MATHEMATICAL ELEMENTS
OF DENSITY FUNCTIONAL THEORY

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We review some of the basic mathematical results about density functional theory.

1. Introduction

Already in classical mechanics it turned out that the microscopic equation describing many particles interacting via the Coulomb force cannot be solved analytically. Approximation schemes are indispensably. The idea of describing such systems by effective equations depending only on a few variables of interest, like the density of matter and its velocity field has a long history that dates back to at least to Euler [1–3] long before the advent of quantum mechanics. In quantum mechanics of atoms and other fermionic systems the need for such an effective description was also immediately recognized. Only two years after Heisenberg’s [4] fundamental discovery Thomas [5] and Fermi [6,7] introduced the first — in today’s language — density functional theory which is now known as Thomas–Fermi theory. Although relatively simple it is not only of historical importance. As we will see in Section 4.1 it becomes asymptotically exact for heavy atoms and serves as a mathematical tool to prove fundamental features of matter like its stability and, closely related, the existence of the thermodynamic limit of Coulomb systems. Later, various corrections of the theory were made, e.g., Dirac [8] took the exchange energy into account and Weizsäcker [9] inhomogeneities of the electron gas. A detailed overview over these early
developments is offered by Gombas [10]. The subject received an immense push with an observation of Hohenberg and Kohn [11]. They argued that there is at most one external potential for a system of $N$ fermions interacting via Coulomb potentials for which a given one-particle density with particle number $N$ is its ground state density. They concluded from this that there is a functional of the form

$$\mathcal{E}^{HK}(\rho) + \int_{\mathbb{R}^3} d\mathbf{x} \, V(\mathbf{x}) \rho(\mathbf{x})$$

whose minimizer is a reduced one-particle electronic ground state density of the Hamiltonian

$$H_{V,N} := \sum_{n=1}^{N} \left( -\frac{1}{2} \Delta_n + V(x_n) \right) + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}.$$  

(As usual the colon in connection with an equality sign indicates a definition where the defined quantity is on the side of the colon.) The functional $\mathcal{E}^{HK}$ depends only on the kinetic energy operator and the interaction energy of the electrons which are assumed to be the nonrelativistic kinetic energy and the Coulomb force. Both choices, namely nonrelativistic kinetic energy and Coulomb interaction, are made only for convenience and definiteness at this point. Although Hohenberg and Kohn merely claimed the existence of such a functional without offering any construction of $\mathcal{E}^{HK}$, it nevertheless triggered a tsunami of results on the subject that is still gathering momentum sixty years after its publication.

2. Elements of quantum mechanics of electrons

2.1. Electronic Hilbert spaces

We write $\mathcal{H}_1$ for the one-electron Hilbert space. The $N$-electron Hilbert space is its antisymmetric tensor product

$$\mathcal{H}_N := \bigwedge_{n=1}^{N} \mathcal{H}_1,$$

and finally the Fock space of electrons is

$$\mathcal{F} := \bigoplus_{N=0}^{\infty} \mathcal{H}_N$$

with the understanding that $\mathcal{H}_0 := \mathbb{C}$. The summand $\mathcal{H}_0$ is also called the vacuum space.
To be concrete we focus on the case of nonrelativistic quantum mechanics where $\mathcal{H}_1 = L^2(\Gamma)$ is the space of functions $\psi$ of the space-spin variable $x := (x, \sigma) \in \Gamma := \mathbb{R}^3 \times \{1, 2\}$ with finite scalar product $(\psi, \psi) < \infty$. Here

$$(\psi, \tilde{\psi}) := \int_{\Gamma} dx \overline{\psi(x)} \tilde{\psi}(x) := \sum_{\sigma = 1}^2 \int_{\mathbb{R}^3} dx \overline{\psi(x, \sigma)} \tilde{\psi}(x, \sigma)$$

(2.3)

using the notation $\int_{\Gamma} dx := \int_{\mathbb{R}^3} dx \sum_{\sigma = 1}^2$.

The $N$-electron Hilbert space $\mathcal{H}_N$ is the space of antisymmetric functions $\psi$ of space-spin variables with $(\psi, \psi) < \infty$ where

$$(\psi, \tilde{\psi})_N := \int_{F_N} dx_1 \cdots dx_N \overline{\psi(x_1, \ldots, x_N)} \tilde{\psi}(x_1, \ldots, x_N).$$

(2.4)

Eventually $\mathfrak{F}$ is the space of all sequences $\psi := (\psi_0, \psi_1, \psi_2, \ldots)$ with $\psi_N \in \mathcal{H}_N$ such that $(\psi, \psi)_{\mathfrak{F}} < \infty$ with

$$(\psi, \tilde{\psi})_{\mathfrak{F}} := \sum_{N=0}^{\infty} (\psi_N, \tilde{\psi}_N)_N.$$  

(2.5)

In the following we will drop any indices with scalar products.

### 2.2. Electronic states

From an abstract point of view, a state $\omega$ is simply a continuous linear functional on the bounded operators $\mathfrak{B}(\mathfrak{H})$ of the underlying Hilbert space $\mathfrak{H}$, which is also positive and normalized, i.e.,

- For all $A \in \mathfrak{B}(\mathfrak{H})$ we have $\omega(A^* A) \in \mathbb{R}_+$ (positivity).
- $\omega(1) = 1$ (normalization).

Given any $f, g \in \mathfrak{H}$ we will use the physics notation $|g\rangle \langle f|$ for the operator

$$\mathfrak{H} \rightarrow \mathfrak{H},$$

$$h \mapsto (f, h)g.$$  

(2.6)

In particular, if $f$ is normalized, then $|f\rangle \langle f|$ is the orthogonal projection onto the one-dimensional subspace spanned by $f$. Given any set of orthonormal vectors $\xi_1, \xi_2, \ldots \in \mathfrak{H}$ and nonnegative weights $w_1, w_2, \ldots \in \mathbb{R}_+$ with $w_1 + w_2 + \cdots = 1$

$$d := w_1 |\xi_1\rangle \langle \xi_1| + w_2 |\xi_2\rangle \langle \xi_2| + \cdots.$$  

(2.7)
is called a density matrix. To each density matrix one can associate in
natural way a state $\omega_d$ via the relation

$$\omega_d(A) := \text{tr}(Ad).$$

(2.8)

If there is a single normalized vector $\psi \in H_N$ such that $d = |\psi\rangle\langle\psi|$ then
$\omega_{|\psi\rangle\langle\psi|}$ is called a pure state which — in abuse of notation — is also written
for brevity as $\rho_{\psi}$. We have

$$\omega_{\psi}(A) := \omega_{|\psi\rangle\langle\psi|}(A) = \text{tr}(A|\psi\rangle\langle\psi|) = (\psi, A\psi).$$

(2.9)

Because of the above relations, it is customary — although strictly speaking
abusing notation again — to address normalized vectors in a Hilbert space
also as states, in fact as pure states, and density matrices with rank larger
than one as mixed states.

The Hilbert spaces of relevance for us will be the Fock space $\mathfrak{F}$ and its
summands, i.e., the $N$-electron spaces $H_N$.

2.3. Creation and annihilation operators

For our discussion it is handy to use creation and annihilation operators. Given $f \in \mathfrak{F}_1$ and $\psi = (\psi_0, \psi_1, \ldots) \in \mathfrak{F}$ we define $a(f) : \mathfrak{F} \to \mathfrak{F}$ component-wise — abusing notation writing $\psi_N$ instead of $(0, \ldots, \psi_N, 0, \ldots)$ — by

$$[a(f)(\psi_N)](x_1, \ldots, x_{N-1}) := \left\{ \begin{array}{ll}
\sqrt{N} \int_{\Gamma} dx f(x) \psi_N(x, x_1, \ldots, x_{N-1}) & \text{for } N \geq 1, \\
0 & \text{for } N = 0. \end{array} \right.$$

(2.10)

Three properties are obvious for all $f \in \mathfrak{F}_1$:

- the family $a$ is conjugate linear in $f$,
- the operators $a(f)$ are bounded and linear on $\mathfrak{F}$,
- the operators $a(f)$ map the $N$-particle sector of the Fock space to
its $(N-1)$-particle sector (for all $N \geq 1$).

The adjoint operators $a^*(f)$ are called creation operators. We claim that
they are also given component-wise by the formula

$$[a^*(f)(\phi)](x_0, \ldots, x_{N-1}) := \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} (-1)^n f(x_n) \phi(x_1, \ldots, \hat{x}_n, \ldots, x_{N-1})$$

(2.11)
where the hat indicates the omission of the variable below it. Obviously these operators are also bounded, linear, and map $\mathcal{H}_N$ to $\mathcal{H}_{N+1}$. That (2.11) gives indeed the adjoint operator can be seen as follows. Suppose $\phi \in \mathcal{H}_{N-1}$ and $\psi \in \mathcal{H}_N$ then
\[
(\phi, a(f)\psi) = \sqrt{N} \int_{\Gamma^{N-1}} dx_1 \cdots dx_{N-1} \phi(x_1, \ldots, x_{N-1}) \int_{\Gamma} dx_0 f(x_0) \psi(x_0, \ldots, x_{N-1})
= \sqrt{N} \int_{\Gamma^N} dx_0 \cdots dx_{N-1} f(x_0) \phi(x_1, \ldots, x_{N-1}) \psi(x_0, \ldots, x_{N-1})
= \int_{\Gamma^N} dx_0 \cdots dx_{N-1} \sum_{n=0}^{N-1} (-1)^n \sqrt{N} f(x_n) \phi(x_1, \ldots, x_n, \ldots, x_{N-1})
= [a^*(f)(0) | x_0, \ldots, x_{N-1})]
\times \psi(x_0, \ldots, x_{N-1}).
\] (2.12)

For given orthonormal basis $\xi_1, \xi_2, \ldots$ of $\mathcal{H}_1$ the short hand
\[
a^*_n := a^*(\xi_n), \quad a_n := a(\xi_n)
\] (2.13)
is customary. One even extends these to “eigenstates” of position by writing $a^*_x := a^*(\delta_x \delta_{\cdot, \sigma})$ or of momentum by writing $a^*_p := a^*(\exp(i\cdot p) \delta_{\cdot, \sigma}/(2\pi)^2)$ and of other observables. These expressions become meaningful when “integrated” against a suitable test function in the sense of a distribution, e.g., we have
\[
a^*(f) =: \int_{\Gamma} dx f(x)a^*_x, \quad a^*(\mathcal{F}(f)) =: \int_{\Gamma} dp f(p)a^*_p
\] (2.14)
where we write $\mathcal{F}(f)$ for the Fourier transform of $f$. It is also common to write them as
\[
a_x = \sum_n \xi_n(x)a(\xi_n), \quad a^*_x = \sum_n \overline{\xi_n(x)}a^*(\xi_n)
\] (2.15)
(see, e.g., Schweber [12, Chapter 6.e, Formulae (63) and (64)]) using Parseval’s identity.

