博士論文

論文題目

Binding stability of molecules in density-matrix-functional theories

（密度行列汎関数理論における分子の安定性）

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Chapter 1

Introduction

1 Many-Particle systems

We consider a problem of N electrons and K static nuclei (Born-Oppenheimer approximation). The K nuclei have charges $\underline{Z} = (Z_1, \ldots, Z_K) \in (\mathbb{R}_+ \cup \{0\})^K$ and are located at $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$. We use the units $\hbar = m = c = e = 1$. These are

- m = mass of the electron
- $e = -1\times$ charge of the electron
- $\hbar$ = Planck's constant divided by 2π
- c = speed of light.

The nonrelativistic quantum mechanical model for a molecule is described by the Hamiltonian

$$H(N, \underline{Z}, \underline{R}) \coloneqq \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_{x_i} - V_{\underline{R}}(x_i) \right) + \sum_{1 \le i < j \le N} W(|x_i - x_j|) + U_{\underline{R}},$$

where Δ_{x_i} is the three-dimensional Laplacian with respect to the coordinate $x_i \in \mathbb{R}^3$ and

$$V_{\underline{R}}(x) \coloneqq \sum_{j=1}^{K} \frac{Z_j}{|x - R_j|},$$
$$W(|x-y|) \coloneqq \frac{1}{|x-y|},$$
$$U_{\underline{R}} \coloneqq \sum_{1 \le i < j \le K} \frac{Z_i Z_j}{|R_i - R_j|}.$$

Here $V_{\underline{R}}(x)$ is the electron-nucleus attractive Coulomb interaction, $W(|x-y|)$ is the electron-electron repulsive interaction, and $U_{\underline{R}}$ is the nucleus-nucleus repulsive interaction. For N electrons system, the wave functions obey the Pauli exclusion principle, that is, ψ must be anti-symmetric:

$$\psi(\dots, x_i, \dots, x_j, \dots) = -\psi(\dots, x_j, \dots, x_i, \dots)$$

for $i \neq j$. For the sake of simplicity, we ignore the electron spin. The subspace of $L^2(\mathbb{R}^{3N})$ consisting of all anti-symmetric function is denoted by $\bigwedge^N L^2(\mathbb{R}^3)$. It is well-known that $H(N, \underline{Z}, \underline{R})$ is the self-adjoint operator on $\bigwedge^N L^2(\mathbb{R}^3)$ and bounded from below.

The ground state energy of the system is given by the bottom of the spectrum, namely

$$E(N, \underline{Z}, \underline{R}) \coloneqq \inf \operatorname{spec} H(N, \underline{Z}, \underline{R}) = \inf \left\{ \frac{\langle \psi, H(N, \underline{Z}, \underline{R})\psi \rangle_{L^2}}{\langle \psi, \psi \rangle_{L^2}} : \psi \in \bigwedge^N L^2(\mathbb{R}^3) \right\}.$$

If $E(N, \underline{Z}, \underline{R})$ is an eigenvalue of $H(N, \underline{Z}, \underline{R})$, the corresponding eigenfunction is called the ground state.

We are interested in the properties of the ground states of $H(N, \underline{Z}, \underline{R})$. The HVZ theorem [29] states that the essential spectrum of $H(N, \underline{Z}, \underline{R})$ is given by

$$\operatorname{ess.spec} H(N, \underline{Z}, \underline{R}) = [E(N-1, \underline{Z}, \underline{R}), +\infty).$$

In particular, if one cannot move the excess electrons infinitely far away without changing energy, that is, $E(N, \underline{Z}, \underline{R}) < E(N-1, \underline{Z}, \underline{R})$, then $E(N, \underline{Z}, \underline{R})$ is the discrete eigenvalue of $H(N, \underline{Z}, \underline{R})$, and therefore there is a ground state ψ. In other words, the electrons can be bound by a collection of nuclei.

Zhislin showed that the binding $E(N, \underline{Z}, \underline{R}) < E(N-1, \underline{Z}, \underline{R})$ occurs if, at least, $N < Z + 1$, where $Z = \sum_{j=1}^{K} Z_j$.

On the other hand, it is also known that the system is not bound if for a given N the total nuclear charge becomes sufficiently small. More precisely, Lieb [33] proved that the system has no ground state if $N \geq 2Z + K$. This implies instability of the di-anion H^{2-} ($N = 3$, $Z = 1$, and $K = 1$). In the usual fermionic case (electrons system), experimental [3] and numerical [26, 43] evidence suggests that there are no stable di-anions X^{2-}, that is, fermionic atoms and molecules are not bound if $N > Z + cK$ with c close to 1, or possibly 2. Rigorous proof of this fact (called the ionization conjecture) is a long standing open problem in mathematical physics literature, except in the context of approximate theories such as [6, 24, 25, 28, 32, 49].

Although one might think the bound on the maximum ionization $N - Z$ is a consequence of Coulomb potential, if particles are boson (i.e., the wave functions are in the whole of $L^2(\mathbb{R}^{3N})$, not $\bigwedge^N L^2(\mathbb{R}^3)$), the ionization is as large as $N \sim 1.21Z$ for an atom with large Z. Here $1.21Z$ is exact (the lower bound was shown by Benguria and Lieb [8], and the upper bound was shown by Solovej [48], or see [4]). Hence the particle symmetry (the Pauli exclusion principle) is essential for the ionization conjecture.

Lieb, Sigal, Simon and Thirring [34] showed that the asymptotic neutrality $N/Z \to 1$ as $Z \to \infty$ for fermion models. Asymptotically, it was improved to $N \leq Z + \mathcal{O}(Z^{5/7})$ by Seco, Sigal and Solovej [42], and by Fefferman and Seco [18].

For the molecular case, we define the Born-Oppenheimer energy by

$$E(N, \underline{Z}) := \inf_{\underline{R} \in \mathbb{R}^{3K}} E(N, \underline{Z}, \underline{R}).$$

Lieb and Thirring [39] showed that a molecule is stable, namely

(a) There is at least one configuration $\underline{R}$ such that

$$E(N, \underline{Z}) = E(N, \underline{Z}, \underline{R}).$$

(b)

$$E(N, \underline{Z}) < \lim_{\lambda \to \infty} \inf \left\{ E(N, \underline{Z}, \underline{R}) \colon \max_{i \neq j} |R_i - R_j| > \lambda \right\}.$$

Then the asymptotic neutrality was shown by Solovej [47] (for $K = 2$) and by Ruskai and Solovej [41] (for all K).

Intuitively, the stability of atoms and molecules is related to the size of the system. In order to compute the size of atoms and molecules, Thomas-Fermi theory is useful.

2 Thomas-Fermi theory

Thomas-Fermi (TF) theory is defined by an energy functional

$$\mathcal{E}_{\underline{R}}(\rho) \coloneqq \frac{3}{10}(3\pi^2)^{2/3}\int_{\mathbb{R}^3}\rho(x)^{5/3}\,dx - \int_{\mathbb{R}^3}V_{\underline{R}}(x)\rho(x)\,dx + D[\rho],$$

where

$$D[\rho] \coloneqq \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\rho(x)|x-y|^{-1}\rho(y)\,dx\,dy$$

is the direct Coulomb energy of a charge density. The Thomas-Fermi energy is defined by

$$E^{\mathrm{TF}}(N,\underline{Z},\underline{R}) \coloneqq \inf\left\{\mathcal{E}_{\underline{R}}(\rho)\colon 0\le\rho,\ \int_{\mathbb{R}^3}\rho(x)\,dx = N,\ \rho\in L^{5/3}(\mathbb{R}^3)\right\},$$

and its minimizer exists if $N \le Z$ (see [32, 35]).

TF theory is the semiclassical approximation for the many-electrons system in the following sense. First, we define the one-particle density matrix by

$$\gamma_\psi(x,y) \coloneqq N\int_{\mathbb{R}^{3(N-1)}}\psi(x,x_2,\dots,x_N)\psi^*(y,x_2,\dots,x_N)\,dx_2\cdots dx_N$$

for any state $\psi \in \bigwedge^N L^2(\mathbb{R}^3)$. If we define its density by

$$\rho_\psi(x) \coloneqq N\int_{\mathbb{R}^{3(N-1)}}|\psi(x,x_2,\dots,x_N)|^2\,dx_2\cdots dx_N$$

then the kinetic energy is asymptotically

$$\left\langle\psi, -\frac{1}{2}\sum_{j=1}^N\Delta_j\psi\right\rangle = \mathrm{tr}\left(-\frac{1}{2}\Delta\gamma_\psi\right) \sim \frac{3}{10}(3\pi^2)^{2/3}\int_{\mathbb{R}^3}\rho_\psi(x)^{5/3}\,dx$$

for large N [35].

Moreover, It was shown (see [27, 32, 35]) that

$$E(N, \underline{Z}, \underline{R}) = E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}) + U_{\underline{R}} + o(Z^{7/3})$$

under suitable assumptions (for instance, $\min_{i \neq j} |R_i - R_j| > cZ^{-1/3}$ and $N = Z$). If we define $V^Z_{\underline{R}}(x) \coloneqq \sum_{j=1}^K Z_j Z |x - Z^{-1/3} R_j|^{-1}$ and $\rho_Z(x) \coloneqq Z^2 \rho(Z^{1/3} x)$ for given ρ, then we have the scaling properties

$$\mathcal{E}^{\mathrm{TF}}(\rho_Z; V^Z_{\underline{R}}) = Z^{7/3} \mathcal{E}^{\mathrm{TF}}(\rho; V_{\underline{R}})$$

and

$$\int_{\mathbb{R}^3} \rho_Z(x)\, dx = Z \int_{\mathbb{R}^3} \rho(x)\, dx.$$

Let $\rho_\psi(x)$ is the one particle density for the ground state ψ. Then, as $Z \to \infty$,

$$Z^{-2} \rho_\psi(Z^{-1/3} x) \to \rho^{\mathrm{TF}}(x),$$

where ρ^{TF} is the TF density (minimizer). In other words, ρ_ψ and ρ^{TF} become concentrated within a distance $Z^{-1/3}$ of the various nuclei.

In the TF model, the most noticeable feature is instability of molecules. Indeed, Teller's no-binding theorem [32, 35] asserts that the TF energy of a collection of fixed nuclei and TF electrons always strictly decreases if one arbitrarily separate the nuclei into K independent atoms:

$$E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}) + U_{\underline{R}} > \sum_{j=1}^K E^{\mathrm{TF}}_{\mathrm{atom}}(N_j, Z_j)$$

for any $\sum_{j=1}^K N_j = N$. It is usually considered that Teller's theorem and instability of any negative ion (if $N > Z$ then no TF minimizer exist) are the defect of TF theory, but their properties are the very strong tools in mathematical physics. For example, Lieb and Thirring [38] proved the stability of matter via Thomas-Fermi theory.

Thomas-Fermi theory is the original density functional theory, that is, the approximation method to represent the ground state energy of many electrons systems in terms of the one particle density functional.

3 Hartree-Fock theory

We consider an N electrons state $\psi \in \bigwedge L^2(\mathbb{R}^3)$ normalized as

$$\int_{\mathbb{R}^{3N}} |\psi(x_1, \ldots, x_N)|^2\, dx_1 \cdots dx_N = 1.$$

Then the exchange correlation energy X_{xc} is defined by

$$\left\langle \psi, \sum_{i<j} |x_i - x_j|^{-1} \psi \right\rangle = D[\rho_\psi] - X_{\mathrm{xc}}.$$

We recall the simplest anti-symmetric function $\psi \in \bigwedge L^2(\mathbb{R}^3)$ is Slater determinant, namely

$$\psi(x) = (N!)^{-1/2} \det\{\varphi_i(x_j)\}_{i,j=1}^N,$$

where N functions $\varphi_i \in L^2(\mathbb{R}^3)$, $i = 1, \ldots, N$, are orthonormal

$$\int_{\mathbb{R}^3} \varphi_i(x)^* \varphi_j(x)\, dx = \delta_{i,j}.$$

Using this state, we obtain

$$X_{\mathrm{xc}} = X(\gamma_\psi) \coloneqq \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\gamma_\psi(x,y)|^2}{|x-y|}\, dx\, dy,$$

where

$$\gamma(x,y) = \sum_{i=1}^N \varphi_i(x) \varphi_i(y)^*.$$

We define the general one particle density matrix γ as any linear, self-adjoint operator satisfying $0 \leq \gamma \leq 1$ and $\operatorname{tr} \gamma = N$. The condition of $\gamma \leq 1$ is, due to Coleman [15], a representation of the Pauli exclusion principle in term of one particle density matrices.

