - E^{\mathrm{rHF}}_Z| \leq \max\{c_{4.6a}, c_{4.6b}\}Z^{\frac{7}{3}-\frac{2}{33}}$. We combine these bounds and write $C_{\mathbf{Z}} = \max\{Z_1, Z_2\}/m_{\mathbf{Z}}$ so that for all $R \leq Cm_{\mathbf{Z}}^{-\frac{1}{3}}$:

$$R^7|D^{\mathrm{rHF}}_{\mathbf{Z},R} - D^{\mathrm{TF}}_{\mathbf{Z},R}| \leq C^{\frac{75}{11}}\max\{c_{4.6a}, c_{4.6b}\}\left(1 + C_{\mathbf{Z}}^{\frac{7}{3}-\frac{2}{33}} + (1+C_{\mathbf{Z}})^{\frac{7}{3}-\frac{2}{33}}\right)R^{\frac{2}{11}}.$$

This bound, together with (6.16) and $\varepsilon_{6.1} := \varepsilon_0\frac{\eta-7}{\eta-\varepsilon_0} < \frac{2}{11}$, completes the proof. □

It is evident from the proof, or more specifically (6.16), that we do not require the quotient $\max\{Z_1, Z_2\}/m_{\mathbf{Z}}$ to be bounded if we consider the behaviour of $D^{\mathrm{rHF}}_{\mathbf{Z},R}$ as $m_{\mathbf{Z}} \to \infty$. From (6.16) and (3.41) we therefore obtain the following Corollary, which confirms the conjecture (1.5) in reduced Hartree-Fock theory:

Corollary 6.5.

$$\limsup_{m_Z\to\infty}\left|D^{\mathrm{rHF}}_{\boldsymbol{Z},R} - D^{\mathrm{TF}}_{\infty,1}R^{-7}\right| = o(R^{-7}), \qquad \textit{as } R \to 0.$$

CHAPTER 7

Numerics

In the previous Chapters we looked at the Born-Oppenheimer potential in the limit $m_{\mathbf{Z}} \to \infty$, because it is a way to make a mathematically rigorous statement about the behaviour of $D_{\mathbf{Z},R}$ and since TF theory has a limit as $m_{\mathbf{Z}} \to \infty$. Now how fast is the asymptotic behaviour in (1.6) (or Corollary 6.5) reached? The honest answer is that the constants from Theorem 6.1 are immense, so this result gives no quantitative insight for reasonable values of $Z < 100$.

To obtain a better understanding about the validity of (1.6) for finite $|\mathbf{Z}|$, we have compared numerical values for homonuclear diatomic Born-Oppenheimer potentials. Numbers for different homonuclear diatomics in HF theory had been computed in [13] and we were given their data. For TF theory, we computed $D^{\mathrm{TF}}_{(Z,Z),R}$ via the identity (3.42). This means that we had to determine the values $\int \varphi^{5/2}$ and $\lim_{|x|\to 0}(\varphi(x) - Z|x|^{-1})$ for both the atomic and diatomic TF potentials. These functions satisfy the nonlinear Thomas-Fermi partial differential equation (3.3) and by choosing $c_{\mathrm{TF}}^{3/2} = 4\pi$ in this chapter, the PDE is free of constants and reads

$$\Delta\varphi = \varphi^{3/2}, \qquad \lim_{|x|\to\infty} \varphi(x)|x|^4 = 144.$$

We solve this equation both in the atomic and diatomic case numerically.

Remark: (Correctness of numerical values)
As this is not a thesis in numerical analysis, we do not derive any error estimates. In the atomic case, the correctness of our results relies on the internal capabilities of `Wolfram Mathematica` to carry out numerical computation with prescribed precision. Whereas for the diatomic case, we have no claim on the exactness of the computations. We only deduce *a posteriori*, that our values are sufficiently exact for our *qualitative* comparison of Born-Oppenheimer potentials. This is based on two observations: Firstly, the values are consistent when computed with different software platforms and slightly different approaches. Secondly, and most importantly, the TF values show a good agreement with the HF values, which have been obtained by completely different methods.

Before presenting the results for the Born-Oppenheimer curve, we describe the solution process. We do this separately for the atomic and diatomic case, because the former reduces to an ODE.

1. Solving the atomic ODE

The atomic TF potential is radial and due to the TF scaling (1.3) fully determined by a single function $\varphi_1^{\mathrm{TF}}(x) = f(|x|)|x|^{-1}$. Here $f \in C^\infty((0,\infty)) \cap C([0,\infty))$ is the unique solution to the nonlinear ordinary differential equation

$$\begin{cases} f''(r) = \frac{(f(r))^{3/2}}{\sqrt{r}}, & \forall r > 0, \\ f(0) = 1, \\ \lim\limits_{r\to\infty} f(r)r^3 = 144. \end{cases} \tag{7.1}$$

Since $\varphi_1^{\mathrm{TF}} > 0$, we in particular have $f > 0$. This ODE has been studied many times by physicists and mathematicians, both numerically and analytically. We do not give a full account and instead refer to the references of authors mentioned here.

One can attempt to solve this problem numerically on a finite domain $[0, r_\infty]$, varying the guessed initial slope $c_0 = f'(0)$ until the solution is sufficiently close to the Sommerfeld asymptotic at r_∞. This assumes r_∞ is chosen large enough that the $12^2 r^{-3}$-asymptotic is valid. Furthermore, it typically requires a high number of correct digits of c_0. The importance of the value c_0 has been noted by many authors and it has been computed to higher and higher accuracy over the past decades. Among them is the result $c_0 \approx -1.588071022611375312718684508$ from [40] and this agrees, with the exception of the last digit, with the 30-digit result that has been reported 2014 in [41].[1]

We propose an iterative approach that allows one to compute c_0 to a much higher accuracy with relatively few computational resources. It is based on the following observation: For any $c \in \mathbb{R}$, let y_c be the (maximal) solution to the initial value problem

$$\begin{cases} y''(r) = \frac{(y(r))^{3/2}}{\sqrt{r}}, \\ y(0) = 1, \\ y'(0) = c. \end{cases}$$

[1]See also the Table 1 in [41] for an overview of computed values since Fermi in 1928.

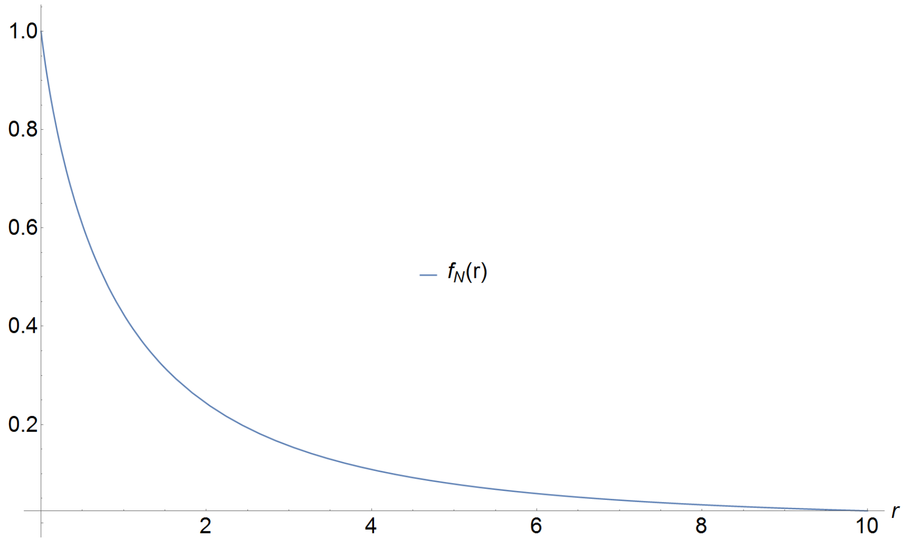


FIGURE 1. Numerical solution to (7.1). It describes the integral over (r, ∞) of a single-electron density in atomic TF theory.

Then $y_{c_0} = f$, where f solves (7.1), and it is defined on all of $[0, \infty)$. According to Hille [20, 42], if $c < c_0$ then $y_c(a) = 0$ at some $a > 0$ and if $c > c_0$, then y' will be positive at some point. This leads to the following algorithm: We guess an initial c and solve for y_c, starting at $r = 0$ until $\tilde{r}$, the first r where either y_c or y_c' vanish, is reached. Then we adjust c accordingly and repeat the process. This yields two sequences $c_n, \tilde{r}_n$ and we expect that $\tilde{r}_n \to \infty$ and $c_n \to c_0$.

Implementing this in Mathematica (see the appendix C.1), one observes that r_n is increasing and c_n is strictly decreasing when starting from an initial guess $c > c_0$. Stopping at the 81$^{\text{st}}$ correct digit, we obtain

$$
\begin{aligned}
c_0 = &- 1.588071022611375312718684509423950109452... \\
&\qquad ...7466216748256167656774181665519611543092 6..., \qquad (7.2)
\end{aligned}
$$

which in particular confirms the mentioned 30-digit result. The corresponding distance up to where this system was solved is about $\tilde{r} \approx 10^{10}$. The execution time to get the next digit reached up to 30 minutes and we therefore stopped here. Note that this was performed on a single desktop computer, so it is in principle possible to obtain far more digits with only a moderate use of computational resources. For our purposes, (7.2) is sufficient. Using this 81-digit approximation, we computed a numerical solution f_N to (7.1) up to $r_\infty = 10^{10}$ in Mathematica, which is displayed in Figure 1. Note that the graph describes the integral over the outside part of the electron density, because $f_N(r) = \int_{|y| \geq r} \varrho_1^{\mathrm{TF}}(y) dy$. We also give a plot of

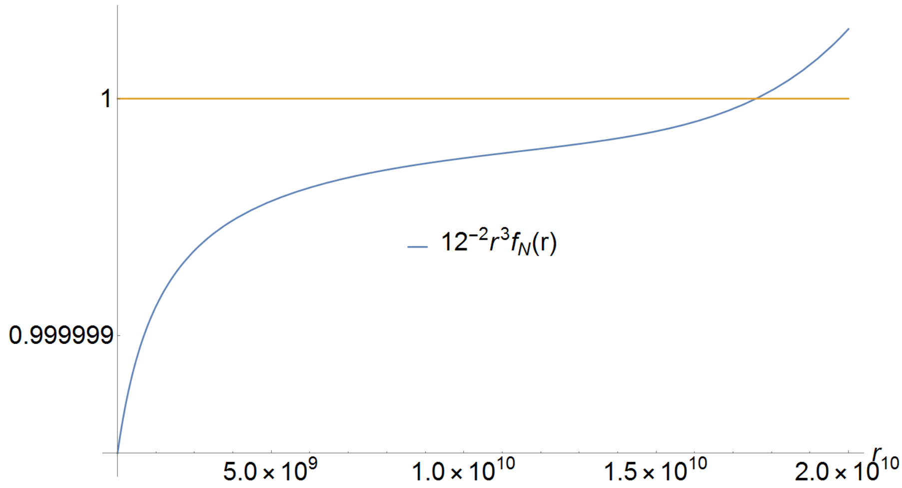


FIGURE 2. Relative deviation from the Sommerfeld asymptotic at r_∞.

the the relative distance of f_N to the Sommerfeld-asymptotic in Figure 2. For the normalization integral we have

$$1 = \int \varrho_1^{\mathrm{TF}} \approx \int_0^{r_\infty} f_N(r)^{3/2} r^{1/2} dr = 1 + 6.65211 \times 10^{-18}$$

so that we can confirm this solution to be highly accurate. With the goal of computing $D^{\mathrm{TF}}_{(Z,Z),R}$ in mind, we also determined

$$\int \left(\varphi_1^{\mathrm{TF}}(x)\right)^{5/2} dx \approx \int \left(f_N(r)\right)^{5/2} r^{-1/2} dr = 1.1343364447224109384754 56. \quad (7.3)$$

All these calculations for the atomic ODE where performed in Mathematica, version 11.1.1.0, in particular by use of the `NDSolve` and `NIntegrate` commands and suitably increasing the `WorkingPrecision`. Details are given in the appendix C.1 and C.2.

2. Solving the diatomic homonuclear PDE

2.1. The problem and its reformulations. We are interested in a (numerical) approximation to the *homonuclear* diatomic TF potential, the positive solution $\varphi^{\mathrm{TF}}_{(Z,Z),R} \in C^\infty(\mathbb{R}^3 \setminus \{0, R\nu\})$ of the problem

$$\begin{cases} \Delta\varphi^{\mathrm{TF}} = (\varphi)^{3/2} & \text{in } \mathbb{R}^3 \setminus \{0, R\nu\}, \\ \varphi(x)|x|^4 \to 144 & \text{as } |x| \to \infty, \\ \varphi(x)|x-p| \to Z & \text{as } x \to p \in \{0, R\nu\}. \end{cases} \quad (7.4)$$

From a mathematical point of view, this problem is well-posed (the solution exists and is unique). But it is not suited to be solved numerically because, a) the solution is singular at $\{0, R\nu\}$, b) solving a three-dimensional problem is usually computationally expensive and c) the 'Dirichlet condition at infinity' is not directly implementable on a computer.

To deal with a), we regularize the problem by solving for

$$u(x) = \varphi^{\mathrm{TF}}_{(Z,Z),R}(x) - Z|x|^{-1} - Z|x-R\nu|^{-1} = -\varrho^{\mathrm{TF}}_{(Z,Z),R} * |x|^{-1}$$

instead. Note that by Proposition 2.2, $u \in C(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0, R\nu\})$. Furthermore, since $\varphi^{\mathrm{TF}}_{(Z,Z),R}$ is rotationally invariant with respect to the axis ν and reflection symmetric across $\mathbb{H}_{R\nu/2}$, so is u. Using cylindrical coordinates (ρ, z, θ) with origin at $x = R\nu/2$ and z-axis in direction ν, we reduce the PDE to a 2-dimensional problem in the quadrant $\rho > 0, z > 0$, thus dealing with b). Finally, for c), we truncate the quadrant at $|(\rho, z)| = r_\infty$ and *impose* the approximate Dirichlet condition

$$u(\rho, z) = g(\rho, z) := \frac{144}{|(\rho, z)|^4} - \frac{Z}{|(\rho, z + R/2)|} - \frac{Z}{|(\rho, z - R/2)|} \qquad \text{on } |(\rho, z)| = r_\infty.$$

Let $\Omega = \{(\rho, z) \in \mathbb{R}^2_+ : |(\rho, z)| \le r_\infty\}$ and $\Gamma_D = \{(\rho, z) \in \mathbb{R}^2_+ : |(\rho, z)| = r_\infty\}$, $\Gamma_N = \partial\Omega \setminus \Gamma_D$. These sets all depend on r_∞, which we omit in the notation. We arrive at the following reformulation of (7.4) for a bounded domain: Given $R, Z, r_\infty > 0$, find $u(\rho, z)$ such that

$$\begin{cases} \nabla\rho\nabla u = n(\rho, u) & \text{in } \Omega, \\ u = g & \text{on } \Gamma_D, \\ \partial_n u = 0 & \text{on } \Gamma_N, \end{cases} \tag{7.5}$$

with the nonlinearity $n(\rho, u) := \rho(u + Z|(\rho, z + R/2)|^{-1} + Z|(\rho, z - R/2)|^{-1})^{3/2}$. To compute approximations via the finite element method, we note that (7.5) is equivalent to the variational problem of finding $u \in H^1_{g,\Gamma_D}(\Omega)$ such that

$$0 = F(u, v) := \langle \rho\nabla u, \nabla v\rangle_{L^2(\Omega)} + \langle n(u), v\rangle_{L^2(\Omega)} \; \forall v \in H^1_{0,\Gamma_D}(\Omega). \tag{7.6}$$

2.2. Solution via the finite element method. We use the FEniCS platform to compute an approximate solution $\tilde{u} \in V(\mathcal{M}, k)$ to the discrete version of (7.6), obtained by restricting to $V(\mathcal{M}, k) \cap H^1_{0,\Gamma_D}$.[2] Here $V_k(\mathcal{M}, k)$ denotes the finite-dimensional vector space of continuous functions over $\overline{\Omega}$, whose restriction to any simplex of the triangular mesh $\mathcal{M}$ is a polynomial of degree at most k.

[2]Note that F is not linear in the first argument. The solution to the discrete problem is therefore approximated by a Newton iteration.

The mesh $\mathcal{M}$ is generated by the automated adaptive algorithm that was proposed in [43] and has been implemented in FEniCS. The algorithm takes as an input a goal function M and determines an *a posteriori* error indicator η_M, which is *assumed* to approximate

$$\eta_M(\tilde{u}) \approx |M(u) - M(\tilde{u})|,$$

where u solves (7.6) and $\tilde{u}$ is its approximation in $V(\mathcal{M}, k)$. The initial mesh is then successively refined and $\tilde{u}$ recomputed for this mesh, until $\eta_M(\tilde{u})$ is less than the chosen tolerance.[3] Since our goal is to compute $D^{\mathrm{TF}}_{(Z,Z),R}$ via (3.42), we chose M to be the 5/2-integral of the TF-potential, so

$$M(u) = \int_\Omega \left(u(\rho, z) + Z|(\rho, z + R/2)|^{-1} + Z|(\rho, z - R/2)|^{-1}\right)^{5/2} \rho d\rho dz.$$

A commented and relatively short example of code that computes the solution with $R = 10, Z = 1$ and $r_\infty = 30$ can be found in the appendix C.3. We in particular chose quartic Lagrange elements (polynomials of degree $k = 4$ on a triangular mesh). The initial mesh was uniform with 11037 cells. The final mesh was reached after 20 adaptations and had 33158 cells, clustered at the singularity $(\rho, z) = (0, R/2)$. The chosen tolerance for the goal function was 10^{-12} and at each adaptation step, the Newton algorithm for $F(u; v) = 0$ converged to a relative or absolute tolerance of 10^{-10}. Varying the cutoff radius r_∞ had only a negligible effect. The solution has been visualized in Figures 3, 4 and 5 using ParaView 5.4.1.[4] We recall that we actually solved for $u(x) = -\varrho^{\mathrm{TF}}_{(Z,Z),R} * |x|^{-1}$, hence these Figures show the electric potential generated by the diatomic electron density in TF theory.

The L^1-mean-deviation of the computed $\tilde{u}$ to g on Γ_D is 3×10^{-17} and the normalization integral over the region equals 1.9946668775417533. This is reasonably close to the expected value $2 - \frac{2^3}{5^3 3} = 1.9786...$, which itself is an approximation, assuming that the Sommerfeld asymptotic holds at $r_\infty = 30$. For the goal functional, we find

$$\int \left(\varphi^{\mathrm{TF}}_{(1,1),10}(x)\right)^{5/2} dx \approx 2.2705744545893682.$$

These values seem to be consistent with the ones obtained by other FEM calculations we carried out:

[3]The refinement uses the Dörfler marking strategy: The cells c_j of $\mathcal{M}$ are ordered such that $\eta_M(\tilde{u}\mathbb{1}_{c_j})$ decreases. Then the first k cells such that $\sum_{j=1}^k \eta_M(\tilde{u}\mathbb{1}_{c_j}) \geq \frac{1}{2}\eta_M(\tilde{u})$ are refined.

[4]The Figures actually only show a linear fit between the vertices of the mesh. The actual solution is much more regular and built up from quartic functions.

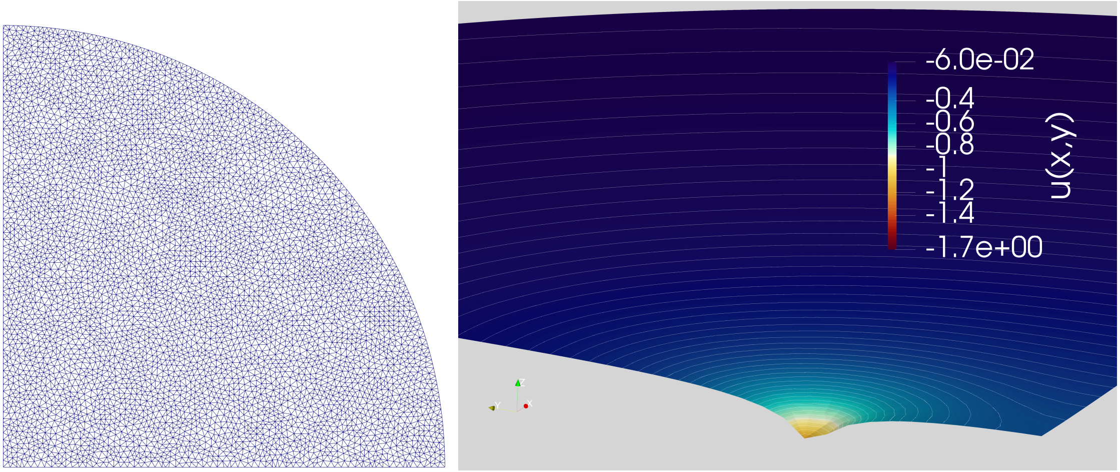


FIGURE 3. Initial mesh and solution of the goal-oriented adaptive method.

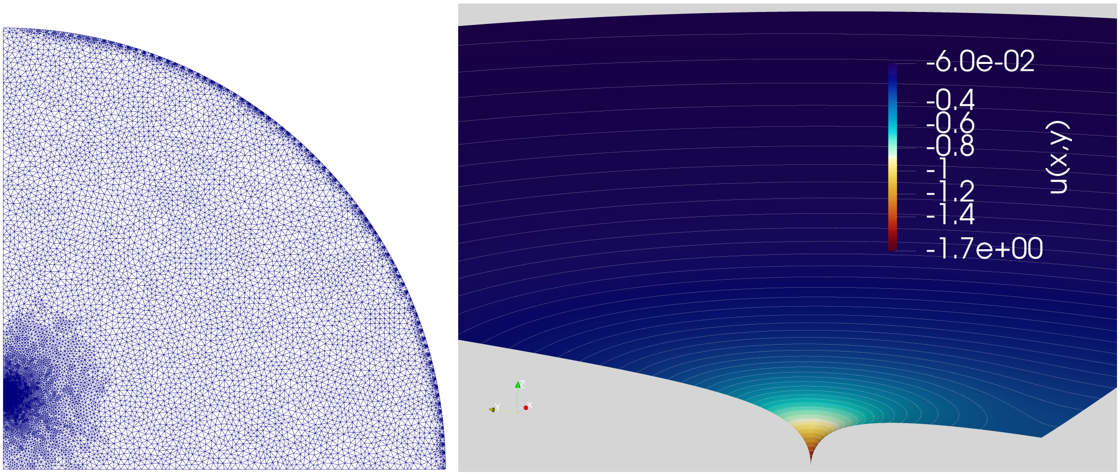


FIGURE 4. Final mesh and solution of the goal-oriented adaptive method.