Eventually we mention that the creation and annihilation operators fulfill the canonical anticommutation relations (Jordan and Wigner [13, Formulae (36) and (40)]
\[
a(f)a(g) + a(g)a(f) = a^*(f)a^*(g) + a^*(g)a^*(f) = 0,
\]
a\[
a^*(f)a(g) + a(g)a^*(f) = (g, f).
\] (2.16)
2.4. Reduced densities and density matrices

Given a state $\omega \in \mathcal{B}(\mathcal{F})'$ and $f, g \in \mathcal{H}_1$ we define the sesquilinear form

$$q_\omega : \mathcal{H}_1 \times \mathcal{H}_1 \to \mathbb{C},$$

$$(f, g) \mapsto \omega(a^*(f)a(g)). \tag{2.17}$$

We have $0 \leq \omega(a^*(f)a(f)) \leq \omega(a^*(f)a(f)) + \omega(a(f)a^*(f)) = (f, f)$, i.e., $q_\omega$ defines a positive linear operator $\gamma_\omega$ bounded from above by one. Moreover $\gamma_\omega$ is trace class, and, if $\omega$ lives on $\mathcal{B}(\mathcal{H}_N)$ only, then $\text{tr}(\gamma_\omega) = N$.

It is enough to show the trace class property for the case that $\omega$ is a pure $N$-electron state $\psi \in \mathcal{H}_N$. Then

$$q_{|\psi\rangle\langle\psi|}(f, g) := \text{tr}(a^*(f)a(g)|\psi\rangle\langle\psi|) = (a(f)\psi, a(g)\psi)$$

$$= \int_{\Gamma_{N-1}} dx_1 \cdots dx_{N-1} a(f)\psi(x_1, \ldots, x_{N-1})a(g)\psi(x_1, \ldots, x_{N-1})$$

$$= \int_{\Gamma} dx \int_{\Gamma} dy g(x)$$

$$\times N \int_{\Gamma_{N-1}} dx_1 \cdots dx_{N-1} \psi(x_1, \ldots, x_{N-1})\overline{\psi(y_1, \ldots, y_{N-1})} f(y)$$

$$= \int_{\Gamma} dx \int_{\Gamma} dy \gamma_\psi(x, y)f(y) = (g, \gamma_\psi f). \tag{2.18}$$

Since $0 \leq q_\omega(f, f) \leq (f, f)$, we have also that $0 \leq \gamma_\omega \leq 1$. Because of the positivity of $\gamma_\omega$, it suffices to show that its trace exists. By (2.18) we have

$$\text{tr}(\gamma_\omega) = \sum_{n=1}^{\infty} q_{|\psi\rangle\langle\psi|}[\xi_n]$$

$$= \sum_{n=1}^{\infty} \int_{\Gamma} dx \int_{\Gamma} dy \overline{\xi_n(x)}$$

$$\times N \int_{\Gamma_{N-1}} dx_1 \cdots dx_{N-1} \psi(x_1, \ldots, x_{N-1})\overline{\psi(y_1, \ldots, y_{N-1})}\xi_n(y)$$

$$= \int_{\Gamma} dx N \int_{\Gamma_{N-1}} dx_1 \cdots dx_{N-1} \psi(x_1, \ldots, x_{N-1})\overline{\psi(x_1, \ldots, x_{N-1})} = N \tag{2.19}$$

where we used Parseval’s identity to arrive at the last line.
The operator $\gamma_\omega$ is called the one-particle reduced density matrix of $\omega$, $\gamma_\omega(x,y)$ is its integral kernel, and the (spin summed) one-particle reduced density is

$$\rho_{\gamma_\omega}(x) := \sum_\sigma \sum_n \lambda_n |\xi_n(x)|^2$$

where the $\{\xi_1, \xi_2, \ldots\}$ is a complete orthonormal set of eigenvectors of $\gamma_\omega$, known as natural orbitals, and the $\lambda_n$ are the corresponding eigenvalues. Formally $\rho_\omega(x)$ is the spin-summed diagonal $\sum_\sigma \gamma_\omega(x,\sigma,x,\sigma)$ of the reduced one-particle density matrix. Using the above notation, we have

$$\omega(a_x a_y^\ast) = \gamma_\omega(x,y)$$

for the kernel of $\gamma_\omega$.

This generalizes to $k$ particles: the $k$-particle reduced density matrix $\gamma_\omega^{(k)}$ of a state $\omega$ has the integral kernel

$$\gamma_\omega^{(k)}(x_1, \ldots, x_k, y_1, \ldots, y_k) := \frac{1}{k!} \omega(a_{x_k} \cdots a_{x_1} a_{y_1}^\ast \cdots a_{y_k}^\ast).$$

The $k$-particle reduced density

$$\rho_\omega^{(k)}(x_1, \ldots, x_k) = \sum_{\sigma_1, \ldots, \sigma_k} \gamma_\omega^{(k)}(x_1, \ldots, x_k, x_1, \ldots, x_k)$$

is the spin-summed diagonal of the $k$-particle density matrix.

2.5. Observables

2.5.1. The number operator

The space

$$Q_N := \left\{ (\psi_0, \psi_1, \ldots) \in \mathfrak{S} \left| \sum_{N=1}^{\infty} N \int_{\Gamma^N} dx |\psi_N(x)|^2 < \infty \right. \right\}$$

is dense in $\mathfrak{S}$ and the number of electrons in a state $\psi = (\psi_0, \psi_1, \ldots)$ is given by the quadratic form

$$q_N[\psi] := \int_{\Gamma} dx (a_x \psi, a_x \psi) = \sum_{N=1}^{\infty} N \int_{\Gamma^N} dx |\psi_N(x)|^2.$$ 

It is well defined on $Q_N$, closed, and bounded from below. The associated selfadjoint operator defined according to Friedrichs is called the number operator $N$. In a common abuse of notation it is written as $N = \int_{\Gamma} dx a_x^\ast a_x$. 
2.5.2. The electronic Hamiltonian

The one-particle kinetic energy operator is a positive, selfadjoint, and translation-invariant operator which in nonrelativistic quantum mechanics is \(-\frac{1}{2}p^2 \otimes 1_{C2}\) with \(p := -i\nabla\). We should write \(V \otimes 1_{C2}\) for the one-particle external potential when spin independent; but as usual we will omit factors that are one. We will assume that the kinetic energy controls the one-particle potential, technically

\[
\exists a \in [0, 1), \exists M \in \mathbb{R} \forall f \in H^1(\Gamma) \left| \int_\Gamma dx |f(x)|^2 V(x) \right| \leq \int_\Gamma dx \left( a^2 |\nabla f(x)|^2 + M |f(x)|^2 \right). \tag{2.26}
\]

Here

\[
H^1(\Gamma) := \left\{ f \in L^2(\Gamma) \left| \int_\Gamma d\xi |\xi F(f)(\xi)|^2 < \infty \right\}, \tag{2.27}
\]

i.e., a state \(f\) is in \(H^1(\Gamma)\) if it has finite kinetic energy. The space \(H^1\) is called the Sobolev space of order one. It naturally characterizes all states that have a finite energy in nonrelativistic quantum mechanics.

We write

\[
Q_H := \left\{ (\psi_0, \psi_1, \ldots) \in \mathfrak{H} \left| \sum_{N=1}^{\infty} \int_\Gamma d\xi |\xi F(\psi_N)(\xi)|^2 < \infty \right\} \tag{2.28}
\]

for the space of all \(\psi \in \mathfrak{H}\) which have finite kinetic energy. The energy \(E(\psi)\) of the electrons in a state \(\psi \in Q_H\),

\[
E_V[\psi] := \int_\Gamma dx \left( \frac{1}{2} \| p_x a_x \psi \|_2^2 + V(x) \| a_x \psi \|_2^2 \right) + \frac{1}{2} \int_\Gamma dx \int_\Gamma dy \frac{\langle \psi, a_x^* a_y a_x \psi \rangle}{|x - y|}
\]

\[
= \sum_{N=1}^{\infty} \int_\Gamma dx \left( \frac{N}{2} |\nabla x_1 \psi_N(x)|^2 + V(x_1) |\psi_N(x)|^2 \right) + \frac{N}{2} |\psi_N(x)|^2
\]

\[
= \sum_{N=1}^{\infty} \int_\Gamma dx \left[ \sum_{n=1}^{N} \left( \frac{1}{2} |\nabla x_n \psi_N(x)|^2 + V(x_n) |\psi_N(x)|^2 \right) \right]
\]

\[
+ \sum_{1 \leq m < n \leq N} \frac{|\psi_N(x)|^2}{|x_m - x_n|}, \tag{2.29}
\]

is well defined and \(E_V|_{\mathfrak{H}_N}\) is closed and bounded from below by \(-MN\). The selfadjoint operator associated to it according to Friedrichs is the \(N\)-electron Hamiltonian \(H_{V,N}\) giving meaning to (1.2) as a selfadjoint opera-
The direct sum of these Hamiltonians is the second quantized Hamiltonian $H$. Furthermore, we remark that, e.g., in the case of a Coulomb potential $V(x) = -Z/|x|$, i.e., the standard atomic Hamiltonian,

$$E - Z/|\cdot| \geq \inf \{ \sigma(H - Z/|\cdot|, 2Z+1) \| \psi \|^2 \}$$

which is a consequence of the fact that there are no arbitrarily negative ions.

In fact, Lieb [14] showed that less than $2Z + 1$ electrons can be bound. (We will exhibit the argument leading to this bound in the proof of Theorem 4.14 in the context of the Thomas–Fermi–Weizsäcker functional). In this case, $E_V$ is bounded from below and the Friedrichs extension in the entire Fock space is directly possible.

We finish the section by rewriting (2.29) in terms of the one-particle density matrix $\gamma$ and the two-particle density $\rho^{(2)}$. It can be read off from the third line of (2.29) and gives

$$E_V[\psi] = \text{tr}\left( (-\frac{1}{2}\Delta + V) \gamma \psi \right) + \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho^{(2)}(x,y)}{|x-y|}.$$  

(2.31)

### 3. The Hohenberg–Kohn theorem

As mentioned above, Hohenberg’s and Kohn’s original argument merely supports the existence of the functional $E_{HK}$. The underlying mathematical question raised by the argument is indeed intriguing and has been the subject of recent investigation. We will, however, not expand on these results and refer to Garrigue [15–17].