The Hartree-Fock (HF) functional is defined by

$$\mathcal{E}^{\mathrm{HF}}_{\underline{R}}(\gamma) \coloneqq \left[\operatorname{tr} \left(-\frac{1}{2}\Delta - V_{\underline{R}} \right) \gamma \right] + D[\rho_\gamma] - X(\gamma),$$

where $\rho_\gamma(x) = \gamma(x,x) = \sum_{j \geq 1} \lambda_j |\varphi_j(x)|^2$, with $\gamma \varphi_j = \lambda_j \varphi_j$, is the electrons density of γ. Hartree-Fock theory is widely used in quantum chemistry and physics. We note Hartree-Fock theory is not a density functional but a density matrix functional theory.

The Hartree-Fock energy is defined by

$$E^{\mathrm{HF}}(N, \underline{Z}, \underline{R}) \coloneqq \inf\{\mathcal{E}^{\mathrm{HF}}_{\underline{R}}(\gamma) \colon \gamma \in \mathcal{P}_N\},$$

where

$$\mathcal{P}_N \coloneqq \{\gamma\colon 0 \le \gamma \le 1,\ \mathrm{tr}\,\gamma = N,\ \mathrm{tr}(-\Delta+1)^{1/2}\gamma(-\Delta+1)^{1/2} < \infty\}.$$

A HF minimizer does exist when $N < Z + 1$ (see [36]).

Furthermore, by Lieb's variational principle [31], it holds that

$$E^{\mathrm{HF}}(N, \underline{Z}, \underline{R}) = \inf\{\mathcal{E}^{\mathrm{HF}}_{\underline{R}}(\gamma)\colon \gamma \in \mathcal{P}_N,\ \gamma^2 = \gamma\}$$

and $E(N, \underline{Z}, \underline{R}) \le E^{\mathrm{HF}}(N, \underline{Z}, \underline{R})$.

For the atomic case ($K = 1$), the ionization conjecture was shown by Solovej [49]. Moreover, he investigated the radius of atom. Here we define the radius R^{HF}_Z by

$$\int_{|x|\ge R^{\mathrm{HF}}_Z} \rho^{\mathrm{HF}}(x)\,dx = 1$$

for Hartree-Fock minimizing density ρ^{HF}. Then Solovej proved that there exist universal constants C_1, C_2 such that

$$C_1 \le R^{\mathrm{HF}}_Z \le C_2.$$

It is believed that this is true for the Hamiltonian $H(N, \underline{Z}, \underline{R})$, but no proof is known.

As defined before, we set a Born-Oppenheimer energy for Hartree-Fock functional by

$$E^{\mathrm{HF}}(N, \underline{Z}) \coloneqq \inf_{\underline{R}\in\mathbb{R}^{3K}} \{E^{\mathrm{HF}}(N, \underline{Z}, \underline{R}) + U_{\underline{R}}\}.$$

Catto and Lions [11–14] give a necessary and sufficient condition for the stability of molecules in Hartree-Fock theories. Let $\gamma(x,y) = \sum_{j=1}^N \varphi_j(x)\varphi_j(y)^*$ be a Hartree-Fock state. They showed that any minimizing sequence $(\underline{R}^n, \varphi^n_j)^\infty_{n=1} \subset \mathbb{R}^{3K} \times (H^1(\mathbb{R}^3))^N$ for $E^{\mathrm{HF}}(N, \underline{Z})$ is relatively compact if and only if

$$E^{\mathrm{HF}}(N, \underline{Z}) < E^{\mathrm{HF}}(N - M, \underline{Z_1}) + E^{\mathrm{HF}}(M, \underline{Z_2})$$

for all $0 \le M \le N$ and for any configuration $\underline{Z_1}$, $\underline{Z_2}$.

However, the stability of Hartree-Fock molecule is still open even in the hydrogen molecule case $N = 2$, $K = 2$.

4 Müller theory

Müller functional which was introduced by Müller [40] is defined by

$$\mathcal{E}^{\mathrm{M}}_{\underline{R}}(\gamma) \coloneqq \left[\mathrm{tr}\left(-\frac{1}{2}\Delta - V_{\underline{R}}\right)\gamma\right] + D[\rho_\gamma] - X(\gamma^{1/2}),$$

where

$$X(\gamma^{1/2}) \coloneqq \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma^{1/2}(x,y)|^2}{|x-y|}\,dx\,dy$$

and

$$\gamma^{1/2}(x,y) = \sum_{j=1}^{\infty} \lambda_j^{1/2}\varphi_j(x)\varphi_j(y)^*, \quad \gamma\varphi_j = \lambda_j\varphi_j.$$

The Müller energy is

$$E^{\mathrm{M}}(N,\underline{Z},\underline{R}) = \inf\{\mathcal{E}^{\mathrm{M}}_{\underline{R}}(\gamma)\colon \gamma\in\mathcal{P}_N\}.$$

It was shown in [21] that Müller functional has a minimizer if $N \le Z$.

As mentioned above, the Hartree-Fock minimizers are projection $\gamma = \gamma^2$, and hence $\mathcal{E}^{\mathrm{HF}}_{\underline{R}}(\gamma) = \mathcal{E}^{\mathrm{M}}_{\underline{R}}(\gamma)$. Thus Müller functional is a genelarization of HF functional, and it is always the case $E^{\mathrm{M}}(N,\underline{Z},\underline{R}) \le E^{\mathrm{HF}}(N,\underline{Z},\underline{R})$.

According to numerical computations, $E^{\mathrm{M}}(N,\underline{Z},\underline{R})$ is always a lower bound of $E(N,\underline{Z},\underline{R})$. For $N = 2$, this lower bound is rigorously proven by [21].

For the neutral atom $N = Z$, Siedentop [45] showed the energy asymptotics

$$E^{\mathrm{M}}_{\mathrm{atom}}(Z) = E^{\mathrm{HF}}_{\mathrm{atom}}(Z) + o(Z^{5/3}) \quad \text{as } Z\to\infty.$$

In particular, for $Z\in\mathbb{N}$

$$E^{\mathrm{M}}_{\mathrm{atom}}(Z) = E_{\mathrm{atom}}(Z) + o(Z^{5/3})$$

because $E_{\mathrm{atom}}(Z) = E^{\mathrm{HF}}_{\mathrm{atom}}(Z) + o(Z^{5/3})$ by [5].

An important property of Müller functional is the convexity. Indeed, the term $D[\rho_\gamma]$ is strictly convex in ρ_γ. According to Fefferman and de la Llave [17]

$$|x-y|^{-1} = \int_0^\infty dr \int_{\mathbb{R}^3} \chi_{B_{z,r}}(x)\chi_{B_{z,r}}(y)\,dz,$$

and hence we can write

$$X(\gamma^{1/2}) = \int_0^\infty dr \int_{\mathbb{R}^3} dz \iint_{\mathbb{R}^3\times\mathbb{R}^3} |\gamma^{1/2}(x,y|^2 \chi_{B_{z,r}}(x)\chi_{B_{z,r}}(y)\, dx\, dy.$$

By the Wigner-Yanase-Dyson-Lieb concavity [30], $\operatorname{tr}(B^\dagger\gamma^{1/2}B\gamma^{1/2})$ is a concave function of γ. Therefore, $\mathcal{E}^{\mathrm{M}}_{\underline{R}}$ is a convex function of γ.

We note that $\rho_\gamma(x)\rho_\gamma(y) - |\gamma^{1/2}(x,y)|^2$ is not necessarily positive as a function of x, y. This nonpositivity prevents the application of "the multiplication by $|x|$ strategy" [33] to show a bound on the maximum ionization.

Nevertheless, it was shown the ionization conjecture for atoms [25], that is, if there is a Müller minimizer in the atomic case $K = 1$, then $N \le Z + C$. In addition, a bound on the atomic radii of Müller atom was proven:

$$C_1 \le R^{\mathrm{M}}_Z \le C_2.$$

Here C_1, C_2 are the universal constants.

The purpose of this thesis is to study the molecular theory for Müller functional.

In the Chapter 2, we investigate the Born-Oppenheimer energy of Müller functional

$$E^{\mathrm{M}}(N,\underline{Z}) \coloneqq \inf_{\underline{R}\in\mathbb{R}^{3K}} \{E^{\mathrm{M}}(N,\underline{Z},\underline{R}) + U_{\underline{R}}\}. \tag{1.1}$$

We will say that the molecular system is stable if there exists a density-matrix γ with $\operatorname{tr}\gamma = N$ such that $E(N,\underline{Z}) = \mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}}$ for some $\underline{R} \in \mathbb{R}^{3K}$.

Now we set

$$\widehat{\mathcal{E}}_{\underline{R}}(\gamma) = \mathcal{E}_{\underline{R}}(\gamma) + \frac{\operatorname{tr}\gamma}{8},$$

and a relaxed problem

$$\widehat{E}_{\le}(N,Z,\underline{R}) = \inf\left\{\widehat{\mathcal{E}}_{\underline{R}}(\gamma)\colon 0 \le \gamma \le 1,\ \operatorname{tr}\gamma \le N\right\}.$$

Physically, this functional might be interpreted as the binding energy because it is known

$$-\frac{N}{8} = \inf\left\{\operatorname{tr}\left[\left(-\frac{1}{2}\Delta\right)\gamma\right] + D[\rho_\gamma] - X(\gamma^{1/2})\colon\ \operatorname{tr}\gamma \le N\right\}.$$

Also we define the Born-Oppenheimer energy for this functional by

$$\widehat{E}_{\le}(N,\underline{Z}) = \inf_{\underline{R}}\left\{\widehat{E}_{\le}(N,Z,\underline{R}) + U_{\underline{R}}\right\}. \tag{1.2}$$

Our results in this thesis are following.

Theorem (Chapter 2. Theorem 1.1)**.** *Any minimizing sequence* $(\underline{R}_n)_n \subset \mathbb{R}^{3K}$ *for (1.2) is bounded if and only if*

$$\widehat{E}_{\leq}(N, \underline{Z}) < \widehat{E}(N_1, \underline{Z_1}) + \widehat{E}(N_2, \underline{Z_2}) \tag{1.3}$$

for all $N_i \geq 0$, $i = 1, 2$, *such that* $N_1 + N_2 \leq N$ *and for any configuration* $\underline{Z_1} = (Z_{j(1)}, \ldots, Z_{j(p)})$ *and* $\underline{Z_2} = (Z_{j(p+1)}, \ldots, Z_{j(K)})$, j *permutation of* $\{1, \ldots, K\}$.

Theorem (Chapter 2. Theorem 1.2)**.** *We assume* $\widehat{E}_{\leq}(N, \underline{Z}) = E(N, \underline{Z}) + N/8$. *Then any minimizing sequence* $(\underline{R}_n)_n \subset \mathbb{R}^{3K}$ *for (1.1) is bounded if and only if*

$$E(N, \underline{Z}) < E(N_1, \underline{Z_1}) + E(N_2, \underline{Z_2}) \tag{1.4}$$

for all $N_i \geq 0$, $i = 1, 2$, *such that* $N_1 + N_2 = N$ *and for any configuration* $\underline{Z_1} = (Z_{j(1)}, \ldots, Z_{j(p)})$ *and* $\underline{Z_2} = (Z_{j(p+1)}, \ldots, Z_{j(K)})$, j *permutation of* $\{1, \ldots, K\}$.

Remark 4.1. For $N \leq Z$, a minimizer of the Müller energy has trace N. Thus $\widehat{E}_{\leq}(N, \underline{Z}) = E(N, \underline{Z}) + N/8$ for $N \leq Z$ and the molecules are stable when the binding inequality (1.4) hold.

Theorem (Chapter 2. Theorem 1.3)**.** *We assume* $N \leq c_1 Z$ *and* $Z_{\min} \coloneqq \min\{Z_1, \ldots, Z_K\} \geq c_2 Z$ *with some constants* $c_i > 0$, $i = 1, 2$, *independent of* Z. *If there exist a stable configuration* $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$ *and a density matrix* $\gamma \in \mathcal{P}_N$ *such that* $\mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}} = E(N, \underline{Z})$, *then there exist* $C_0 > 0$ *depending only on* $Z_1, \ldots, Z_K$, *and* K, $c_i > 0$ *such that*

$$Z - N \leq C_0 Z^{1-\delta} \tag{1.5}$$

for some $\delta > 0$.

Moreover, if we put $R_{\min} \coloneqq \min_{i \neq j} |R_i - R_j|$, *then there is a constant* $C > 0$ *depending on the same quantities as above* C_0 *so that*

$$R_{\min} > C Z^{-(1/3)(1-\varepsilon)}, \tag{1.6}$$

where $\varepsilon = 2/77$.

Remark 4.2. (1.5) gives a bound on the excess positive charge. The estimate (1.6) states that the molecular radii in the frame work of the Müller theory are much larger than the Thomas-Fermi atomic radii, namely $Z^{-1/3}$. This is the crucial fact for the proof of (1.5).

Chapter 2

Binding stability of molecules in Müller theory

Abstract. We give a necessary and sufficient condition for the stability of molecules in Müller theory. Furthermore, it is shown that if a system is stable in Born-Oppenheimer approximation, then the bound on the excess positive charge $Z - N \leq cZ^{1-\varepsilon}$ follows.