(1) In FEniCS, we computed solutions without adaptation by specifying a (non-uniform) mesh, refined around $(\rho, z) = (0, R/2)$. Details are in the appendix C.4.
(2) In Mathematica, we iterated the solution to the linearised PDE, that is we computed $\Delta\varphi_{n+1} = \varphi_{n+1}\sqrt{\varphi_n}$, starting from $\varphi_0 = 0$ on a mesh with refinement around $(\rho, z) = (0, R/2)$. Details are in the appendix C.5.
(3) We thank Guillaume Legendre from Paris-Dauphine who kindly helped us to compute a solution in FreeFem++ by an adaptive method. Details are in the appendix C.6.

The best argument for the correctness of our computation is the agreement of our computed values for the Thomas-Fermi Born-Oppenheimer curve with the HF values, which we discuss below

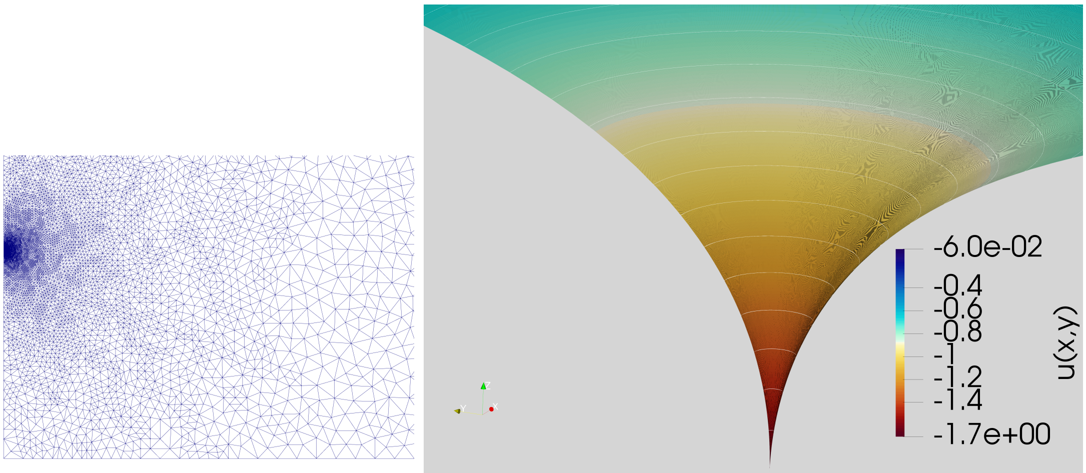


Figure 5. Final mesh and solution, zoomed to the singularity.

3. Comparison to HF values

Numerical HF-calculations for Hydrogen, Helium, Nitrogen, Neon, Argon, Lithium, Sodium, Potassium and Rubidium have been reported in [13]. They show, with the exception of hydrogen, an astonishing agreement of the electronic part of the rescaled Born-Oppenheimer curves $(2Z)^{-\frac{7}{3}}\left(D^{\mathrm{HF}}_{(Z,Z),R} - \frac{Z^2}{R}\right)$ at small $(2Z)^{1/3}R$ for different values of Z. The nuclear repulsion Z^2/R has been taken out because in this scaling, it is the same for all elements and dominates the electronic contribution at small r. In TF theory these curves are really just a single function in $r = (2Z)^{1/3}R$, since by the TF scaling (1.3),

$$(2Z)^{-\frac{7}{3}}\left(D^{\mathrm{TF}}_{(Z,Z),R} - \frac{Z^2}{R}\right) = D^{\mathrm{TF}}_{(\frac{1}{2},\frac{1}{2}),r} - \frac{1}{4r} =: D(r).$$

In order to compute this function via (3.42), we used the atomic values (7.2) and (7.3). The corresponding diatomic values $\|\varphi^{\mathrm{TF}}_{(Z,Z),R}\|_{5/2}$ and $(\varphi^{\mathrm{TF}}_{(Z,Z),R} - Z/|\cdot|)(0)$ were obtained via the goal-oriented adaptation in FEniCS. Note that we expect the diatomic values to be close to (7.2) and (7.3) and since we are interested in their difference (see (3.42)), we need to compute fairly accurate values also in the diatomic case.

We computed the solution of $\varphi^{\mathrm{TF}}_{(Z,Z),R}$ in atomic units, that is $c_{\mathrm{TF}} = \frac{1}{2}(3\pi^2)^{2/3}$ for $Z \in \{0.5, 1, 2\}$ and for 130 values of $r = R(2Z)^{1/3}$ between 0.001 and 12. We chose $r_\infty = 30$ and quartic Lagrange elements on an initial mesh with about 2 cells per unit length. The Newton algorithm at each iteration of the adaptive algorithm converged to relative or absolute precision 10^{-11}, which was also the chosen tolerance for the goal function.[5] Most of the computations have been carried out in the first half of 2018 on a cluster at Paris-Dauphine and the code can be found in the appendix C.7. We provide Tables of the computed values in the appendix C.8. We see that the relative and absolute deviations between the three datasets with respect to $Z \in \{0.5, 1, 2\}$, displayed in Figure 2 on page 129 and Figure 1 on page 129, are small.

Since $(E^{\mathrm{TF}}_{(Z,Z),R} - Z^2/R) \xrightarrow[R\to 0]{} E^{\mathrm{TF}}_{2Z}$, the TF scaling (1.3) implies

$$\lim_{r\downarrow 0} D^{\mathrm{TF}}(r) = E^{\mathrm{TF}}_1(1 - 2^{-4/3}) \approx -0.4636$$

and this seems to hold for our numerical values.[6] We display $D^{\mathrm{TF}}(r)$, the electronic part of the rescaled potential, together with the HF values from [13] in Figures 6,7 and 8. The absolute and relative deviations to the HF values, computed from an interpolation of $D^{\mathrm{TF}}(r)$, are shown in Figures 9 and 10.

The agreement of these curves is astonishing and far better than what we hoped for at the start of our numerical investigation and implies that our TF computations must be correct.[7] We conclude: Our computations indicate that the universal behaviour of the Born-Oppenheimer curve for the region of small internuclear distances, which we understand for heavy atoms, also holds for lighter atoms:

The small-R regime of Born-Oppenheimer curves is truly universal.

[5]With the exception of a few values, for which we chose 10^{-10} as the tolerance of M. They are marked with a * in tables 1, 4 and 7. See also the comments in the appendix C.7.

[6]We obtained the value $E^{\mathrm{TF}}_1 = -3.67874523/c_{\mathrm{TF}}$ from the solution f_N that we computed in Chapter 1. It is consistent with the value given in [4].

[7]We do not claim exactness or any concrete degree of accuracy.

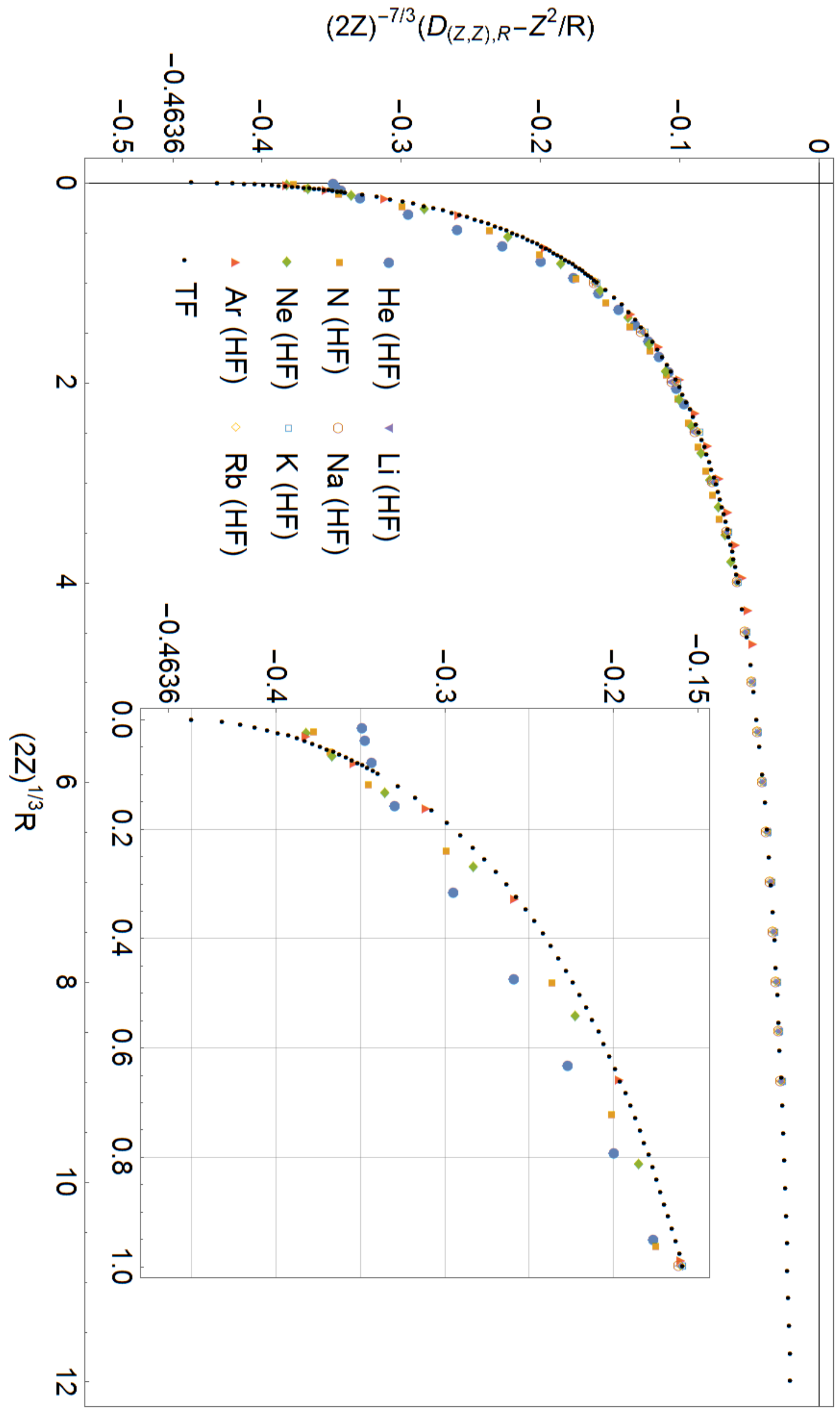


FIGURE 6. Comparison of numerically obtained Born-Oppenheimer curves in Thomas-Fermi (TF) and Hartree-Fock (HF) theory for $(2Z)^{1/3}R = r \in [0.001, 12]$ and for small values of r in $[0.001, 0.1]$.

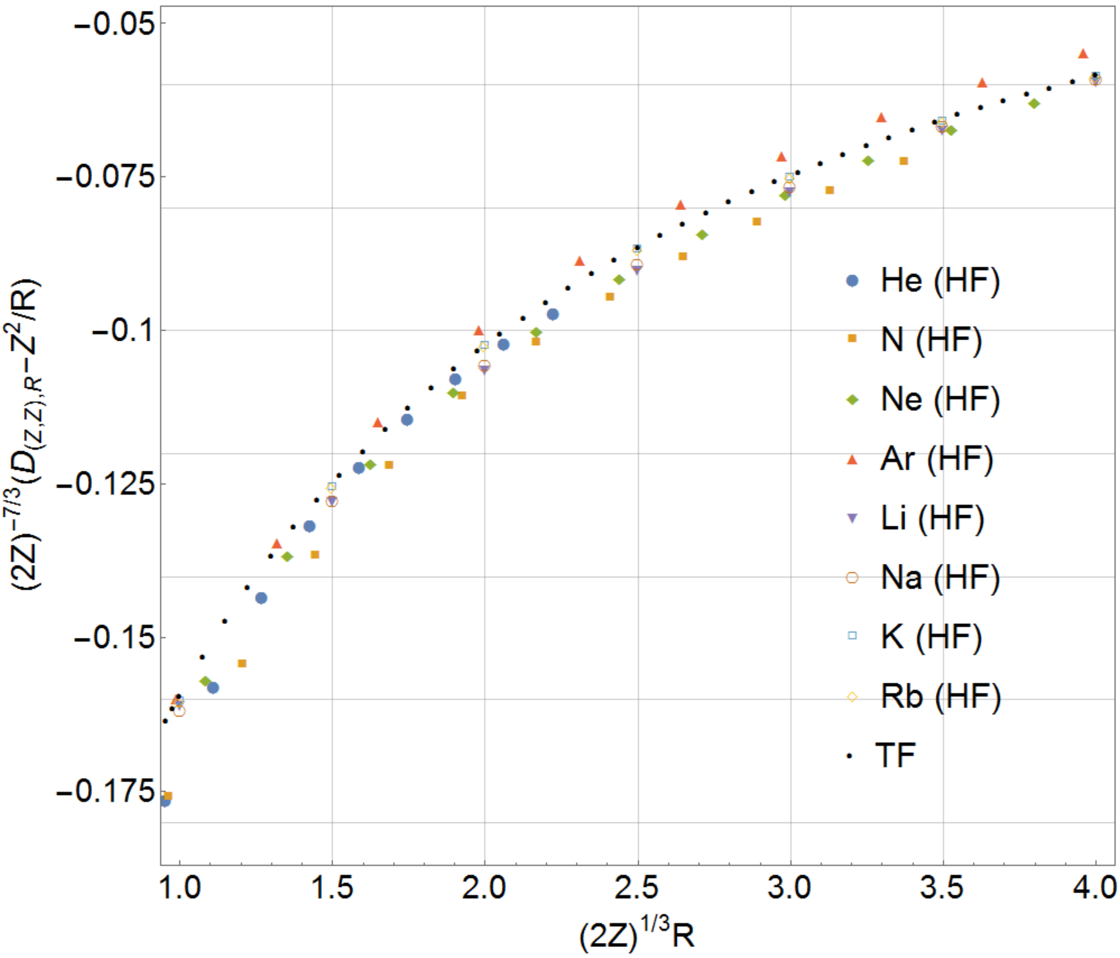


FIGURE 7. Comparison of numerically obtained Born-Oppenheimer curves in Thomas-Fermi (TF) and Hartree-Fock (HF) theory for $(2Z)^{1/3}R = r \in [1, 4]$.

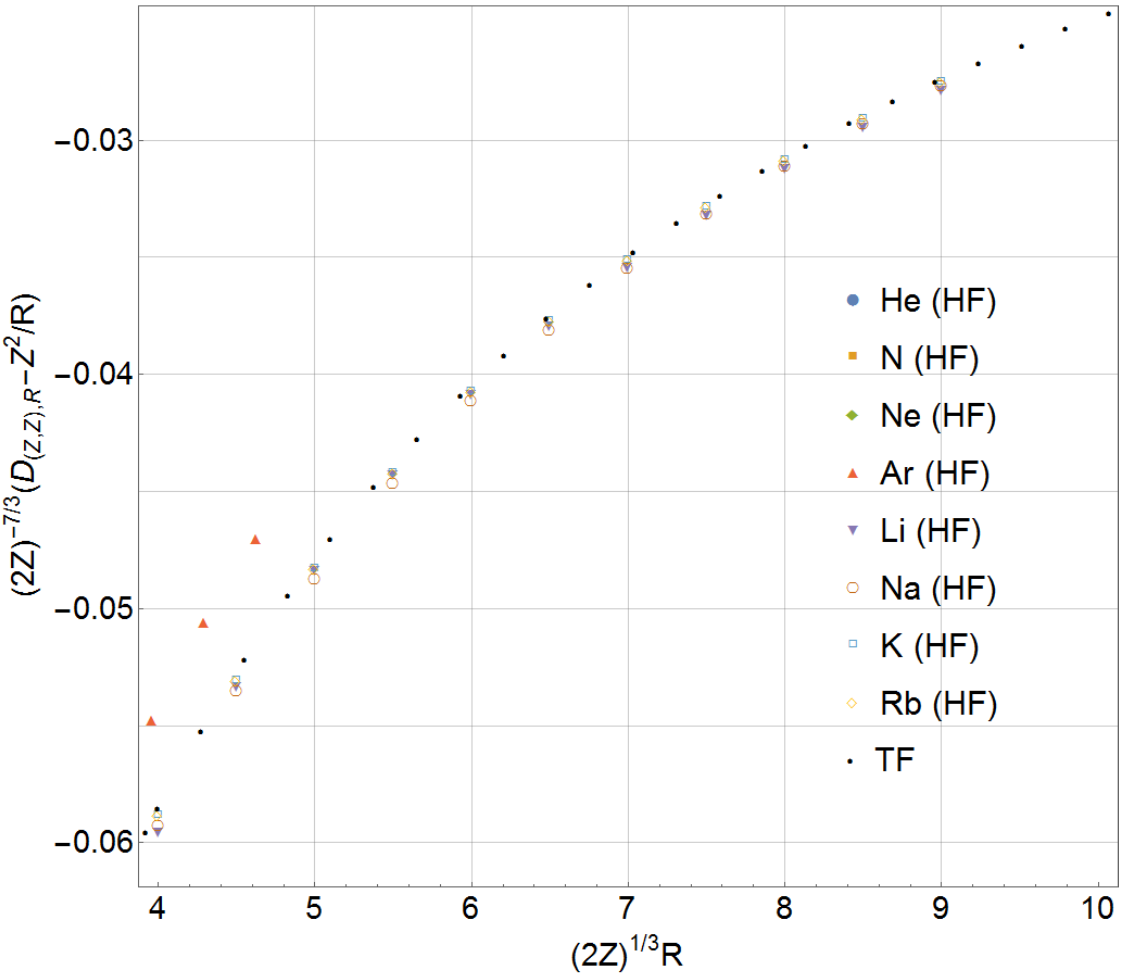


FIGURE 8. Comparison of numerically obtained Born-Oppenheimer curves in Thomas-Fermi (TF) and Hartree-Fock (HF) theory for $(2Z)^{1/3}R = r \in [4, 10]$.

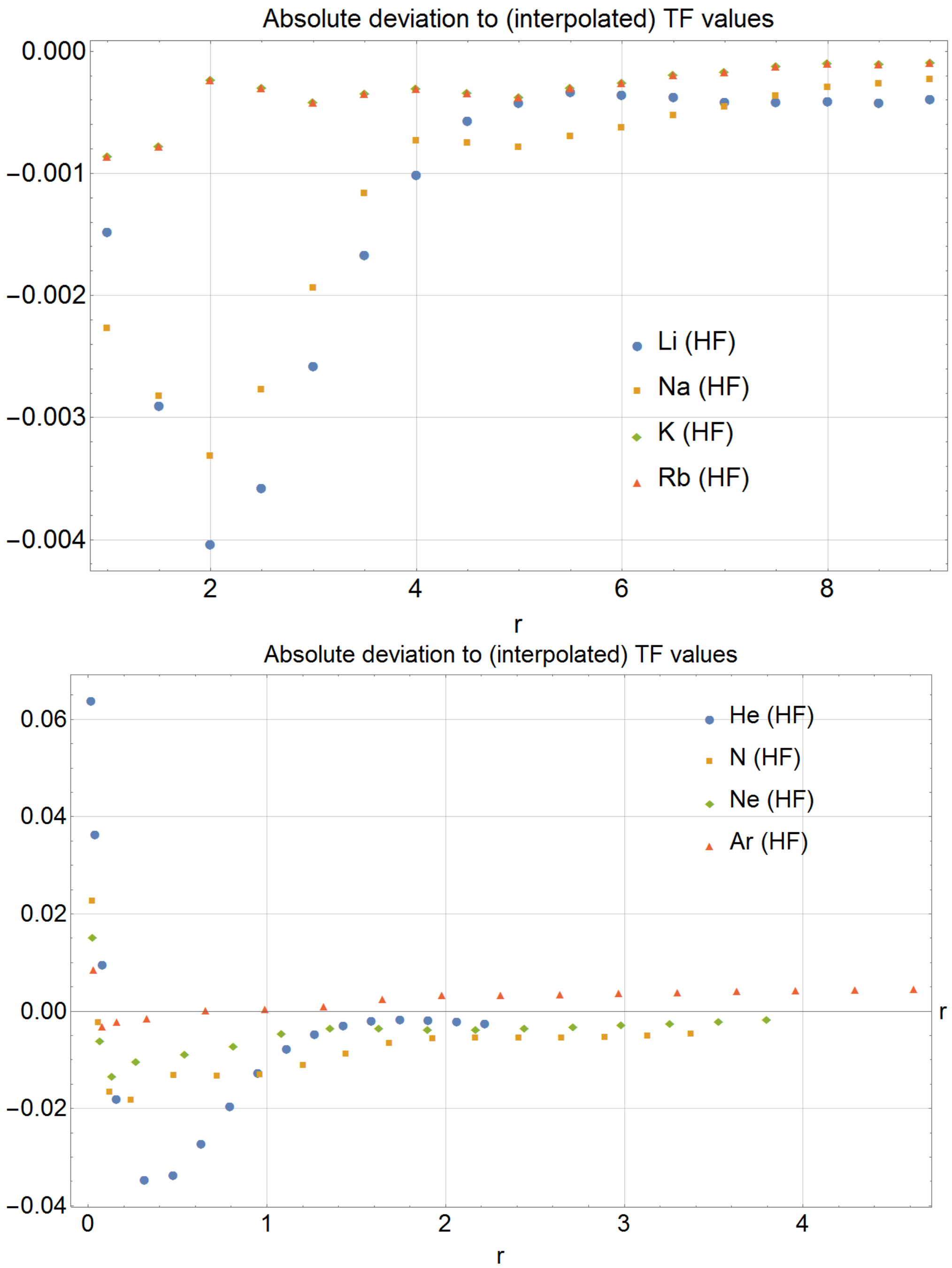
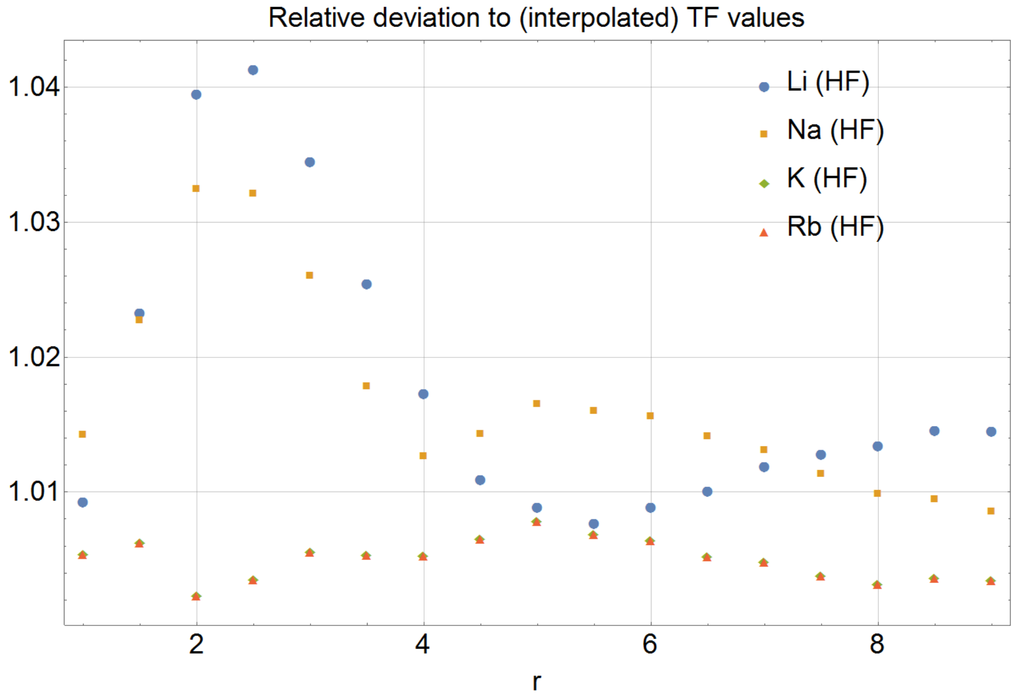


FIGURE 9. Absolute deviation of the (interpolated) TF Born-Oppenheimer curve to HF values.