Instead, we will present a variational construction of the Hohenberg–Kohn functional. An early version is due to Percus [18] who outlined the idea in the context of vanishing electron–electron interaction. It is known as Levy–Lieb constraint search going back to Levy [19] and Lieb [20]. The variational argument does not only show the existence of such a functional but also indicates a way on how to approximate the Hohenberg–Kohn functional. Again we will present it in the context of nonrelativistic quantum mechanics with Coulomb interactions among the electrons.

**Definition 3.1:** For $N \in \mathbb{R}_+$ we set

$$\mathcal{A} := \{ \rho \mid \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3) \},$$

$$\mathcal{A}_N := \{ \rho \in \mathcal{A} \mid \int_{\mathbb{R}^3} \rho \leq N \},$$

$$\mathcal{A}_{\rho N} := \{ \rho \in \mathcal{A} \mid \int_{\mathbb{R}^3} \rho = N \}.$$  

(3.1)

*Here and below $\int_{\mathbb{R}^3} \rho$ abbreviates $\int_{\mathbb{R}^3} dx \rho(x)$, and similarly for $\int_{\mathbb{R}^3} \sigma$ and the like.*
If \( N \in \mathbb{N} \) we call \( \mathcal{A}_{\partial N} \) the set of \( N \)-particle densities. We call the functional \( E_{HK} : \mathcal{A}_{\partial N} \to \mathbb{R}_+ \cup \{\infty\} \),

\[
\rho \mapsto \inf \left\{ \mathcal{E}_V[\psi] - \int_{\mathbb{R}^3} d\mathbf{x} \: V(\mathbf{x}) \rho(\mathbf{x}) \ \bigg| \ \psi \in \mathcal{H}_N \cap H^1(\Gamma_N), \ ||\psi|| = 1, \ \rho_\psi = \rho \right\} 
\]

(3.2)

the Hohenberg–Kohn functional.

In (3.2) we use the standard convention that the infimum over the empty set is \( \infty \), which in the case at hand occurs, if there is no pure \( N \)-electron state \( \psi \in \mathcal{H}_N \) of finite kinetic energy such that its one-particle density \( \rho_\psi \) equals the given \( \rho \). Such densities are called non-\( N \)-representable densities. In other words, nonrepresentable densities do not contribute to the infimum.

The following immediate observation holds (Percus [18], Levy [19], and Lieb [20]).

**Theorem 3.2:** We have

\[
\inf \{ \sigma(H_{V,N}) \} = \inf \left\{ E_{HK}(\rho) + \int_{\mathbb{R}^3} d\mathbf{x} \: V(\mathbf{x}) \rho(\mathbf{x}) \ \bigg| \ \rho \in \mathcal{A}_{\partial N} \right\}. 
\]

(3.3)

Furthermore, if \( H_{V,N} \) has a ground state, a minimizer of the right side exists and is the one-particle density of a ground state.

In other words, this observation justifies the functional’s name: \( E_{HK} \) is the universal, i.e., independent of the external potential \( V \), functional of the reduced one-particle density matrix which, when \( \int_{\mathbb{R}^3} d\mathbf{x} \: V(\mathbf{x}) \rho(\mathbf{x}) \) is added, yields the exact quantum ground state energy as minimal value and an exact quantum one-particle ground state density as minimizer. In other words, it is the functional whose existence Hohenberg and Kohn showed.

This construction has various more or less immediate extensions:

**Spin-dependent potentials** (Barth and Hedin [21]): The functional depends on the diagonal of \( \gamma \), the space-spin density, instead of \( \rho \), the space density, only.

**Magnetic fields and Spin** (Rajagopal and Callaway [22]): The functional depends on the electric current which, in state \( \psi \), is \( j_\psi(\mathbf{x}) := (a_x \psi, p_x a_x \psi) \).

**k-body potentials** (Müller et al. [23]): The functional depends on the \( k \)-body density.

**General one-body potentials** (Gilbert [24]): The functional depends on the reduced one-particle density matrix \( \gamma \).
As mentioned above, Hohenberg’s and Kohn’s original argument for the existence of $E^{\text{HK}}$ is nonconstructive. In contrast, although the construction appears difficult to be carried through completely, it nevertheless offers an approximation scheme. An example of such a scheme actually predates the work of Hohenberg and Kohn. It is based on an idea of Macke [25] carried through by March and Young [26] for one-dimensional fermions (see also Percus [18]). We will outline the idea suppressing the spin-dependence and interaction to exhibit it more clearly: Given any density $\rho$ on $\mathbb{R}$ with mass $N$ and with $\sqrt{\rho'}$ square integrable, we define a Slater determinant $\psi$ with orbitals

$$\phi_n(x) := \sqrt{Y'(x)} \exp(i2\pi(n-a)Y(x)), \ n = 1, \ldots, N, \ a \in \mathbb{R},$$

$$Y : \mathbb{R} \to (0,1), \ Y(x) := \int_{-\infty}^{x} dt \frac{\rho(t)}{N}, \quad (3.4)$$

also known as Macke orbitals. We immediately read off that these are orthonormal and their density is

$$\rho_{\psi}(x) = \sum_{n=1}^{N} |\phi_n(x)|^2 = \rho(x). \quad (3.5)$$

Moreover, a small calculation and optimization in the parameter $a$ shows

$$E^{\text{HK}}(\rho) \leq \frac{1}{2} \int_{\mathbb{R}} dx \left[ \sqrt{\rho'}(x)^2 + \frac{\pi^2}{3} \left( 1 - \frac{1}{N^2} \right) \rho(x)^3 \right] \quad (3.6)$$

which — apart from the $-N^{-2}$ — is the one-dimensional Thomas–Fermi–Weizsäcker functional of the kinetic energy (March and Young [26]).

Müller [27] found a generalization of (3.4) to all dimensions $d$ such that the orbitals fulfill (3.5) for given $d$-dimensional density $\rho(x)$, namely

$$\phi_{\nu}(x) := \sqrt{\det(J(x))} \exp(i2\pi(n_{\nu}-a)Y(x)) \quad (3.7)$$

for $n_{\nu} \in \mathbb{Z}^d$ with $\nu = 1, \ldots, n$, and $a \in \mathbb{R}^d$ with

$$Y : \mathbb{R}^d \to (0,1)^d,$$

$$x \mapsto \left( \begin{array}{c} \int_{-\infty}^{x_1} dt_1 \rho(t_1, x_2, \ldots, x_d) \\ \int_{-\infty}^{x_2} dt_1 \rho(t_1, x_2, \ldots, x_d) \\ \vdots \\ \int_{-\infty}^{x_d} dt_1 \cdots \int_{-\infty}^{t_{d-1}} dt_{d-1} \int_{-\infty}^{x_d} dt_d \rho(t_1, \ldots, t_d) \\ \int_{-\infty}^{x_1} dt_1 \cdots \int_{-\infty}^{t_{d-1}} dt_{d-1} \int_{-\infty}^{x_d} dt_d \rho(t_1, \ldots, t_d) \end{array} \right) \quad (3.8)$$

where $J$ is the Jacobian of $Y$. These orbitals are also orthonormal. The Jacobian is the determinant of a tridiagonal matrix, i.e., $J$ is just the product
of the diagonal. It is a telescopic product yielding $\rho(x)/N$. However the corresponding Slater determinant reproduces merely the Weizsäcker part of the kinetic energy but not the Thomas–Fermi part.

Note that March and Young [26] proposed a choice for the orbitals (3.7) with a different $Y$. They postulated properties of the transform of $R(d)$ to $(0,1)^d$ which, however, lead to a contradiction. One may, however, salvage the argument in three dimensions by a slight modification which is suitable for spherical potential and, in this way, obtain the Hellmann-Weizsäcker functional [28]

$$E_{\text{HW}}(\vec{\rho}) := \frac{1}{2} \sum_{l=0}^{\infty} \int_0^{\infty} dr \left( \sqrt{\rho_l'(r)^2 + \frac{l(l+1)}{r^2}} \rho_l(r) + \frac{\pi^2}{3} \frac{\rho_l^3(r)}{(2l+1)^2} \right)$$

$$+ \sum_{l=0}^{\infty} \int_0^{\infty} dr \frac{V(r)}{\rho_l(r)}$$

$$+ \frac{1}{2} \sum_{l,l'=0}^{\infty} \int_0^{\infty} dr \int_0^{\infty} dr' \rho_l(r) \rho_{l'}(r') \frac{\max\{r,r'\}}{r}$$  \hspace{1cm} (3.9)

with $\vec{\rho} = (\rho_0, \rho_1, \ldots)$ instead of the Thomas–Fermi–Weizsäcker functional as an upper bound. We assume that $\rho_0 \geq 0$, $\rho_1 \geq 0$, \ldots, $\sum_{l=0}^{\infty} \int_0^{\infty} dr \sqrt{\rho_l(r)^2} < \infty$ and $\sum_{l=0}^{\infty} \rho_l \leq N$, the electron number. The function $\rho_l$ with $l \in \mathbb{N}_0$ may be interpreted as the radial densities of electrons in angular momentum channel $l$.

Although infinitely many $l$ are allowed, it turns out that the minimizer has only finitely many. Using Hardy’s inequality, we obtain a lower bound with the gradient term dropped and $l(l+1)$ replaced by $(l + \frac{1}{2})^2$. The resulting function would give a positive contribution for high angular momenta [29]. See also a bound on the total charge obtained by the same argument yielding (4.85) (Benguria et al. [30]).

The following modification of (3.3) — additionally with spin included — shows that $E_{\text{HW}}(\vec{\rho})$ is an upper bound on the ground-state energy inf\{\(\sigma(H_{V,N})\)\} of the $N$-electron system:

$$\phi_{n,l,m,s}(x) := \sqrt{\frac{Y_l(|x|)}{|x|}} \exp(i2\pi(n_l - a_l)Y_l(|x|))Y_{l,m}(x/|x|)\delta_{s,\sigma}$$  \hspace{1cm} (3.10)

for $n = 1, \ldots, N_{l,m,s} \in \mathbb{N}_0$, $m = -l, \ldots, l$, $s = 1, 2$, $\sum_{l,m,s} N_{l,m,s} = N$, and $a_l \in \mathbb{R}$ with

$$Y_l : (0, \infty) \to (0,1)^d, \quad r \mapsto \frac{\int_0^r dt \rho_l(t)}{\int_0^{\infty} dt \rho_l(t)}$$  \hspace{1cm} (3.11)

for all $l \in \mathbb{N}_0$ with $\int_0^{\infty} \rho_l > 0$ (see Ladanyi [31] and [32]).
4. Some results on concrete density functionals

In the following we will spotlight some of the basic density functionals and density matrix functionals. To simplify the notation we concentrate on the atomic case although there are generalizations to molecules and other more general external potentials.