1 Introduction

We consider a molecule with $N > 0$ electrons and K nuclei. We say that a self-adjoint operator γ is an one-body density-matrix if $0 \leq \gamma \leq 1$ on $L^2(\mathbb{R}^3)$ and $\operatorname{tr} \gamma < +\infty$. Then the Müller functional is defined by

$$\mathcal{E}_{\underline{R}}(\gamma) = \operatorname{tr}\left[\left(-\frac{1}{2}\Delta - V_{\underline{R}}\right)\gamma\right] + D[\rho_\gamma] - X(\gamma^{1/2}),$$

where $D[\rho_\gamma]$ is the direct part of Coulomb energy defined by

$$D[\rho_\gamma] = D(\rho_\gamma, \rho_\gamma) = \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy$$

and the Müller exchange energy is defined by

$$X(\gamma^{1/2}) = \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma^{1/2}(x,y)|^2}{|x-y|}dxdy.$$

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Here $\gamma^{1/2}(x,y) = \sum_{i\geq 1} \lambda_i^{1/2} \varphi_i(x)\varphi_i^*(y)$, with $\gamma\varphi_i = \lambda_i\varphi_i$, and $\rho_\gamma(x) = \gamma(x,x)$ is the one-particle electron density. Our potential is

$$V_{\underline{R}}(x) = \sum_{i=1}^{K} \frac{Z_i}{|x - R_i|}, \quad Z = \sum_{i=1}^{K} Z_i,$$

where $\underline{Z} = (Z_1, \ldots, Z_K) \in \mathbb{R}_+^K$ are the charges of fixed nuclei located at $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$.

For $N > 0$ (not necessarily integer valued) and $Z_i \geq 0$, we now define the ground state energy in Müller theory by

$$E_{\underline{R}}(N, Z) = \inf \{\mathcal{E}_{\underline{R}}(\gamma) \colon \gamma \in \mathcal{P}, \operatorname{tr} \gamma = N\}$$

where $\mathcal{P} = \{\gamma \colon \gamma = \gamma^\dagger, 0 \leq \gamma \leq 1, (-\Delta + 1)^{1/2}\gamma(-\Delta + 1)^{1/2} \in \mathcal{S}^1\}$, $\mathcal{S}^1$ is the set of trace-class operators. When $N \leq Z$, it was shown by Frank et. al. [21] that $E_{\underline{R}}(N, Z)$ has a minimizer.

In this paper, we will investigate minimization of the Müller energy over the nuclear positions R_j, that is, the Born-Oppenheimer energy of a molecule defined as

$$E(N, \underline{Z}) = \inf_{\underline{R}} \{E_{\underline{R}}(N, Z) + U_{\underline{R}}\}, \tag{2.1}$$

where $U_{\underline{R}}$ is the nuclear-nuclear repulsion

$$U_{\underline{R}} = \sum_{i<j} \frac{Z_i Z_j}{|R_i - R_j|}.$$

Our purpose is to explore the stability of molecules in Müller theories. Following, we will say that the molecular system is stable if there exists a density-matrix γ with $\operatorname{tr} \gamma = N$ such that $E(N, \underline{Z}) = \mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}}$ for some $\underline{R} \in \mathbb{R}^{3K}$.

Analogously to a series of works [11–14] by Catto and Lions on the Thomas-Fermi and Hartree type theories, we prove that any molecular system is stable under the Müller theory if and only if all possible two molecules can be bound.

It is well-known that, due to the classical work of Lieb and Thirring [39], neutral atoms and molecules are stable in the nonrelativistic Schrödinger theory. In particular, it was shown that the R^{-6} attractive interaction energy, among molecules for large separation R, appears from the dipole-dipole interaction. On the other hand, density-functional theory may not have the

same feature, since it deals only with single particle densities, as pointed out in [39]. In Thomas-Fermi theory, two neutral molecules can never be bound by Teller's no-binding theorem [32, 35]. We refer to [10–14, 32] for other Thomas-Fermi type theories and Hartree-Fock theories. We recall Müller theory is not a density functional but a density-matrix theory. Namely, this theory describe the energy as a functional of the one-body density matrix $\gamma(x, y)$, rather than a one-particle density $\rho(x)$. Our purpose of this paper is to extend the method of [11–14] to investigate the Müller theory of molecules.

Let us define

$$\widehat{\mathcal{E}}_{\underline{R}}(\gamma) = \mathcal{E}_{\underline{R}}(\gamma) + \frac{\operatorname{tr}\gamma}{8}.$$

We note that

$$-\frac{N}{8} = E_\infty(N) = \inf\left\{\mathcal{E}_\infty(\gamma)\colon\ \operatorname{tr}\gamma = N\right\}$$

by [21, Propositon 1], where

$$\mathcal{E}_\infty(\gamma) \coloneqq \operatorname{tr}\left(-\frac{1}{2}\Delta\right)\gamma + D[\rho_\gamma] - X(\gamma^{1/2}).$$

For technical reason, we set a relaxed problem

$$\widehat{E}_{\leq}(N, \underline{Z}) = \inf_{\underline{R}}\left\{\widehat{E}_{\leq}(N, Z, \underline{R}) + U_{\underline{R}}\right\}, \tag{2.2}$$

where

$$\widehat{E}_{\leq}(N, Z, \underline{R}) = \inf\left\{\widehat{\mathcal{E}}_{\underline{R}}(\gamma)\colon \gamma \in \mathcal{P}, \operatorname{tr}\gamma \leq N\right\}.$$

For any $N > 0$, $Z > 0$, it was shown in [21], $\widehat{E}_{\leq}(N, Z, \underline{R})$ has a minimizer.

Our results are following.

Theorem 1.1. *Any minimizing sequence $(\underline{R}_n)_n \subset \mathbb{R}^{3K}$ for (2.2) is bounded if and only if*

$$\widehat{E}_{\leq}(N, \underline{Z}) < \widehat{E}(N_1, \underline{Z_1}) + \widehat{E}(N_2, \underline{Z_2}) \tag{2.3}$$

for all $N_i \geq 0$, $i = 1, 2$, such that $N_1 + N_2 \leq N$ and for any configuration $\underline{Z_1} = (Z_{j(1)}, \ldots, Z_{j(p)})$ and $\underline{Z_2} = (Z_{j(p+1)}, \ldots, Z_{j(K)})$, j permutation of $\{1, \ldots, K\}$.

As mentioned above, for $N \leq Z$, a minimizer of Müller energy has trace N. Thus $\widehat{E}_{\leq}(N, \underline{Z}) = E(N, \underline{Z}) + N/8$ and the molecules are stable when the binding inequality hold. Moreover,

Theorem 1.2. *We assume* $\widehat{E}_{\leq}(N, \underline{Z}) = E(N, \underline{Z}) + N/8$. *Then any minimizing sequence* $(\underline{R}_n)_n \subset \mathbb{R}^{3K}$ *for (2.1) is bounded if and only if*

$$E(N, \underline{Z}) < E(N_1, \underline{Z_1}) + E(N_2, \underline{Z_2}) \tag{2.4}$$

for all $N_i \geq 0$, $i = 1, 2$, *such that* $N_1 + N_2 = N$ *and for any configuration* $\underline{Z_1} = (Z_{j(1)}, \ldots, Z_{j(p)})$ *and* $\underline{Z_2} = (Z_{j(p+1)}, \ldots, Z_{j(K)})$, j *permutation of* $\{1, \ldots, K\}$.

It is expected that the binding occur for $N \leq Z$ molecules or ions, though it is an open question. Even in the Hartree-Fock theory, the stability of molecules is still open except in special cases [10–14].

One main purpose of this article is the following.

Theorem 1.3 (Bound on the excess positive charge)**.** *We assume* $N \leq c_1 Z$ *and* $Z_{\min} \coloneqq \min\{Z_1, \ldots, Z_K\} \geq c_2 Z$ *with some constants* $c_i > 0$, $i = 1, 2$, *independent of* Z. *If there exist a stable configuration* $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$ *and a density matrix* $\gamma \in \mathcal{P}$ *such that* $\mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}} = E(N, \underline{Z})$, *then there exist* $C_0 > 0$ *depending only on* $Z_1, \ldots, Z_K$, *and* K, $c_i > 0$ *such that*

$$Z - N \leq C_0 Z^{1-\delta} \tag{2.5}$$

for some $\delta > 0$.

Moreover, if we put $R_{\min} \coloneqq \min_{i \neq j} |R_i - R_j|$, *then there is a constant* $C > 0$ *depending on the same quantities as above* C_0 *so that*

$$R_{\min} > C Z^{-(1/3)(1-\varepsilon)}, \tag{2.6}$$

where $\varepsilon = 2/77$.

Remark 1.4. It is expected that if a Müller minimizer exists, then $N \leq CZ$ holds. In fact, for atomic case, if there is a minimizer then $N \leq Z + \text{const.}$ holds by [25]. However, the proof works only for atomic case, and it is still an open issue for molecular case.

Remark 1.5. The estimate (2.6) states that the molecular radii in the frame work of Müller theory are much larger than the Thomas-Fermi atomic radii, namely $Z^{-1/3}$. Thus the Thomas-Fermi density of the molecule is of order of the sum of atomic densities. Solovej and Ruskai [41,47] showed by using this type estimate that the asymptotic neutrality $N - Z = o(Z)$ for molecules in nonrelativistic Schrödinger theory.

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2 di-atomic case

First, we consider a simple di-atomic case. Without loss of generality, we may assume

$$V_{\underline{R}}(x) = V_R(x) = \frac{Z_1}{|x|} + \frac{Z_2}{|x - R\hat{e}|}, \quad U_{\underline{R}} = U_R = \frac{Z_1 Z_2}{R},$$

where $R > 0$, and $\hat{e} \in \mathbb{R}^3$ is an unit vector. Then our minimizing problem is

$$\widehat{E}_{\leq}(N, Z) = \inf_{R>0} \left\{ \widehat{E}_{\leq}(N, Z, R) + \frac{Z_1 Z_2}{R} \right\}. \tag{2.7}$$

In this section our main result is

Theorem 2.1. *Any minimizing sequence for (2.7) is bounded if and only if*

$$\widehat{E}_{\leq}(N, Z) < \widehat{E}_{\mathrm{atom}}(N_1, Z_1) + \widehat{E}_{\mathrm{atom}}(N_2, Z_2), \tag{2.8}$$

for all $0 \leq N_i$, $i = 1, 2$, *such that* $N_1 + N_2 \leq N$. *Here*

$$\widehat{E}_{\mathrm{atom}}(N, Z) = \inf\{\widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma) \colon \gamma \in \mathcal{P}, \operatorname{tr} \gamma = N\},$$

and

$$\widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma) = \operatorname{tr}\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma + D[\rho_\gamma] - X(\gamma^{1/2}) + \frac{\operatorname{tr}\gamma}{8}.$$

The next Lemma corresponds to the 'if' part of theorem.

Lemma 2.2. *For all $N_i \geq 0$, $i = 1, 2$, with $N_1 + N_2 \leq N$, we have*

$$\begin{aligned} \widehat{E}_{\leq}(N, Z) &\leq \limsup_{R\to\infty} (\widehat{E}_{\leq}(N, Z, R) + U_R) \\ &\leq \widehat{E}_{\mathrm{atom}}(N_1, Z_1) + \widehat{E}_{\mathrm{atom}}(N_2, Z_2). \end{aligned} \tag{2.9}$$

It immediately follows that

Corollary 2.3. *We assume $\widehat{E}(N, Z) = \widehat{E}_{\leq}(N, Z)$. For all $N_i \geq 0$, $i = 1, 2$, with $N_1 + N_2 \leq N$, we have*

$$\begin{aligned} E(N, Z) &\leq \limsup_{R\to\infty} (E_{\leq}(N, Z, R) + U_R) \\ &\leq E_{\mathrm{atom}}(N_1, Z_1) + E_{\mathrm{atom}}(N_2, Z_2). \end{aligned} \tag{2.10}$$

We shall prove Lemma 2.2. The following lemma is obtained by the same proof in [28, Lemma 1].