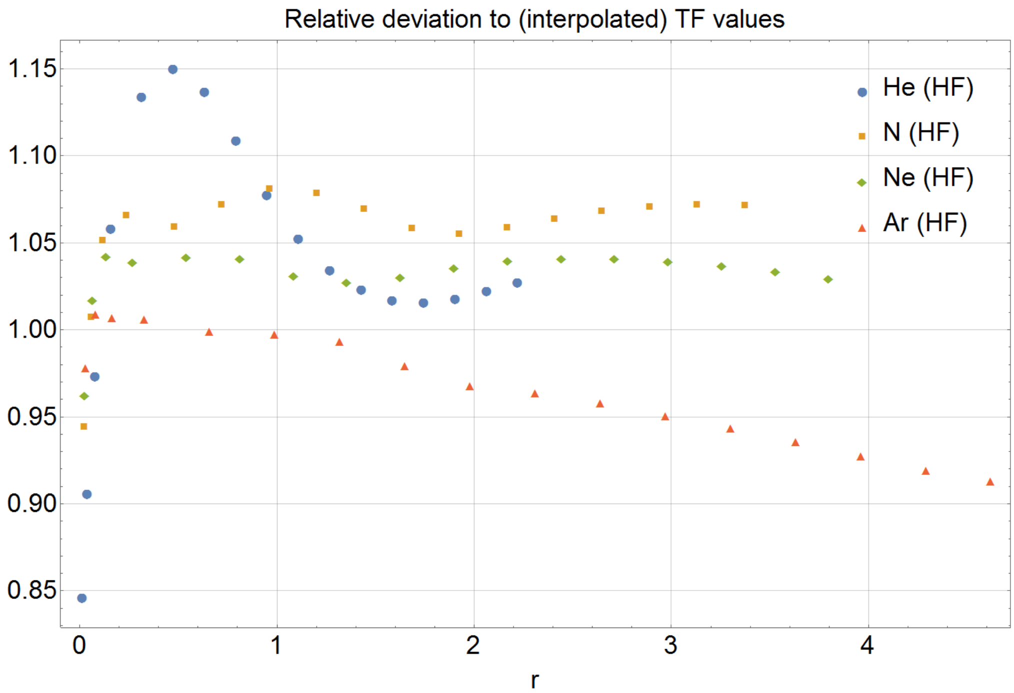


FIGURE 10. Relative deviation of the (interpolated) TF Born-Oppenheimer curve to HF values.

CHAPTER 8

Conclusions and perspectives

1. Summary

We have proven the conjectured [11] universality of diatomic Born-Oppenheimer curves for the Hartree-Fock model without the exchange term in Theorem 6.1. To do this, we showed in Lemmas 3.22 and 6.4 that the Born-Oppenheimer curves of TF theory and rHF theory can be determined from appropriate outside TF models. These are appropriate in the sense that the corresponding outside potentials agree, to leading order in the separation distance r, with TF-screened potentials. It is crucial that this holds for all r less than a constant, independent of the nuclear charge. In the atomic case, this was already known [12]. We have proved it for the diatomic case in Theorem 5.1, using the universality of positive solutions to the TF differential equation, which we studied in Chapter 3.3.1.

We also provided a numerical investigation of the TF Born-Oppenheimer curve at small nuclear charges and separations by solving the nonlinear TF differential equation. For the well-studied atomic ODE, we presented an algorithm that allows to compute the initial slope accurately. To solve the more complicated (homonuclear) diatomic PDE, we used the finite element method. The resulting agreement between the repulsive part of the TF and HF Born-Oppenheimer curves exceeds our expectations. This both strengthens the conjectured universality (1.5) for (full) HF theory and suggests that it is already valid for lighter atoms.

2. Perspectives for future research

We end this thesis by listing possible future research projects:

(1) The conjecture (1.5) for quantum mechanics is a major open problem. By the results of this thesis, it would suffice to show that the Born-Oppenheimer curves (of infinitely large atoms) in quantum mechanics and rHF theory agree to leading order in $R \to 0$.
(2) The conjecture (1.5) is still open in HF theory and a proof by the methods we outlined in this thesis might be possible. The exchange term between electrons

localized to the balls $B(0,r)$ and $B(R\nu, r)$,

$$\mathcal{X}_{R,r}[\gamma] := \frac{1}{2} \int\limits_{B(0,r)} \int\limits_{B(R\nu,r)} \frac{|\gamma(x,y)|^2}{|x-y|} dxdy,$$

is the main obstacle we encountered. However, we did not find a suitable bound on $|\mathcal{X}_{R,r}[\gamma^{HF}_{\mathbf{Z},R}]|$ to show that it can be controlled *independently* of $Z \in \mathbb{N}$ to the relevant order $o(R^{-7})$ for $r << R$.

(3) Our main result (1.6) can certainly be improved or extended:
   (a) One can try to optimize the constants, but we do not believe that this leads to a substantial improvement as long as the proof is based on the iteration coupled with the asymptotic of TF potentials.
   (b) Obtaining the next order in $R \to 0$ would certainly be of interest.
   (c) Going beyond the diatomic case and extending the universality to any Born-Oppenheimer surface. This should in most places be a straightforward (but notationally expensive) generalization of this thesis. Though we note that it might be difficult to obtain suitable Sommerfeld type bounds in the 'multi-atomic outside', which are needed to replace Lemma 3.12.

(4) There are still open problems in the TF theory of infinitely large atoms. For example, we do not know the value of $D^{TF}_{\infty,1}$. One could try to probe it numerically or analytically via the formula (3.43). The latter is related to another problem: While we have pointwise convergence of $\varphi^{\mathrm{TF}}_Z(x)$ towards $c_{\mathrm{S}}|x|^{-4}$ for $Z \to \infty$, there is no known analytic expression of the limiting function $\varphi^{\mathrm{TF}}_{\infty,R}$ in the diatomic case. We only know that it is the unique positive solution to the TF PDE with strong singularities $c_{\mathrm{S}}|x|^{-4}$ both at 0 and $R\nu$.

APPENDIX A

Outside harmonic functions and the Kelvin transform

We assume the reader is familiar with the basic theory of harmonic functions, in particular on bounded sets of $\mathbb{R}^3$. The Kelvin transform is a useful tool that allows one to translate the study of harmonic functions on unbounded sets which vanish at infinity to the study of harmonic functions on a bounded set. Most, if not all, of what we discuss here can be found in textbooks like [22, Vol. 3].

Definition A.1. Let $I_T : \mathbb{R}^3 \setminus \{0\} \to \mathbb{R}^3 \setminus \{0\}$ be the **inversion at the sphere** $\partial B(0,T)$, given by $I_T(x) = x\frac{T^2}{|x|^2}$. The **Kelvin transform** $K_T u$ with respect to the sphere $\partial B(0,T)$ of a real-valued function u with domain $\Omega \subset \mathbb{R}^3$ is defined on $I_T(\Omega \setminus \{0\})$ by

$$K_T u(x) = \frac{T}{|x|} u(I_T(x)).$$

Lemma A.2. *Let $\Omega \subset \mathbb{R}^3$ be open. Then $K_T K_T u(x) = u(x)$ for all $x \in \Omega \setminus \{0\}$ and*

$$u \text{ is harmonic in } \Omega \setminus \{0\} \Leftrightarrow K_T u \text{ is harmonic in } I_T(\Omega \setminus \{0\}).$$

Moreover, if $0 \in \Omega$, then

$$u \text{ is harmonic in } \Omega \Leftrightarrow K_T u \text{ is harmonic in } I_T(\Omega) \text{ and } \lim_{|x|\to\infty} K_T u(x) = 0.$$

Proof. That $K_T K_T u(x) = u(x)$ is checked by computation. Another straightforward computation shows that

$$\Delta[K_T u(x)] = \frac{T^5}{|x|^5} \Delta u(I_T(x)) \qquad \forall x \in I_T(\Omega \setminus \{0\}),$$

which proves the first equivalence. For the second, we first note that if $0 \in \Omega$, then $I_T(\Omega \setminus \{0\})$ contains the complement of a ball. Hence $\lim_{|x|\to\infty} K_T u(x) = 0$. On the other hand, if $K_T u$ is given, then we set $u = K_T K_T u$ on $\Omega \setminus \{0\}$ and note that $0 \in \Omega$ and $\lim_{|x|\to\infty} K_T u(x) = 0$ imply

$$\lim_{\substack{x\to 0\\ x\neq 0}} |x| u(x) = 0. \tag{A.1}$$

According to the first equivalence, it remains to verify that if $u(x)$ is harmonic in $\Omega\setminus\{0\}$ and satisfies (A.1), then it can be extended to $x = 0$ such that it is harmonic in all of Ω: Abbreviating $B(0,r)$ by B_r, we fix some $r > 0$ such that $B_r \subset \Omega$ and consider the unique v that is harmonic in all of B_r and equals u on ∂B_r. By (A.1), we can find for any $\epsilon > 0$ some $\delta \in (0, r)$ such that $|u(x) - v(x)| \le \epsilon |x|^{-1}$ in $\overline{B_\delta} \setminus \{0\}$. Since $u, v, \epsilon|x|^{-1}$ are harmonic in $B_r \setminus \{0\}$, the maximum principle implies that also $|u(x) - v(x)| \le \epsilon|x|^{-1}$ in $B_r \setminus B_\delta$ and thus (by the former bound) also in $B_r \setminus \{0\}$. Taking $\epsilon \to 0$, we obtain $u = v$ in $B_r \setminus \{0\}$ and end the proof by defining $u(0) = v(0)$. □

Examples

(1) The constant function $f(x) = c$ is the basic example of a harmonic function on a ball $B(0,T)$. Its Kelvin transform $K_T f(x) = \frac{Tc}{|x|}$ is the basic example of a nontrivial harmonic function that vanishes at infinity.

(2) We recall that the Poisson kernel for the ball of radius $r = |\xi|$,

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

is harmonic in $x \in B(0,r)$. We use the formula $\left| x\frac{|\xi|^2}{|x|^2} - \xi \right| = \frac{|\xi|}{|x|} |x - \xi|$ to compute for its Kelvin transform in x with respect to $\partial B(0,r)$:

$$K_r P_r(x, \xi) = \frac{1}{4\pi r} \frac{r^3}{|x|^3} \frac{|x|^2 - r^2}{|xr^2/|x|^2 - \xi|^3} = -P_r(x, \xi).$$

This implies that $-P_r$ is the Poisson kernel for the outside $B(0,r)^c$ in the following sense: For any $g \in C(\partial B(0,r))$, the function $x \mapsto -\int\limits_{\partial B(0,r)} P_r(x,\xi) g(\xi) d\xi$ is the unique solution to

$$\begin{cases} \Delta u = 0 & \text{in } \overline{B(0,r)}^c \\ u = g & \text{on } \partial B(0,r) \\ \lim\limits_{|x|\to\infty} u(x) = 0. \end{cases}$$

The mean value-property for harmonic functions on a ball has a reformulation for outside harmonic functions:

Proposition A.3. *Assume u is a harmonic function on an open set $\Omega \supset B(0,T)^c$ that satisfies $\lim\limits_{|x|\to\infty} u(x) = 0$. Then*

$$t \fint_{\partial B(0,t)} u = T K_T u(0) \qquad \forall t > T.$$

Proof. We use Lemma A.2 to write $u = K_T K_T u$ and compute by a change of coordinates that

$$t \fint_{\partial B(0,t)} u = T \fint_{\partial B(0,T^2/t)} K_T u.$$

Since $K_T u$ is harmonic in $B(0, T)$, the claim then follows from the mean value property for $K_T u$. $\square$

APPENDIX B

Computations

Lemma B.1. *Let $\Omega \subset \mathbb{R}^3$ be open, $\omega^-, \omega^+ \in C^\infty(\Omega)$ and assume that there exists an open set $\mathcal{S} \subset \Omega$, containing $\mathbb{R}^2 \times \{0\} \cap \Omega$, and such that*

$$\omega^-(x_1, x_2, x_3) = \omega^+(x_1, x_2, -x_3) \quad \forall (x_1, x_2, x_3) \in \mathcal{S}. \tag{B.1}$$

Let $\mathbb{H}^\pm := \mathbb{R}^2 \times \mathbb{R}^\pm$ and $\delta(x_3)[\phi] := \int_{\mathbb{R}^2} \phi(x_1, x_2, 0) dx_1 dx_2$, $\forall \phi \in C_c^\infty(\mathbb{R}^3)$. Then

$$\Delta(\omega^- \mathbb{1}_{\mathbb{H}^-} + \omega^+ \mathbb{1}_{\mathbb{H}^+}) = (\Delta\omega^-)\mathbb{1}_{\mathbb{H}^-} + (\Delta\omega^+)\mathbb{1}_{\mathbb{H}^+} + 2(\partial_3 \omega^+)\delta(x_3)$$

distributionally in Ω.

Proof. We pick $\phi \in C_c^\infty(\Omega)$ and note that simply by definition,

$$\Delta(\omega^- \mathbb{1}_{\mathbb{H}^-} + \omega^+ \mathbb{1}_{\mathbb{H}^+})[\phi] = \sum_{k=1}^{3} \left\langle \omega^- \mathbb{1}_{\mathbb{H}^-} + \omega^+ \mathbb{1}_{\mathbb{H}^+}, \partial_k^2 \phi \right\rangle_{L^2}.$$

Integrating by parts and noting that the due to (B.1), the boundary terms cancel, we find that this equals $-\sum_{k=1}^{3} \langle (\partial_k \omega^-)\mathbb{1}_{\mathbb{H}^-} + (\partial_k \omega)^+ \mathbb{1}_{\mathbb{H}^+}, \partial_k \phi \rangle_{L^2}$. Integrating by parts once more, we conclude

$$\begin{aligned} &\Delta(\omega^- \mathbb{1}_{\mathbb{H}^-} + \omega^+ \mathbb{1}_{\mathbb{H}^+})[\phi] \\ &= \sum_{k=1}^{3} \left\langle (\partial_k^2 \omega^-)\mathbb{1}_{\mathbb{H}^-} + (\partial_k^2 \omega)^+ \mathbb{1}_{\mathbb{H}^+}, \phi \right\rangle_{L^2} + \int\limits_{\mathbb{R}^2 \times \{0\}} (\partial_3 \omega^+ - \partial_3 \omega^-) \phi d\sigma \\ &= (\Delta\omega^-)\mathbb{1}_{\mathbb{H}^-}[\phi] + (\Delta\omega^+)\mathbb{1}_{\mathbb{H}^+}[\phi] + (\partial_3 \omega^+ - \partial_3 \omega^-)\delta(x_3)[\phi]. \end{aligned}$$

We note (B.1) implies $\partial_3 \omega^+ = -\partial_3 \omega^-$ on $\mathbb{R}^2 \times \{0\} \cap \Omega$, which ends the proof. □

Lemma B.2. *Let $r < R/2$, F be given by* (3.24) *and assume $W \in \mathcal{H}(\mathcal{O}_r)$. Then $F \in H^1(\mathbb{R}^3), FW \in L^6(\mathbb{R}^3), \nabla F W \in L^2(\mathbb{R}^3)$ and*

$$\|\nabla F W\|_2^2 = \int (\nabla F)^2 W^2.$$

Proof. Let A_0 denote $B(0, 3r) \setminus B(0, 2r) \cap \mathbb{H}^-_{R\nu/2}$ and $A_{R\nu}$ denote $B(R\nu, 3r) \setminus B(R\nu, 2r) \cap \mathbb{H}^+_{R\nu/2}$. We consider $f(x) = \sum_{p \in \{0, R\omega\}} \frac{x-p}{r|x-p|} \mathbb{1}_{A_p}$ and show that it equals ∇F in the weak sense. Note that$(x-p)/(r|x-p|)$ is smooth in a neighbourhood of $\overline{A}_p$. Hence we may integrate by parts to deduce that for any $\phi \in C_c^\infty(\mathbb{R}^3)$,

$k = 1, 2, 3$:

$$\int_{\mathbb{R}^3} F\partial_k\phi = \int_{\partial\mathcal{O}_{3r}} n_k(x)\phi + \int_{\partial A_0} n_k(x)\frac{|x|-2r}{r}\phi + \int_{\partial A_{R\nu}} n_k(x)\frac{|x-R\nu|-2r}{r}\phi - \int f_k\phi.$$

As $\frac{|x-p|-2r}{r} = 0$ on $\partial A_p \cap \partial B(p,2r)$, and $\frac{|x-p|-2r}{r} = 1$ on $\partial A_p \cap \partial B(p,3r) = \partial A_p \cap \partial\mathcal{O}_{3r}$, while $\int_{\partial\mathcal{O}_{3r}} n_k(x)\phi = -\int_{\partial\mathcal{I}_{3r}} n_k(x)\phi$,

$$\int_{\mathbb{R}^3} F\partial_k\phi = -\int f_k\phi + \int\limits_{\partial A_0\cap\mathbb{H}^-_{R\nu/2}} n_k(x)\frac{|x|-2r}{r}\phi + \int\limits_{\partial A_{R\nu}\cap\mathbb{H}^-_{R\nu/2}} n_k(x)\frac{|x-R\nu|-2r}{r}\phi.$$

Here the last two summands either cancel each other (if $r \geq R/6$) or vanish (if $r < R/6$). Hence $f = \nabla F$ weakly and since $f \in L^2(\mathbb{R}^3)$, we conclude $F \in H^1(\mathbb{R}^3)$. We now consider the function FW. Note that W is smooth on a neighbourhood of the support of F, hence $\nabla(FW) = (\nabla F)W + F(\nabla W)$ weakly. We integrate by parts

$$\int \partial_k F(FW\partial_k W) = -\int\limits_{A_0\cup A_{R\nu}} \big(FW\partial_k F\partial_k W + F^2(\partial_k W)^2 + F^2W\partial_k^2 W\big) + \sum_{p\in\{0,R\omega\}} \int_{\partial A_p} n_k F^2 W\partial_k W.$$

Here the last line actually equals $\sum\limits_{p\in\{0,R\omega\}} \int\limits_{\partial\mathcal{I}_{3r}} n_k W\partial_k W = -\int\limits_{\partial\mathcal{O}_{3r}} n_k\frac{1}{2}\partial_k(W)^2$, since the contributions from the integrals over $\partial\mathbb{H}_{R\nu/2}\cap\mathcal{I}_{3r}$ cancel each other, and since $F = 0$ on $\partial\mathcal{O}_{2r}$. Moreover we have (3.11) and from (3.46) with $V^{(R\nu/2)}_{R/2+r} = W$ on $B(R\nu/2, R/2+r)^c$ we deduce that $|\partial_k W(x)| \leq \|W\|_\infty \frac{5(R/2+r)}{|x-R\nu/2|^2-(R/2+r)^2}$ for $|x - R\nu/2| > R/2+r$. These decay properties are sufficient to integrate by parts (using a cut-off at $T > R/2+r$ and taking $T\to\infty$ with dominated convergence). We therefore deduce that

$$\sum_{p\in\{0,R\omega\}} \int_{\partial A_p} n_k F^2 W\partial_k W = -\int\limits_{\partial\mathcal{O}_{3r}} n_k\frac{1}{2}\partial_k(W)^2 = -\frac{1}{2}\int\limits_{\mathcal{O}_{3r}} F^2\partial_k^2(W)^2.$$

Overall, we find (after summing over $k = 1, 2, 3$) that

$$2\int FW\nabla F\nabla W = -\int F^2(\nabla W)^2 - \int F^2 W\Delta W = -\int F^2(\nabla W)^2.$$

This immediately implies the claimed identity

$$\|\nabla(FW)\|_2^2 = \int W^2(\nabla F)^2.$$

With the right hand side being bounded by $\|W\|_\infty^2 \|\nabla F\|_2^2 < \infty$, we conclude $FW \in H^1(\mathbb{R}^3)$. $\square$

Proposition B.3. *If $\rho \in L^{6/5}(\mathbb{R}^3)$ and $g \in L^2(\mathbb{R}^3)$ is normalized and radial, then*

$$\mathcal{D}(\rho * g^2) \leq \mathcal{D}(\rho).$$

Proof. We have $g^2 * |x|^{-1} \leq |x|^{-1}$ by Newton's theorem. This implies

$$\int\int \frac{g^2(x-w)g^2(y-z)}{|x-y|} dxdy \leq \int \frac{g^2(x)}{|w-z+x|} dx \leq \frac{1}{|w-z|}.$$

$\square$

APPENDIX C

Numerical scripts

We now give the source code and selected parts of the resulting output of the scripts we used for the numerical investigation.

1. Mathematica - atomic TF ODE, computing initial slope

```
TestUpperBound[c_, ndsolveOpts_, bvprec_] :=
  (flag = {0, 0};
    NDSolve[{y''[x] == (y[x]^(3/2))/Sqrt[x], y[10^(-bvprec)] == 1,
      y'[10^(-bvprec)] == c}, y, {x, 10^(-bvprec), Infinity},
      Method -> {"EventLocator", "Event" -> {Re[y[x]], Re[y'[x]]},
      "EventAction" :> {Throw[flag = {False, x}, "StopIntegration"],
      Throw[flag = {True, x}, "StopIntegration"]}}, ndsolveOpts,
      AccuracyGoal -> Infinity];
  flag)

ComputeDigits[cStart_, digitStart_, digitGoal_, ndsolveOpts_, bvprec_: 1000] :=
  Block[{c = cStart, currentDigit = digitStart},
    Print["loopcount | correct digits (after decimal point) |",
          " c | critical x | TestUpperBound execution time"];
    For[i = 0, currentDigit <= digitGoal, i++,
       timedFlag =         Flatten[Timing[TestUpperBound[c, ndsolveOpts, bvprec]]];
       Switch[timedFlag[[2]],
       0, Print["ERROR: TestUpperBound returned the flag zero"];,
       True, c -= 10^-currentDigit;,
       False, c += 10^-currentDigit; currentDigit++;
       Print[i, " | ", currentDigit - 1, " | ", N[c, currentDigit], " | ",
             N[timedFlag[[3]], 3], " | ", timedFlag[[1]]];
       ]
    ]
  ];

ComputeDigits[-15/15, 1, 80, {MaxSteps->Infinity,WorkingPrecision->currentDigit*2 + 50}]
```

This code computes the first 81 digits of the initial slope for the atomic TF PDE (7.1). We already announced the result in (7.2). To compute more digits, the setting `WorkingPrecision -> currentDigit*2 + 50` might need to be increased accordingly.