4.1. Thomas–Fermi theory

4.1.1. Definition and basic properties

The Thomas–Fermi functional (Lenz [33]) of an atom with nuclear charge \( Z \) is

\[
E_{TF}^Z(\rho) := \int_{\mathbb{R}^3} dx \left( \frac{3}{5} \gamma_{TF} \rho(x)^{\frac{5}{3}} - \frac{Z}{|x|} \rho(x) \right) + \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho(x) \rho(y)}{|x-y|} \quad =: D[\rho]
\]

(4.1)

where \( \gamma_{TF} \) is a positive constant, namely \( (\hbar^2/2m)(6\pi^2/q)^2/3 \) which for electrons \((q = 2)\) is \((3\pi^2)^{2/3}/2\) in Hartree units \((\hbar = m = 1)\).

We will collect some (mostly) known results. We refer to Lieb and Simon [34], Simon [35, Section 9], Lieb [36], and Lieb and Loss [37] for other reviews and references.

As usual we write \( S(\mathbb{R}^3) \) for the Schwartz space of fast decaying functions in \( C^\infty(\mathbb{R}^3) \) and \( S'(\mathbb{R}^3) \) for its dual, the tempered distributions. (See, e.g., Lieb and Loss [37] for more details.)

**Definition 4.1:** We write

\[
\mathcal{C} := \left\{ \rho \in S'(\mathbb{R}^3) \mid \int_{\mathbb{R}^3} d\xi \left| \mathcal{F}(\rho)(\xi) \right|^2/|\xi|^2 < \infty \right\},
\]

\[
\mathcal{I} := \left\{ \rho \in L^4(\mathbb{R}^3) \mid \rho \geq 0, \ D[\rho] < \infty \right\},
\]

\[
\mathcal{I}_N := \left\{ \rho \in \mathcal{I} \mid \int_{\mathbb{R}^3} \rho \leq N \right\},
\]

\[
\mathcal{I}_{\partial N} := \left\{ \rho \in \mathcal{I}_N \mid \int_{\mathbb{R}^3} \rho = N \right\}.
\]

(4.2)

for the set of all tempered distributions \( \rho \) with finite electron-electron interaction TF-energy, those positive distributions which have also finite kinetic energy, and those with corresponding constraints on their masses.
Note that $C$ is a Hilbert space with the scalar product

$$D(\rho, \sigma) := \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho(x) \sigma(y)}{|x - y|}$$

$$= 2\pi \int_{\mathbb{R}^3} d\xi \frac{F(\rho)(\xi) F(\sigma)(\xi)}{\xi^2},$$

(4.3)

the sesquilinear form associated with the positive quadratic form $D$. The fact that for any $\rho \in C$ one has $D[\rho] > 0$ unless $\rho = 0$, which is immediate from its Fourier representation, is known as Onsager’s inequality.

One of the key observations which elevates Thomas–Fermi theory to an important tool in the analysis of many electron systems is the Lieb–Thirring inequality (Lieb and Thirring [38, 39]).

**Theorem 4.2:** There exists a positive constant $\gamma_{LT}$ such that for all one-particle density matrices $\gamma$ with finite kinetic energy, i.e., for all $\gamma \in \mathcal{S}^1(L^2(\Gamma))$ with $0 \leq \gamma \leq 1$ and $\Delta \gamma \in \mathcal{S}^1(L^2(\Gamma))$

$$\text{tr}(\frac{1}{2} \Delta \gamma) \geq \frac{3}{5} \gamma_{LT} \int_{\mathbb{R}^3} dx \rho_{\gamma}(x)^{\frac{5}{2}}.$$  

(4.4)

A dual formulation is

**Theorem 4.3:** There is a constant $L > 0$ such that for all $\varphi \in L^\frac{5}{2}(\mathbb{R}^3)$

$$\text{tr}(\frac{1}{2} \Delta - \varphi)_- \geq -L \int_{\mathbb{R}^3} dx \varphi_+(x)^{\frac{5}{2}}.$$  

(4.5)

(We indicate the positive part of a function or operator by an index $+$, and by an index $-$ the negative part [which we pick negative, i.e., $f = f_+ + f_-$].)

It is a longstanding conjecture, called the Lieb–Thirring conjecture, that the optimal constant is given by semi-classical phase space counting, e.g., $\gamma_{LT} = \gamma_{TF}$. (Note that the conjectured optimal constant depends on the number of spin states $q$ per electron, namely $\gamma = (6\pi^2/q)^{\frac{5}{2}}/2.$) It is known, that $\gamma$ cannot be larger than the classical one because of asymptotic results for the sum of eigenvalues. Although over the years there have been considerable efforts in proving the Lieb–Thirring conjecture, they merely yielded improvements of the lower bound on $\gamma$ but not the conjectured value. On the other hand there have been also considerable efforts in disproving the conjecture. However, these were not successful either.

We will not prove the Lieb–Thirring inequality and their extensions. We refer instead to Nam’s [40] review in these proceedings and make freely use
of it. See also Benguria and Loewe \[11\].

**Theorem 4.4:** The Thomas–Fermi functional $\mathcal{E}_Z^{\text{TF}}$ is well defined on $\mathcal{I}$ and bounded from below.

**Proof:** Obviously the kinetic energy and the electron-electron energy are well defined and finite for every $\rho \in \mathcal{I}$. To show that this holds also for the nuclear potential we decompose the Coulomb potential $1/|x|$: We write $\sigma := \delta(R - |x|)/(4\pi R^2)$ for a unit charge smeared out homogeneously on a sphere of radius $R$ centered at the origin. Obviously $\sigma \in C^1$, since

$$D[\sigma] = \frac{1}{2} \int_0^\infty \frac{4\pi r^2}{4\pi R^2} \int_0^\infty ds \frac{4\pi s^2}{4\pi R^2} \frac{\delta(r - r)\delta(R - s)}{\max\{r, s\}} = \frac{1}{2R}. \quad (4.6)$$

We set

$$V_l : \sigma * |\cdot|^{-1} = \begin{cases} 1/|x| & \text{for } |x| \geq R, \\ 1/R & \text{for } |x| < R, \end{cases}$$

$$V_k := \frac{1}{|\cdot|} - V_l \quad (4.7)$$

yielding a decomposition of the Coulomb potential into its long range regular part and its short range singular part. Thus, using Hölder's inequality on the short-range part and the Schwarz inequality on the long-range part we get

$$\int_{\mathbb{R}^3} dx \frac{\rho(x)}{|x|} \leq \int_{|x| < R} dx \frac{\rho(x)}{|x|} + 2D(\rho, \sigma)$$

$$\leq \left( \int_{|x| < R} \frac{dx}{|x|^2} \right)^{\frac{2}{3}} \|\rho\|_\frac{2}{3} + 2D(\rho, \sigma)$$

$$\leq (8\pi)^{\frac{2}{3}} R^{\frac{2}{3}} \|\rho\|_\frac{2}{3} + 2\sqrt{D[\sigma]D[\rho]}$$

$$\leq (8\pi)^{\frac{2}{3}} R^{\frac{2}{3}} \|\rho\|_\frac{2}{3} + 2\sqrt{D[\rho]/(2R)}. \quad (4.8)$$

Thus, also the nuclear-electron energy is finite. Using this bound in the functional and minimizing in $\|\rho\|_\frac{2}{3}$ and $D[\rho]$ gives

$$\mathcal{E}_Z^{\text{TF}}(\rho) \geq \frac{3}{5} \gamma_{\text{TF}} \|\rho\|_\frac{5}{2} - (8\pi)^{\frac{2}{3}} R^{\frac{2}{3}} Z \|\rho\|_\frac{2}{3} + D[\rho] - Z \sqrt{2D[\rho]/R}$$

$$\geq -\frac{32\sqrt{2}}{15\pi} Z^\frac{2}{3} R^\frac{2}{3} - \frac{Z^2}{2R} = \frac{2^{\frac{4}{3}} 3^{\frac{1}{3}}}{(5\pi)^{\frac{2}{3}}} Z^\frac{2}{3} \approx -1.46 Z^\frac{2}{3}. \quad (4.9)$$

after picking $R = (15\pi)^{\frac{2}{3}}/(2^{\frac{4}{3}} Z^\frac{2}{3})$. \qed
**Lemma 4.5:** The Thomas–Fermi functional and its restrictions to $\mathcal{I}_N$ and $\mathcal{I}_{\partial N}$ are strictly convex, i.e., the sets $\mathcal{I}$, $\mathcal{I}_N$, and $\mathcal{I}_{\partial N}$ are convex sets and for every $t \in (0, 1)$ and $\rho, \tau \in \mathcal{I}$ we have

$$t \mathcal{E}_Z^{\text{TF}}(\rho) + (1-t) \mathcal{E}_Z^{\text{TF}}(\tau) \geq \mathcal{E}_Z^{\text{TF}}(t \rho + (1-t) \tau) \quad (4.10)$$

with equality if and only if $\rho = \tau$.

**Proof:** The convexity of the above three sets is obvious and so is the strict convexity of the kinetic energy. The nuclear potential is linear. It remains the electron-electron interaction:

$$D[t \rho + (1-t) \tau] = t^2 D[\rho] + (1-t)^2 D[\tau] + 2t(1-t) D(\rho, \tau)$$

$$\leq t^2 D[\rho] + (1-t)^2 D[\tau] + 2t(1-t) \sqrt{D[\rho] D[\tau]}$$

$$= \left( t \sqrt{D[\rho]} + (1-t) \sqrt{D[\tau]} \right)^2$$

$$\leq t D[\rho] + (1-t) D[\tau]. \quad (4.11)$$

where the first inequality is true because of the Schwarz inequality and the last because of the convexity of the square.

We define

$$E^{\text{TF}}(Z, N) := \inf \{ \mathcal{E}_Z^{\text{TF}}(\mathcal{I}_N) \}, \quad E^{\text{TF}}(Z) := \inf \{ \mathcal{E}_Z^{\text{TF}}(\mathcal{I}) \}. \quad (4.12)$$

**Lemma 4.6:** For fixed $Z \in \mathbb{R}^+$ the function $E^{\text{TF}}(Z, \cdot) : \mathbb{R}^+ \rightarrow \mathbb{R}$ is monotone decreasing and convex.