Lemma 2.4. *Let $Z \geq 0$, $N > 0$ and $\operatorname{tr}\gamma = N$. Then, for any $\varepsilon > 0$ there exists a σ having a compactly supported integral kernel, $\operatorname{tr}\sigma = N$ and*

$$|\mathcal{E}_R(\gamma) - \mathcal{E}_R(\sigma)| \leq \varepsilon.$$

Proof of Lemma 2.2. It is trivial for $N_1 = 0$ (or equivalently, $N_2 = 0$). Let $\varepsilon > 0$, $N_i > 0$, $i = 1, 2$, and $N_1 + N_2 \leq N$. We may assume $\widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma_i) \leq \widehat{E}_{\mathrm{atom}}(N_i, Z_i) + \varepsilon/3$, $\operatorname{tr}\gamma_i = N_i$, and the kernel of γ_i is compactly supported in a ball with radius $r > 0$. Let $\widehat{\gamma}_{2R} = \tau_{-R}\gamma_2\tau_R$ with translation τ. We then define a trial density-matrix by

$$\gamma_R = \gamma_1 + \widehat{\gamma}_{2_R}.$$

Clearly $0 \leq \gamma \leq 1$, $\operatorname{tr}\gamma \leq N$, and $\gamma_1\widehat{\gamma}_{2_R} = 0$ for large R, by construction. Thus we can compute $X(\gamma_R^{1/2}) = X(\gamma_1^{1/2}) + X(\widehat{\gamma}_{2R}^{1/2})$. Furthermore, it is easy to see that

$$2D[\rho_{\gamma_1}, \rho_{\widehat{\gamma_2}_R}] = \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_{\gamma_1}(x)\rho_{\widehat{\gamma_2}_R}(y)}{|x-y|}\,dx\,dy \leq \frac{N_1N_2}{R-2r}.$$

Using the translation invariant of the functional $\mathcal{E}_\infty(\gamma)$, we may find

$$\begin{aligned} \widehat{E}_{\leq}(N, Z, R) + \frac{Z_1Z_2}{R} &\leq \widehat{\mathcal{E}}_R(\gamma_R) + \frac{Z_1Z_2}{R} \\ &\leq \sum_{i=1,2} \widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma_i) + 2D(\rho_{\gamma_1}, \rho_{\widehat{\gamma_2}_R}) + \frac{Z_1Z_2}{R} \\ &\leq \sum_{i=1,2} \widehat{E}_{\mathrm{atom}}(N_i, Z_i) + \varepsilon/3 + \frac{N_1N_2}{R-2r} + \frac{Z_1Z_2}{R}, \end{aligned}$$

for sufficiently large $R > 0$. Hence for any given $\varepsilon > 0$ and $N_1 + N_2 \leq N$, it hold that

$$\limsup_{R\to\infty} \left(\widehat{E}_{\leq}(N, Z, R) + \frac{Z_1 Z_2}{R} \right) \leq \widehat{E}_{\mathrm{atom}}(N_1, Z_1) + \widehat{E}_{\mathrm{atom}}(N_2, Z_2) + \varepsilon,$$

which shows (2.9).

□

Lemma 2.2 implies that if any minimizing sequence $(R_n)_n$ for (2.7) is bounded, then binding inequality (2.8) hold. Indeed, assume contrary $\widehat{E}(N, Z) = \widehat{E}_{\mathrm{atom}}(N_1, Z_1) + \widehat{E}_{\mathrm{atom}}(N_2, Z_2)$ for some $N_1 + N_2 \leq N$. Then, by Lemma 2.2, $\lim_{R\to\infty}(\widehat{E}_{\leq}(N, Z, R) + U_R) = \widehat{E}(N, Z)$. This contradicts to the assumption that any minimizing sequence is bounded. Hence, the 'if' part of Theorem 2.1 is followed.

Proof of Theorem 2.1. We shall show that 'only if' part. Assume contrary there is a minimizing sequence $(R_n)_n$ for $\widehat{E}_{\leq}(N, Z)$ so that $R_n \to \infty$. Then we may assume that there exist density-matrices $\gamma_n \in \mathcal{P}$ so that $\widehat{\mathcal{E}}_{R_n}(\gamma) + U_{R_n} \to \widehat{E}_{\leq}(N, Z)$ as $n \to \infty$. Using the hydrogen bound, it follows that

$$\operatorname{tr} Z_j |x - R_j|^{-1} \gamma \leq \frac{Z_j \varepsilon}{4Z} \operatorname{tr}(-\Delta)\gamma + \frac{Z_j Z}{\varepsilon} \operatorname{tr} \gamma,$$

for any positive number $\varepsilon > 0$. Hence $\operatorname{tr} V_R \gamma \leq \varepsilon/4 \operatorname{tr}(-\Delta\gamma) + Z^2/\varepsilon \operatorname{tr} \gamma$, for any $\varepsilon > 0$. Moreover, the hydrogen bound also implies that

Lemma 2.5 (Lemma 1 of [21])**.** *For any $\varepsilon > 0$ it hold that*

$$X(\gamma^{1/2}) \leq \frac{\varepsilon}{4} \operatorname{tr}(-\Delta\gamma) + \frac{1}{4\varepsilon} \operatorname{tr} \gamma.$$

Now we get the following bound as [21, Equation (57)]:

$$\frac{1}{2}(1 - \varepsilon) \operatorname{tr}(-\Delta)\gamma_n \leq \widehat{\mathcal{E}}_{R_n}(\gamma_n) + U_{R_n} + \frac{1}{\varepsilon} \left(Z^2 + \frac{1}{4} \right) \operatorname{tr} \gamma_n \tag{2.11}$$

Hence $(-\Delta + 1)^{1/2} \gamma_n (-\Delta + 1)^{1/2}$ is bounded in $\mathcal{S}^1$, and thus, by the Banach-Alaoglu theorem, after passing to a subsequence if necessaly we may assume that $\operatorname{tr} K\gamma_n \to \operatorname{tr} K\gamma$ for some γ and for any operator K such that $(-\Delta +$

$1)^{1/2}K(-\Delta+1)^{1/2}$ is compact. In particular, for any function $f \in L^p(\mathbb{R}^3)$ $(3/2 \le p < \infty)$

$$\int_{\mathbb{R}^3} f(x)\rho_{\gamma_n}(x)\,dx = \operatorname{tr} f\gamma_n \to \operatorname{tr} f\gamma = \int_{\mathbb{R}^3} f(x)\rho_{\gamma}(x)\,dx. \tag{2.12}$$

We note that $0 \le \gamma \le 1$ and

$$M = \operatorname{tr}\gamma \le \liminf_{n\to\infty} \operatorname{tr}\gamma_n = \widetilde{N} \le N \tag{2.13}$$

by the lower-semicontinuity of the $\mathcal{S}^1$ norm.

We may show that $\gamma \not\equiv 0$ from [21, Proposition 1]. In fact, for some $\delta > 0$

$$\widehat{E}_{\mathrm{atom}}(N, Z_1) \le -\delta.$$

From Lemma 2.2,

$$\limsup_{R\to\infty} \widehat{E}_R(N, Z) \le \widehat{E}_{\mathrm{atom}}(N, Z_1).$$

Thus, $\widehat{\mathcal{E}}_{R_n}(\gamma_n) + U_{R_n} \le -\varepsilon$ for some $\varepsilon > 0$ and sufficiently large n. Hence, we have

$$-\varepsilon \ge \widehat{\mathcal{E}}_{R_n}(\gamma_n) + U_{R_n} \ge -\operatorname{tr} V_{R_n}\gamma_n,$$

and thus

$$\operatorname{tr} V_{R_n}\gamma_n \ge \varepsilon,$$

where $V_{R_n} = Z_1|x|^{-1} + Z_2|x - R_n e|^{-1}$. Thus $\gamma \not\equiv 0$.

If $M = \widetilde{N}$, then $\lim_{n\to\infty} \operatorname{tr}\gamma_n = \operatorname{tr}\gamma$. Thus $\gamma_n \to \gamma$ as $n \to \infty$ in $\mathcal{S}^1$ by [46, Theorem A.6]. Then

$$\int_{\mathbb{R}^3} \rho_{\gamma_n}(x)|x - R_n\hat{e}|^{-1}dx \to 0$$

by $R_n \to \infty$. From the lower-semicontinuity of our functionals [21, Proposition 3], we have

$$\widehat{E}_{\le}(N, Z) \ge \liminf_{n\to\infty} \widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma_n) \ge \widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma) \ge \widehat{E}_{\mathrm{atom}}(\widetilde{N}, Z_1) \ge \widehat{E}_{\le}(N, Z),$$

and thus $\widehat{E}_{\le}(N, Z) = \widehat{E}_{\mathrm{atom}}(\widetilde{N}, Z_1)$ with $\widetilde{N} \le N$. Then we have finished the proof in this case.

Let

$$(\chi^0)^2 + (\chi^1)^2 = 1$$

with $\chi^0 \in C^\infty(\mathbb{R}^3)$, radial, $\chi^0(0) = 1$, $\chi^0(r) < 1$ if $r > 0$, $\chi^0(r) = 0$ if $r \geq 2$. For each j $\operatorname{tr}(\chi^0(|x|/L))^2\gamma_j$, is a continuous function of $L > 0$ which increases from 0 to $\operatorname{tr}\gamma_j$. Now $\operatorname{tr}\gamma_j > M$ for large j, and thus we can choose L_j such that $\operatorname{tr}\gamma_j^0 \coloneqq \operatorname{tr}(\chi^0(|x|/L_j))^2\gamma = M$, $L_j \to \infty$, and then $\gamma_j^0 \to \gamma$ in $\mathcal{S}^1$. We write $\chi_j^\nu(x/L_j) \coloneqq \chi^\nu(|x|/L_j)$ and $\gamma_j^\nu = \chi_j^\nu\gamma_j\chi_j^\nu$ for each $\nu = 0, 1$.

From the IMS formula,

$$\operatorname{tr}(-\Delta\gamma_n) = \sum_{\nu=0,1} \left[\operatorname{tr}(-\Delta\gamma_N^\nu) - \operatorname{tr}|\nabla\chi_n^\nu|^2\gamma_n\right].$$

Clearly,

$$D[\rho_{\gamma_j}] = D[\rho_{\gamma_j^0}] + D[\rho_{\gamma_j^1}] + 2D(\rho_{\gamma_j^0}, \rho_{\gamma_j^1}) \geq D[\rho_{\gamma_j^0}] + D[\rho_{\gamma_j^1}]$$

since $\rho_{\gamma_j}^\nu \geq 0$. For the potential term,

$$\operatorname{tr}(|x|^{-1}\gamma_n) = \operatorname{tr}(|x|^{-1}\gamma_n^0) + o(1).$$

and

$$\operatorname{tr}(|x - R_n\hat{e}|^{-1}\gamma_n) = \operatorname{tr}(|x - R_n\hat{e}|^{-1}\gamma_n^1) + o(1),$$

because $R_n \to \infty$. Indeed, we may split

$$\begin{aligned}\operatorname{tr}(|x - R_n\hat{e}|^{-1}\gamma_n^0) &= \int_{\mathbb{R}^3} \frac{\rho_{\gamma_n^0}(x)}{|x - R_n\hat{e}|}\,dx \\ &= \int_{\mathbb{R}^3} \left(\frac{\rho_{\gamma_n^0}(x) - \rho_\gamma(x)}{|x - R_n\hat{e}|} + \frac{\rho_\gamma(x)}{|x - R_n\hat{e}|}\right) dx.\end{aligned} \tag{2.14}$$

We see that the second term converges to 0 by Young's inequality. For the first term, we split $\rho_{\gamma_n^0}(x) - \rho_\gamma(x) = (\sqrt{\rho_{\gamma_n^0}(x)} + \sqrt{\rho_\gamma(x)})(\sqrt{\rho_{\gamma_n^0}(x)} - \sqrt{\rho_\gamma(x)})$. We know that $\sqrt{\rho_{\gamma_n^0}} \to \sqrt{\rho_\gamma}$ strongly in $L^2(\mathbb{R}^3)$ by $\gamma_n^0 \to \gamma$ in $\mathcal{S}^1$, and thus the first term also converges to 0. For the exchange term, we have $X(\gamma_j^{1/2}) \leq X((\gamma_j^0)^{1/2}) + X((\gamma_j^1)^{1/2}) + o(1)$ as [21]. Let $\widetilde{\gamma}_n = \tau_{-R_n\hat{e}}\gamma_n^1\tau_{R_n\hat{e}}$. It is clear that $\operatorname{tr}\widetilde{\gamma}_n = K - M$ with some $K \leq N$. By the translation invariants for the functional $\mathcal{E}_\infty(\gamma)$, we have

$$\begin{aligned}\widehat{\mathcal{E}}_{R_n}(\gamma_n) + U_{R_n} &\geq \widehat{\mathcal{E}}_{\text{atom}}(\gamma_n^0) + \widehat{\mathcal{E}}_{\text{atom}}(\widetilde{\gamma}_n) + o(1) \\ &\geq \widehat{\mathcal{E}}_{\text{atom}}(\gamma_n^0) + \widehat{E}_{\text{atom}}(K - M; Z_2) + o(1).\end{aligned}$$

Hence, again by the lower-semicontinuity, we arrive at

$$\begin{aligned}\widehat{E}_{\leq}(N,Z) &\geq \liminf_{n\to\infty} \widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma_n^0) + \widehat{E}_{\mathrm{atom}}(K-M,Z_2) \\ &\geq \widehat{\mathcal{E}}_{\mathrm{atom}}(\gamma) + \widehat{E}_{\mathrm{atom}}(K-M,Z_2).\end{aligned}$$

Thus $\widehat{E}_{\leq}(N,Z) \geq \widehat{E}_{\mathrm{atom}}(M,Z_1)+\widehat{E}_{\mathrm{atom}}(K-M,Z_2)$ with $K \leq N$. By Lemma 2.2, this is equal.