2. Mathematica - atomic TF ODE, computing integrals of the solution

```
(* 81-digit approximation to the initial velocity *)
c = -1588071022611375312718684509423950109452746621674825616765677418\
6655196115430926 *10^-80;
(* boundary value precision: 10^-bvprec as approximation to zero *)
bvprec = 1000;
```

```
* compute a solution *)
Timing[f =
NDSolveValue[{f''[x] ==  (f[x]^(3/2))/Sqrt[x], f[10^(-bvprec)] == 1,
f'[10^(-bvprec)] == c}, f, {x, 10^(-bvprec), Infinity},
Method -> {"EventLocator", "Event" -> {Re[f[x]], Re[f'[x]]},
"EventAction" :> {Throw[Print["solution becomes negative"],
"StopIntegration"],
Throw[Print["derivative becomes positive"],
"StopIntegration"]}}, MaxSteps -> Infinity,
WorkingPrecision -> 200, AccuracyGoal -> Infinity] ]

* Normalization : 3/2 - integral *)
NIntegrate[( u[r]/ r )^(3/2)*r^2, {r, 0, 10^9},
WorkingPrecision -> 100, MaxRecursion -> 200,
Method -> {"DuffyCoordinates"}]

(* The 5/2-integral *)
NIntegrate[( f[r]/ r )^(5/2)*r^2, {r, 0, 10^9},
WorkingPrecision -> 100, MaxRecursion -> 200,
Method -> {"DuffyCoordinates"}]
```

3. FEniCS - diatomic TF PDE, adaptive mesh refinement

```
from fenics import *
from mshr import *
# Parameters
R, Z, r_max, mesh_res, deg_FSpace, adapt_tol = 10.0, 1.0, 30.0, 2.0, 4, 1E-12
DualVariationalSolverParameters = {'linear_solver':'mumps', 'preconditioner':'none'}
NewtonSolverParameters = {'linear_solver':'mumps', 'preconditioner':'none',\
                          'maximum_iterations':25, 'relative_tolerance':1E-10, \
                          'absolute_tolerance':1E-10}

# Create mesh
domain = Rectangle(Point(0, 0),Point(r_max, r_max)) * Circle(Point(0, 0), r_max)
mesh = generate_mesh(domain, mesh_res*r_max)
x = SpatialCoordinate(mesh)

# Choose function space
V = FunctionSpace(mesh, 'P', deg_FSpace)

# Define Dirichlet BC
class Boundary_arc(SubDomain):
def inside(self, x, on_boundary):
    return on_boundary and near(x[1]*x[1]+x[0]*x[0], r_max*r_max, 1/(mesh_res*mesh_res))
bnd_arc = Boundary_arc()
dbc_function = Expression('144.0*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                          - Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                          - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5)',\
degree=deg_FSpace+3, Z=Z, R=R)
dbc = DirichletBC(V, dbc_function, bnd_arc)

# Define variational problem
u = Function(V)
v = TestFunction(V)
def nl(u):                      # the nonlinearity
    return x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                    + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 1.5)
F = (x[0]*Dx(u, 0)*Dx(v, 0) + x[0]*Dx(u, 1)*Dx(v, 1) + nl(u)*v)*dx
```

```
NLproblem = NonlinearVariationalProblem(F, u, dbc, derivative(F, u))

# Choose goal function
def I(u):                   # integrand of the goal functional
    return x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                  + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 2.5)
goalFunctional = I(u)*dx()

# Load parameters for the solver
solver = AdaptiveNonlinearVariationalSolver(NLproblem, goalFunctional)
for key in DualVariationalSolverParameters.keys():
    solver.parameters["error_control"]["dual_variational_solver"][key] \
                                                  =DualVariationalSolverParameters[key]
for key in NewtonSolverParameters.keys():
    solver.parameters["nonlinear_variational_solver"]["newton_solver"][key] \
                                                           =NewtonSolverParameters[key]
# Solve to chosen tolerance
solver.solve(adapt_tol)
solver.summary()

# Post-processing: computing key values
u0, u1 = u.root_node(), u.leaf_node()
mesh0, mesh1 = mesh.root_node(), mesh.leaf_node()

def computeDBCdeviation(u, mesh):    # L1-mean-deviation from |x|^{-4} at |(r,z)|=r_max
    x = SpatialCoordinate(mesh)
    class Boundary_arc(SubDomain):
    def inside(self, x, on_boundary):
        return on_boundary and near(x[1]*x[1]+x[0]*x[0],r_max*r_max,1/(mesh_res*mesh_res))
    bnd_arc = Boundary_arc()
    boundary_marker = MeshFunction('size_t', mesh, 1)
    boundary_marker.set_all(0)
    bnd_arc.mark(boundary_marker, 1)
    ds = Measure('ds', domain=mesh, subdomain_data=boundary_marker)
    integrand = abs( 144.0*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                  - Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                  - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5) -  u )*ds(1)
    return assemble(integrand)/assemble(1.0*ds(1))

def computeN(u, mesh):          # computes the 3/2-integral of the TF potential
    x = SpatialCoordinate(mesh)
    return assemble( (x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                      + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 1.5))*dx(mesh))

def computeI(u, mesh):          # computes the 5/2-integral of the TF potential
    x = SpatialCoordinate(mesh)
    return assemble( (x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                      + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 2.5))*dx(mesh))

print('* checking solution:')
print('* the mesh has ', mesh1.num_cells(), ' cells')
print('*   u(0,R/2) =', u1(0, R/2))
print('*   other values for reference: u(0,0) =', u1(0, 0),'u(R/2,R/2) =', u1(R/2,R/2))
print('*   DBC L^1-mean - error = ', computeDBCdeviation(u1, mesh1))
print('*   norm integral =', computeN(u1,mesh1))
print('*   5/2-integral =', computeI(u1,mesh1))

# Save inititial and final solution
File("./initialSolution.pvd")<<u0
File("./initialMesh.pvd")<<mesh0
File("./finalSolution.pvd")<<u1
```

```python
File("./finalMesh.pvd")<<mesh1
print('* files saved')
```

The output, computed with FEniCS (version 2017.2.0) is

```
Generating forms required for error control, this may take some time...
Solving variational problem adaptively
Adaptive iteration 0
Solving nonlinear variational problem.
Newton iteration 0: r (abs) = 6.783e+01 (tol = 1.000e-10) r (rel) = 1.000e+00 (tol = 1.000e-10)
Newton iteration 1: r (abs) = 3.023e-01 (tol = 1.000e-10) r (rel) = 4.456e-03 (tol = 1.000e-10)
Newton iteration 2: r (abs) = 5.070e-02 (tol = 1.000e-10) r (rel) = 7.475e-04 (tol = 1.000e-10)
Newton iteration 3: r (abs) = 8.663e-03 (tol = 1.000e-10) r (rel) = 1.277e-04 (tol = 1.000e-10)
Newton iteration 4: r (abs) = 1.291e-03 (tol = 1.000e-10) r (rel) = 1.903e-05 (tol = 1.000e-10)
Newton iteration 5: r (abs) = 1.174e-04 (tol = 1.000e-10) r (rel) = 1.731e-06 (tol = 1.000e-10)
Newton iteration 6: r (abs) = 2.098e-06 (tol = 1.000e-10) r (rel) = 3.093e-08 (tol = 1.000e-10)
Newton iteration 7: r (abs) = 7.802e-10 (tol = 1.000e-10) r (rel) = 1.150e-11 (tol = 1.000e-10)
Newton solver finished in 7 iterations and 7 linear solver iterations.
Value of goal functional is 3.26416.
Solving linear variational problem.
```

[...shortened...]

```
Solving linear variational problem.
Interpolate from parent to child
Adaptive iteration 19
Solving nonlinear variational problem.
Newton iteration 0: r (abs) = 8.593e-07 (tol = 1.000e-10) r (rel) = 1.000e+00 (tol = 1.000e-10)
Newton iteration 1: r (abs) = 4.051e-13 (tol = 1.000e-10) r (rel) = 4.714e-07 (tol = 1.000e-10)
Newton solver finished in 1 iterations and 1 linear solver iterations.
Value of goal functional is 2.2703.
Solving linear variational problem.
Interpolate from parent to child
Adaptive iteration 20
Solving nonlinear variational problem.
Newton iteration 0: r (abs) = 5.606e-07 (tol = 1.000e-10) r (rel) = 1.000e+00 (tol = 1.000e-10)
Newton iteration 1: r (abs) = 4.417e-13 (tol = 1.000e-10) r (rel) = 7.879e-07 (tol = 1.000e-10)
Newton solver finished in 1 iterations and 1 linear solver iterations.
Value of goal functional is 2.27057.
Solving linear variational problem.
Error estimate (-9.57088e-13) is less than tolerance (1e-12), returning.

Parameters used for adaptive solve:

<Parameter set "adaptive_solver" containing 9 parameter(s) and parameter set(s)>

Summary of adaptive data:

Level  |  functional_value  error_estimate  tolerance  num_cells  num_dofs
-------------------------------------------------------------------------
0      |          3.264162       -0.010129   0.000000      11037     88911
1      |          3.158429       -0.000427   0.000000      11053     89043
2      |          2.777008       -0.001792   0.000000      11075     89223
3      |          2.721439        0.000053   0.000000      11093     89375
4      |          2.491673       -0.000335   0.000000      11112     89529
5      |          2.468215        0.000071   0.000000      11160     89917
6      |          2.303986       -0.000094   0.000000      11249     90635
7      |          2.266971        0.000046   0.000000      11381     91699
8      |          2.222136        0.000000   0.000000      11474     92449
9      |          2.230807       -0.000003   0.000000      11683     94131
10     |          2.259771        0.000000   0.000000      11852     95493
11     |          2.258466       -0.000000   0.000000      12103     97511
12     |          2.265862        0.000000   0.000000      12539    101015
13     |          2.272983       -0.000000   0.000000      13180    106157
14     |          2.263525        0.000000   0.000000      13970    112493
15     |          2.264986       -0.000000   0.000000      15182    122205
```

```
16     |          2.268548       -0.000000   0.000000      16908    136041
17     |          2.269340       -0.000000   0.000000      19260    154961
18     |          2.269900       -0.000000   0.000000      22795    183431
19     |          2.270295       -0.000000   0.000000      27348    220153
20     |          2.270574       -0.000000   0.000000      33158    266997

Time spent for adaptive solve (in seconds):

Level  |  solve_primal  estimate_error  compute_indicators  mark_mesh  adapt_mesh    update
-------------------------------------------------------------------------------------------
0      |      9.208241       23.663189            5.363592   0.002125    0.010022  1.179448
1      |      4.221241       23.319697            5.386556   0.002444    0.010720  1.200100
2      |      3.046274       23.369060            5.373303   0.001891    0.010764  1.214095
3      |      3.066056       23.385281            5.409247   0.002444    0.010016  1.201023
4      |      3.080649       23.478264            5.400889   0.002252    0.010484  1.203576
5      |      3.075266       24.371523            5.576660   0.002003    0.011696  1.235868
6      |      1.984070       24.360442            5.471968   0.004134    0.012544  1.224390
7      |      1.913949       24.179397            5.501364   0.002064    0.010569  1.255297
8      |      1.906317       24.524191            5.589666   0.002178    0.011523  1.234173
9      |      1.933703       25.288347            5.659840   0.002085    0.010918  1.300461
10     |      1.995260       24.789270            5.737451   0.003315    0.011784  1.319455
11     |      2.008165       25.536868            5.748632   0.002243    0.014242  1.304454
12     |      2.029139       26.240016            6.027200   0.002287    0.013032  1.417212
13     |      2.138478       27.699916            6.229285   0.002393    0.015441  1.497606
14     |      2.355474       29.730266            6.754882   0.002459    0.017526  1.601863
15     |      2.479236       32.282786            7.504119   0.002746    0.018254  1.868430
16     |      2.868611       36.474745            8.236986   0.004338    0.024493  2.117345
17     |      3.632538       42.187332            9.212110   0.003844    0.035564  2.640248
18     |      4.050414       50.285739           11.194264   0.005411    0.036573  2.971103
19     |      5.172756       60.524524           13.252918   0.006073    0.045058  3.665315
20     |      6.041358       72.943783                   0          0           0         0

* checking solution:
* the mesh has  33158  cells
*   u(0,R/2) = -1.6876006141
*   other values for reference: u(0,0) = -0.372222749099 u(R/2,R/2) = -0.273224691014
*   DBC L^1-mean - error =  3.06702236293715e-17
*   norm integral = 1.9946668775417533
*   5/2-integral = 2.2705744545893682
* files saved
```

4. FEniCS - diatomic TF PDE, manual mesh refinement

```python
from fenics import *
from mshr import *
import numpy

# Parameters
R, Z, r_max, mesh_res, deg_FSpace = 10.0, 1.0, 30.0, 1.0, 4
NewtonSolverParameters = {'linear_solver':'cg', 'preconditioner':'petsc_amg',\
                          'maximum_iterations':25, 'relative_tolerance':1E-14,\
                          'absolute_tolerance':1E-14}

refinewidth, refinepower, refinesteps = 1.5, 4.0, 15

# Create mesh and refine at singularity
domain = Rectangle(Point(0, 0),Point(r_max, r_max)) * Circle(Point(0, 0), r_max)
mesh = generate_mesh(domain, mesh_res*r_max)
for width in numpy.linspace(pow(refinewidth, 1/refinepower), 0, refinesteps,\
                            endpoint=False):
    class singRegion(SubDomain):    #the region which is to be refined
    def inside(self, x, on_boundary):
        return x[0]*x[0] +(x[1]-R/2)*(x[1]-R/2)<= pow(width, 2.0*refinepower)
```

```
    sing_region = singRegion()
    refinefct_sing = MeshFunction('bool', mesh, 1)
    refinefct_sing.set_all(False)
    sing_region.mark(refinefct_sing, True)
    mesh = refine(mesh, refinefct_sing)
x = SpatialCoordinate(mesh)

# Choose function space
V = FunctionSpace(mesh, 'P', deg_FSpace)

# Define Dirichlet BC
class Boundary_arc(SubDomain):
    def inside(self, x, on_boundary):
        return on_boundary and near(x[1]*x[1]+x[0]*x[0],r_max*r_max,1/(mesh_res*mesh_res))
    bnd_arc = Boundary_arc()
    dbc_function = Expression('144.0*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                              - Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                              - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5)',\
                                degree=deg_FSpace+3, Z=Z, R=R)
dbc = DirichletBC(V, dbc_function, bnd_arc)

# Define variational problem
u = Function(V)
v = TestFunction(V)
def nl(u):                      # the nonlinearity
    return x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                      + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 1.5)
F = (x[0]*Dx(u, 0)*Dx(v, 0) + x[0]*Dx(u, 1)*Dx(v, 1) + nl(u)*v)*dx
NLproblem = NonlinearVariationalProblem(F, u, dbc, derivative(F, u))


# Load parameters for the solver
solver = NonlinearVariationalSolver(NLproblem)
for key in NewtonSolverParameters.keys():
    solver.parameters["newton_solver"][key] = NewtonSolverParameters[key]

# Solve to chosen tolerance
solver.solve()


# Post-processing: computing key values
def computeDBCdeviation(u, mesh):     # L1-mean-deviation to |x|^{-4} at |(r,z)|=r_max
    x = SpatialCoordinate(mesh)
    class Boundary_arc(SubDomain):
        def inside(self, x, on_boundary):
            return on_boundary and near(x[1]*x[1]+x[0]*x[0],r_max*r_max,\
                                                               1/(mesh_res*mesh_res))
    bnd_arc = Boundary_arc()
    boundary_marker = MeshFunction('size_t', mesh, 1)
    boundary_marker.set_all(0)
    bnd_arc.mark(boundary_marker, 1)
    ds = Measure('ds', domain=mesh, subdomain_data=boundary_marker)
    integrand = abs( 144.0*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                    -Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                    - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5) -  u )*ds(1)
    return assemble(integrand)/assemble(1.0*ds(1))

def computeN(u, mesh):          # computes the 3/2-integral of the TF potential
    x = SpatialCoordinate(mesh)
    return assemble( (x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                        + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 1.5))*dx(mesh))
```

```
def computeI(u, mesh):          # computes the 5/2-integral of the TF potential
    x = SpatialCoordinate(mesh)
    return assemble( (x[0]*pow(u + Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                        + Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5), 2.5))*dx(mesh))

print('* checking solution:')
print('* the mesh has ', mesh.num_cells(), ' cells')
print('*   u(0,R/2) =', u(0, R/2))
print('*   other values for reference: u(0,0) =', u(0, 0),'u(R/2,R/2) =', u(R/2,R/2))
print('*   DBC L^1-mean - error = ', computeDBCdeviation(u, mesh))
print('*   norm integral =', computeN(u,mesh))
print('*   5/2-integral =', computeI(u,mesh))

# Save initital and final solution
File("./Solution.pvd")<<u
File("./Mesh.pvd")<<mesh
print('* files saved')
```

The output, computed with FEniCS (version 2017.2.0) is

```
Solving nonlinear variational problem.
Newton iteration 0: r (abs) = 5.709e+01 (tol = 1.000e-14) r (rel) = 1.000e+00 (tol = 1.000e-14)
Newton iteration 1: r (abs) = 6.035e-01 (tol = 1.000e-14) r (rel) = 1.057e-02 (tol = 1.000e-14)
Newton iteration 2: r (abs) = 1.010e-01 (tol = 1.000e-14) r (rel) = 1.768e-03 (tol = 1.000e-14)
Newton iteration 3: r (abs) = 1.723e-02 (tol = 1.000e-14) r (rel) = 3.017e-04 (tol = 1.000e-14)
Newton iteration 4: r (abs) = 2.560e-03 (tol = 1.000e-14) r (rel) = 4.483e-05 (tol = 1.000e-14)
Newton iteration 5: r (abs) = 2.321e-04 (tol = 1.000e-14) r (rel) = 4.066e-06 (tol = 1.000e-14)
Newton iteration 6: r (abs) = 4.136e-06 (tol = 1.000e-14) r (rel) = 7.245e-08 (tol = 1.000e-14)
Newton iteration 7: r (abs) = 1.536e-09 (tol = 1.000e-14) r (rel) = 2.690e-11 (tol = 1.000e-14)
Newton iteration 8: r (abs) = 1.699e-13 (tol = 1.000e-14) r (rel) = 2.977e-15 (tol = 1.000e-14)
Newton solver finished in 8 iterations and 194 linear solver iterations.
* checking solution:
* the mesh has  52126  cells
*   u(0,R/2) = -1.68593974737
*   other values for reference: u(0,0) = -0.372222745936 u(R/2,R/2) = -0.273224677036
*   DBC L^1-mean - error =  4.582810113789804e-13
*   norm integral = 1.9946662046282755
*   5/2-integral = 2.268624708287004
* files saved
```

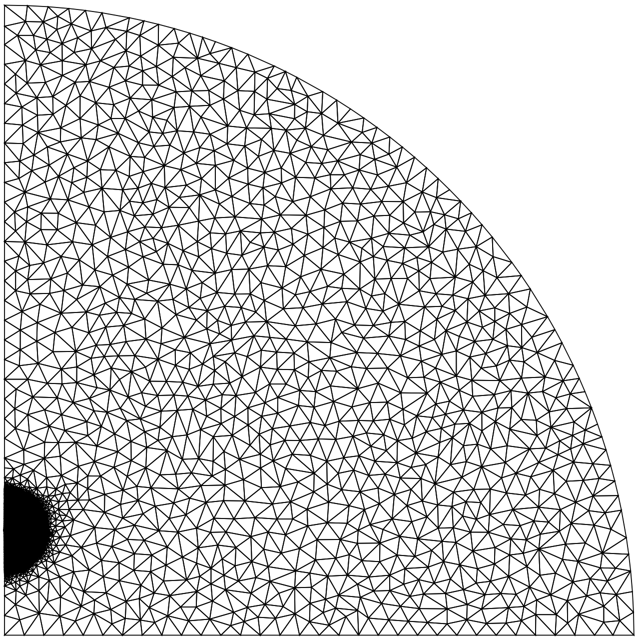
5. Mathematica - diatomic TF PDE, iteration of a linearised PDE

```
Needs["NDSolve`FEM`"]
rmax = 30;
R = 10;
Z = 1;
(* nuclear potential *)
V[Z_, R_, r_, z_] :=
Z/Sqrt[r^2 + (z - R/2)^2] + Z/Sqrt[r^2 + (z + R/2)^2];
Options[mesh] = {meshres -> 1, refineMeshres -> 10, refineWidth -> 1,
refineScaling -> 1};
(* create a mesh *)
mesh[R_, OptionsPattern[]] :=
ToElementMesh[
ImplicitRegion[
0 <= Sqrt[r^2 + z^2] <= rmax, {{r, 0, rmax}, {z, 0, rmax}}],
MeshRefinementFunction ->
Function[{vertices, area},
Block[{r, z}, {r, z} = Mean[vertices];
If[Sqrt[r^2 + (R/2 - z)^2] <= OptionValue[refineWidth],
```

```
area > 1/OptionValue[refineMeshres]*(Sqrt[r^2 + (R/2 - z)^2]/
OptionValue[refineWidth])^OptionValue[refineScaling],
area > 1/OptionValue[meshres]]]]];

(* solving linearised PDE with given guess 'uInit' *)

solveLinear[Z_, R_, uInit_, mesh_] :=
Assuming[{u \[Element] Reals, r \[Element] Reals,
z \[Element] Reals},
NDSolveValue[{r D[u[r, z], {r, 2}] + D[u[r, z], {r, 1}] +
r D[u[r, z], {z, 2}] -
r* (V[Z, R, r, z] + u[r, z])*Abs[V[Z, R, r, z] + uInit]^(1/2) ==
0, DirichletCondition[
u[r, z] == 12^2 (r^2 + z^2)^-2 - V[Z, R, r, z],
r^2 + z^2 == (rmax)^2]}, u, {r, z} \[Element] mesh]]

(* iterating the initial guess *)
iterationSolve[Z_, R_, mesh_, iMax_] :=
Module[{sol = solveLinear[Z, R, 0, mesh]},
Do[sol = solveLinear[Z, R, sol[r, z], mesh];
Print["u(0,R/2)=", FullForm[ sol[10^-10, R/2]]], iMax];
Print["u(0,R/2)=", FullForm[ sol[10^-10, R/2]], " | u(0,0)=",
FullForm[ sol[10^-10, 10^-10]], " | u(R/2,R/2)=",
FullForm[ sol[R/2, R/2]], " | 5/2-Integral: ",
FullForm[
NIntegrate[
r*Abs[sol[r, z] + V[Z, R, r, z]]^(5/2), {r, z} \[Element] mesh]],
" | Norm Integral: ",
FullForm[
NIntegrate[
r*Abs[sol[r, z] + V[Z, R, r, z]]^(3/2), {r, z} \[Element] mesh]]];
sol]

(* compute solution with keyvalues and visualise it *)
m = mesh[R, meshres -> 2, refineMeshres -> 10000, refineWidth -> 2.0,
refineScaling -> 1.3];
m["Wireframe"]
Timing[fct = iterationSolve[Z, R, m, 10];]
Plot3D[fct[r, z], {r, z} \[Element] m, PlotRange -> All]
```