**Proof:** The monotony is obvious, since $N \leq N'$ implies $\mathcal{I}_N \subset \mathcal{I}_{N'}$.

To prove the convexity, we pick $N_1, N_2, \alpha_1, \alpha_2 \in \mathbb{R}_+$ so that $\alpha_1 + \alpha_2 = 1$. Then

$$E^{\text{TF}}(Z, \alpha_1 N_1 + \alpha_2 N_2)$$

$$= \inf \left\{ \mathcal{E}_Z^{\text{TF}}(\rho) \left| \rho \in \mathcal{I}, \int_{\mathbb{R}^3} \rho \leq \alpha_1 N_1 + \alpha_2 N_2 \right\} \right.$$
\[ \leq \inf \left\{ \alpha_1 \mathcal{E}^{\text{TF}}_Z (\rho) \mid \rho \in \mathcal{I}, \int_{\mathbb{R}^3} \rho \leq N_1 \right\} \]
\[ + \inf \left\{ \alpha_2 \mathcal{E}^{\text{TF}}_Z (\sigma) \mid \sigma \in \mathcal{I}, \int_{\mathbb{R}^3} \sigma \leq N_2 \right\} \]
\[ = \alpha_1 E^{\text{TF}} (Z, N_1) + \alpha_2 E^{\text{TF}} (Z, N_2) \quad (4.13) \]

which is the desired inequality proving convexity. \(\square\)

**Theorem 4.7:** The Thomas–Fermi functional and its restriction to \(\mathcal{I}_N\) have a unique minimizer.

**Proof:** The uniqueness follows from the strict convexity of \(\mathcal{E}^{\text{TF}}_Z\). Suppose that \(\rho\) and \(\tau\) are two minimizers. Then, we are led to a contradiction

\[ \mathcal{E}^{\text{TF}}_Z \left( \frac{1}{2} (\rho + \tau) \right) < \frac{1}{2} \left( \mathcal{E}^{\text{TF}}_Z (\rho) + \mathcal{E}^{\text{TF}}_Z (\tau) \right) = \inf \{ \mathcal{E}^{\text{TF}}_Z (\mathcal{I}) \} \quad (4.14) \]

unless \(\rho = \tau\) showing there is at most one minimizer in \(\mathcal{I}\).

We now turn to the existence of a minimizer. We begin by noting that because of (4.9) the functional \(\mathcal{E}^{\text{TF}}_Z\) is bounded from below on \(\mathcal{I}\), i.e., \(\inf \mathcal{E}^{\text{TF}}_Z (\mathcal{I}) > -\infty\). Assume that \(\rho_n \in \mathcal{I}\) is a minimizing sequence, i.e.,

\[ \lim_{n \to \infty} \mathcal{E}^{\text{TF}}_Z (\rho_n) = \inf \{ \mathcal{E}^{\text{TF}}_Z (\mathcal{I}) \} \quad (4.15) \]

which, of course, is also true for any subsequence of \(\rho_n\). Again by (4.9) we see that both the \(L^\infty\)-norm and the Coulomb-norm of \(\rho_n\) are bounded, since otherwise there would be a subsequence of \(\rho_n\) which is minimizing and also drive the Thomas–Fermi functional to \(+\infty\) which is certainly not true, since \(0 \in \mathcal{I}\) and \(\mathcal{E}^{\text{TF}}_Z (0) = 0 < \infty\).

Now, since \(\rho_n\) is bounded in \(L^\infty\)-norm and \(L^\frac{3}{2}\) is reflexive, the Banach–Alaoglu theorem gives a minimizing subsequence — which we call in abuse of notation again \(\rho_n\) — which converges weakly in \(L^\frac{3}{2}\) to some \(\rho \in L^\frac{3}{2} (\mathbb{R}^3)\).

Now, this sequence is also bounded in the Coulomb norm

\[ \| \rho \|_c := \sqrt{D[\rho]} \quad (4.16) \]

associated with the scalar product \(D\) in \(\mathcal{C}\). Since \(\mathcal{C}\) is a Hilbert space and therefore reflexive, we can pick again an appropriate subsequence of this subsequence, again denoted by \(\rho_n\), which also converges weakly in the Coulomb scalar product to some \(\hat{\rho} \in \mathcal{C}\). But actually, those two limits are equal: Both convergences imply convergence as a tempered distribution.
Therefore, we have for any \( f \in \mathcal{S}(\mathbb{R}^3) \)
\[
\int_{\mathbb{R}^3} \rho f = \lim_{n \to \infty} \int_{\mathbb{R}^3} \rho_n f = \lim_{n \to \infty} 2D(\rho_n, -\Delta f/(4\pi)) = 2D(\hat{\rho}, -\Delta f/(4\pi)) = \int_{\mathbb{R}^3} \hat{\rho} f.
\]  
(4.17)

Since this holds for all \( f \in \mathcal{S}(\mathbb{R}^3) \), we have \( \rho = \hat{\rho} \in L^{\frac{5}{3}}(\mathbb{R}^3) \cap \mathcal{C} \). In other words, the subsequence \( \rho_n \) is minimizing and converges weakly in \( L^{\frac{5}{3}}(\mathbb{R}^3) \) and \( \mathcal{C} \) to \( \rho \).

Now we note that \( \rho \geq 0 \) almost everywhere. Suppose that there is a set \( \mathcal{N} \subset \mathbb{R}^3 \) with \( \int_{\mathcal{N}} > 0 \) and \( \rho(\mathcal{N}) < 0 \). Then there exists a radius \( R \in \mathbb{R}^+ \) such that \( \int \chi_R \rho < 0 \) where \( \chi_R \) denotes the characteristic function of the ball of radius \( R \) centered at the origin intersected with \( \mathcal{N} \). This function is, of course, in any \( L^p \) space, in particular in \( L^{\frac{5}{2}} \), the dual space of \( L^{\frac{3}{5}} \). Then we are led to the following contradiction
\[
0 > \int_{\mathbb{R}^3} \chi_R \rho = \lim_{n \to \infty} \int_{\mathbb{R}^3} \chi_R \rho_n \geq 0.
\]  
(4.18)

Thus, \( \rho \) is nonnegative and with the above result that \( \rho \in L^{\frac{5}{3}}(\mathbb{R}^3) \cap \mathcal{C} \) we conclude that \( \rho \in \mathcal{I} \).

We claim that the function \( \rho \), which we just constructed, is a minimizer. We prove this term by term:

**The kinetic energy:** Since \( \rho \in L^{\frac{5}{3}} \), we have \( \hat{\rho} \in L^\frac{5}{2} \). Thus
\[
\int \hat{\rho}^\frac{5}{2} = \int \hat{\rho}^\frac{5}{2} \rho = \lim_{n \to \infty} \int \hat{\rho}^\frac{5}{2} \rho_n \leq \liminf_{n \to \infty} \left( \int \hat{\rho}_n^\frac{5}{2} \right)^\frac{2}{5} \left( \int \rho_n^\frac{5}{2} \right)^\frac{3}{5}.
\]  
(4.19)

by weak convergence in \( L^\frac{5}{2} \) and Hölder’s inequality. Therefore
\[
\int \rho^\frac{5}{2} \leq \liminf_{n \to \infty} \int \rho_n^\frac{5}{2}.
\]  
(4.20)

**The nuclear potential:** Since \( V_k \in L^\frac{5}{2} \), we have because of weak convergence in \( L^\frac{5}{2} \)
\[
\int V_k \rho = \lim_{n \to \infty} \int V_k \rho_n
\]  
(4.21)

and since \( \sigma \in \mathcal{C} \) we have because of weak convergence in \( \mathcal{C} \)
\[
\int V_l \rho = 2D(\sigma, \rho) = 2 \lim_{n \to \infty} D(\sigma, \rho_n) = \lim_{n \to \infty} V_l \rho_n.
\]  
(4.22)

**The electron-electron-potential:** Since \( \rho \in \mathcal{C} \) we have
\[
D[\rho] = D(\rho, \rho) = \lim_{n \to \infty} D(\rho, \rho_n) \leq \liminf_{n \to \infty} \sqrt{D[\rho] D[\rho_n]}
\]  
(4.23)
Mathematical elements of density functional theory

by Schwarz’s inequality and thus

\[ D[\rho] \leq \lim_{n \to \infty} \inf \ D[\rho_n]. \]  (4.24)

Putting all terms together yields

\[ \mathcal{E}^{\text{TF}}_Z (\rho) \leq \lim_{n \to \infty} \inf \mathcal{E}^{\text{TF}}_Z (\rho_n). \]  (4.25)

In other words, \( \rho \) is the unique minimizer on \( I \).

The argument for \( I_N \) is almost identical and therefore skipped here. \( \square \)

We are now interested in some properties of the minimizer and the minimal energy.

**Theorem 4.8:** The minimizer \( \rho_Z \) of \( \mathcal{E}^{\text{TF}}_Z \) on \( I \) is spherically symmetric, decreasing and convex in the radial variable \( |x| \), \( \int_{\mathbb{R}^3} \rho_Z = Z \), and it fulfills the Thomas–Fermi equation

\[ \gamma_{\text{TF}} \rho_Z^2 = \varphi Z := Z | \cdot |^{-1} - \rho_Z * | \cdot |^{-1} \]  (4.26)

almost everywhere in \( \mathbb{R}^3 \) and the scaling relations

\[ \rho_Z(x) = Z^2 \rho_1 (Z^{7/3} x), \ E^{\text{TF}}(Z) = E^{\text{TF}}(1)Z^{7/3}. \]  (4.27)

Before turning to the proof, we would like to comment on this result:

- Since there is a minimizer of the Thomas–Fermi functional in \( I \) this ensures the existence of a solution of the Thomas–Fermi equation in \( I \).
- Numerically \( E^{\text{TF}}(1) = -0.7687 \) [Ha].
  
  On the one hand this compares with \(-0.5\) [Ha] for the ground state energy of the Schrödinger Hamiltonian of hydrogen. That it reproduces the order of magnitude of a one-electron system – despite counting also the self-energy – is astonishing, since, as we will see, Thomas–Fermi theory, traditionally called a statistical theory of atoms, becomes correct for large electron numbers and is not meant for small electron numbers. However, the fact that it is lower than the quantum energy and therefore lower when dropping the electron-electron interaction, is a particular case of a long standing conjecture of Lieb and Thirring (see, e.g., Nam [40] in these proceedings).