□

We recall $E_\infty(N) = -N/8$ for the Müller case $X^{1/2}$. The next theorem which is the diatomic case of Theorem 1.2 follows.

Theorem 2.6. *We assume $\widehat{E}_{\leq}(N,Z) = E(N,Z) + N/8$. Then, any minimizing sequence for (2.1) is bounded if and only if*

$$E(N,Z) < E_{\mathrm{atom}}(N_1,Z_1) + E_{\mathrm{atom}}(N_2,Z_2) \tag{2.15}$$

for all $N_1 + N_2 = N$, $0 \leq N_i$, $i = 1,2$.

Proof of Theorem 2.6. In the proof of the previous theorem, we may take $K = N$ when $\widehat{E}_{\leq}(N,Z) = E(N,Z) + N/8$. Thus the molecules are stable if and only if (2.8) hold for all $N_1 + N_2 = N$. Then, the binding (2.15) and (2.8) are equivalent for $N_1 + N_2 = N$. □

3 General case

First, we need the following proposition.

Proposition 3.1. It is always the case

$$\widehat{E}_{\leq}(N,\underline{Z}) \leq \widehat{E}_{\leq}(N_1,\underline{Z_1}) + \widehat{E}_{\leq}(N_2,\underline{Z_2}) \tag{2.16}$$

for all $N_i \geq 0$, $i = 1,2$, such that $N_1 + N_2 \leq N$.

Proof of Proposition 3.1. Let $\varepsilon > 0$. As proof of Lemma 2.2, we can take γ_i^n and $\underline{R_i^n}$, $i = 1,2$, such that

$$\widehat{\mathcal{E}}_{\underline{R_i^n}}(\gamma_i^n) + U_{\underline{R_i^n}} \leq \widehat{E}_{\leq}(N_i,\underline{Z_i}) + \frac{1}{n},$$

$i = 1, 2$. Moreover, we may assume that their kernel have the compact support in the ball. Let $\hat{\gamma}_2^n = \tau_{-B}\gamma_2^n\tau_B$, with $B \in \mathbb{R}^3$. We define $\gamma^n = \gamma_1^n + \hat{\gamma}_2^n$ as diatomic case. Then, for $\underline{R}^n = (R^n_{j(1)}, \dots, R^n_{j(p)}, R^n_{j(p+1)} + B_n, R^n_{j(p+2)} + B_n, \dots, R^n_{j(K)} + B_n)$ with large $|B_n|$,

$$\begin{aligned}\widehat{E}_{\le}(N, \underline{Z}) &\le \widehat{E}_{\underline{R}^n}(N, Z) + U_{\underline{R}^n} \le \widehat{\mathcal{E}}_{\underline{R}^n}(\gamma^n) + U_{\underline{R}^n} \\ &\le \widehat{E}_{\le}(N_1, \underline{Z_1}) + \widehat{E}_{\le}(N_2, \underline{Z_2}) + \frac{3}{n} \\ &\le \widehat{E}_{\le}(N_1, \underline{Z_1}) + \widehat{E}_{\le}(N_2, \underline{Z_2}) + \varepsilon.\end{aligned}$$

Here we have choosen $3/n \le \varepsilon$.

□

Remark 3.2. It is immediately followed the 'if' part of Theorem 2.3 by this Lemma. Suppose that any minimizing sequence for (2.2) is bounded in $\mathbb{R}^{3K}$. If $\widehat{E}_{\le}(N, \underline{Z}) = \widehat{E}_{\le}(N_1, \underline{Z_1}) + \widehat{E}_{\le}(N_2, \underline{Z_2})$ for some configuration, then the above $\underline{R}^n$ is a minimizing sequence and clearly not bounded.

Proof of Theorem 1.1. We only show the 'if only' part by contradiction. Let $\widehat{\mathcal{E}}_{\underline{R}^n}(\gamma_n) + U_{\underline{R}^n} \to \widehat{E}_{\le}(N, \underline{Z})$ and suppose this $\underline{R}^n$ is not bounded. As proof of di-atomic case, we may assume $\gamma_n \to \gamma \not\equiv 0$ in a sense, and the relation (2.13) holds. If $\operatorname{tr}\gamma = M = \widetilde{N}$, then $\gamma_n \to \gamma$ in S^1. Then, after passing by subsequence if necessaly,

$$\widehat{E}_{\le}(N, \underline{Z}) \ge \liminf_{n\to\infty}(\widehat{\mathcal{E}}_{\underline{R}^n}(\gamma_n) + U_{\underline{R}^n}) \ge \widehat{\mathcal{E}}_{\underline{R}}(\gamma),$$

where $\underline{R} \in \mathbb{R}^{3(K-L)}$, L is the number of i such that $|R_i^n| \to \infty$. Hence $\widehat{E}_{\le}(N, \underline{Z}) = \widehat{E}(\widetilde{N}, \underline{\widetilde{Z}})$ with $\widetilde{N} \le N$ and thus $\widehat{E}_{\le}(N, \underline{Z}) \ge \widehat{E}_{\le}(N, \underline{\widetilde{Z}})$. The proof is done when $M = \widetilde{N}$.

Next, we consider the case of $M < \widetilde{N}$. We may split $\gamma_n = \gamma_n^0 + \gamma_n^1$, $\gamma_n^0 \to \gamma$ in S^1. Let $J = \{j \colon R_j^n \text{ remain bounded}\}$, If $J = \emptyset$, passing to a subsequence if necessary, we may $|R_j^n| \to \infty$ for all j. Then,

$$\operatorname{tr}(|x - R_j^n|^{-1}\gamma_n) = \operatorname{tr}(|x - R_j^n|^{-1}\gamma_n^1) + o(1).$$

as the same reason of (2.14). Thus we get

$$\begin{aligned}\widehat{\mathcal{E}}_{\underline{R}^n}(\gamma_n) + U_{\underline{R}^n} &\ge \widehat{\mathcal{E}}_\infty(\gamma_n^0) + \widehat{\mathcal{E}}_{\underline{R}^n}(\gamma_n^1) + U_{\underline{R}_n} + o(1) \\ &\ge \widehat{\mathcal{E}}_\infty(\gamma_n^0) + \widehat{E}(K - M, Z) + o(1).\end{aligned}$$

Thus

$$\widehat{E}_{\leq}(N, \underline{Z}) \geq \widehat{E}_{\infty}(M) + \widehat{E}(K - M, Z).$$

The proof is done.

If $J \neq \emptyset$, then, by passing to a subsequence if necessary, we may assume that $R_j^n \to R_j$ for $j \in J$ and $|R_i| \to \infty$ for $i \notin J$. Then, for $j \in J$ we see that

$$\mathrm{tr}(|x - R_j^n|^{-1}\gamma_n) = \mathrm{tr}(|x - R_j|^{-1}\gamma_n^0) + o(1).$$

For $j \notin J$,

$$\mathrm{tr}(|x - R_j^n|^{-1}\gamma_n) = \mathrm{tr}(|x - R_j^n|^{-1}\gamma_n^1) + o(1).$$

Hence we arrive at

$$\widehat{E}_{\leq}(N, Z) \geq \widehat{E}(M, Z_1) + \widehat{E}(K - M, Z_2),$$

where $Z_1 = \{Z_j \colon j \in J\}$ and $Z_2 = \{Z_j \colon j \notin J\}$. This completes the proof. □

We now turn to the

Proof of Theorem 1.2. If $\widehat{E}_{\leq}(N, Z) = E_{\leq}(N, Z) + N/8$, then we can take $K = N$ in the above proofs. Therefore, any minimizing sequence is bounded if and only if the binding condition (2.3) hold for all $N_1 + N_2 = N$. For $N_1 + N_2 = N$ the condition (2.3) and (2.4) are equivalent. Thus Theorem 1.2 follows. □

4 A lower bound on the size of molecules

In this section we prove the estimate (2.6) in Theorem 1.3. First, we use the united atom bound for Müller theory.

Proposition 4.1 (united atom bound)**.** For any $N > 0$ and for any configuration $\underline{R} \in \mathbb{R}^{3K}$ we have

$$E_{\underline{R}}(N, Z) \geq E_{\mathrm{atom}}(N, Z).$$

Proof. Let $\varepsilon > 0$ and $E_{\underline{R}}(N, Z) \geq \mathcal{E}_{\underline{R}}(\gamma) + \varepsilon$. Then

$$\mathcal{E}_{\underline{R}}(\gamma) = \sum_{j=1}^{K} \frac{Z_j}{Z} \left[\mathrm{tr}\left(-\frac{1}{2}\Delta - Z|x - R_j|^{-1} \right) \gamma + D[\rho_\gamma] - X(\gamma^{1/2}) \right].$$

Since the energy of $E_{\mathrm{atom}}(N, Z)$ is independent of nucler positions R_j, the conclusion follows. □

From this bound we have

$$E(N, \underline{Z}) \geq E_{\text{atom}}(N, Z) + \frac{Z_i Z_j}{|R_i - R_j|}$$

where $R_{\min} = |R_i - R_j|$. We now deduce from Lemma 2.5 that

$$E_{\text{atom}}(N, Z) \geq \text{tr}\left(-\frac{1}{4}\Delta\right)\gamma - \text{tr}(Z|x|^{-1})\gamma + D[\rho_\gamma] - \frac{N}{4}.$$

For the bound of kinetic energy term, we need the

Theorem 4.2 (Lieb-Thirring kinetic energy inequality [37])**.**

$$\text{tr}\left(-\frac{\Delta}{2}\gamma\right) \geq \frac{3}{10}L\int_{\mathbb{R}^3}\rho_\gamma(x)^{5/3}\,dx,$$

with a constant L (see [16, 19]).

Hence we infer that

$$E_{\text{atom}}(N, Z) \geq \frac{3}{10}C\int_{\mathbb{R}^3}\rho(x)^{5/3}\,dx - \text{tr}(Z|x|^{-1})\gamma + D[\rho] - \frac{N}{4}.$$

Next, we introduce the Thomas-Fermi (TF) theory [32, 35] by

$$\mathcal{E}^{TF}_{\underline{\mathrm{R}}}(\rho) = \frac{3}{10}(3\pi^2)^{2/3}A\int_{\mathbb{R}^3}\rho(x)^{5/3}\,dx + \int_{\mathbb{R}^3}V_R(x)\rho(x)\,dx + D[\rho],$$

and define the lowest energy by

$$E^{TF}_{\underline{R}}(N, Z, A) = \inf\left\{\mathcal{E}^{TF}_{\underline{R}}(\rho)\colon 0 \leq \rho, \int_{\mathbb{R}^3}\rho(x)\,dx = N, \rho \in L^{5/3}(\mathbb{R}^3)\right\}.$$

From the scaling property of Thomas-Fermi functional [32], we see $E^{\text{TF}}_{\text{atom}}(N, Z, A) \geq -CZ^{7/3}$. Consequently, we arrive at

$$E(N, Z) \geq -CZ^{7/3} + \frac{Z_i Z_j}{|R_i - R_j|}.$$

Hence we have $|R_i - R_j| \geq CZ^{-1/3}$.

Next, we shall improve this bound by comparison with Thomas-Fermi theory. In order to compare our functional with Thomas-Fermi one, we need the following semiclassical approximation. The following results are taken from [49, Lemma 8.2] (we use the optimal $\delta > 0$ as in [25, Lemma 11]).

Lemma 4.3. *For fixed $s > 0$ and smooth $g\colon \mathbb{R}^3 \to [0,1]$ satisfying $\operatorname{supp} g \subset \{|x| < s\}$, $\int g^2 = 1$, $\int |\nabla g|^2 \leq Cs^{-2}$ it follows that*

(i) For any $V\colon \mathbb{R}^3 \to \mathbb{R}$ with $[V]_+$, $[V - V \star g^2]_+ \in L^{5/2}$ and for any $0 \leq \gamma \leq 1$

$$\operatorname{tr}\left(-\frac{\Delta}{2} - V\right)\gamma \geq -2^{5/2}(15\pi^2)^{-1}\int [V]_+^{5/2} - Cs^{-2}\operatorname{tr}\gamma \\ - C\left(\int [V]_+^{5/2}\right)^{3/5}\left(\int [V - V\star g^2]_+^{5/2}\right)^{2/5},$$

where the symbol $[x]_+$ stands for $\max\{0, x\}$.