Running this code in Mathematica 11.1.1.0 yields:

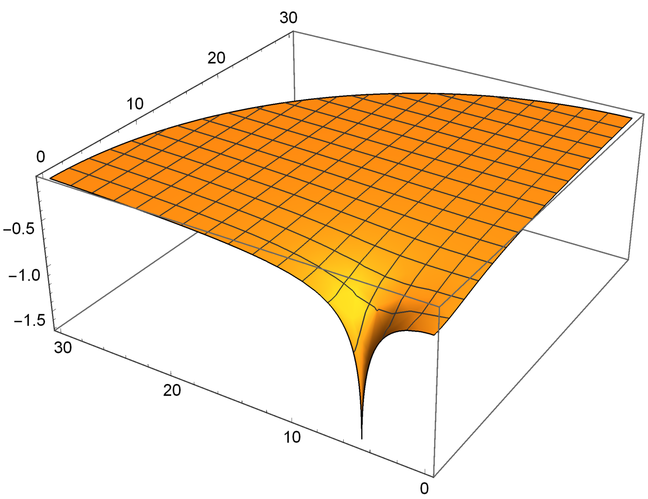
Out[27]=



```
u(0,R/2)=-1.6471782708093052`
u(0,R/2)=-1.6993489792365883`
u(0,R/2)=-1.6833254246589233`
u(0,R/2)=-1.6890169263567612`
u(0,R/2)=-1.686888508913609`
u(0,R/2)=-1.6877232623840073`
u(0,R/2)=-1.6873878945110405`
u(0,R/2)=-1.68752514475297`
u(0,R/2)=-1.687468355407517`
u(0,R/2)=-1.6874920358980305`
u(0,R/2)=-1.6874920358980305` | u(0,0)=-0.3722092604038237` | u(R/2,R/2)=
 -0.2732143239122185` | 5/2-Integral: 2.270568100129982` | Norm Integral: 1.99402605246405`
```

Out[28]= {806.572, Null}

Out[29]=



6. FreeFem++ - diatomic TF PDE, adaptive mesh refinement

Console output of a FreeFem++ script (including the source code), mainly written by Guillaume Legendre from Paris-Dauphine.

```
-- FreeFem++ v  3.590000 (date jeu. 22 févr. 2018 13:41:54)
Load: lg_fem lg_mesh lg_mesh3 eigenvalue
1 : load "medit"(load: loadLibary C:\Program Files (x86)\FreeFem++\\.\medit = 0);
2 : load "Element_P4"(load: loadLibary C:\Program Files (x86)\FreeFem++\\.\Element_P4 = 0);
3 :
4 : // Parameters
5 : real R=10; // distance between the nuclei
6 : real Z=1; // nuclear charge
7 : real rmax=30;
8 : real meshres=2;
9 : int maxiter=30;
10 : real reltol=1e-13,abstol=1e-13;
11 :
12 : // Create mesh
13 : border bndbot(t=0,rmax){x=t;y=0;label=0;}
14 : border bndarc(t=0,pi/2){x=rmax*cos(t);y=rmax*sin(t);label=1;}
15 : border bndleft(t=0,rmax){x=0;y=rmax-t;label=2;}
16 : mesh themesh=buildmesh(bndbot(rmax*meshres)+bndarc(floor(pi*rmax*meshres/2)) \
                                                            +bndleft(rmax*meshres));
17 : plot(themesh,wait=1);
18 :
19 : // Choose function space
20 : fespace V(themesh,P4);
21 : V u,v,delta;
22 :
23 : // Function of the Dirichlet BC
24 : func g=144*pow(x*x+y*y,-2)-Z*(pow(x*x+(y-R/2)*(y-R/2),-0.5) + pow(x*x+(y+R/2)*(y+R/2),-0.5));
25 :
26 : // Obtain a first crude approximation and use it to refine adaptively the mesh
27 : // Initialize Newton algorithm
28 : solve Newtoninit1(u,v)=int2d(themesh)(x*(dx(u)*dx(v)+dy(u)*dy(v)))+on(1,u=g);
29 : int n;
30 : for (n=1;n<6;n++) // Newton loop
31 : {
32 :    cout << "Newton loop - iter " << n+1 << endl;
33 :    solve Newtonloop(delta,v)=
34 :          int2d(themesh)(x*(dx(delta)*dx(v)+dy(delta)*dy(v) \
                                                     + 1.5*pow(u+Z*(pow(x*x+(y-R/2)*(y-R/2),-0.5)
35 :          + pow(x*x+(y+R/2)*(y+R/2),-0.5)),0.5)*delta*v))\
                                                       -int2d(themesh)(x*(dx(u)*dx(v)+dy(u)*dy(v)
36 :          + pow(u+Z*(pow(x*x+(y-R/2)*(y-R/2),-0.5) + pow(x*x+(y+R/2)*(y+R/2),-0.5)),1.5)*v))
37 :         +on(1,delta=0);
38 :    u[]-=delta[];
39 : }
40 :
41 : cout << "* Checking the crude computed solution " << endl;
42 : cout << " - value at the singular point: u(0,R/2)=" << u(0,R/2) << endl;
43 : cout << " - other values for reference: u(0,0)=" << u(0,0) << " and u(R/2,R/2)=" \
                                                                       << u(R/2,R/2) << endl;
44 : cout << " - L^1-mean error of the DBC: " \
                  << int1d(themesh,1)(abs(g(x,y)-u))/int1d(themesh,1)(1.) << endl;
45 : cout << " - norm integral: "<<int2d(themesh,qforder=10)(x*pow(u+Z*pow(x*x+(y-R/2)*(y-R/2),-0.5)
46 :                                 + Z*pow(x*x+(y+R/2)*(y+R/2),-0.5),1.5)) << endl;
47 : cout << " - 5/2-integral: "<<int2d(themesh,qforder=10)(x*pow(u+Z*pow(x*x+(y-R/2)*(y-R/2),-0.5)
48 :                                 + Z*pow(x*x+(y+R/2)*(y+R/2),-0.5),2.5))<<endl;
49 :
50 : // Using the crude approximation, compute an adaptive solution
51 : int nAdapt;
52 : for (nAdapt=1; nAdapt<5; nAdapt++)
53 : {
54 :       cout << "* Adaptive solve Nr"<< nAdapt << endl;
```

```
55 :       themesh=adaptmesh(themesh, u*u, err=0.00001, nbvx=100000);
56 :       u=u; // to delete the old mesh
57 :
58 :       //plot(themesh,wait=1);
59 :
60 :       // Initialize Newton algorithm
61 :       solve Newtoninit2(u,v)=int2d(themesh)(x*(dx(u)*dx(v)+dy(u)*dy(v)))+on(1,u=g);
62 :       real err=0.;
63 :       for (n=0;n<maxiter;n++)  // Newton loop
64 :       {
65 :       cout << "Newton loop - iter " << n+1 << endl;
66 :       solve Newtonloop(delta,v)=
67 :             int2d(themesh)(x*(dx(delta)*dx(v)+dy(delta)*dy(v) \
                                          + 1.5*pow(u+Z*(pow(x*x+(y-R/2)*(y-R/2),-0.5)
68 :             + pow(x*x+(y+R/2)*(y+R/2),-0.5)),0.5)*delta*v)) \
                                          - int2d(themesh)(x*(dx(u)*dx(v)+dy(u)*dy(v)
69 :             + pow(u+Z*(pow(x*x+(y-R/2)*(y-R/2),-0.5) + pow(x*x+(y+R/2)*(y+R/2),-0.5)),1.5)*v))
70 :             + on(1,delta=0);
71 :       err=delta[].linfty/u[].linfty;
72 :       cout << err << endl;
73 :       if (err<reltol) break;
74 :       u[]-=delta[];
75 :       }
76 :
77 :       cout << "* Checking the solution after "<< nAdapt << " adaptive refinements"  << endl;
78 :       cout << " - value at the singular point: u(0,R/2)=" << u(0,R/2) << endl;
79 :       cout << " - other values for reference: u(0,0)=" << u(0,0) << " and u(R/2,R/2)=" \
                                                                       << u(R/2,R/2) << endl;
80 :       cout << " - L^1-mean error of the DBC: " \
                                 << int1d(themesh,1)(abs(g(x,y)-u))/int1d(themesh,1)(1.) << endl;
81 :       cout << " - norm integral: " \
                            << int2d(themesh,qforder=10)(x*pow(u+Z*pow(x*x+(y-R/2)*(y-R/2),-0.5)
82 :                                         + Z*pow(x*x+(y+R/2)*(y+R/2),-0.5),1.5)) << endl;
83 :       cout << " - 5/2-integral: " \
                            << int2d(themesh,qforder=10)(x*pow(u+Z*pow(x*x+(y-R/2)*(y-R/2),-0.5)
84 :                                         + Z*pow(x*x+(y+R/2)*(y+R/2),-0.5),2.5))<<endl;
85 : }
86 :
87 : plot(u,wait=1);
88 :  sizestack + 1024 =12696  ( 11672 )

--  mesh:  Nb of Triangles =   6486, Nb of Vertices 3351
-- Solve :
min -0.0683959  max -0.0655818
Newton loop - iter 2
-- Solve :
min -2.51652e-038  max 1.18275
Newton loop - iter 3
-- Solve :
min -9.61846e-039  max 0.0855815
Newton loop - iter 4
-- Solve :
min -3.41291e-039  max 0.0152144
Newton loop - iter 5
-- Solve :
min -1.3211e-039  max 0.00201599
Newton loop - iter 6
-- Solve :
min -3.42002e-040  max 0.000190066
* Checking the crude computed solution
- value at the singular point: u(0,R/2)=-1.33176
- other values for reference: u(0,0)=-0.371801 and u(R/2,R/2)=-0.273268
- L^1-mean error of the DBC: 1.94856e-014
- norm integral: 1.99573
- 5/2-integral: 1.87149
* Adaptive solve Nr1
```

[...shortened...]

```
* Adaptive solve Nr4
number of required edges : 0
Warning not enough vertices  to split all internal edges
we lost 8 Edges Sorry
-- adaptmesh Regulary:  Nb triangles 197935 , h  min 3.7191e-005 , h max 8.76814
area =  706.849 , M area = 267814 , M area/( |Khat| nt) 3.12471
infiny-regulaty:  min 0.20914  max 56.6738
anisomax  37.8286, beta max = 1.63733 min  0.0382142
--  mesh:  Nb of Triangles = 197935, Nb of Vertices 100000
-- Solve :
min -0.0683942  max -0.0655818
Newton loop - iter 1
-- Solve :
min 2.66596e-039  max 1.53406
22.4296
Newton loop - iter 2
-- Solve :
min -1.41009e-041  max 0.0850776
0.0531537
Newton loop - iter 3
-- Solve :
min -1.34967e-040  max 0.0151762
0.00903394
Newton loop - iter 4
-- Solve :
min -7.37165e-041  max 0.0020098
0.00119188
Newton loop - iter 5
-- Solve :
min -1.83554e-041  max 0.00018934
0.000112259
Newton loop - iter 6
-- Solve :
min -7.76166e-043  max 4.83639e-006
2.86745e-006
Newton loop - iter 7
-- Solve :
min -8.65091e-046  max 4.59061e-009
2.72173e-009
Newton loop - iter 8
-- Solve :
min -2.78027e-015  max 4.55294e-015
2.6994e-015
* Checking the solution after 4 adaptive refinements
- value at the singular point: u(0,R/2)=-1.6898
- other values for reference: u(0,0)=-0.372208 and u(R/2,R/2)=-0.2732
- L^1-mean error of the DBC: 8.33542e-016
- norm integral: 1.99467
- 5/2-integral: 2.26341
times: compile 0.052s, execution 1012.82s,  mpirank:0
######## We forget of deleting   766 Nb pointer,   0Bytes   ,  mpirank 0, memory leak =0
CodeAlloc : nb ptr  3779,  size :414704 mpirank: 0
Ok: Normal End
```

7. Collecting data for the comparison of Born-Oppenheimer curves

For the computation of the values that lead to Figure 6, we ran the following script. It imports the custom file `libr_DTF`, which we provide below after some comments about the execution.

```
#-------------------------------------------------------------------------------
#-------------------------------------------------------------------------------
```

```
#       Computes a solution of the diatomic TF PDE
#       in atomic units, that is cD=2^{7/2}/(3*pi))
#       for several choices of R, Z, running over a
#       range of  R*(2Z)^{1/3} to compare with the
#       HF values from GILKA/SOLOVEJ/TAYLOR.
#       Results are saved to a .csv-file.
#-----------------------------------------------------------------------------------------
#-----------------------------------------------------------------------------------------



from fenics import *
import time
import datetime
import csv
import math
import numpy
import libr_DTF



# --- default values for parameters
Prm = libr_DTF.param(R=2.0, Z=1.0, r_max=30.0, cD=pow(2.0,3.5)/(3.0*math.pi), \
                                    mesh_res=2.0, deg_FSpace=4, adapt_tol=1E-11 )
DualVariationalSolverParameters = {'linear_solver':'mumps', 'preconditioner':'none'}
NewtonSolverParameters = {'linear_solver':'mumps', 'preconditioner':'none',\
                          'maximum_iterations':25, 'relative_tolerance':1E-11, \
                          'absolute_tolerance':1E-11}


CSVFilePath = './logs/sweep.csv'
set_log_level(ERROR)

# --- start of program ---
t0 = time.time()

print('')
print('*----------------------------------------')
print('*------- start of FEniCS program -------')
print('* on the',str(datetime.datetime.now().strftime("%d.%m.%y")),'at',libr_DTF.tStamp())
print('*----------------------------------------')
print('')


# --- write header for the .csv file ---
print(libr_DTF.tStamp(),'* write information of the current session into \
                        the current logfile at',CSVFilePath)
comment = " you find a copy of the corresponding source files at " + \
            libr_DTF.logSourceFiles([__file__,"libr_DTF.py"],"./logs/")
csv.register_dialect('comma_separated', delimiter=',')
with open(CSVFilePath, 'a', newline='') as f:
writer = csv.writer(f,dialect='comma_separated')
writer.writerow([datetime.datetime.now().strftime("%d.%m.%y"), \
                 datetime.datetime.now().strftime("%H:%M:%S"), comment])
writer.writerow(["R","Z","D(R,Z)","Z*R^3","R^7*D(R,Z)","u(0,R/2)", "I(u)", \
                 "I(u) deg = 100", "N(u)", "L^1-mean deviation", "rmax", \
                 "solve time (s)", "computing time for values (s)", "nr of cells", \
                 "initital mesh resolution", "adaptive tolerance","FE degree","cD", \
                 "Newton solver parameters", "Dual solver parameters"])
```

```
# --- start loop ---

libr_DTF.printParameters(Prm,NewtonSolverParameters,DualVariationalSolverParameters)

RHOvalues = numpy.linspace(0.001, 0.1, num = 20, endpoint = False)
Zvalues = [0.5, 1.0, 2.0]

print(libr_DTF.tStamp(),'* Executing a nested loop: \
                           Within each value of R(2Z)^{1/3} from ', RHOvalues)
print(libr_DTF.tStamp(),'*                          Z runs over ', Zvalues)

for Rho in RHOvalues:
    for Z in Zvalues:
        PrmLoop = Prm._replace(R=Rho*pow(2*Z,-1.0/3.0), Z=Z)
        print(libr_DTF.tStamp(),'* R(2Z)^{1/3} = ', Rho, 'Z =',PrmLoop.Z, 'R =', \
                                             PrmLoop.R, ' | Solving...')
        t0 = time.time()
        (u,mesh) = libr_DTF.computeSolution_adaptive(PrmLoop, NewtonSolverParameters, \
                                               DualVariationalSolverParameters)
        t1 = time.time()
        print(libr_DTF.tStamp(),'* computing values...')
        Nu = assemble( libr_DTF.N(u, PrmLoop)*dx(mesh))
        Iu = assemble( libr_DTF.I(u, PrmLoop)*dx(mesh))
        Iu_100 = assemble( libr_DTF.I(u, PrmLoop)*dx(mesh,\
                                          metadata={'quadrature_degree': 100}))
        L1dev = libr_DTF.L1MeanError_DBC(u, mesh, PrmLoop)
        DissEn = libr_DTF.dissocEnergy(u(0,PrmLoop.R/2), Iu_100, PrmLoop)
        t2 = time.time()
        with open(CSVFilePath, 'a', newline='') as f:
            writer = csv.writer(f,dialect='comma_separated')
            writer.writerow([PrmLoop.R, PrmLoop.Z, DissEn, PrmLoop.Z*pow(PrmLoop.R,3.0),\
                             pow(PrmLoop.R,7.0)*DissEn, u(0,PrmLoop.R/2), Iu, Iu_100 , \
                             Nu, L1dev, PrmLoop.r_max, round(t1-t0,2), round(t2-t1,2), \
                             mesh.num_cells(), PrmLoop.mesh_res, PrmLoop.adapt_tol, \
                             DualVariationalSolverParameters])
        print(libr_DTF.tStamp(),'*   ...values saved to',CSVFilePath)

print('')
print('*-------------------------------------')
print('*------- end of FEniCS program -------')
print('* runtime:', round(time.time()-t0, 2), 's')
print('*-------------------------------------')
print('')
```

During the execution of this code, an error occurred, ending in:

```
17:30:43 * R(2Z)^{1/3} =  0.0703 Z = 0.5 R = 0.0703  | Solving...
17:30:44 * solving adaptively...
17:43:12 *   finished solving in  748.02  s
17:43:12 * computing values...
17:43:21 *   ...values saved to ./logs/sweep.csv
17:43:21 * R(2Z)^{1/3} =  0.0703 Z = 1.0 R = 0.05579714697668221  | Solving...
17:43:22 * solving adaptively...
18:04:54 *   finished solving in  1292.56  s
18:04:54 * computing values...
18:05:21 *   ...values saved to ./logs/sweep.csv
18:05:21 * R(2Z)^{1/3} =  0.0703 Z = 2.0 R = 0.044286224903804794  | Solving...
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
```

```
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
Calling FFC just-in-time (JIT) compiler, this may take some time.
18:05:34 * solving adaptively...
Traceback (most recent call last):
File "/home/users/samojlow/sweep.py", line 74, in <module>
(u,mesh) = libr_DTF.computeSolution_adaptive(PrmLoop, NewtonSolverParameters, \
                                                        DualVariationalSolverParameters)
File "/mnt/nfs/users-data/users/samojlow/libr_DTF.py", line 185, in computeSolution_adaptive
solver.solve(p.adapt_tol)
File "/usr/lib/python3/dist-packages/dolfin/fem/adaptivesolving.py", line 124, in solve
cpp.AdaptiveNonlinearVariationalSolver.solve(self, tol)
RuntimeError:

*** -------------------------------------------------------------------------
*** DOLFIN encountered an error. If you are not able to resolve this issue
*** using the information listed below, you can ask for help at
***
***     fenics-support@googlegroups.com
***
*** Remember to include the error message listed below and, if possible,
*** include a *minimal* running example to reproduce the error.
***
*** -------------------------------------------------------------------------
*** Error:   Unable to solve linear system using PETSc Krylov solver.
*** Reason:  Solution failed to converge in 0 iterations (PETSc reason DIVERGED_PCSETUP_FAILED, \
                                                          residual norm ||r|| = 0.000000e+00).
*** Where:   This error was encountered inside PETScKrylovSolver.cpp.
*** Process: 0
***
*** DOLFIN version: 2017.2.0
*** Git changeset:  unknown
*** -------------------------------------------------------------------------

/var/spool/torque/mom_priv/jobs/2720.cluster.ceremade.dauphine.fr.SC: line 30: \
                                   171634 Aborted                 (core dumped) python3 ~/sweep.py
```

We continued the calculation for the remaining values $R(2Z)^{1/3} \in \{...\}$ with a lower goal tolerance of 10^{-10} in the script above. Moreover, we also also ran the script (for the initial goal tolerance of 10^{-11} and without any errors) three more times with the line

`RHOvalues = numpy.linspace(0.001, 0.1, num = 20, endpoint = False)`

replaced by

`RHOvalues = numpy.linspace(0.1, 1, num = 40, endpoint = False)`,

`RHOvalues = numpy.linspace(1, 4, num = 40, endpoint = False)`

and

`RHOvalues = numpy.linspace(4, 12, num = 30, endpoint = True)`.