  On the other hand the value \(-0.7687Z^{7/3}\) [Ha] compares with \(-1.46Z^{7/3}\) [Ha] in (4.9) showing that that estimate does not only produce the correct power law but also a numerical factor of the right order of magnitude.
Since the unrestricted minimizer has charge $Z$, there are no negative ions in Thomas–Fermi theory. This might look strange at first sight, since negative ions are known to exist. However, doubly or higher negatively charged ions are unknown (Massey [42, 43]), i.e., the prediction is off by one only. Moreover, Thomas–Fermi theory plays an essential role in bounding the excess charge of atoms in more elaborate models like Hartree–Fock theory. There it is used to successively screen out the inner electrons (Solovej [44]).

Proof: Spherical symmetry: The density $\rho^R$ defined by $\rho^R(x) = \rho_Z(Rx)$ is again a minimizer for any rotation $R$ about the origin. Therefore, since the minimizer is unique, $\rho^R = \rho_Z$. Since this holds for all $R$, the minimizer must be spherically symmetric.

Upper bound on the number of electrons: We will use Benguria’s famous — unfortunately unpublished — variational argument: Suppose $\int_{\mathbb{R}^3} \rho_Z > Z$. Then there is a radius $R \in \mathbb{R}_+$ such that $\int_{|x| \leq R} \rho_Z = Z$. Set

$$n(x) := \begin{cases} 
\rho_Z(x) & \text{for } |x| \leq R \\
0 & \text{for } |x| > R
\end{cases}$$

(4.28)

and $\delta := \rho_Z - n$ where $\delta$ is not vanishing almost everywhere. We claim that $n$ has a lower energy than the infimum unless $\delta$ vanishes:

$$E_{TF}^Z(n) - E_{TF}^Z(\rho_Z) = -\frac{3}{5} \int_{\mathbb{R}^3} \rho \delta(x)^2 + \int_{\mathbb{R}^3} \frac{Z}{|x|} \delta(x) - 2D(n, \delta) - D[\delta] < 0$$

(4.29)

where the underbraced quantity vanishes because the electric potential of $n$ outside the ball of radius $R$ is exactly $Z/|x|$ by Newton’s theorem. The last inequality in (4.29) is strict, since $\delta$ does not vanishes almost everywhere. This, of course, contradicts the fact that $\rho_Z$ is a minimizer. Therefore the supposition is absurd and

$$\int_{\mathbb{R}^3} \rho_Z \leq Z.$$  

(4.30)

Thomas–Fermi equation: We defer the lower bound on the charge of $\rho_Z$ and first turn to the Thomas–Fermi equation. We begin with the Thomas–Fermi potential $\varphi_Z$. The electronic potential of the minimizer $\psi := \rho_Z^* |.|^{-1}$
is Hölder continuous: For any nonzero \( a \in \mathbb{R}^3 \) we have

\[
|\psi(x + a) - \psi(x)| = \left| \int_{\mathbb{R}^3} dy \rho_Z(y) \left( \frac{1}{|x - y + a|} - \frac{1}{|x - y|} \right) \right|
\]

\[
\leq \int_{\mathbb{R}^3} dy \rho_Z(y) \frac{|a|}{|x - y + a||x - y|}
\]

\[
\leq \|\rho_Z\|_{L^1} |a| \left( \int_{\mathbb{R}^3} dy |y - a - |x - y||^{-2} \right)^{\frac{1}{2}}
\]

\[
\leq C\|\rho_Z\|_{L^1} |a|^{\frac{1}{2}}
\]  

which shows the Hölder continuity. Thus the Thomas–Fermi potential is continuous outside the origin where it is also subharmonic, since

\[
-\frac{1}{4\pi} \Delta \varphi_Z = Z \delta_0 - \rho_Z.
\]  

(4.32)

Pick now any positive \( R \) and \( \epsilon \) and set

\[
\chi := \rho_Z \text{sgn}(\gamma_{TF} \rho_Z^2 - \varphi_Z).
\]  

(4.33)

Note that \( \rho_Z + \alpha \chi \in I \) for all \( \alpha \in [-1, 1] \). Moreover,

\[
F(\alpha) := \mathcal{E}_Z^{TF}(\rho_Z + \alpha \chi) - \mathcal{E}_Z^{TF}(\rho_Z)
\]  

(4.34)

is continuously differentiable in \( \alpha \) for \( \alpha \in (-1, 1) \) and

\[
0 = F'(0) = \gamma_{TF} \int_{\mathbb{R}^3} dx \rho_Z(x) \hat{\varphi}(x) - \int_{\mathbb{R}^3} dx \frac{Z \chi(x)}{|x|} + 2D(\chi, \rho_Z)
\]

\[
= \int_{\mathbb{R}^3} dx \left| \gamma_{TF} \rho_Z(x) \hat{\varphi}(x) - \varphi_Z(x) \right| \rho_Z(x),
\]  

(4.35)

since \( \rho_Z \) is the minimizer. Thus,

\[
\gamma_{TF} \rho_Z(x) \hat{\varphi}(x) - \varphi_Z(x) = 0 \text{ for almost all } x \text{ such that } \rho_Z(x) > 0.
\]  

(4.36)

Repeating the above argument but picking \( \chi \) as the characteristic function of any ball \( B_R(y) \cap N \) with \( y \in \mathbb{R}^3 \) and \( R > 0 \) as a perturbing function, where \( N := \{x \in \mathbb{R}^3 | \rho_Z(x) = 0 \} \), yields

\[
0 \leq F'(0) = \int_{B_R(y) \cap N} dx \left( -\varphi_Z(x) \right).
\]  

(4.37)

(Note that we cannot conclude equality, since \( \alpha \) is restricted to \([0, \infty)\) because of the requirement that \( \rho_Z + \alpha \chi \in I \).

Since \( \psi \) is continuous by (4.31) and \( \varphi_Z = Z/|\cdot| - \psi \), there exists a neighborhood of the origin which is disjoint from \( N \). But outside the origin \( \varphi_Z \) is continuous. Thus \( \varphi_Z \leq 0 \) on \( N \). However, from (4.30) we know because of
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spherical symmetry and Newton’s theorem that \( \varphi_Z \geq 0 \) everywhere. Thus \( \varphi_Z = 0 \) on \( \mathcal{N} \).

Combining this with \( \Theta \mathcal{Z} \) yields
\[
\gamma_{\text{TF}} \rho_Z(x) = \varphi_Z(x) \quad (4.38)
\]
almost everywhere on \( \mathbb{R}^3 \), i.e., yields the claimed formula \( \Theta \mathcal{Z} \). (We note in passing — since not needed in our proof — that one can actually show that \( \rho_Z > 0 \) everywhere. But since \( \varphi_Z \) can only vanish if \( \rho_Z \) has compact support, this implies that \( \mathcal{N} = \emptyset \).)

**Lower bound on the number of electrons:** Now suppose \( \int_{\mathbb{R}^3} \rho_Z < Z \). Then, by Newton’s theorem there exist \( R > 0 \) and \( \epsilon > 0 \) such that for \( |x| > R \) we have \( \varphi_Z(x) \geq \epsilon/|x| \). Thus, by \( \Theta \mathcal{Z} \) and \( \Theta \mathcal{Z} \), we have
\[
Z \geq \int_{\mathbb{R}^3} \rho_Z = \int_{\mathbb{R}^3} (\varphi_Z(x)/\gamma_{\text{TF}})^{\frac{3}{2}} \left( \epsilon/\gamma_{\text{TF}} \right)^{\frac{1}{2}} \int_{|x| > R} \frac{dx}{|x|^2} = \infty \quad (4.39)
\]
which is a contradiction. Thus, also \( \int_{\mathbb{R}^3} \rho_Z \geq Z \) and therefore \( \int_{\mathbb{R}^3} \rho_Z = Z \) as claimed.

**Decrease of the minimizer:** For showing that the minimizer \( \rho_Z \) is decreasing in the radial variable, we remark that by the Thomas–Fermi equation \( \Theta \mathcal{Z} \) it suffices to show that the radial derivative of the Thomas–Fermi potential \( \varphi_Z \) is negative. Thus we compute for \( x \neq 0 \) and get using Newton’s theorem
\[
\frac{x}{|x|} \cdot \nabla \varphi_Z(x) = \frac{x}{|x|} \cdot \nabla \left( \frac{Z}{|x|} - \int_{\mathbb{R}^3} \frac{\rho_Z(y)}{\max\{ |x|, |y| \}} dy \right)
= -Z \frac{|x|}{|x|^2} + \int_{|y| < |x|} \frac{dy \rho_Z(y)}{|y|^2} \leq 0 \quad (4.40)
\]
using \( \Theta \mathcal{Z} \) in the last step. This proves that \( \rho_Z \) is decreasing in the radial variable. Differentiating again yields
\[
\left( \frac{x}{|x|} \cdot \nabla \right)^2 \varphi_Z(x) = \frac{2}{|x|^3} \left( Z - \int_{|y| < |x|} dy \rho_Z(y) \right) + \frac{4\pi \rho_Z(x)}{|x|^2} \geq 4\pi \rho_Z(x) \geq 0 \quad (4.41)
\]
using that \( \int_{\mathbb{R}^3} \rho_Z = Z \). This shows the convexity of \( \varphi_Z \) which, in turn, implies the the convexity of \( \varphi_Z^\frac{3}{2} \) and thus the claimed convexity of \( \rho_Z \).

**Scaling relations:** For any \( \rho \in \mathcal{I} \) a straightforward computation shows
\[
\mathcal{E}_Z^{\text{TF}} (Z^2 \rho(Z^\frac{1}{2})) = Z^\frac{1}{2} \mathcal{E}_1^{\text{TF}} (\rho). \quad (4.42)
\]
The scaling relations follow. \( \square \)
Theorem 4.8 implies that minimizers of the Thomas–Fermi functional fulfill the Thomas–Fermi equation. The reverse is also true:

**Theorem 4.9:** If $\rho \in I$ fulfills (4.26), then it minimizes $E_{TF}^Z$ on $I$.

We remark that this implies that the solution of the Thomas–Fermi equation is unique in $I$, since there is exactly one minimizer of the Thomas–Fermi functional in $I$. In particular $\rho$ is equal to $\rho_Z$, the unique minimizer of the Thomas–Fermi functional on $I$.