(ii) If $[V]_+ \in L^{5/2} \cap L^{3/2}$, then there is a density matrix γ so that $\rho_\gamma = 2^{5/2}(6\pi^2)^{-1}[V]_+^{3/2} \star g^2$,

$$\operatorname{tr}\left(-\frac{\Delta}{2}\gamma\right) \leq 2^{3/2}(5\pi^2)^{-1}\int [V]_+^{5/2} + Cs^{-2}\int [V]_+^{3/2}$$

We introduce the TF potential for the molecule as the function

$$\varphi_{\mathrm{mol}}^{\mathrm{TF}}(x) \coloneqq \sum_{i=1}^{K} Z_i|x - R_i|^{-1} - \int_{\mathbb{R}^3} \frac{\rho_{\mathrm{mol}}^{\mathrm{TF}}(y)}{|x-y|}\,dy,$$

where $\rho_{\mathrm{mol}}^{\mathrm{TF}}$ is the unique minimizing density for $E^{\mathrm{TF}}(N, Z, \underline{R}) = E^{\mathrm{TF}}(N, Z, \underline{R}, 1)$ (when $N > Z$ we take the minimizer for the neutral molecule). First, we shall show that

Lemma 4.4. *For any configuration $\underline{R} \in \mathbb{R}^{3K}$ and density-matrix γ we have*

$$\mathcal{E}_{\underline{R}}(\gamma) \geq \mathcal{E}^{\mathrm{TF}}(\rho_{\mathrm{mol}}^{\mathrm{TF}}) + D\left[\rho_\gamma - \rho_{\mathrm{mol}}^{\mathrm{TF}}\right] - CZ^{25/11}. \tag{2.17}$$

Proof of Lemma 2.17. We can write

$$\mathcal{E}_{\underline{R}}(\gamma) = \operatorname{tr}\left(-\frac{\Delta}{2} - \varphi_{\mathrm{mol}}^{\mathrm{TF}}\right)\gamma + D\left[\rho_\gamma - \rho_{\mathrm{mol}}^{\mathrm{TF}}\right] - D\left[\rho_{\mathrm{mol}}^{\mathrm{TF}}\right] - X(\gamma^{1/2}).$$

According to $N \leq CZ$, we may bound the exchange term by

$$X(\gamma^{1/2}) \leq CZ^{5/3}.$$

Indeed, we infer from Hardy's inequality that

$$\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma^{1/2}(x,y)|^2}{|x-y|}\,dx\,dy \\
&\quad\le \left(\iint_{\mathbb{R}^3\times\mathbb{R}^3} |\gamma^{1/2}(x,y)|^2\,dx\,dy\right)^{1/2} \left(\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma^{1/2}(x,y)|^2}{|x-y|^2}\,dx\,dy\right)^{1/2} \\
&\quad\le 4N^{1/2}(\mathrm{tr}(-\Delta)\gamma)^{1/2}.
\end{aligned}$$

We recall $\mathrm{tr}(-\Delta)\gamma \le CZ^{7/3}$ by the energy bound.

Next, from Lemma 4.3 (i) we have

$$\begin{aligned}
&\mathrm{tr}\left(-\frac{\Delta}{2} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} + \mu(N,Z,\underline{R})\right)\gamma \\
&\quad\ge -2^{5/2}(15\pi)^{-1}\int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \mu(N,Z,\underline{R})]_+^{5/2} - Cs^{-2}\,\mathrm{tr}\,\gamma \\
&\qquad - C\left(\int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \mu(N,Z,\underline{R})]_+^{5/2}\right)^{3/5}\left(\int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} \star g^2]_+^{5/2}\right)^{2/5}.
\end{aligned}$$

Here $\mu(N,Z,\underline{R}) \ge 0$ is the chemical potential for the molecule. It is known (see [32]) that the functions $\rho^{\mathrm{TF}}_{\mathrm{mol}}$ and $\varphi^{\mathrm{TF}}_{\mathrm{mol}}$ satisfy the TF equation

$$\rho^{\mathrm{TF}}_{\mathrm{mol}}(x)^{2/3} = 2^{5/3}(6\pi^2)^{-2/3}[\varphi^{\mathrm{TF}}_{\mathrm{mol}}(x) - \mu(N,Z,\underline{R})]_+. \tag{2.18}$$

Using the TF equation and scaling property in Thomas-Fermi theory, we have

$$\int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \mu(N,Z,\underline{R})]_+^{5/2} \le C\int (\rho^{\mathrm{TF}}_{\mathrm{mol}})^{5/3} \le CZ^{7/3}.$$

Since V_R is superharmonic, it follows that $V_{\underline{R}} - V_{\underline{R}} \star g^2 \ge 0$ by the maximum principle. To see this, we note that $V_{\underline{R}} \star g^2$ is a continuous function going to zero at infinity, and therefore $\psi \coloneqq V_{\underline{R}} - V_{\underline{R}} \star g^2 \to \infty$ as $x \to R_i$ for any i. Since ψ is continuous away from the R_i, $A \coloneqq \{x\colon \psi(x) < 0\}$ is open and disjoint from the R_i. Thus $-\Delta\psi \le 0$ on A. It is clear that $\psi(x) \to 0$ as $|x| \to \infty$ and hence A is empty by the maximum principle. Hence $\psi \ge 0$.

From the fact that $\rho^{\mathrm{TF}}_{\mathrm{mol}}(x) \sim |x - R_j|^{-3/2}$ near the R_j [32], we can repeat the above arguments for $\psi = \rho^{\mathrm{TF}}_{\mathrm{mol}} - \rho^{\mathrm{TF}}_{\mathrm{mol}} \star |x|^{-1}$. Thus, $\rho^{\mathrm{TF}}_{\mathrm{mol}} \star |x|^{-1} - \rho^{\mathrm{TF}}_{\mathrm{mol}} \star g^2 \star |x|^{-1} \ge 0$. We recall Newton's theorem

$$\int_{\mathbb{S}^2} |x-y|^{-1}\frac{d\nu(y)}{4\pi} = \min(|x|^{-1}, |y|^{-1})$$

for any $x \in \mathbb{R}^3$. Then

$$V_{\underline{R}} - V_{\underline{R}} \star g^2 \leq \sum_{j=1}^{K} Z_j \left(|x - R_j|^{-1} \mathbb{1}(|x - R_j| \leq s) \right). \tag{2.19}$$

Using this bound, we obtain

$$\begin{aligned} \int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} \star g^2]_+^{5/2} &\leq \int [V_{\underline{R}} - V_{\underline{R}} \star g^2]_+^{5/2} \\ &\leq Z^{5/2} \sum_{i=1}^{K} \int_{|x-R_i| \leq s} |x - R_i|^{-5/2} \, dx \\ &\leq C Z^{5/2} s^{1/2}, \end{aligned}$$

where we have used the convexity of $x^{5/2}$. Hence

$$\begin{aligned} \mathrm{tr} \left(-\frac{\Delta}{2} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} \right) \gamma \geq -2^{5/2} (15\pi^2)^{-1} \int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \mu(N, Z, \underline{R})]_+^{5/2} - C s^{-2} Z \\ - C Z^{12/5} s^{1/5} - \mu(N, Z, \underline{R}) N. \end{aligned}$$

Optimizing over $s > 0$ we get

$$\begin{aligned} &\mathrm{tr} \left(-\frac{\Delta}{2} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} \right) \gamma \\ &\quad \geq -2^{5/2} (15\pi^2)^{-1} \int [\varphi^{\mathrm{TF}}_{\mathrm{mol}} - \mu(N, Z, \underline{R})]_+^{5/2} - \mu(N, Z, \underline{R}) N - C Z^{25/11} \\ &\quad = -\frac{3}{10} (2/3) (3\pi^2)^{2/3} \int \left[\left(\rho^{\mathrm{TF}}_{\mathrm{mol}} \right)^{5/3} - \mu(N, Z, \underline{R}) \right]_+^{5/2} \\ &\qquad - \mu(N, Z, \underline{R}) N - C Z^{25/11} \end{aligned}$$

Using the relation obtained from the TF equation

$$-\mu(N, Z, \underline{R}) N - D\left[\rho^{\mathrm{TF}}_{\mathrm{mol}}\right] = \frac{3}{10} (5/3) (3\pi^2)^{2/3} \int \left(\rho^{\mathrm{TF}}_{\mathrm{mol}} \right)^{5/3} - \int \rho^{\mathrm{TF}}_{\mathrm{mol}} V_{\underline{R}} + D\left[\rho^{\mathrm{TF}}_{\mathrm{mol}}\right],$$

we learn

$$\mathrm{tr} \left(-\frac{\Delta}{2} - \varphi^{\mathrm{TF}}_{\mathrm{mol}} \right) \gamma \geq \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}_{\mathrm{mol}}) + D\left[\rho_\gamma - \rho^{\mathrm{TF}}_{\mathrm{mol}}\right] - C Z^{25/11},$$

which shows (2.17). □

We denote

$$\Gamma(N, \underline{Z}, \underline{R}) \coloneqq E^{\mathrm{TF}}_{\mathrm{mol}}(N, Z, \underline{R}) - \inf \left\{ \sum_{j=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(N_j, Z_j) \colon \sum_{j=1}^{K} N_j = N \right\}.$$

It was shown in [41, Proof of Theorem 8] that for any pair (R_i, R_j) from $\underline{R}$ there is a decomposition $(N_1, \dots, N_K)$ with $\sum_j N_j = N$ so that

$$\Gamma(N, \underline{Z}, \underline{R}) \geq \Gamma(N_i + N_j, (Z_i, Z_j), (R_i, R_j)).$$

From the result in [7] Γ is smallest in the neutral case. It was shown in [9] that $\Gamma(N_i + N_j, (Z_i, Z_j), l(R_i, R_j))l^7$ is an increasing function of l for the neutral case. By $|R_i - R_j| > C_0(Z_i + Z_j)^{-1/3}$, with $(R_i, R_j) = R(Z_i + Z_j)^{-1/3}|R_i - R_j|^{-1}(R_i, R_j)$, we see $R > C_0$. We put $\underline{z_{ij}} \coloneqq (Z_i + Z_j)^{-1}(Z_i, Z_j)$ and $\underline{r_{ij}} \coloneqq |R_i - R_j|^{-1}(R_i, R_j)$ for convenience. Then

$$\begin{aligned} \Gamma(N_i + N_j, (Z_i, Z_j), (R_i, R_j)) &\geq (Z_i + Z_j)^{7/3} \Gamma(1, \underline{z_{ij}}, R\underline{z_{ij}}) \\ &\geq |R_i - R_j|^{-7} C_0^7 \Gamma(1, \underline{z_{ij}}, C_0 \underline{r_{ij}}) \\ &= C|R_i - R_j|^{-7}. \end{aligned}$$

Here we have used the scaling property of Thomas-Fermi theory.

Combining these results,

$$\mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}} \geq \sum_{i=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(N_i, Z_i) - CZ^{25/11} + D\left[\rho_\gamma - \rho^{\mathrm{TF}}_{\mathrm{mol}}\right] + CR^{-7}_{\mathrm{min}}.$$

Next, we show the upper bound for the energy of Müller atom.

Lemma 4.5. *For any $N > 0$ and $Z > 0$*

$$E_{\mathrm{atom}}(N, Z) \leq \mathcal{E}^{\mathrm{TF}}_{\mathrm{atom}}(N, Z) + CZ^{11/5}. \tag{2.20}$$

Proof. First, we introduce the reduced Hartree-Fock functional by

$$\mathcal{E}^{\mathrm{RHF}}_{\mathrm{atom}}(\gamma) \coloneqq \mathrm{tr}\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma + D[\rho_\gamma].$$

It is clear that

$$E_{\mathrm{atom}}(N, Z) \leq \inf\{\mathcal{E}^{\mathrm{RHF}}_{\mathrm{atom}}(\gamma) \colon 0 \leq \gamma \leq 1,\ \mathrm{tr}\,\gamma = N\}$$

We introduce the atomic Thomas-Fermi potential by

$$\varphi^{\mathrm{TF}}_{\mathrm{atom}}(x) = Z|x|^{-1} - \rho^{\mathrm{TF}}_{\mathrm{atom}} \star |x|^{-1},$$

where ρ_{atom} is the minimizer for atomic ($K = 1$) Thomas-Fermi functional $E^{\mathrm{TF}}_{\mathrm{atom}}(N, Z)$ (in the negative ionic situation $N > Z$, we take the neutral TF minimizer). We apply Lemma 4.3 (2) with $V = \varphi^{\mathrm{TF}}_{\mathrm{atom}} - \mu$ (μ is the chemical potential for the TF atom) and a spherically symmetric g to obtain a density matrix γ'. Because of the Thomas-Fermi equation we see that

$$\rho_{\gamma'} = 2^{5/2}(6\pi^2)^{-1}(\varphi^{\mathrm{TF}}_{\mathrm{atom}} - \mu)^{3/2} \star g^2 = \rho^{\mathrm{TF}}_{\mathrm{atom}} \star g^2.$$

Since

$$\operatorname{tr}\gamma' = \int \rho_{\gamma'} = \int \rho^{\mathrm{TF}}_{\mathrm{atom}} = N,$$

we obtain

$$\inf\{\mathcal{E}^{\mathrm{RHF}}(\gamma) \colon 0 \le \gamma \le 1,\, \operatorname{tr}\gamma = N\} \le \mathcal{E}^{\mathrm{RHF}}(\gamma').$$