The content of `libr_DTF` which was called in the previous script:

```
#-----------------------------------------------------------------------------------------
#-----------------------------------------------------------------------------------------
#       Collection of methods used to compute
#       a solution of the diatomic TF PDE
```

```
#-------------------------------------------------------------------------------------
#-------------------------------------------------------------------------------------

from fenics import *
from mshr import *
import numpy
import time
import datetime
import math
from collections import namedtuple

# --- parameter 'struct' to be used ---
param = namedtuple('param',['R','Z','r_max','mesh_res','cD','deg_FSpace','adapt_tol'])
refine_param = namedtuple('refine_param', ['steps','width','power','meshres'])


# --- collection of methods ---
r = Expression('x[0]', degree=1)    # coordinate function, used in some methods below
z = Expression('x[1]', degree=1)    # coordinate function, used in some methods below


def logSourceFiles(fileList, subfolder= "./"):  # save scripts (fileList) to a subfolder
LogFileName = subfolder + datetime.datetime.now().strftime("%y%m%d_%Hh%Mm%Ss.sourcecode")
for file in fileList:
with open(LogFileName,'a') as f:
f.write('sourcecode of '+file+':\n')
f.write(open(file).read())
f.write('sourcecode of '+file+' ends here.\n')
return LogFileName


def printParameters(param, NewtonSolverParameters, DualVariationalSolverParameters, \
                                                                        refineP=None):
    print(tStamp(),'* parameters are currently:')
        if(refineP != None):
            print(tStamp(),'*   refine_steps=', refineP.steps,'| refine_width=', \
                  refineP.width, '| refine_power=', refineP.power, '| refine_meshres=', \
                  refineP.meshres)
        print(tStamp(),'*   R=', param.R,'| Z=', param.Z, "| r_max=", param.r_max, \
              '| cD=', param.cD, '| mesh_res =', param.mesh_res,'| degFSPace=', \
              param.deg_FSpace, '| adapt_tol=', param.adapt_tol)
        print(tStamp(),'*   NewtonSolverParameters=', NewtonSolverParameters)
        print(tStamp(),'*   DualVariationalSolverParameters=', \
                                                   DualVariationalSolverParameters)

def tStamp():
    return str(datetime.datetime.now().strftime("%H:%M:%S"))

def N(u, p):
    return p.cD*r*pow(u + p.Z*pow(r*r+(z-p.R/2)*(z-p.R/2), -0.5) \
                        + p.Z*pow(r*r+(z+p.R/2)*(z+p.R/2), -0.5), 1.5)
def I(u, p):
    return p.cD*r*pow(u + p.Z*pow(r*r+(z-p.R/2)*(z-p.R/2), -0.5) \
                        + p.Z*pow(r*r+(z+p.R/2)*(z+p.R/2), -0.5), 2.5)

def dissocEnergy(u0, kinInt, p):
    u0Atomic = -1.793738623165210568576124990031006513754290266429542050207003066029928
    kinIntAtomic = 1.2812418736894361212823553262361613505
    return 1/10*(kinInt - 2*pow(p.Z, 7.0/3.0)*kinIntAtomic) +  p.Z*(u0 + p.Z/(p.R) \
                        - pow(p.Z,(4.0/3.0))*u0Atomic)
```

```
def L1MeanError_DBC(u, mesh, p):    # L1-mean-deviation to |x|^{-4} at |(r,z)|=r_max
    class Boundary_arc(SubDomain):
        def inside(self, x, on_boundary):
            return on_boundary and  near(x[1]*x[1]+x[0]*x[0],p.r_max*p.r_max, \
                                                        1/(p.mesh_res*p.mesh_res))
    bnd_arc = Boundary_arc()
    boundary_marker = MeshFunction('size_t', mesh, 1)
    boundary_marker.set_all(0)
    bnd_arc.mark(boundary_marker, 1)
    ds = Measure('ds', domain=mesh, subdomain_data=boundary_marker)
    integrand = abs( 144.0*pow(p.cD, -0.5)*pow(r*r+z*z, -2.0) \
                            - p.Z*pow(r*r+(z-p.R/2)*(z-p.R/2), -0.5) \
                            - p.Z*pow(r*r+(z+p.R/2)*(z+p.R/2), -0.5) -  u )*ds(1)
    return assemble(integrand)/assemble(1.0*ds(1))

def checkSolution(u, mesh, p):      # computes and outputs some nummbers
    print(tStamp(),'* checking solution:')
    print(tStamp(),'*   computing values...')
    Norm = assemble(N(u, p)*dx(mesh))
    Idefault = assemble(I(u, p)*dx(mesh))
    I50 = assemble(I(u, p)*dx(mesh,metadata={'quadrature_degree': 50}))
    I100 = assemble(I(u, p)*dx(mesh,metadata={'quadrature_degree': 100}))
    DissocEn = dissocEnergy(u(0, p.R/2), I100, p)
    L1error = L1MeanError_DBC(u, mesh, p)
    print(tStamp(),'*   ...finished:')
    print(tStamp(),'*   u(0,R/2) =', u(0, p.R/2))
    print(tStamp(),'*   N(u) =', Norm)
    print(tStamp(),'*   I(u) =', Idefault, 'computed with degree = auto/default')
    print(tStamp(),'*   I(u) =', I50, 'computed with degree = 50')
    print(tStamp(),'*   I(u) =', I100, 'computed with degree = 100')
    print(tStamp(),'*   D(Z,R) = ', DissocEn, 'with I(u) for degree = 100')
    print(tStamp(),'*   ZR^3 = ', p.Z*pow(p.R,3.0))
    print(tStamp(),'*   D(ZR^3,1) = ', pow(p.R,7.0)*DissocEn)
    print(tStamp(),'*   other values for reference: u(0,0) =', u(0, 0),'u(R/2,R/2) =', \
                                                                    u(p.R/2,p.R/2))
    print(tStamp(),'*   DBC L^1-mean - error = ', L1error)


def computeSolution_refinemesh(p, refine_p, NewtonSolverParameters): #solves w. manually
                                                                     #refined mesh
    # --- create the mesh, define (and initialize) the boundary at r_max ---
    domain = Rectangle(Point(0, 0), Point(p.r_max, p.r_max))*Circle(Point(0, 0), p.r_max)
    mesh = generate_mesh(domain, refine_p.meshres*p.r_max)
    class Boundary_arc(SubDomain):
        def inside(self, x, on_boundary):
            return on_boundary and near(x[1]*x[1]+x[0]*x[0], p.r_max*p.r_max, \
                                                            1/(p.mesh_res*p.mesh_res))
    bnd_arc = Boundary_arc()

    # --- refine at the singularity
    print(tStamp(),'* refining mesh...')
    for width  in numpy.linspace(pow( refine_p.width,1/refine_p.power ) , 0, \
                                                    refine_p.steps, endpoint=False ):
        class singRegion(SubDomain):    #the region which is to be refined
            def inside(self, x, on_boundary):
                return x[0]*x[0]+(x[1]-p.R/2)*(x[1]-p.R/2)<=pow(width,2.0*refine_p.power)
        sing_region = singRegion()
        refinefct_sing = MeshFunction('bool', mesh, 1)
        refinefct_sing.set_all(False)
        sing_region.mark(refinefct_sing, True)
        mesh = refine(mesh, refinefct_sing)
```

```
    print(tStamp(),'*   finished refining mesh')

    # --- Choose functionspace and define the Dirichlet BC ---
    V = FunctionSpace(mesh, 'P', p.deg_FSpace)
    dbc_function = Expression('144.0*pow(cD, -0.5)*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                                - Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                                - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5)',\
                                  degree=p.deg_FSpace+3, Z=p.Z, R=p.R, cD=p.cD)

    dbc = DirichletBC(V, dbc_function, bnd_arc)

    # --- define functions, variational form and goal functional ---
    u = Function(V)
    v = TestFunction(V)
    def nl(u):          #nonlinear term of the problem
        return p.cD*r*pow(u + p.Z*pow(r*r+(z-p.R/2)*(z-p.R/2), -0.5) \
                          + p.Z*pow(r*r+(z+p.R/2)*(z+p.R/2), -0.5), 1.5)
    F = (r*Dx(u, 0)*Dx(v, 0) + r*Dx(u, 1)*Dx(v, 1) + nl(u)*v)*dx
    dF = derivative(F, u)
    NLproblem = NonlinearVariationalProblem(F, u, dbc, dF)

    # --- Create a solver and load its parameters ---
    solver = NonlinearVariationalSolver(NLproblem)
    for key in NewtonSolverParameters.keys():
        solver.parameters["newton_solver"][key] = NewtonSolverParameters[key]

    # --- run the solver, return BOTH solution and final mesh ---
    print(tStamp(),'* solving over a refined mesh...')
    t0_solve = time.time()
    solver.solve()
    print(tStamp(),'*   finished solving in ',round(time.time()-t0_solve,2),' s')
    return (u, mesh)

def computeSolution_adaptive(p, NewtonSolverParameters, DualVariationalSolverParameters,\
    show_solver_summary=False, starting_mesh=None):  # solves w. adaptive mesh refinement
    # --- create the mesh, define (and initialize) the boundary at r_max ---
    if(starting_mesh==None):
        domain = Rectangle(Point(0, 0), Point(p.r_max, p.r_max)) * Circle(Point(0, 0), \
                                                                               p.r_max)
        mesh = generate_mesh(domain, p.mesh_res*p.r_max)
        else:
            mesh = starting_mesh
            class Boundary_arc(SubDomain):
    def inside(self, x, on_boundary):
        return on_boundary and near( x[1]*x[1]+x[0]*x[0], p.r_max*p.r_max, \
                                                     1/(p.mesh_res*p.mesh_res))
    bnd_arc = Boundary_arc()

    # --- Choose functionspace and define the Dirichlet BC ---
    V = FunctionSpace(mesh, 'P', p.deg_FSpace)
    dbc_function = Expression('144.0*pow(cD, -0.5)*pow(x[0]*x[0]+x[1]*x[1], -2.0) \
                                   - Z*pow(x[0]*x[0]+(x[1]-R/2)*(x[1]-R/2), -0.5) \
                                   - Z*pow(x[0]*x[0]+(x[1]+R/2)*(x[1]+R/2), -0.5)',\
                                     degree=p.deg_FSpace+3, Z=p.Z, R=p.R, cD=p.cD)

    dbc = DirichletBC(V, dbc_function, bnd_arc)

    # --- define functions, variational form and goal functional ---
    u = Function(V)
    v = TestFunction(V)
    def nl(u):          #nonlinear term of the problem
```

```
        return p.cD*r*pow(u + p.Z*pow(r*r+(z-p.R/2)*(z-p.R/2), -0.5) \
                            + p.Z*pow(r*r+(z+p.R/2)*(z+p.R/2), -0.5), 1.5)
    F = (r*Dx(u, 0)*Dx(v, 0) + r*Dx(u, 1)*Dx(v, 1) + nl(u)*v)*dx
    dF = derivative(F, u)
    NLproblem = NonlinearVariationalProblem(F, u, dbc, dF)
    goalFunctional = I(u, p)*dx()

    # --- Create a solver and load its parameters ---
    solver = AdaptiveNonlinearVariationalSolver(NLproblem, goalFunctional)
    for key in DualVariationalSolverParameters.keys():
        solver.parameters["error_control"]["dual_variational_solver"][key] \
                                            = DualVariationalSolverParameters[key]
    for key in NewtonSolverParameters.keys():
        solver.parameters["nonlinear_variational_solver"]["newton_solver"][key] \
                                                     = NewtonSolverParameters[key]

    # --- run the solver, return BOTH solution and final mesh ---
    print(tStamp(),'* solving adaptively...')
    t0_solve = time.time()
    solver.solve(p.adapt_tol)
    print(tStamp(),'*   finished solving in ',round(time.time()-t0_solve,2),' s')
    if(show_solver_summary):
        print(tStamp(),'*   the solver summary is (needs log level INFO or less):')
    solver.summary()
    return (u.leaf_node(), mesh.leaf_node())
```

8. Values for the comparison of Born-Oppenheimer curves

We here only give a selection of the data that the script C.7 gathered. In particular because the solving time is machine dependent and because the L^1-mean deviation at Γ_D was always less than 10^{-16}, with the precise value being of little interest. The relative deviation for $D(r)$, computed from (7.3), (7.2) and these values, is shown in Figure 2 on page 129 and the absolute deviation is displayed in Figure 1 on page 129.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.001	-1.76141	1.24905	-0.450725	1.00472	22738
0.00595	-1.71554	1.20315	-0.43238	1.00472	52740
0.0109	-1.68793	1.17591	-0.421299	1.00472	16151
0.01585	-1.66662	1.15475	-0.41276	1.00472	25998
0.0208	-1.64863	1.13692	-0.405549	1.00472	31781
0.02575	-1.63263	1.12127	-0.399114	1.00472	27035
0.0307	-1.61824	1.10715	-0.393331	1.00472	27155
0.03565	-1.60525	1.09434	-0.388114	1.00472	46185
0.0406	-1.59296	1.08247	-0.383158	1.00472	22457
0.04555	-1.58157	1.07142	-0.378567	1.00472	26012
0.0505	-1.57099	1.0611	-0.374309	1.00472	30961
0.05545	-1.56081	1.05135	-0.370192	1.00472	23770
0.0604	-1.55117	1.04207	-0.366303	1.00472	25150
0.06535	-1.54215	1.03335	-0.362661	1.00472	49004
0.0703	-1.53326	1.02492	-0.359061	1.00472	18941
0.07525*	-1.52456*	1.01709*	-0.355496*	1.00472*	16574*
0.0802*	-1.51673*	1.00935*	-0.352352*	1.00472*	18059*
0.08515*	-1.5089*	1.00178*	-0.349195*	1.00472*	17739*
0.0901*	-1.50157*	0.994724*	-0.346236*	1.00472*	21789*
0.09505*	-1.49429*	0.987889*	-0.343277*	1.00472*	23112*
0.1	-1.48729	0.981314	-0.340435	1.00472	27466
0.1225	-1.45778	0.953811	-0.328435	1.00471	24332
0.145	-1.43185	0.929842	-0.317862	1.00471	30829
0.1675	-1.40812	0.908586	-0.308125	1.00471	18909
0.19	-1.3867	0.888971	-0.299375	1.00471	27119
0.2125	-1.36711	0.871402	-0.291338	1.0047	35299
0.235	-1.34881	0.855406	-0.28379	1.0047	22923
0.2575	-1.33177	0.840551	-0.276754	1.0047	25331
0.28	-1.31566	0.826711	-0.27008	1.00469	15014
0.3025	-1.30088	0.814039	-0.263962	1.00469	15931
0.325	-1.28695	0.802496	-0.258146	1.00468	29536
0.3475	-1.27374	0.791427	-0.252652	1.00468	31426
0.37	-1.2611	0.780679	-0.247407	1.00468	34415
0.3925	-1.24915	0.770887	-0.242412	1.00467	27145
0.415	-1.23784	0.761638	-0.237679	1.00467	35431
0.4375	-1.22643	0.752919	-0.232846	1.00466	16142
0.46	-1.21659	0.74463	-0.228757	1.00466	23802
0.4825	-1.20673	0.736871	-0.224601	1.00466	35817
0.505	-1.19719	0.729722	-0.220546	1.00465	29121
0.5275	-1.18809	0.722317	-0.216738	1.00465	27036
0.55	-1.17931	0.715781	-0.212999	1.00464	26416
0.5725	-1.17074	0.709187	-0.209376	1.00464	14390
0.595	-1.16285	0.703097	-0.206036	1.00463	26314

TABLE 1. Values are for $Z = 0.5$ and those with * are computed to tolerance 10^{-10} of the goal functional (instead of 10^{-11}).

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.6175	-1.15504	0.697332	-0.20271	1.00463	27585
0.64	-1.1475	0.691713	-0.199504	1.00462	29471
0.6625	-1.14026	0.686381	-0.196417	1.00462	27303
0.685	-1.13323	0.681257	-0.193413	1.00461	27479
0.7075	-1.1264	0.676326	-0.190492	1.00461	21358
0.73	-1.11991	0.671798	-0.187701	1.0046	26739
0.7525	-1.1134	0.667071	-0.184916	1.0046	21347
0.775	-1.10736	0.662806	-0.182325	1.00459	30231
0.7975	-1.10143	0.658688	-0.179771	1.00459	30007
0.82	-1.0956	0.65461	-0.177263	1.00458	26493
0.8425	-1.08988	0.650806	-0.174784	1.00458	19028
0.865	-1.08458	0.647053	-0.172506	1.00457	26409
0.8875	-1.07928	0.643504	-0.170213	1.00457	33852
0.91	-1.07406	0.64003	-0.167951	1.00456	22770
0.9325	-1.06912	0.636692	-0.165814	1.00456	25962
0.955	-1.06415	0.633518	-0.163647	1.00455	22696
0.9775	-1.05937	0.63047	-0.161563	1.00455	17616
1.	-1.05493	0.627425	-0.159647	1.00454	33821
1.075	-1.04027	0.618127	-0.153246	1.00452	34747
1.15	-1.02681	0.609803	-0.147346	1.0045	19509
1.225	-1.01436	0.602288	-0.141877	1.00448	19925
1.3	-1.00305	0.595582	-0.136889	1.00446	26535
1.375	-0.992414	0.589459	-0.132185	1.00444	27986
1.45	-0.98236	0.583858	-0.127717	1.00442	21947
1.525	-0.973206	0.578876	-0.123639	1.0044	27687
1.6	-0.964277	0.574292	-0.119633	1.00438	17313
1.675	-0.956342	0.56993	-0.116101	1.00436	23577
1.75	-0.948702	0.566068	-0.112667	1.00434	38170
1.825	-0.941272	0.562457	-0.109313	1.00432	17108
1.9	-0.93448	0.5598	-0.106184	1.0043	24239
1.975	-0.928111	0.556132	-0.103365	1.00428	25330
2.05	-0.922066	0.553318	-0.100624	1.00426	35993
2.125	-0.916153	0.550696	-0.0979302	1.00424	20513
2.2	-0.910739	0.548944	-0.0953984	1.00421	25907
2.275	-0.90561	0.546079	-0.0931204	1.00419	33345
2.35	-0.900491	0.544231	-0.0907456	1.00417	23534
2.425	-0.895768	0.542018	-0.0886057	1.00415	21664
2.5	-0.891321	0.540258	-0.0865578	1.00413	20400
2.575	-0.886962	0.538528	-0.0845513	1.0041	20905
2.65	-0.882845	0.53801	-0.0825446	1.00408	20958
2.725	-0.878919	0.535426	-0.0808401	1.00406	21109
2.8	-0.875215	0.534238	-0.0791069	1.00404	23670
2.875	-0.871559	0.532783	-0.0774244	1.00401	23681
2.95	-0.868186	0.531581	-0.0758582	1.00399	25710

TABLE 2. Values are for $Z = 0.5$.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
3.025	-0.864854	0.53045	-0.0743054	1.00397	26050
3.1	-0.861586	0.529615	-0.0727547	1.00395	23150
3.175	-0.858516	0.528351	-0.0713464	1.00392	19585
3.25	-0.85549	0.527366	-0.0699316	1.0039	20803
3.325	-0.852529	0.526875	-0.0685004	1.00388	18045
3.4	-0.850043	0.525682	-0.0673767	1.00385	29352
3.475	-0.846986	0.525009	-0.0659152	1.00383	16847
3.55	-0.844574	0.524279	-0.0647825	1.00381	16700
3.625	-0.842541	0.523468	-0.063847	1.00378	31202
3.7	-0.840139	0.522774	-0.0627151	1.00376	31189
3.775	-0.837889	0.522196	-0.0616484	1.00374	31062
3.85	-0.835541	0.521609	-0.060533	1.00371	18187
3.925	-0.833271	0.521	-0.0594587	1.00369	19399
4.	-0.83148	0.520446	-0.0586185	1.00367	30167
4.27586	-0.824414	0.51869	-0.0552612	1.00358	37287
4.55172	-0.818139	0.517245	-0.0522681	1.00349	30710
4.82759	-0.812214	0.516023	-0.0494281	1.0034	17450
5.10345	-0.807341	0.514994	-0.0470944	1.00331	39313
5.37931	-0.802693	0.514119	-0.0448579	1.00322	28327
5.65517	-0.798484	0.513406	-0.0428248	1.00313	28621
5.93103	-0.794668	0.512823	-0.0409753	1.00304	38601
6.2069	-0.790882	0.512272	-0.0391373	1.00294	17041
6.48276	-0.787852	0.511817	-0.0376676	1.00285	38571
6.75862	-0.784852	0.51141	-0.0362084	1.00276	33414
7.03448	-0.78209	0.511089	-0.0348593	1.00266	29722
7.31034	-0.779544	0.510837	-0.0336117	1.00256	32472
7.58621	-0.776931	0.510557	-0.0323333	1.00247	17149
7.86207	-0.774877	0.510308	-0.031331	1.00237	32460
8.13793	-0.772767	0.510091	-0.0302977	1.00227	27037
8.41379	-0.770898	0.509932	-0.0293793	1.00217	30578
8.68966	-0.76903	0.509854	-0.028453	1.00207	31140
8.96552	-0.766834	0.509637	-0.0273765	1.00197	13928
9.24138	-0.765617	0.509537	-0.026778	1.00186	30388
9.51724	-0.764045	0.509402	-0.0260056	1.00176	30609
9.7931	-0.76266	0.509369	-0.0253165	1.00165	30509
10.069	-0.761323	0.509376	-0.0246475	1.00155	31464
10.3448	-0.759663	0.509177	-0.0238372	1.00144	15475
10.6207	-0.758578	0.509051	-0.0233073	1.00133	24192
10.8966	-0.757509	0.509028	-0.0227749	1.00122	30394
11.1724	-0.756421	0.509024	-0.0222316	1.00111	30195
11.4483	-0.755292	0.508913	-0.021678	1.001	26644
11.7241	-0.75407	0.508905	-0.0210677	1.00088	15736
12.	-0.753335	0.508899	-0.0207008	1.00077	32731

TABLE 3. Values are for $Z = 0.5$.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.001	-4.43871	6.29491	-0.450768	2.00336	43544
0.00595	-4.32277	6.06371	-0.43235	2.00336	78294
0.0109	-4.25382	5.92651	-0.421391	2.00336	49055
0.01585	-4.19992	5.81997	-0.41281	2.00336	60682
0.0208	-4.15436	5.73018	-0.405551	2.00336	41828
0.02575	-4.11396	5.65067	-0.399114	2.00336	18731
0.0307	-4.07806	5.57997	-0.393393	2.00336	46151
0.03565	-4.04485	5.5152	-0.388088	2.00336	34757
0.0406	-4.01429	5.45549	-0.383208	2.00336	88900
0.04555	-3.98539	5.39989	-0.378578	2.00336	22484
0.0505	-3.95822	5.34738	-0.374228	2.00336	21073
0.05545	-3.93302	5.29835	-0.370201	2.00336	25144
0.0604	-3.90901	5.252	-0.366357	2.00336	59127
0.06535	-3.88593	5.20773	-0.362655	2.00336	55936
0.0703	-3.86388	5.16547	-0.359118	2.00336	56864
0.07525*	-3.84271*	5.12652*	-0.355691*	2.00336*	32829*
0.0802*	-3.82203*	5.08634*	-0.352384*	2.00336*	31657*
0.08515*	-3.80254*	5.04912*	-0.349255*	2.00336*	23561*
0.0901*	-3.78367*	5.01335*	-0.346221*	2.00336*	21133*
0.09505*	-3.76545*	4.97869*	-0.343294*	2.00335*	25240*
0.1	-3.74755	4.94554	-0.3404	2.00335	26841
0.1225	-3.67371	4.80712	-0.328494	2.00335	69627
0.145	-3.60779	4.68574	-0.317824	2.00335	33782
0.1675	-3.54838	4.57756	-0.30818	2.00335	29720
0.19	-3.49431	4.48007	-0.299387	2.00334	21366
0.2125	-3.44481	4.39159	-0.291321	2.00334	30962
0.235	-3.39881	4.31061	-0.283799	2.00334	34621
0.2575	-3.35608	4.23613	-0.276799	2.00333	40705
0.28	-3.31602	4.16881	-0.270186	2.00333	43725
0.3025	-3.27845	4.10331	-0.264031	2.00333	27064
0.325	-3.24316	4.04298	-0.258224	2.00332	56235
0.3475	-3.20972	3.98691	-0.252702	2.00332	44449
0.37	-3.17803	3.93441	-0.247455	2.00331	50732
0.3925	-3.14794	3.88505	-0.242465	2.00331	46174
0.415	-3.11896	3.8384	-0.23764	2.00331	19241
0.4375	-3.09194	3.79537	-0.233133	2.0033	57522
0.46	-3.06584	3.75295	-0.228796	2.0033	33599
0.4825	-3.04042	3.71331	-0.224538	2.00329	20966
0.505	-3.01688	3.67604	-0.220607	2.00329	33511
0.5275	-2.99387	3.64061	-0.216744	2.00328	24513
0.55	-2.97203	3.60669	-0.213083	2.00328	83648
0.5725	-2.95072	3.57432	-0.209496	2.00327	49768
0.595	-2.93025	3.54342	-0.206048	2.00327	33825

TABLE 4. Values are for $Z = 1.0$ and those with * are computed to tolerance 10^{-10} of the goal functional (instead of 10^{-11}).