**Proof:** Suppose that $\sigma, \rho \in I$ and $\rho$ fulfills (4.26). We set $\delta := \sigma - \rho$. The condition that both $\rho$ and $\sigma$ are nonnegative implies that $\delta \geq -\rho$. We set

$$F(t) := E_{TF}^Z(\rho + t\delta) - E_{TF}^Z(\rho). \quad (4.43)$$

In this notation, we wish to show that $F(1) \geq 0$. We compute

$$F(1) = \int_0^1 d\tau F(\tau)$$

$$= \int_0^1 d\tau \left[ \int_{\mathbb{R}^3} d\mathbf{x} \delta(\mathbf{x}) \left( \gamma_{TF}(\rho(\mathbf{x}) + \tau\delta(\mathbf{x}))^{\frac{2}{3}} - \varphi_Z(\mathbf{x}) \right) + 2\tau D[\delta] \right]$$

$$= \int_0^1 d\tau \left[ \int_{\mathbb{R}^3} d\mathbf{x} \delta(\mathbf{x}) \left( (\rho(\mathbf{x}) + \tau\delta(\mathbf{x}))^{\frac{2}{3}} - \rho(\mathbf{x})^{\frac{2}{3}} \right) + 2\tau D[\delta] \right]$$

$$\geq D[\delta] \geq 0 \quad (4.44)$$

where the first inequality holds because of $\delta \geq -\rho$ and therefore the integrand of the space integral is positive regardless of the sign of $\delta(x)$.

We remark that both inequalities are strict unless $\delta$ vanishes almost everywhere, i.e., we have $E_{TF}^Z(\sigma) > E_{TF}^Z(\rho)$ unless $\rho = \sigma$ almost everywhere.

**Theorem 4.10:** For $N \leq Z$ the minimizer of the Thomas–Fermi functional on $I_N$ occurs in $I_{\partial N}$; whereas for $N > Z$ the minimizer occurs in $I_{\partial Z}$. In fact the Thomas–Fermi functional has no minimizer in $I_{\partial N}$ for $N > Z$.

**Proof:** 1. $N \leq Z$. Suppose $\rho$ minimizes $E_{TF}^Z$ on $I_N$ and $N_{\min} := \int_{\mathbb{R}^3} \rho < N$. Then $\rho$ is also a minimizer of the Thomas–Fermi functional for all $N' \in [N_{\min}, N]$, i.e., $E_{TF}(Z, N') = C$ for all $N' \in [N_{\min}, N]$. We will show that this leads to a contradiction. Since, by Theorem 4.8, $E_{TF}(Z, N)$ is monotone decreasing and convex, we even have that $E_{Z,N'}^Z = C$ for all $N' \geq N_{\min}$, in particular $N' = Z$. However, for this case, we know the
The minimizer is $\rho_Z$ which is certainly different from $\rho$, since $\int_{\mathbb{R}^3} \rho_Z > \int_{\mathbb{R}^3} \rho$ by assumption; but this contradicts the uniqueness of the minimizer, i.e., since $\rho \in \mathcal{I}_N$, we have $\int_{\mathbb{R}^3} \rho = N$.

2. $N > Z$. By Theorem 4.8 the unique minimizer on $\mathcal{I}$ occurs in $\mathcal{I}_Z$. But of course, it is also a minimizer in $\mathcal{I}_N$.

Finally, to show that there is no minimizer in $\mathcal{I}_{\partial N}$ for $N > Z$, we note that

$$\inf \{ \mathcal{E}_{TF}^Z (\mathcal{I}_N) \} = \inf \{ \mathcal{E}_{TF}^Z (\mathcal{I}_{\partial N}) \}.$$  \hspace{1cm} (4.45)

This is obvious for $N \leq Z$ and can be achieved for $N > Z$ by pushing the charge exceeding $Z$ to infinity and diluting it there: We pick a nonnegative $g \in C_0^\infty (\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} g = N - Z$ and use $\sigma_\lambda := \rho_Z + \lambda^3 g(\lambda x)$ with $\lambda > 0$ as trial function. Then, obviously, $\sigma_\lambda \in \mathcal{I}_{\partial N}$. We claim that

$$\mathcal{E}_{TF}^Z (\sigma_\lambda) \rightarrow \mathcal{E}_{TF}^Z (\rho_Z)$$  \hspace{1cm} (4.46)

as $\lambda \rightarrow 0$. If (4.46) were true, then, indeed, (4.45) would hold and the proof would be complete.

We prove the remaining convergence (4.46) term by term:

1. The kinetic energy: By the inverse triangular inequality we have

$$0 \leq \| \sigma_\lambda \|_\bullet - \| \rho_Z \|_\bullet \leq \| \sigma_\lambda - \rho_Z \|_\bullet = \| \lambda^3 g(\lambda \cdot) \|_\bullet = \lambda^\frac{4}{3} \| g \|_\bullet \rightarrow 0$$  \hspace{1cm} (4.47)

as $\lambda \rightarrow 0$.

2. The nuclear attraction: Obviously, as $\lambda \rightarrow 0$

$$\int_{\mathbb{R}^3} dx \frac{\rho_Z(x) + \lambda^3 g(\lambda x)}{|x|} = \int_{\mathbb{R}^3} dx \frac{\rho_Z(x)}{|x|} + \lambda \int_{\mathbb{R}^3} dx \frac{g(x)}{|x|} = \lambda \int_{\mathbb{R}^3} dx \frac{g(x)}{|x|} \rightarrow 0.$$  \hspace{1cm} (4.48)

3. The electron-electron repulsion: By the inverse triangular inequality for the Coulomb norm (4.16) we have

$$0 \leq \| \sigma_\lambda \|_c - \| \rho_Z \|_c \leq \| \sigma_\lambda - \rho_Z \|_c = \| \lambda^3 g(\lambda \cdot) \|_c = \sqrt{\lambda} \| g \|_c \rightarrow 0$$  \hspace{1cm} (4.49)

as $\lambda \rightarrow 0$. \hfill \Box

4.1.2. Asymptotic exactness of Thomas–Fermi theory

The heuristic derivation of the Thomas–Fermi theory — see, e.g., Gom- bas [10] for a textbook treatment — may be viewed as a semiclassical
approximation with effective Planck constant $Z^{-\frac{1}{3}}$. It is therefore reasonable to guess that it describes large — say for simplicity — neutral atoms correctly. We will see in this subsection that this is indeed the case for the ground-state energy $E^S(Z) := \inf \{ \sigma(H_{Z/|x|}, Z) \}$ and the reduced one-particle ground-state density. We begin with the energy:

**Theorem 4.11:**

$$E^S(Z) = E^{TF}(Z) + O(Z^{\frac{25}{11}}) \quad (4.50)$$

as $Z \to \infty$.

There are several proofs of this result. The historical first one uses Courant’s [45, 6th Chapter, §4] Dirichlet-Neumann bracketing (Lieb and Simon [34]) and is close to the heuristic derivation. Here we will use coherent states (see, e.g., Thirring [46]) which were used in this context by Lieb [36] and Thirring [47]. We are guided by their presentations. However, we start the lower bound differently by using a different correlation inequality.

Before embarking on the proof we introduce coherent states and review some properties which we will use. Given $g \in H^1(\mathbb{R}^3)$ with $\|g\|_2 = 1$, $q, p \in \mathbb{R}^3$, and $s \in \{1, 2\}$ we call the function

$$f_{p, q, s} : \Gamma := \mathbb{R}^3 \times \{1, 2\} \to \mathbb{C}, \quad x \mapsto e^{ip \cdot x}g(x - q)\delta_{s, \sigma} \quad (4.51)$$

a coherent state. The perhaps most well known coherent states use a Gaussian as $g$, since they yield equality in the Heisenberg uncertainty relation. Here, however, it will be practical to pick $g$ as function of compact support. To be definite we pick it as the ground state of a particle in a ball of radius $R$ with Dirichlet boundary conditions continued by zero outside that ball. We pick

$$g_R(x) := R^{-\frac{1}{2}}g_1(x/R) \quad (4.52)$$

where

$$g_1(x) = \begin{cases} \frac{\sin(\pi|x|)}{\sqrt{2\pi|x|}} & \text{for } |x| < 1 \\ 0 & \text{for } |x| > 1 \end{cases} \quad (4.53)$$

and $R$ is a positive parameter that will be optimized later.

We set $z := (p, q, s) \in P := \mathbb{R}^6 \times \{1, 2\}$, $f_p, dz := \int_{\mathbb{R}^3} dp \int_{\mathbb{R}^3} dq \sum_{s=1, 2}$, and $\Pi_z := |f_z\rangle \langle f_z|$ where $\bar{dp}$ denotes the volume element divided by the
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cube of the Planck constant \( h \) (in Hartree units \( h = 2\pi \)). We will pick the radius \( R \) later. These states have easily verified interesting properties:

\[
\int_P dz \Pi_z = 1,
\]

\[
0 \leq \gamma(z) \leq 1 \implies 0 \leq \int_P dz \gamma(z) \Pi_z \leq 1,
\] (4.54)

\[
\int_P dz \gamma(z) = \text{tr} \left( \int_P dz \gamma(z) \Pi_z \right)
\] (4.55)

where the integrals are understood in the weak sense, i.e., e.g., \( \int_P dz \gamma(z) \Pi_z \) is the operator \( O \) whose matrix elements \( \langle f, O g \rangle \) are \( \int_P dz \gamma(z)(f, \Pi_z g) \) for every \( f, g \in L^2(\Gamma, dx) \). (As reminder, the notation \( A \leq B \) for two selfadjoint operators means, that the domain \( D(B) \) of \( B \) is included in \( D(A) \) and for all \( f \in D(B) \) the inequality \( \langle f, Af \rangle \leq \langle f, Bf \rangle \) holds.)