Again, by Lemma 4.3 (ii),

$$\begin{aligned}
\mathcal{E}^{\mathrm{RHF}}(\gamma') &\le 2^{3/2}(5\pi^2)^{-1}\int [V]_+^{5/2} + Cs^{-2}\int [V]_+^{3/2} \\
&\quad - \int Z|x|^{-1}(\rho^{\mathrm{TF}}_{\mathrm{atom}} \star g^2(x))\,dx + D\left[\rho^{\mathrm{TF}}_{\mathrm{atom}} \star g^2\right] \\
&\le 2^{3/2}(5\pi^2)^{-1}\int [V]_+^{5/2} - \int [\varphi^{\mathrm{TF}}_{\mathrm{atom}} - \mu]\rho^{\mathrm{TF}}_{\mathrm{atom}}(x)\,dx - \mu N \\
&\quad - D\left[\rho^{\mathrm{TF}}_{\mathrm{atom}}\right] + Z\int (|x|^{-1} - |x|^{-1} \star g^2)\rho^{\mathrm{TF}}_{\mathrm{atom}}(x)\,dx \\
&\qquad + Cs^{-2}\int \rho^{\mathrm{TF}}_{\mathrm{atom}} \\
&= -2^{5/2}(15\pi^2)^{-1}\int [\varphi^{\mathrm{TF}}_{\mathrm{atom}} - \mu]_+^{5/2} - D\left[\rho^{\mathrm{TF}}_{\mathrm{atom}}\right] - \mu N \\
&\quad + Cs^{-2}\int \rho^{\mathrm{TF}}_{\mathrm{atom}} + Z\int (|x|^{-1} - |x|^{-1} \star g^2)\rho^{\mathrm{TF}}_{\mathrm{atom}} \\
&= \mathcal{E}^{\mathrm{TF}}_{\mathrm{atom}}(\rho^{\mathrm{TF}}_{\mathrm{atom}}) + Cs^{-2}\int \rho^{\mathrm{TF}}_{\mathrm{atom}} + Z\int (|x|^{-1} - |x|^{-1} \star g^2)\rho^{\mathrm{TF}}_{\mathrm{atom}}.
\end{aligned} \tag{2.21}$$

In the second inequality, we have used

$$[g^2 \star |x|^{-1} \star g^2](x-y) \leq |x-y|^{-1}, \tag{2.22}$$

as an operator and function. This is shown, for instance, by using the Fourier transform. By Newton's theorem,

$$0 \leq |x|^{-1} - |x|^{-1} \star g^2 = |x|^{-1} \mathbb{1}(|x| \leq s).$$

Then, by the Hölder inequality,

$$\begin{aligned} Z \int & (|x|^{-1} - |x|^{-1} \star g^2) \rho_{\mathrm{atom}}^{\mathrm{TF}} \\ & \leq Z \left(\int (\rho_{\mathrm{atom}}^{\mathrm{TF}})^{5/3} \right)^{3/5} \left(\int (|x|^{-1} - |x|^{-1} \star g^2)^{5/2} \right)^{2/5} \\ & \leq CZ \left(\int (Z|x|^{-1})^{5/2} \right)^{3/5} \left(\int_{|x| \leq s} |x|^{-5/2} \right)^{2/5} dx \\ & \leq CZ^{5/2} s^{1/2}, \end{aligned} \tag{2.23}$$

where we have used the Thomas-Fermi equation in the second inequality. Thus, after optimization in s,

$$\mathcal{E}^{\mathrm{RHF}}(\gamma') \leq \mathcal{E}_{\mathrm{atom}}^{\mathrm{TF}}(\rho_{\mathrm{atom}}^{\mathrm{TF}}) + CZ^{11/5}.$$

This shows the desired upper bound. □

Inserting this, we obtain

$$E(N,Z) \geq \sum_{j=1}^{K} E_{\mathrm{atom}}(N_j, Z_j) - CZ^{25/11} + D[\rho_\gamma - \rho_{\mathrm{mol}}^{\mathrm{TF}}] + CR_{\mathrm{min}}^{-7}. \tag{2.24}$$

This completes the proof.

Remark 4.6. It immediately follows that

$$D[\rho_\gamma - \rho_{\mathrm{mol}}^{\mathrm{TF}}] \leq CZ^{25/11}, \tag{2.25}$$

and $R_{\mathrm{min}} \geq CZ^{-(1/3)(1-\varepsilon)}$ with $\varepsilon = 2/77$. These bounds are the crucial ingredients for comparring with Thomas-Fermi theory.

5 Bound on the Excess Positive Charge

We assume that the molecule is stable in a configuration $\underline{R} \in \mathbb{R}^{3K}$ and $N < Z$. Let γ be a minimizer for the stable molecule. The next lemma allows us to localize the Müller functional [25, Lemma 6].

Lemma 5.1 (IMS-type formula)**.** *For any quadratic partition of unity* $\sum_{j=0}^{n} \theta_j^2 = 1$ *with* $\nabla\theta_j \in L^\infty$ *and for any density matrix* $\gamma \in \mathcal{S}^1$*, we have*

$$\begin{aligned}\sum_{j=0}^{n} \mathcal{E}_{\underline{R}}(\theta_j\gamma\theta_j) - \mathcal{E}_{\underline{R}}(\gamma) \\ \leq \int_{\mathbb{R}^3} \sum_{j=0}^{n} |\nabla\theta_j(x)|^2 \rho_\gamma(x)\, dx \\ + \sum_{i<j}^{n} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\theta_j(x)^2(|\gamma^{1/2}(x,y)|^2 - \rho_\gamma(x)\rho_\gamma(y))\theta_j(y)^2}{|x-y|}\, dx\, dy\end{aligned} \tag{2.26}$$

As in [41] we choose smooth localizing function $0 \leq \theta_j \in C^\infty(\mathbb{R}^3)$, $j = 0, \ldots, K$ having the following properties.

(i) For $j \geq 1$ we have $\theta_j(x) = \theta(|x - R_j|/R_{\min})$, with smooth θ satisfying $0 \leq \theta \leq 1$ and $\theta(t) = 1$ if $t < 1/5$ and $\theta(t) = 0$ if $t > 1/4$.

(ii) $\sum_{j=0}^{K} \theta_j(x)^2 = 1$ (which defines θ_0).
These properties imply

(iii) $|\nabla\theta_j(x)| \leq CR_{\min}^{-1}$ for all j.

For any $M_1 + M_2 \leq M$ we have

$$E_{\text{atom}}(M) \leq E_{\text{atom}}(M_1) + E_\infty(M_2).$$

The proof of this is the same as Proposition 3.1 (or, see [28, Lemma 2]). Using proposition 3.1, we have

$$\begin{aligned}\mathcal{E}_{\underline{R}}(\gamma) + U_{\underline{R}} &\leq \sum_{j=1}^{K} E_{\text{atom}}(N_j, Z_j) \\ &\leq \sum_{j=1}^{K} (E_{\text{atom}}(N_j^{(1)}, Z_j) + E_\infty(N_j^{(2)})\end{aligned}$$

for a minimizer γ and for any $\sum_{j=1}^{K}(N_j^{(1)}+N_j^{(2)})=N$. We note that

$$\sum_{j=1}^{K} E_\infty(N_j^{(2)}) = -\sum_{j=1}^{K}\frac{N_j^{(2)}}{8} = -\frac{N^{(2)}}{8} = E_\infty(N^{(2)})$$

and take $N_j^{(1)}=\mathrm{tr}(\theta_j\gamma\theta_j)$, $j=1,\dots,K$, and $N^{(2)}=\mathrm{tr}(\theta_0\gamma\theta_0)$. Then

$$\mathcal{E}_{\underline{R}}(\gamma)+U_{\underline{R}} \le \sum_{j=1}^{K}\mathcal{E}_{\mathrm{atom}}(\theta_j\gamma\theta_j)+\mathcal{E}_\infty(\theta_0\gamma\theta_0) \tag{2.27}$$

Combining (2.27) and the IMS-type formula in Lemma 5.1

$$\begin{aligned}
0 &\le \sum_{j=1}^{K}\mathcal{E}_{\mathrm{atom}}(\theta_j\gamma\theta_j)+\mathcal{E}_\infty(\theta_0\gamma\theta_0)-\mathcal{E}_{\underline{R}}(\gamma)-U_{\underline{R}}\\
&= \sum_{j=0}^{K}\mathcal{E}_{\underline{R}}(\theta_j\gamma\theta_j)+\mathrm{tr}(V_{\underline{R}}\theta_0\gamma\theta_0)-\mathcal{E}_{\underline{R}}(\gamma)-U_{\underline{R}}\\
&\quad+\sum_{1\le i<j\le K}\left(\int_{\mathbb{R}^3}\frac{Z_i\theta_j(x)^2}{|x-R_j|}\rho_\gamma(x)\,dx+\int_{\mathbb{R}^3}\frac{Z_j\theta_i(x)^2}{|x-R_i|}\rho_\gamma(x)\,dx\right)\\
&\le \int_{\mathbb{R}^3}\sum_{j=0}^{K}|\nabla\theta_j(x)|^2\rho_\gamma(x)\,dx+\sum_{1\le i<j\le K}I_{ij}+\sum_{j=1}^{K}I_{0j},
\end{aligned} \tag{2.28}$$

where we have denoted

$$\begin{aligned}
I_{ij} \coloneqq &-\frac{Z_iZ_j}{|R_i-R_j|}+\int_{\mathbb{R}^3}\frac{Z_i\theta_j(x)^2}{|x-R_j|}\rho_\gamma(x)\,dx+\int_{\mathbb{R}^3}\frac{Z_j\theta_i(x)^2}{|x-R_i|}\rho_\gamma(x)\,dx\\
&+\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\theta_i(x)^2(|\gamma^{1/2}(x,y)|^2-\rho_\gamma(x)\rho_\gamma(y))\theta_j(y)^2}{|x-y|}\,dx\,dy
\end{aligned} \tag{2.29}$$

and

$$\begin{aligned}
I_{0j} \coloneqq &\int_{\mathbb{R}^3}\frac{Z_j\theta_0(x)^2}{|x-R_j|}\rho_\gamma(x)\,dx\\
&+\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\theta_0(x)^2(|\gamma^{1/2}(x,y)|^2-\rho_\gamma(x)\rho_\gamma(y))\theta_j(y)^2}{|x-y|}\,dx\,dy
\end{aligned}$$

For the first term in (2.28) we learn from the property (iii) of the functions θ_j that

$$\int_{\mathbb{R}^3} \sum_{j=0}^{K} |\nabla \theta_j(x)|^2 \rho_\gamma(x)\, dx \leq CNR_{\min}^{-2}, \tag{2.30}$$

where the constant C depends on K. For estimate the contributions from I_{ij} we use the following properties in [41, Section 4]. We now define $N_1^{\mathrm{TF}}, \ldots, N_K^{\mathrm{TF}}$ to be the positive numbers that minimize $\sum_{j=1}^K E_{\mathrm{atom}}^{\mathrm{TF}}(N_j^{\mathrm{TF}}, Z_j)$ under the constraint $\sum_{j=1}^K N_j^{\mathrm{TF}} = N$. Then it is well-known that all the chemical potential $\mu_{\mathrm{atom}}(N_j^{\mathrm{TF}}, Z_j)$ for the atoms will be identical

$$\mu_{\mathrm{atom}}(N_j^{\mathrm{TF}}, Z_j) = \mu_{\mathrm{mol}}(N, \underline{Z}, \infty), \quad j = 1, \ldots, K.$$

Lemma 5.2 (Lemma 9 in [41])**.** *Let $\rho_{\mathrm{mol}}^{\mathrm{TF}}$ be the TF density for the molecular. If $CZ^{-1/3} < R' < R_{\min}/2$ then we have for all $j = 1, \ldots, K$*

$$\int_{|x-R_j|<R'} \rho_{\mathrm{mol}}^{\mathrm{TF}}(x)\, dx = N_j^{\mathrm{TF}} + \mathcal{O}(R'^{-3}) \tag{2.31}$$

and if $|x - R_j| > 3R_{\min}/4$

$$\int_{|y-R_j|<R'} \rho_{\mathrm{mol}}^{\mathrm{TF}}(y)|x-y|\, dy = (N_j^{\mathrm{TF}} + \mathcal{O}(R'^{-3}))|x - R_j|^{-1} \tag{2.32}$$

Also we will need the

Lemma 5.3 (Proposition 10 in [41])**.** *If $\mu_{\mathrm{mol}}(N, \underline{Z}, \infty) > 0$ then there are positive constants $\kappa, \kappa' > 0$ depending on $Z_1, \ldots, Z_K$ such that*

$$\kappa < \frac{Z_j - N_j^{\mathrm{TF}}}{Z_i - N_i^{\mathrm{TF}}} < \kappa' \tag{2.33}$$

for all $i \neq j$. If $\mu_{\mathrm{mol}}(N, \underline{Z}, \infty) = 0$ then $Z_j = N_j^{\mathrm{TF}}$.