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.6175	-2.91062	3.51421	-0.202732	2.00326	40334
0.64	-2.89162	3.48699	-0.199503	2.00326	28708
0.6625	-2.87328	3.45914	-0.196415	2.00325	27829
0.685	-2.85579	3.43342	-0.193455	2.00325	37302
0.7075	-2.83826	3.40841	-0.190473	2.00324	25161
0.73	-2.82198	3.38509	-0.187706	2.00324	32440
0.7525	-2.80597	3.36223	-0.184983	2.00323	30443
0.775	-2.79066	3.34047	-0.182376	2.00323	53533
0.7975	-2.7756	3.31953	-0.179804	2.00322	38963
0.82	-2.76047	3.29886	-0.177212	2.00322	20859
0.8425	-2.74668	3.27974	-0.174855	2.00321	30013
0.865	-2.73296	3.26105	-0.172504	2.00321	41178
0.8875	-2.71966	3.24301	-0.170222	2.0032	37254
0.91	-2.70669	3.22591	-0.167988	2.0032	42662
0.9325	-2.694	3.20887	-0.165808	2.00319	51718
0.955	-2.68173	3.19306	-0.163687	2.00319	45845
0.9775	-2.6696	3.1771	-0.161598	2.00318	25997
1.	-2.65806	3.16205	-0.159607	2.00318	28412
1.075	-2.62153	3.11531	-0.153286	2.00316	48282
1.15	-2.58761	3.07412	-0.147372	2.00314	28913
1.225	-2.55653	3.03568	-0.141968	2.00312	43102
1.3	-2.52746	3.0015	-0.136879	2.0031	26789
1.375	-2.50069	2.97075	-0.132176	2.00308	36525
1.45	-2.47572	2.94273	-0.127777	2.00306	42059
1.525	-2.45233	2.91718	-0.123643	2.00304	38010
1.6	-2.43013	2.89474	-0.119683	2.00302	21590
1.675	-2.40989	2.87245	-0.116109	2.003	31766
1.75	-2.39043	2.85284	-0.112638	2.00298	31619
1.825	-2.37215	2.83467	-0.10937	2.00295	26670
1.9	-2.35479	2.81778	-0.106261	2.00293	18346
1.975	-2.33882	2.80282	-0.103389	2.00291	31662
2.05	-2.32356	2.7887	-0.100641	2.00289	42343
2.125	-2.30888	2.77559	-0.0979889	2.00287	39181
2.2	-2.2951	2.76339	-0.0954954	2.00285	26945
2.275	-2.28193	2.75212	-0.0931067	2.00283	32708
2.35	-2.26908	2.74134	-0.090771	2.0028	20670
2.425	-2.25757	2.7319	-0.0886747	2.00278	31887
2.5	-2.24626	2.72264	-0.086614	2.00276	31590
2.575	-2.23522	2.71401	-0.084595	2.00274	31490
2.65	-2.22489	2.70612	-0.0827006	2.00271	27795
2.725	-2.21495	2.6986	-0.0808772	2.00269	31921
2.8	-2.20569	2.69214	-0.0791696	2.00267	55510
2.875	-2.19653	2.68517	-0.077489	2.00265	26946
2.95	-2.18751	2.67887	-0.0758252	2.00262	22396

TABLE 5. Values are for $Z = 1.0$.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
3.025	-2.17925	2.67401	-0.0742818	2.0026	27084
3.1	-2.17142	2.66793	-0.0728498	2.00258	32312
3.175	-2.16356	2.66334	-0.0713811	2.00256	28331
3.25	-2.15547	2.65814	-0.0698782	2.00253	15318
3.325	-2.14903	2.65391	-0.0686851	2.00251	34245
3.4	-2.14183	2.64918	-0.0673491	2.00249	20794
3.475	-2.13541	2.64618	-0.0661357	2.00246	22598
3.55	-2.12916	2.64173	-0.0649838	2.00244	36281
3.625	-2.12268	2.64022	-0.0637269	2.00242	19140
3.7	-2.1167	2.63472	-0.0626501	2.00239	19076
3.775	-2.1102	2.63677	-0.0613194	2.00237	15862
3.85	-2.10558	2.62864	-0.0605641	2.00235	31569
3.925	-2.10013	2.62552	-0.0595457	2.00232	21907
4.	-2.095	2.62284	-0.0585798	2.0023	30562
4.27586	-2.07723	2.6139	-0.0552306	2.00221	36306
4.55172	-2.06138	2.60699	-0.0522232	2.00213	28791
4.82759	-2.04735	2.60064	-0.0495657	2.00204	43091
5.10345	-2.03425	2.59539	-0.0470696	2.00195	31264
5.37931	-2.02273	2.59114	-0.0448685	2.00186	33978
5.65517	-2.01201	2.58757	-0.0428125	2.00177	34961
5.93103	-2.00224	2.58428	-0.0409388	2.00168	29398
6.2069	-1.99345	2.58207	-0.0392401	2.00159	35001
6.48276	-1.98504	2.57939	-0.0376229	2.0015	24791
6.75862	-1.97746	2.57748	-0.0361565	2.00141	29134
7.03448	-1.97094	2.57582	-0.0348967	2.00132	48547
7.31034	-1.96395	2.57408	-0.0335436	2.00122	25374
7.58621	-1.95833	2.57299	-0.0324504	2.00113	48089
7.86207	-1.9525	2.57182	-0.0313176	2.00104	40833
8.13793	-1.94709	2.57087	-0.0302622	2.00094	23486
8.41379	-1.94222	2.57004	-0.0293132	2.00085	35758
8.68966	-1.93767	2.56921	-0.0284253	2.00075	38872
8.96552	-1.93328	2.56851	-0.0275687	2.00065	33970
9.24138	-1.92934	2.56823	-0.0267919	2.00056	69246
9.51724	-1.92532	2.56742	-0.0260112	2.00046	46955
9.7931	-1.92148	2.56705	-0.0252561	2.00036	26842
10.069	-1.91797	2.56637	-0.024574	2.00026	23937
10.3448	-1.91493	2.56751	-0.0239485	2.00016	51526
10.6207	-1.91171	2.56566	-0.0233452	2.00006	29533
10.8966	-1.90874	2.56547	-0.0227609	1.99996	29585
11.1724	-1.90599	2.56525	-0.0222194	1.99985	41918
11.4483	-1.90293	2.56471	-0.0216219	1.99975	20081
11.7241	-1.90072	2.56524	-0.0211727	1.99965	29287
12.	-1.89847	2.56461	-0.0207391	1.99954	51467

TABLE 6. Values are for $Z = 1.0$.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.001	-11.1848	31.7249	-0.450759	4.002	29573
0.00595	-10.8927	30.5595	-0.432351	4.002	34112
0.0109	-10.7189	29.8676	-0.421391	4.002	68778
0.01585	-10.5832	29.3299	-0.412819	4.002	47617
0.0208	-10.4684	28.8769	-0.405566	4.002	236518
0.02575	-10.3672	28.4785	-0.399164	4.002	128261
0.0307	-10.276	28.1208	-0.393389	4.002	45867
0.03565	-10.1927	27.7952	-0.388115	4.002	80789
0.0406	-10.1154	27.4951	-0.383206	4.00199	275505
0.04555	-10.0434	27.2138	-0.378641	4.00199	212755
0.0505	-9.97518	26.9526	-0.3743	4.00199	46055
0.05545	-9.9113	26.7033	-0.370252	4.00199	2288576
0.0604	-9.85027	26.4698	-0.366365	4.00199	121643
0.06535	-9.79217	26.2455	-0.362673	4.00199	426588
0.0703*	-9.73632*	26.0339*	-0.359109*	4.00199	27929*
0.07525*	-9.68029*	25.8304*	-0.355497*	4.00199	15002*
0.0802*	-9.6312*	25.6332*	-0.352409*	4.00199	27673*
0.08515*	-9.58244*	25.4461*	-0.349305*	4.00199	55738*
0.0901*	-9.53382*	25.2702*	-0.34617*	4.00199	21087*
0.09505*	-9.48831*	25.0948*	-0.343276*	4.00199	41286*
0.1	-9.44349	24.925	-0.340415	4.00199	23914
0.1225	-9.2572	24.2268	-0.328495	4.00199	41831
0.145	-9.09135	23.6153	-0.317843	4.00198	50850
0.1675	-8.94196	23.0701	-0.308226	4.00198	45708
0.19	-8.80571	22.5799	-0.299427	4.00198	52087
0.2125	-8.68025	22.1323	-0.29131	4.00198	32628
0.235	-8.56466	21.7246	-0.283813	4.00197	36291
0.2575	-8.45685	21.3484	-0.276804	4.00197	63468
0.28	-8.35611	21.0004	-0.270242	4.00197	97665
0.3025	-8.26177	20.677	-0.264086	4.00196	148209
0.325	-8.17233	20.3753	-0.258231	4.00196	61513
0.3475	-8.08816	20.0937	-0.252712	4.00195	136594
0.37	-8.00821	19.8285	-0.24746	4.00195	70827
0.3925	-7.93242	19.5803	-0.24247	4.00195	935877
0.415	-7.85996	19.3449	-0.23769	4.00194	57361
0.4375	-7.79126	19.1238	-0.233151	4.00194	89164
0.46	-7.72565	18.914	-0.228811	4.00193	660962
0.4825	-7.66275	18.7152	-0.224641	4.00193	147933
0.505	-7.60233	18.5286	-0.220617	4.00192	72445
0.5275	-7.54471	18.3473	-0.216794	4.00192	2121982
0.55	-7.48893	18.1789	-0.213065	4.00192	62732
0.5725	-7.43418	18.0222	-0.20937	4.00191	19629
0.595	-7.38437	17.8589	-0.206091	4.00191	77952

TABLE 7. Values are for $Z = 2.0$ and those with * are computed to tolerance 10^{-10} of the goal functional (instead of 10^{-11}).

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
0.6175	-7.33469	17.7103	-0.202764	4.0019	69499
0.64	-7.28687	17.5688	-0.199555	4.0019	77793
0.6625	-7.2404	17.4342	-0.196426	4.00189	33089
0.685	-7.19635	17.3037	-0.193471	4.00189	66682
0.7075	-7.15326	17.1793	-0.190568	4.00188	186711
0.73	-7.11154	17.0598	-0.187753	4.00188	162601
0.7525	-7.07092	16.9447	-0.185008	4.00187	44535
0.775	-7.03198	16.835	-0.182373	4.00187	60691
0.7975	-6.99419	16.7292	-0.179814	4.00186	67368
0.82	-6.95751	16.6281	-0.177324	4.00186	69853
0.8425	-6.92165	16.5294	-0.174889	4.00185	56066
0.865	-6.88694	16.4349	-0.172527	4.00185	39891
0.8875	-6.85366	16.3452	-0.17026	4.00184	203572
0.91	-6.8205	16.2563	-0.167999	4.00183	31321
0.9325	-6.78893	16.1724	-0.165843	4.00183	170723
0.955	-6.75783	16.0905	-0.163717	4.00182	92091
0.9775	-6.72756	16.0135	-0.161636	4.00182	67838
1.	-6.69854	15.9362	-0.159656	4.00181	391732
1.075	-6.6055	15.7017	-0.153253	4.00179	33916
1.15	-6.52072	15.4889	-0.147414	4.00178	73216
1.225	-6.44212	15.2987	-0.141973	4.00176	45259
1.3	-6.36899	15.1265	-0.136893	4.00174	34320
1.375	-6.30077	14.9721	-0.132129	4.00172	25607
1.45	-6.23787	14.8298	-0.127736	4.0017	30186
1.525	-6.17949	14.7018	-0.123643	4.00168	52233
1.6	-6.12448	14.5841	-0.119775	4.00166	70971
1.675	-6.07255	14.4764	-0.116109	4.00164	50872
1.75	-6.02389	14.3777	-0.112666	4.00162	61188
1.825	-5.97833	14.287	-0.109436	4.0016	103916
1.9	-5.93484	14.2033	-0.106341	4.00158	54233
1.975	-5.89361	14.1254	-0.103401	4.00155	46226
2.05	-5.85443	14.0549	-0.100593	4.00153	19951
2.125	-5.81835	13.9885	-0.0980136	4.00151	85519
2.2	-5.78334	13.9264	-0.0955014	4.00149	40224
2.275	-5.75009	13.8697	-0.093106	4.00147	39486
2.35	-5.71883	13.8168	-0.0908526	4.00145	48088
2.425	-5.6891	13.7688	-0.0887004	4.00143	89144
2.5	-5.66028	13.7223	-0.086614	4.0014	65476
2.575	-5.6326	13.6786	-0.0846067	4.00138	37704
2.65	-5.60687	13.6402	-0.0827315	4.00136	75030
2.725	-5.58195	13.6023	-0.0809188	4.00134	52692
2.8	-5.55812	13.5668	-0.0791822	4.00132	69742
2.875	-5.53501	13.533	-0.0774951	4.0013	37465
2.95	-5.51299	13.502	-0.0758835	4.00127	48955

TABLE 8. Values are for $Z = 2.0$.

$(2Z)^{\frac{1}{3}}R$	$u(0,R/2)$	$\frac{1}{c_{TF}}\int\varphi^{5/2}$	$(2Z)^{\frac{-7}{3}}\left(D^{TF}_{(Z,Z),R}-\frac{Z^2}{R}\right)$	$\int\varrho$	#cells
3.025	-5.49213	13.4738	-0.0743517	4.00125	55820
3.1	-5.47168	13.4458	-0.0728519	4.00123	38956
3.175	-5.45243	13.4205	-0.0714353	4.00121	50048
3.25	-5.43308	13.3958	-0.0700087	4.00118	25566
3.325	-5.41569	13.3738	-0.0687262	4.00116	55423
3.4	-5.39822	13.3522	-0.067435	4.00114	53374
3.475	-5.3812	13.3316	-0.0661761	4.00112	24726
3.55	-5.36487	13.3126	-0.064965	4.00109	26228
3.625	-5.34976	13.2981	-0.0638328	4.00107	69959
3.7	-5.33456	13.278	-0.0627145	4.00105	31274
3.775	-5.32036	13.2622	-0.0616587	4.00103	69651
3.85	-5.30605	13.2463	-0.0605946	4.001	37130
3.925	-5.29265	13.2322	-0.0595948	4.00098	65864
4.	-5.27891	13.2178	-0.0585696	4.00096	26749
4.27586	-5.23491	13.174	-0.0552771	4.00088	79650
4.55172	-5.19447	13.1369	-0.0522395	4.00079	36520
4.82759	-5.1582	13.1102	-0.0494876	4.00071	28419
5.10345	-5.12621	13.0835	-0.0470738	4.00062	29835
5.37931	-5.09699	13.0591	-0.0448693	4.00054	42539
5.65517	-5.06993	13.0399	-0.0428142	4.00045	41616
5.93103	-5.04545	13.0243	-0.0409479	4.00036	24343
6.2069	-5.02348	13.0115	-0.039268	4.00028	110392
6.48276	-5.00274	13.0007	-0.0376769	4.00019	49742
6.75862	-4.98394	12.9917	-0.0362324	4.0001	95280
7.03448	-4.96595	12.9834	-0.0348489	4.00002	43567
7.31034	-4.94954	12.9737	-0.0335945	3.99993	26060
7.58621	-4.93456	12.9677	-0.0324385	3.99984	68394
7.86207	-4.92043	12.9621	-0.031348	3.99975	105070
8.13793	-4.90702	12.958	-0.0303079	3.99966	86990
8.41379	-4.89452	12.9549	-0.0293359	3.99957	101737
8.68966	-4.88245	12.948	-0.0284126	3.99948	23053
8.96552	-4.87156	12.9443	-0.0275693	3.99939	43222
9.24138	-4.86141	12.9435	-0.026773	3.9993	55523
9.51724	-4.85181	12.9391	-0.0260346	3.99921	72386
9.7931	-4.84248	12.937	-0.0253087	3.99912	37578
10.069	-4.83364	12.9351	-0.0246201	3.99903	30938
10.3448	-4.82534	12.9332	-0.023974	3.99893	60966
10.6207	-4.81765	12.9319	-0.0233731	3.99884	109972
10.8966	-4.81013	12.9296	-0.0227903	3.99875	100712
11.1724	-4.80275	12.9281	-0.0222152	3.99865	38828
11.4483	-4.79597	12.9266	-0.0216871	3.99856	44337
11.7241	-4.79	12.9258	-0.0212198	3.99847	57890
12.	-4.7837	12.9249	-0.0207272	3.99837	44632

TABLE 9. Values are for $Z = 2.0$.

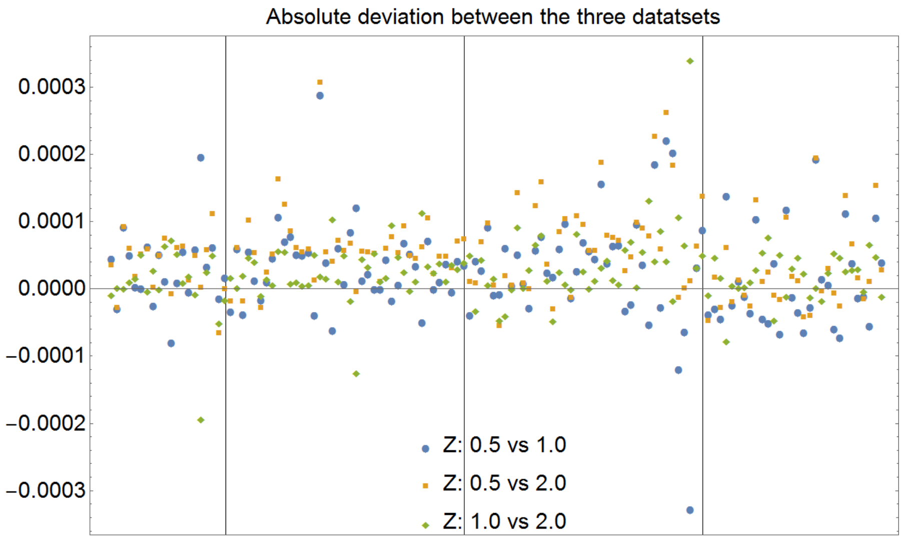


FIGURE 1. Absolute deviation of $D(r)$ between different choices of $Z \in \{0.5, 1, 2\}$ and r ranging from 0.001 to 12. The vertical lines are at $r = (2Z)^{1/3}R = 0.1, 1$ and 4.

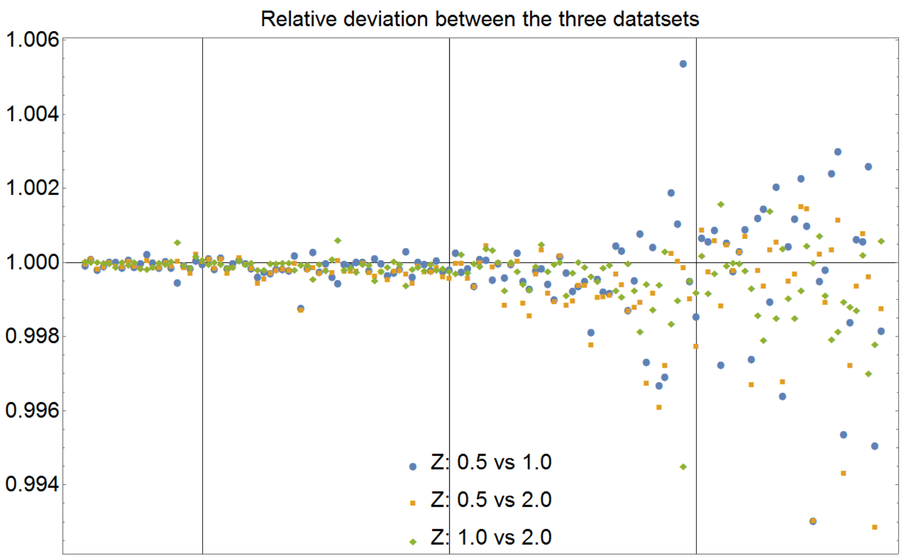


FIGURE 2. Relative deviation of $D(r)$ between different choices of $Z \in \{0.5, 1, 2\}$ and r ranging from 0.001 to 12. The vertical lines are at $r = (2Z)^{1/3}R = 0.1, 1, 4$.

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Software used

(1) FEniCS, version 2017.2. This is an open-source computing platform we used to solve the diatomic TF equation, and in particular for the scripts in appendix C.3, C.4 and C.7. A description of version 1.5 is in [44] and the goal-oriented adaptation has been proposed in [43]. It is freely available under `https://fenicsproject.org/`.

(2) ParaView, version 5.4.1. For the visualization of solutions computed via FEniCS, in particular Figures 3, 4 and 5. It is freely available under `https://www.paraview.org/`. See also [45].

(3) FreeFem++, version 3.59. Another software for the FEM. We used it to cross-check the results from FEniCS, see the appendix C.6. It is freely available at `http://www.freefem.org/`. See also [46].

(4) (Wolfram) Mathematica, version 11.1.1.0 [47] was used to solve the atomic ODE and a linearisation of the diatomic PDE (in appendix C.1, C.5, C.2). All Figures (except 3, 4 and 5) have been created within Mathematica.