In order to compare with Thomas-Fermi theory, we use the

Lemma 5.4. *Let $\beta > 0$ and $R(Z) = (\beta Z^{-1/3(1-\alpha)})$ with $\alpha < \varepsilon = 2/77$ in the previous bound (2.25). For any fixed $1 \leq j \leq K$ let $\lambda(x)$ be a function satisfying*

(a) $\lambda \in C^\infty(\mathbb{R}^3)$ with $0 \leq \lambda(x) \leq 1$.

(b) $\operatorname{supp}\lambda \subset \{x\colon |x-R_j| < R(Z)\}$.

Then there exist $C>0$ *and* $a>0$ *such that for all small* $\alpha<\varepsilon$,

(i)

$$\left|\int_{\mathbb{R}^3} (\rho_\gamma(x)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(x))\lambda(x)\,dx\right| \le CZ^{(1-a)}. \tag{2.34}$$

(ii) If $|y-R_j|>R(Z)$, *we have*

$$\left|\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(x)}{|x-y|}\lambda(x)\,dx\right| \le CZ^{1-a}|y-R_j|^{-1}. \tag{2.35}$$

For the proof we need the following Lemma for Coulomb potential (see [24, Lemma 18]).

Lemma 5.5 (Coulomb potential estimate)**.** *For every* $f\in L^{5/3}(\mathbb{R}^3)\cap L^{6/5}(\mathbb{R}^3)$ *and* $x\in\mathbb{R}^3$, *we have*

$$\left|\int_{|y|<|x|} \frac{f(y)}{|x-y|}\,dy\right| \le C\|f\|_{L^{5/3}}^{5/6}(|x|D(f))^{1/12}. \tag{2.36}$$

Proof of Lemma 5.4. First, we introduce the function

$$\Phi_r(x) \coloneqq \int_{|y|<r} \frac{f(y)}{|x-y|}\,dy$$

Applying the Coulomb potential estimate with $f(y)=(\rho_\gamma(y+R_j)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(y+R_j))\lambda(y+R_j)$, we have

$$\begin{aligned}|\Phi_{|x|}(x)| &= \left|\int_{|y-R_j|<|x|} \frac{\rho_\gamma(y)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(y)}{|x-(y-R_j)|}\lambda(y)\,dy\right| \\ &\le C\|f\|_{L^{5/3}}^{5/6}(|x|D(f))^{1/12}.\end{aligned}$$

By Newton's theorem, we have

$$\begin{aligned}&\int_{|y-R_j|<R(Z)} (\rho_\gamma(y)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(y))\lambda(y)\,dy \\ &\qquad = R(Z)\int_{\mathbb{S}^2}\frac{d\nu}{4\pi}\int_{|y-R_j|<R(Z)} \frac{\rho_\gamma(y)-\rho_{\mathrm{mol}}^{\mathrm{TF}}(y)}{|R(Z)\nu-(y-R_j)|}\lambda(y)\,dy \\ &\qquad = R(Z)\int_{\mathbb{S}^2}\frac{d\nu}{4\pi}\Phi_{R(Z)}(R(Z)\nu) \\ &\qquad \le CR(Z)^{13/12}\|\rho_\gamma-\rho_{\mathrm{mol}}^{\mathrm{TF}}\|_{L^{5/3}}^{5/6}\left(D\left[\rho_\gamma-\rho_{\mathrm{mol}}^{\mathrm{TF}}\right]\right)^{1/12}.\end{aligned}$$

Combining this with (2.25) and the kinetic estimates

$$\int_{\mathbb{R}^3} \rho_\gamma(x)^{5/3}\,dx \le CZ^{7/3}, \quad \int_{\mathbb{R}^3} \rho_{\mathrm{mol}}^{\mathrm{TF}}(x)^{5/3}\,dx \le CZ^{7/3},$$

we find

$$\left|\int_{\mathbb{R}^3} (\rho_\gamma(y) - \rho_{\mathrm{mol}}^{\mathrm{TF}}(y))\lambda(y)\,dy\right| \le CR(Z)^{13/12}Z^{179/132}.$$

Since $179/132 = 49/36 - 1/198$, we have

$$\left|\int_{\mathbb{R}^3} (\rho_\gamma(y) - \rho_{\mathrm{mol}}^{\mathrm{TF}}(y))\lambda(y)\,dy\right| \le C\beta^{13/12}Z^{1-1/198+13\alpha/36}.$$

Thus if we choose $\alpha < 2/143$, the conclusion (i) follows.

Next, we use the well-known property for subharmonic function (see [24, Lemma 6.5]).

Lemma 5.6. *Let f be the real-valued function on $\mathbb{R}^3$. If f is subharmonic for $|x| > r$, continuous for $|x| \ge r$, and vanishing at infinity, then we have*

$$\sup_{|x|\ge r} |x|f(y) = \sup_{|x|=r} |x|f(x).$$

We note that $-\Delta\Phi_r(x) = \mathbb{1}_{|x|<r}(x)f(x)$ and thus harmonic for $|x| > r$. From the Coulomb estimate with $r = R(Z)$ and $\pm f(y) = \pm(\rho_\gamma(y + R_j) - \rho_{\mathrm{mol}}^{\mathrm{TF}}(y + R_j))\lambda(y + R_j)$ we conclude that, on $|y - R_j| > R(Z)$,

$$\begin{aligned}\left|\int_{\mathbb{R}^3} \frac{\rho_\gamma(x) - \rho_{\mathrm{mol}}^{\mathrm{TF}}(x)}{|x-y|}\lambda(x)\,dx\right| &\le CZ^{49/36-1/198}|y - R_j|^{-1}R(Z)^{13/12} \\ &\le CZ^{1-a}|y - R_j|^{-1},\end{aligned}$$

which shows (ii). □

For applying Lemma 5.2 and Lemma 2.34 we choose α and β so that $R_{\min} > 3R(Z)$. If we define $\tilde{\theta}_j(x) = \theta(|x - R_j|/R(Z))$ for $j \ge 1$ then

$$\begin{aligned}\int_{\mathbb{R}^3} \tilde{\theta}_j(x)^2\rho_\gamma(x)\,dx &= \int_{\mathbb{R}^3} \tilde{\theta}_j(x)^2(\rho_\gamma(x) - \rho_{\mathrm{mol}}^{\mathrm{TF}}(x))\,dx \\ &\quad + \int_{\mathbb{R}^3} \tilde{\theta}_j(x)^2\rho_{\mathrm{mol}}^{\mathrm{TF}}(x)\,dx \\ &= N_j^{\mathrm{TF}} + o(Z).\end{aligned}$$

Thus since $\sum_{j=1}^{K} N_j^{\mathrm{TF}} = N$ we conclude

$$\begin{aligned} 0 &\le \sum_{j=1}^{K} \int_{\mathbb{R}^3} \rho_\gamma(x)(\theta_j(x)^2 - \tilde{\theta}_j(x)^2)\, dx \\ &\le \int_{\mathbb{R}^3} \rho_\gamma(x) \left(1 - \sum_{j=1}^{K} \tilde{\theta}_j(x)^2\right) dx \\ &= o(Z). \end{aligned}$$

We also get from (2.35) in Lemma 5.4 that

$$\int_{\mathbb{R}^3} \frac{\tilde{\theta}_j(x)^2 \rho_\gamma(x)}{|x - R_i|}\, dx = \frac{N_j^{\mathrm{TF}} + o(Z)}{|R_i - R_j|}.$$

Using these estimates, we may find

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{\theta_j(x)^2 \rho_\gamma(x)}{|x - R_i|}\, dx &= \int_{\mathbb{R}^3} \frac{\tilde{\theta}_j(x)^2 \rho_\gamma(x)}{|x - R_i|}\, dx \\ &\quad + \int_{\mathbb{R}^3} \frac{(\theta_j(x)^2 - \tilde{\theta}_j(x)^2)\rho_\gamma(x)}{|x - R_i|}\, dx \qquad (2.37) \\ &= \frac{N_j^{\mathrm{TF}} + o(Z)}{|R_i - R_j|}. \end{aligned}$$

Next, we estimate the error term for direct part for I_{ij}. Combining this and (2.32) in Lemma 5.2,

$$
\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\theta_i(x)^2\theta_j(y)^2\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\
&\quad\geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\tilde{\theta}_i(x)^2\theta_j(y)^2\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\
&\quad\geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\tilde{\theta}_i(x)^2\theta_j(y)^2\rho^{\mathrm{TF}}_{\mathrm{mol}}(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\
&\qquad - \frac{CZ^{1-a}}{|R_i-R_j|}\int_{\mathbb{R}^3}\rho_\gamma(x)\theta_j(x)^2\,dx \\
&\quad\geq (N_i^{\mathrm{TF}}+o(Z))\int_{\mathbb{R}^3}\frac{\rho_\gamma(x)\theta_j(x)^2}{|x-R_i|}\,dx \\
&\qquad - \frac{CZ^{1-a}}{|R_i-R_j|}\int_{\mathbb{R}^3}\rho_\gamma(x)\theta_j(x)^2\,dx.
\end{aligned}
$$

Together with (2.37), we obtain

$$
\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\theta_i(x)^2\theta_j(y)^2\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\
&\qquad\geq \frac{(N_i^{\mathrm{TF}}+o(Z))(N_j^{\mathrm{TF}}+o(Z))-o(Z^2)}{|R_i-R_j|}.
\end{aligned}
$$

For the exchange term in (2.29), we simply use

$$
\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\theta_j(x)^2(|\gamma^{1/2}(x,y)|^2\theta_i(y)^2}{|x-y|}\,dx\,dy \\
&\qquad\leq \frac{2}{|R_i-R_j|}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\theta_j(x)^2|\gamma^{1/2}(x,y)|^2\,dx\,dy \\
&\qquad= \frac{2}{|R_i-R_j|}\int_{\mathbb{R}^3}\theta_j(x)^2\rho_\gamma(x)\,dx
\end{aligned}
$$

Thus we arrive at the following estimate for the interaction of two screened nuclei

$$
I_{ij} \leq \frac{-(Z_i-N_i^{\mathrm{TF}}+o(Z))(Z_j-N_j^{\mathrm{TF}}+o(Z))+o(Z^2)}{|R_i-R_j|} \tag{2.38}
$$

Repeating these arguments,

$$I_{0j} \leq \frac{(Z_j - N_j^{\mathrm{TF}} + o(Z))o(Z) + o(Z^2)}{|R_i - R_j|}. \tag{2.39}$$

Inserting the estimates (2.30), (2.38) and (2.39) into (2.28), we get

$$\begin{aligned} 0 \geq & \sum_{1 \leq i < j \leq K} \frac{(Z_i - N_i^{\mathrm{TF}} + o(Z))(Z_j - N_j^{\mathrm{TF}} + o(Z)) + o(Z^2)}{|R_i - R_j|} \\ & - CZ^{1+1/3(1-\varepsilon)} R_{\min}^{-1} \end{aligned}$$

If we write $R_{\min} = |R_{i_0} - R_{j_0}|$ then

$$\begin{aligned} & (Z_{i_0} - N_{i_0}^{\mathrm{TF}})(Z_{j_0} - N_{j_0}^{\mathrm{TF}}) R_{\min}^{-1} \\ & \quad \leq \sum_{1 \leq i < j \leq K} \frac{(Z_i - N_i^{\mathrm{TF}})(Z_j - N_j^{\mathrm{TF}})}{|R_i - R_j|} \\ & \quad \leq CZ^{1-\delta} \sum_{j=1}^{K} (Z_j - N_j^{\mathrm{TF}}) R_{\min}^{-1} + CZ^{2(1-\delta)} R_{\min}^{-1} \end{aligned}$$

for some small $\delta > 0$.

If $Z_{i_0} - N_{i_0}^{\mathrm{TF}} \leq CZ^{1-\delta}$, we find from Lemma 5.3 that $Z_i - N_i^{\mathrm{TF}} \leq CZ^{1-\delta}$ for all i. If $Z_{i_0} - N_{i_0}^{\mathrm{TF}} \geq CZ^{1-\delta}$, then we divide the above inequality by $Z_{i_0} - N_{i_0}^{\mathrm{TF}}$ and get $Z_{j_0} - N_{j_0}^{\mathrm{TF}} \leq CZ^{1-\delta}$ because of Lemma 5.3. Again, by Lemma 5.3, we see that $Z_i - N_i^{\mathrm{TF}} \leq CZ^{1-\delta}$ for all $i = 1, \ldots, K$. Finally, summing this inequality over i, we obtain the desired bound on the excess positive charge

$$Z - N \leq \mathrm{const.} Z^{1-\delta}.$$

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