Errata

The present thesis differs from the submitted version only by typos and minor corrections. More substantial mistakes which we are aware of are listed here, followed by corrected proofs of Theorem 5.1 and 6.1.

i) Page 4: Equation (1.6) holds only for sequences with bounded ratio, meaning $Z_1 \leq Z_2 \leq (cst.)Z_1$. See also viii) and xv) below.

ii) Page 27: In the statement and proof of Lemma 3.13, all appearances of '$c_{\mathrm{TF}}^{-3/2}\varphi^{3/2}$' should be replaced by ϱ, the corresponding TF density.

iii) Page 32: After (3.24), we erroneously claim that $F \in H^1$ but only have $FW \in L^6$ and $\nabla FW \in L^2$. The latter is still sufficient to apply [12, Lemma 9.2]. Similar, Lemma B.2 only proves $FW \in L^6$ and $\nabla FW \in L^2$.

iv) Pages 41 and 42: An assumption on the regularity of $\partial\Omega$ in Proposition 3.19 and Definition 3.20 is missing (C^1 suffices).

v) Page 42: At the end of the proof of Lemma 3.21, the value for $\int_{\mathbb{H}_{R\nu/2}} I_{r,R\nu}$ is false. It equals $\frac{20\pi}{r}\operatorname{arsinh}(r/\sqrt{(R/2)^2-r^2})$ and since $\operatorname{arsinh}(x) \leq x$ for $x \geq 0$, Lemma 3.21 holds with $\frac{5\pi}{4}$ replaced by 10 on the right hand side. Note that $c_{3.22a}$ and $c_{3.22b}$ are now given with this corrected value.

vi) Page 43: The roles of σ, ϵ and σ^*, ε^* in the second and third sentence of Lemma 3.22 have erroneously been swapped. Instead, it should read 'Assume there exist positive $\epsilon, \epsilon^*, \sigma, \sigma^*$ such that $\sup_{\mathcal{O}_r} |V - \Phi^{\mathrm{TF}}_{\mathbf{Z},R,r}| \leq \sigma^* r^{-4+\epsilon^*}$ and $\sup_{B(p,r)^c} |V^{(p)} - \Phi^{\mathrm{TF}}_{Z_p,r}| \leq \sigma r^{-4+\epsilon}$ for $p \in \{0, R\nu\}$. Furthermore assume that $(3/2a^{\mathrm{TF}})^{\frac{1}{\epsilon}} m_{\mathbf{Z}}^{\frac{-1}{3}} \leq r \leq \min\{R/4, (c_{3.14b}/\sigma)^{1/\epsilon}, (c_{3.17}/\sigma^*)^{1/\epsilon^*}\}$.' As a consequence, the proofs of Theorem 6.1 and Lemma 6.3 need to be changed (see xii) below).

vii) Page 57: The first summand on the right hand side of (4.17) should read

$$\frac{8q^{2/3}\pi^{2/3}\left|E_1^{\mathrm{TF}}\right|}{3^{1/3}c_H K_1}\left(r\sup_{\partial\mathcal{O}_r}|\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}|\left(1+\frac{1}{R/2-2}\right)\right)^{7/3}.$$

This is due to the incorrect argument '$\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}(x) \leq \frac{r}{|x|}\sup_{\partial\mathcal{O}_r}\Phi^{\mathrm{rHF}}_{\mathbf{Z},R,r}$' in the proof, which is repaired by using Lemma 3.15 with (3.17) and $E^{\mathrm{TF}}_{(Z,Z),R} \geq 2E^{\mathrm{TF}}_Z$. This mistake mainly changes the value of $c_{5.6b}$.

viii) Page 59 and thereafter: The proof of Theorem 5.1 requires the ratio of the nuclear charges to be bounded. Furthermore, the constant $c_{5.1b}$ we give is ill-defined. It should instead depend on δ. Below we give a proof of the corrected version, which is:

Theorem (5.1, corrected)**.** *There exist $\delta_{5.1} > 0$ and $c_{5.1a}(\lambda), c_{5.1b}(\lambda,\delta) > 0$ such that for all $R, \lambda > 0$, $\delta \in (0, \delta_{5.1}]$ and $\boldsymbol{Z} \in \mathbb{R}^2_+$ with $1 \le |\boldsymbol{Z}| \le \lambda m_{\boldsymbol{Z}}$: If $r \le c_{5.1b}(\lambda,\delta) \min\left\{1, (R/2)^{1+\frac{\delta\xi}{\eta-\delta\xi}}\right\}$, then*

$$\sup_{x\in\partial\mathcal{O}_r} \left| \int_{\mathcal{I}_r} \frac{\varrho^{\mathrm{TF}}_{\boldsymbol{Z},R}(y) - \varrho^{\mathrm{rHF}}_{\boldsymbol{Z},R}(y)}{|x-y|} dy \right| \le c_{5.1a}(\lambda) r^{-4+\delta\xi}. \tag{E.1}$$

ix) Page 64: The set $\Omega_s = \mathcal{O}_s$ in Lemma 5.5 actually depends on $R > 2s$. A better notation would be $\Omega_{s,R}$, in particular for the identity $|\Omega^c_{s,R}| = s^3|\Omega^c_{1,R/s}|$.

x) Page 66: The bound $\mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}} - \varrho_r) \ge \mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{rHF}}(\omega^2_{\mathcal{O}} - \mathbb{1}_{\mathcal{O}_r}))$ is false. Instead, $\mathcal{D}(\varrho^{\mathrm{rHF}}\omega^2_{\mathcal{O}} - \varrho_r) \ge \frac{1}{2}\mathcal{D}(\varrho^{\mathrm{rHF}}\mathbb{1}_{\mathcal{O}_r} - \varrho_r) - \mathcal{D}(\varrho^{\mathrm{rHF}}(\omega^2_{\mathcal{O}} - \mathbb{1}_{\mathcal{O}_r}))$. This only changes constants.

xi) Page 69: Theorem 6.1 requires the stronger assumption $\mathbf{Z} \in [1,\infty)^2$ instead of $\mathbf{Z} \in \mathbb{R}^2_+, |\mathbf{Z}| \ge 1$.

xii) Page 70: Due to viii), we fix ε in Lemma 6.3, so that $c_{5.1b}(\lambda, \varepsilon/\xi)$ only depends on λ. Moreover, because of vi), we need to keep the factor $(Rm_{\mathbf{Z}}^{1/3})^{-\tilde\eta\xi}$ for the corrected proof of Theorem 6.1. With these changes and by defining $c_{6.3a} := c_{3.8b}\left(2^\xi a^{\mathrm{TF}}\tilde\xi/\tilde\eta\right)^{-\tilde\eta} 2^{4(\varepsilon/\eta-2)} + c_{3.8c}2^{4\varepsilon/\eta-\eta}$, the same proof yields:

Lemma (6.3, corrected)**.** *Let $\boldsymbol{Z} \in [1,\infty)^2$ with $|\boldsymbol{Z}| \le \lambda m_{\boldsymbol{Z}}$. There exist $c_{6.3a}, c_{6.3b}(\lambda) > 0$ such that if $2 \ge R \ge 2\left(a^{\mathrm{TF}}\tilde\xi/\tilde\eta\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ and if $r := c_{6.3b}(\lambda)(R/2)^{1+\frac{\varepsilon}{\eta-\varepsilon}} \ge \left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ with $\varepsilon = \min\{\delta_{5.1}\xi, \varepsilon_{5.2}\}$, then for all $s \le r$ and $p \in \{0, R\nu\}$:*

i) $\sup_{B(p,s)^c} \left|\left(\varrho^{\mathrm{rHF}}_{\boldsymbol{Z},R} - \varrho^{\mathrm{TF}}_{Z_p}(\cdot - p)\right)\mathbb{1}_{B(p,s)} * |x|^{-1}\right| \le s^{-4}\left(f_{\boldsymbol{Z},R,s} + \frac{3}{2}c_{5.1a}s^\varepsilon\right)$

ii) $\sup_{B(0,s)^c} \left|\left(\varrho^{\mathrm{rHF}}_{Z_p} - \varrho^{\mathrm{TF}}_{Z_p}\right)\mathbb{1}_{B(0,s)} * |x|^{-1}\right| \le c_{5.2a}s^{-4+\varepsilon}$

iii) $\sup_{\mathcal{O}_s} \left|\left(\varrho^{\mathrm{rHF}}_{\boldsymbol{Z},R} - \varrho^{\mathrm{TF}}_{\boldsymbol{Z},R}\right)\mathbb{1}_{\mathcal{I}_s} * |x|^{-1}\right| \le c_{5.1a}s^{-4+\varepsilon}$

iv) $\sup_{\mathcal{O}_s} \left| \sum_{p\in\{0,R\nu\}} \left(\varrho^{\mathrm{rHF}}_{Z_p}(\cdot - p) - \varrho^{\mathrm{TF}}_{\boldsymbol{Z},R}\right)\mathbb{1}_{B(p,s)} * |x|^{-1}\right| \le s^{-4}2\left(f_{\boldsymbol{Z},R,s} + c_{5.2a}s^\varepsilon\right)$,

where $f_{\boldsymbol{Z},R,s} := c_{3.8b}(s/R)^4\left(Rm_{\boldsymbol{Z}}^{1/3}\right)^{-\tilde\eta\xi} + c_{3.8c}(2s/R)^\eta \le c_{6.3a}s^{\frac{4\varepsilon}{\eta}}$. Furthermore (under the same assumptions),

v) $\mu_r^{(j,p)} = 0$ *and* $\int \varrho_r^{(j,p)} \le c_{3.14a}r^{-3}$ *for* $j \in \{1,2\}$, $p \in \{0, R\nu\}$,

vi) $\mu_r^{(j)} = 0$ *and* $\int \varrho_r^{(j)} \le 2^{7/2}(1+A)^{3/2}c_{\mathrm{S}}r^{-3}$ *for* $j \in \{3,4\}$.

xiii) Page 71 and thereafter: The bounds (6.7) and (6.11) are missing the difference $\mathcal{Q}[V_r^{(j,0)}, V_r^{(j,R\nu)}] - \mathcal{Q}[W_{r,\delta}^{(j,0)}, W_{r,\delta}^{(j,R\nu)}]$, where $W_{r,\delta}^{(j,p)}$ is basically $V_r^{(j,p)}$ but with a smooth cut-off ω_p^2 instead of $\mathbb{1}_{B(p,r)}$. To bound it, we note that (5.4) can be proven to hold with r replaced by t, for all $t \leq r$ and the analogue holds for the atomic rHF density (see also [12, Lemma 12.6]). Hence, via Hölder's inequality and $\int_{|x|-\delta\leq|y|\leq|x|} |x-y|^{-5/2}dx \leq 8\pi\sqrt{\delta}$, we have $\|W_{r,\delta}^{(j,p)} - V_r^{(j,p)}\|_\infty \leq (cst.)(r-\delta)^{-5}(\delta/r)^{1/5}$. We also note that $V_r^{(1,p)} \leq W_{r,\delta}^{(1,p)} \leq V_{r-\delta}^{(1,p)}$ so that overall, by using Lemma 3.21, one deduces

$$|\mathcal{Q}[V_r^{(j,0)}, V_r^{(j,R\nu)}] - \mathcal{Q}[W_{r,\delta}^{(j,0)}, W_{r,\delta}^{(j,R\nu)}]| \leq (cst.)(r-\delta)^{-7}(\delta/r)^{1/5}.$$

We then chose $\delta = r^{21/11}$ in (6.7) and (6.11) which together with the changes from xii) leads to:

Lemma (6.4, corrected). *Let $\boldsymbol{Z} \in [1,\infty)^2$ with $|\boldsymbol{Z}| \leq \lambda m_{\boldsymbol{Z}}$. There exist $c_{6.3a}$, $c_{6.3b}(\lambda) > 0$ such that if $2 \geq R \geq 2\left(a^{\mathrm{TF}}\tilde{\xi}/\tilde{\eta}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ and if $r := c_{6.3b}(\lambda)(R/2)^{1+\frac{\varepsilon}{\eta-\varepsilon}} \geq \left(\frac{3}{2}a^{\mathrm{TF}}\right)^{\frac{1}{\xi}} m_{\boldsymbol{Z}}^{\frac{-1}{3}}$ with $\varepsilon = \min\{\delta_{5.1}\xi, \varepsilon_{5.2}\}$, then*

$$E_r^{(3)} - E_r^{(1,0)} - E_r^{(1,R\nu)} + \mathcal{Q}[V_r^{(1,0)}, V_r^{(1,R\nu)}] - c_{6.4a}(\lambda) r^{-7+\frac{2}{11}} \leq D_{\boldsymbol{Z},R}^{\mathrm{rHF}} \tag{E.2}$$

and

$$E_r^{(4)} - E_r^{(2,0)} - E_r^{(2,R\nu)} + \mathcal{Q}[V_r^{(2,0)}, V_r^{(2,R\nu)}] + c_{6.4b}(\lambda) r^{-7+\frac{2}{11}} \geq D_{\boldsymbol{Z},R}^{\mathrm{rHF}}. \tag{E.3}$$

xiv) Page 75: Due to vi), the proof of Theorem 6.1 does not work and we provide a corrected version below.

xv) Page 75: Corollary 6.5 and the remarks before it are false. We only have

$$\limsup_{\substack{m_{\mathbf{Z}}\to\infty \\ |\mathbf{Z}|\leq(cst.)m_{\mathbf{Z}}}} \left|D_{\mathbf{Z},R}^{\mathrm{rHF}} - D_{\infty,1}^{\mathrm{TF}} R^{-7}\right| = o(R^{-7}), \qquad \text{as } R \to 0.$$

xvi) Page 79: In the text and in Figure 1, '$f_N(r) = \int_{|y|\geq r} \varrho_1^{\mathrm{TF}}(y)dy$' is wrong since $f_N(r) = \int_{|y|\geq r} \varrho_1^{\mathrm{TF}}(y)(1 - r/|y|))dy$.

Corrected proof of Theorem 5.1. Here we prove (E.1).

Proof. We begin by defining the constant $\delta_{5.1} = \min\{\delta_{5.4}, \frac{1}{537/2+66\xi}\}$ and introduce the set $\mathcal{P}_\lambda := (0,\delta_{5.1}] \times \mathbb{R}_+ \times \{\mathbf{Z} \in \mathbb{R}_+^2 : 1 \leq |\mathbf{Z}| \leq \lambda m_{\mathbf{Z}}\}$. Furthermore, let

$$c_{5.1a}(\lambda) = \max\left\{c_{5.3}\left(\tfrac{3}{2}(a^{\mathrm{TF}})^{\frac{1}{\xi}}\lambda^{\frac{1}{3}}\right)^{\frac{49}{12}-\frac{1}{66}}, c_{5.4}\right\}.$$

Step 1 (Reformulating the first step)
Let $\beta_{\mathbf{Z}}(\delta) := (\frac{3}{2}a^{\mathrm{TF}})^{\frac{1}{\xi(1+\delta)}} m_{\mathbf{Z}}^{\frac{-1}{3(1+\delta)}} |\mathbf{Z}|^{\frac{1}{3}}$ then $r_{\mathbf{Z}} := (\beta_{\mathbf{Z}}|\mathbf{Z}|^{-1/3})^{1+\delta} = (\frac{3}{2}a^{\mathrm{TF}})^{\frac{1}{\xi}} m_{\mathbf{Z}}^{\frac{-1}{3}}$.

Since $4+\frac{3}{44}=\frac{49}{12}-\frac{1}{66}$, Lemma 5.3 implies $\mathcal{A}\left(r,\frac{1}{66},c_{5.3}\beta_{\mathbf{Z}}^{\frac{49}{12}-\frac{1}{66}}\right)$ for all $r\leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$. Noting that $\delta\leq\delta_{5.1}<2/537$, we have $\varepsilon(\delta):=\frac{1}{66}-\delta(\frac{49}{12}-\frac{1}{66})>0$ and observe that if $r\leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$ then $r^{1/66}\beta_{\mathbf{Z}}^{\frac{49}{12}-\frac{1}{66}}\leq r^{\varepsilon(\delta)}\beta_{\mathbf{Z}}^{\frac{49}{12}-\frac{1}{66}}\left(\beta_{\mathbf{Z}}|\mathbf{Z}|^{\frac{-1}{3}}\right)^{\frac{1}{66}-\varepsilon(\delta)}\leq r^{\varepsilon(\delta)}\left(\frac{3}{2}(a^{\mathrm{TF}})^{\frac{1}{\xi}}\lambda^{\frac{1}{3}}\right)^{\frac{49}{12}-\frac{1}{66}}$. Here the last inequality used the definitions of $\beta_{\mathbf{Z}},\varepsilon(\delta)$ and the bound $|\mathbf{Z}|\leq\lambda m_{\mathbf{Z}}$. Hence $\mathcal{A}(r,\varepsilon(\delta),c_{5.1a}(\lambda))$ for all $r\leq r_{\mathbf{Z}}^{\frac{1}{1+\delta}}$. The inequality $\delta\leq(\frac{537}{2}+66\xi)^{-1}$ is equivalent to $\delta\xi\leq\varepsilon(\delta)$ so that if $r\leq 1$ then $r^{\varepsilon(\delta)}\leq r^{\delta\xi}$. Overall, we find that

$$\forall(\delta,R,\mathbf{Z})\in\mathcal{P}_\lambda:\ \mathcal{A}\left(r,\delta\xi,c_{5.1a}(\lambda)\right)\ \forall r\leq\min\left\{1,r_{\mathbf{Z}}^{\frac{1}{1+\delta}}\right\}.$$

Step 2 (Iteration) For $(\delta,R,\mathbf{Z})\in\mathcal{P}_\lambda$ we define

$$M(\delta,R,\mathbf{Z}):=\sup\left\{r\in\mathbb{R}:\ \mathcal{A}(s,\delta\xi,c_{5.1a}(\lambda)),\ \forall s\leq r^{\frac{1}{1+\delta}}\right\}.$$

By the same arguments as in Step 2 of the original proof on page 63, we deduce that $M(\delta,R,\mathbf{Z})\geq\min\left\{D(c_{5.1a}(\lambda),\delta\xi,R)\,,c_{3.18a}^{\frac{(\eta+\xi)(1+\delta)}{\eta-\delta\xi}}(R/2)^{\frac{\eta(1+\delta)}{\eta-\delta\xi}}\right\}$ for any $(\delta,R,\mathbf{Z})\in\mathcal{P}_\lambda$ and with D from Lemma 5.4. From here we continue as in Step 3 on page 63 except that we chose $c_{5.1b}(\lambda,\delta):=\min\left\{1/2,(c_{3.17}/c_{5.1a}(\lambda))^{\frac{1}{\delta\xi(1+\delta)}},(c_{3.18b})^{\frac{1}{1+\delta}},c_{3.18a}^{\frac{(\eta+\xi)}{\eta-\delta\xi}}\right\}$. $\square$

Corrected proof of Theorem 6.1

Here we prove: There exists $\varepsilon_{6.1}>0$ and an increasing $\theta:\mathbb{R}_+\to\mathbb{R}_+$ such that for all $R\in(0,2]$ and all $\mathbf{Z}\in[1,\infty)^2$, we have $\left|D_{\mathbf{Z},R}^{\mathrm{TF}}-D_{\mathbf{Z},R}^{\mathrm{rHF}}\right|\leq\theta\left(\frac{|\mathbf{Z}|}{m_{\mathbf{Z}}}\right)R^{-7+\varepsilon_{6.1}}$.

Proof. Let $\varepsilon=\min\{\delta_{5.1}\xi,\varepsilon_{5.2}\}$, $\lambda=|\mathbf{Z}|/m_{\mathbf{Z}}$ and $r=c_{6.3b}(\lambda)(R/2)^{1+\frac{\varepsilon}{\eta-\varepsilon}}$. We assume first that $2\geq R\geq C_1(\lambda)m_{\mathbf{Z}}^{-\frac{1}{3}(1-\alpha)}$ with $\alpha\in(\varepsilon/\eta,1)$ and

$$C_1(\lambda)=2\max\left\{(a^{\mathrm{TF}}\tilde{\xi}/\tilde{\eta})^{\frac{1}{\xi}},((a^{\mathrm{TF}}3/2)^{\frac{1}{\xi}}/c_{6.3b}(\lambda))^{1-\frac{\varepsilon}{\eta}}\right\}.$$

Then $Rm_{\mathbf{Z}}^{\frac{1}{3}}\geq 2(a^{\mathrm{TF}}\tilde{\xi}/\tilde{\eta})^{\frac{1}{\xi}}$ and, because $\alpha\eta>\varepsilon$, also $r\geq(a^{\mathrm{TF}}3/2)^{\frac{1}{\xi}}m_{\mathbf{Z}}^{-\frac{1}{3}}$ so that the assumptions of the corrected Lemmas 6.3 and 6.4 are satisfied. This means that both (6.3) and (6.4) hold, with $\varepsilon_{5.2}$ and $\delta_{5.1}\xi$ replaced by ε. Hence we see that the assumptions of Lemma 3.22 are (using the corrected Lemma 6.3 i), iii)) satisfied for $V^{(p)}=V_r^{(1,p)}$, as well as (using the corrected Lemma 6.3 ii), iv)) for $V^{(p)}=V_r^{(2,p)}$. Note also that $\varepsilon<2/537<2/11$. Combining (3.47) with (E.3) and the corrected Lemma 6.3 iv), and (3.48) with (E.2) and the corrected Lemma 6.3 i), we thus find

$$\left|D_{\mathbf{Z},R}^{\mathrm{rHF}}-D_{\mathbf{Z},R}^{\mathrm{TF}}\right|\leq C_2(\lambda)R^{-7}\left((2r/R)^{-7}r^{\varepsilon}+(2r/R)^{\eta-7}+(2r/R)^{-3}(Rm_{\mathbf{Z}}^{1/3})^{-\tilde{\eta}\xi}\right).$$

We use the definition of r and the inequality $Rm_{\mathbf{Z}}^{1/3} \geq R^{\frac{-\alpha}{1-\alpha}} C_1(\lambda)^{\frac{1}{1-\alpha}}$ to conclude that if $2 \geq R \geq C_1(\lambda) m_{\mathbf{Z}}^{-\frac{1}{3}(1-\alpha)}$, then

$$\left|D_{\mathbf{Z},R}^{\mathrm{rHF}} - D_{\mathbf{Z},R}^{\mathrm{TF}}\right| \leq C_3(\lambda,\alpha) R^{-7+\varepsilon_1(\alpha)}, \tag{E.4}$$

with $\varepsilon_1(\alpha) = \min\left\{\frac{\varepsilon(\eta-7)}{\eta-\varepsilon}, \frac{\alpha\tilde{\eta}\xi}{1-\alpha} - \frac{3\varepsilon}{\eta-\varepsilon}\right\}$.

Let us now assume that $R \leq C_1(\lambda) m_{\mathbf{Z}}^{-\frac{1}{3}(1-\alpha)}$. According to Lemma 4.6, we have $|E_{\mathbf{Z},R}^{\mathrm{TF}} - E_{\mathbf{Z},R}^{\mathrm{rHF}}| \leq \max\{c_{4.6a}, c_{4.6b}\} |\mathbf{Z}|^{\frac{7}{3}-\frac{2}{33}}$ and $|E_Z^{\mathrm{TF}} - E_Z^{\mathrm{rHF}}| \leq \max\{c_{4.6a}, c_{4.6b}\} Z^{\frac{7}{3}-\frac{2}{33}}$. We combine these bounds so that for all $R \leq C_1(\lambda) m_{\mathbf{Z}}^{-\frac{1}{3}(1-\alpha)}$:

$$|D_{\mathbf{Z},R}^{\mathrm{rHF}} - D_{\mathbf{Z},R}^{\mathrm{TF}}| \leq \underbrace{\max\{c_{4.6a}, c_{4.6b}\}\left(1 + (\lambda-1)^{\frac{75}{33}} + \lambda^{\frac{75}{33}}\right) C_1(\lambda)^{\frac{75}{11(1-\alpha)}}}_{=C_4(\lambda,\alpha)} R^{-7+\varepsilon_2(\alpha)}, \tag{E.5}$$

with $\varepsilon_2(\alpha) = \frac{2-77\alpha}{11(1-\alpha)}$. Note that $\varepsilon_2(\alpha) > 0$ for any $\alpha < 2/77$ and $\varepsilon_1(\alpha) > 0$ for all $\alpha > C_5 := (1 + \frac{\tilde{\eta}\xi}{3}(\frac{537\eta}{2\xi} - 1))^{-1}$ because $\varepsilon < \frac{2}{537}\xi$. We also have $C_5 > \varepsilon/\eta$ and since $C_5 < 2/77$, there exists $\alpha_0 = \arg\max_{[C_5, 2/77]} \min\{\varepsilon_1(\alpha), \varepsilon_2(\alpha)\}$ such that $\varepsilon_{6.1} := \min\{\varepsilon_1(\alpha_0), \varepsilon_2(\alpha_0)\} > 0$. We combine (E.4) and (E.5) for $\alpha = \alpha_0$ and complete the proof with $\theta(t) := \inf_{t \leq \lambda} \max\{C_3(\lambda, \alpha_0), C_4(\lambda, \alpha_0)\}$. $\square$