**Proof:** [Theorem 4.11] Upper bound: We pick

\[
\gamma := \int_P dz \theta \left( -\frac{1}{2} p^2 - \varphi_Z(q) \right) \Pi_z
\] (4.56)

which — by (4.54) and (4.55) — is in \( \mathcal{D}_{\partial Z} \) (see (5.1) for the notation). We insert this into the Hartree–Fock variational principle (5.2). Since it is an upper bound on the quantum energy by (5.14) and the exchange term is negative, we get — using our choice of \( g_R \), in particular using that \( g_R \) is the ground state eigenfunction of the Laplacian on the ball of radius \( R \) which has eigenvalue \( \pi^2/R^2 \) —

\[
E_S(Z) \leq E_{HF}^Z(\gamma)
\]

\[
\leq \int_{\frac{1}{2} p^2 - \varphi_Z(q) < 0} dz \int_{\Gamma} dx \left( \frac{1}{2} |\nabla f_z(x)|^2 - \frac{Z |f_z(x)|^2}{|x|} \right)
\]

\[
+ \frac{1}{2} \int_{\Gamma} dx \int_{\Gamma} dy \int_{\frac{1}{2} p^2 - \varphi_Z(q) < 0} dz \int_{\frac{1}{2} p^2 - \varphi_Z(\tilde{q}) < 0} d\tilde{z} \frac{|f_z(x)|^2 |f_{\tilde{z}}(\tilde{y})|^2}{|x - y|}
\]

\[
\leq \int_{\frac{1}{2} p^2 - \varphi_Z(q) < 0} dz \left( \frac{|p|^2}{2} + \frac{\pi^2}{2R^2} - |g_R|^2 \cdot \frac{Z}{|\cdot|}(q) \right)
\]

\[
+ \frac{1}{2} \int_{\mathbb{R}^3} dq \int_{\mathbb{R}^3} d\tilde{q} \frac{1}{|\cdot|} \cdot \frac{1}{|\cdot|} g_R^2(q - \tilde{q}).
\] (4.57)

By Newton’s theorem we have \( |g_R|^2 \cdot |\cdot|^{-1}(q) \geq |q|^{-1} \theta(|q| - R) \) and that
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\[ g_R^2 * | -1 * g_R^2 \langle q - \bar{q} \rangle \leq 1/|q - \bar{q}|. \]  Moreover, a direct computation shows

\[ \rho_Z(q) = \int_{\frac{1}{2}p^2 - \phi_Z(q) < 0} dp \sum_{\sigma = 1}^2 \]

and

\[ \frac{3}{5} \gamma_{\text{TF}} \rho_Z(q) \frac{1}{2} = \int_{\frac{1}{2}p^2 - \phi_Z(q) < 0} dp \sum_{\sigma = 1}^2 \frac{1}{2} |p|^2. \]

Thus, continuing (4.57) we get

\[ E_S(Z) \leq 2 \int_{\mathbb{R}^3} dp \int_{\mathbb{R}^3} dq \left( \frac{|p|^2}{2} - \phi_Z(q) \right) - D[\rho_Z] + \frac{\pi^2 Z}{2R^2} \]

\[ + \int_{|x| < R} dx \frac{Z \rho_Z(x)}{|x|} \]

\[ \leq E^\text{TF}_Z(\rho_Z) + \frac{\pi^2 Z}{2R^2} - \frac{8\pi Z^2 R^3}{\gamma_{\text{TF}}^3} = E^\text{TF}(Z) + CZ \]

where we use \( \gamma_{\text{TF}} \rho(x) \frac{1}{2} \leq Z/|x| \) and picked \( R = Z^{-\frac{1}{3}} \) which proves the upper bound.

**Lower bound:** The first step of the lower bound is to eliminate the correlation in favor of a mean field using a correlation inequality. There are several ways of doing so. We will use the one by Mancas et al. [48, Formula (14)]

\[ \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|} \geq \sum_{n=1}^N \int_{|y - x_n| > R(x_n)} \frac{dy \sigma(y)}{|x_n - y|} - D[\sigma] \]

where \( \sigma \in \mathcal{C} \) will be specified later with \( \int \sigma > \frac{1}{2} \) and \( R(x) \) is defined by

\[ \int_{|y - x| < R(x)} dy \sigma(y) = \frac{1}{2}, \]

i.e., it is a ball, called the exchange hole, centered at \( x \) with radius \( R(x) \) containing exactly half an electron.

The right side of (4.61) can be estimated further: we have

\[ \int_{|x - y| \leq R(x)} dy \frac{\sigma(y)}{|x - y|} \leq \frac{1}{2} \sqrt{9\pi(M \sigma)(x)} \]

by [48, Formula (19)] where \( Mf \) denotes the maximal function of the function \( f \), i.e.,

\[ (Mf)(x) := \sup_{R > 0} \left\{ \frac{\int_{|x - y| < R} dy \ f(y)}{\frac{4\pi}{3} R^3} \right\}. \]
Thus (4.61) implies
\[ \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|} \geq \sum_{n=1}^{N} \left( \int_{\mathbb{R}^3} \frac{dy \sigma(y)}{|x_n - y|} - \frac{3\sqrt{9\pi}}{2} \sqrt{(M\sigma)(x_n)} \right) - D[\sigma]. \tag{4.65} \]

This allows us to estimate
\[ H - \frac{Z}{| \cdot |} \hbar \leq \sum_{n=1}^{N} \left( -\frac{1}{2} \Delta_n - \varphi_\sigma(x_n) - \frac{1}{2} \sqrt{9\pi(M\sigma)(x_n)} \right) - D[\sigma]. \tag{4.66} \]

with \( \varphi_\sigma = \frac{Z}{| \cdot |} - \sigma * | \cdot |^{-1} \). Thus we get the lower bound
\[ E^S(Z) \geq \inf_{\gamma \in D_N} \left\{ \text{tr} \left[ \left( -\frac{1}{2} \Delta - \varphi_\sigma - \frac{1}{2} \sqrt{9\pi(M\sigma)} \right) \gamma \right] \right\} - D[\sigma]. \tag{4.67} \]

Next note that for \( \xi \in H^1(\Gamma) \)
\[ \| \nabla \xi \|^2 = \int_\Omega d(x, \nabla f_z) \cdot (\nabla f_z, \xi) = \int_\Omega p^2(\xi, \Pi_z \xi) - \| \nabla g_R \|^2 \tag{4.68} \]
and
\[ \int_{\Gamma} d\gamma \varphi_\sigma * g_R^2(\xi(x))^2 = \int_\Omega d\gamma \varphi_\sigma(q)(\xi, \Pi_z \xi). \tag{4.69} \]

Furthermore, by Newton’s theorem,
\[ \varphi_\sigma * g_R^2 = \frac{Z}{| \cdot |} \int_{\mathbb{R}^3} \frac{dy g_R^2(y)^2}{|x - y|} - 2D(g_R^2, \sigma) \]
\[ \geq - \int_{\mathbb{R}^3} \frac{\sigma(y)}{|x - y|} + \left\{ \begin{array}{ll} \frac{Z}{|x|} & \text{for } |x| > R \\ 0 & \text{for } |x| \leq R \end{array} \right\} \tag{4.70} \]
i.e.,
\[ \int_{\Gamma} d\gamma \varphi_\sigma(x) |\xi(x)|^2 \leq \int_{\Gamma} d\gamma \varphi_\sigma * g_R^2(x) |\xi(x)|^2 + \int_{|x| > R} dx \frac{Z}{|x|} |\xi(x)|^2. \tag{4.71} \]

We write now \( \gamma = \sum_n \lambda_n |\xi_n\rangle \langle \xi_n| \) in its spectral representation with orthonormal eigenvectors \( \xi_1, \xi_2, \ldots \in H^1(\Gamma) \) and weights \( 0 \leq \lambda_1, \lambda_2, \ldots \leq 1 \), set \( \xi = \xi_n \) in (4.69) and (4.71), multiply by \( \lambda_n \), and sum over \( n \). Continuing
we get for $\epsilon_1, \epsilon_2 \in (0, 1/2)$

$$E^R(Z, N) \geq \int_P dz \left[ (1 - \epsilon_1 - \epsilon_2) \frac{p^2}{2} - \varphi_\sigma(q) \right] \left( \gamma \Pi_z - D[\sigma] \right) + \frac{1 - \epsilon_1 - \epsilon_2}{2R^2} \pi^2 N + \text{tr} \left( -\frac{\epsilon_2}{2} \Delta - \frac{Z \chi_{B_R(0)}}{1} \right) - \inf_{0 \leq \gamma \leq 1, (1-\Delta)\gamma \in \Theta^1(G)} \text{tr} \left( \left[ -\frac{\epsilon_2}{2} \Delta - \frac{1}{2} \sqrt{9\pi M(\sigma)} \right] \gamma \right)$$

where we used $0 \leq \gamma \leq 1$ and therefore $0 \leq \text{tr}(\gamma \Pi_z) \leq 1$ and we used the Lieb–Thirring inequality in both forms (4.3) and (4.4).

It is now appropriate to choose $N$ and $\sigma$. We pick $N = Z$ and $\sigma$ as the minimizer of the first term of the fourth line of (4.72) which amounts to the minimizer of the Thomas–Fermi functional but with a different Thomas–Fermi constant, namely instead of $(3\pi^2)\frac{5}{2}$ the constant $\tilde{\gamma} := (1-\epsilon_1-\epsilon_2)(3\pi^2)\frac{5}{2}$. Rescaling the Thomas–Fermi functional, we get that this term becomes $(1-\epsilon_1-\epsilon_2)^{-1}E^{TF}(Z)$.

Eventually we turn to the last line of (4.72). Obviously, the maximal function is homogeneous for positive constants, is monotone, i.e., $0 \leq f \leq g$ implies $M(f) \leq M(g)$. Moreover $\sigma(x) \leq (Z/(\tilde{\gamma}|x|^2))^{\frac{1}{2}}$ by (4.20), and $1/|x|^2$ is an eigenfunction of the maximal operator with eigenvalue $C_{3/2, 3}$ by (4.1). Thus, the last line of (4.72) is bounded from below as follows

$$\inf_{\rho \in L^\infty, \int_{\mathbb{R}^3} \rho \leq N} \int_{\mathbb{R}^3} dx \left( \frac{3}{5} \epsilon_2 \gamma_{LT} \rho(x)^{\frac{5}{2}} - \frac{1}{2} \sqrt{9\pi M(\sigma)(x)} \rho(x) \right) \geq \inf_{\rho \in L^\infty, \int_{\mathbb{R}^3} \rho \leq N} \int_{\mathbb{R}^3} dx \left( \frac{3}{5} \epsilon_2 \gamma_{LT} \rho(x)^{\frac{5}{2}} - \frac{1}{2} \sqrt{9\pi C_{3/2, 3}} \frac{Z^{\frac{1}{2}}}{\tilde{\gamma}^{\frac{1}{2}} |x|^2} \rho(x) \right) \geq -CZ^{\frac{1}{2}}/\epsilon_2^{\frac{1}{2}}. \quad (4.73)$$
Thus

$$E^S(Z) \geq E^{TF}(Z) - C \left[ (\epsilon_1 + \epsilon_2)Z^{3/2} + \frac{Z^{3/2}R^2}{\epsilon_1^{3/2}} + \frac{Z^{3/2}R^2}{\epsilon_2} \right].$$

(4.74)

Optimizing first in $R$ and $\epsilon_1$ yields an error term of the order $O(Z^{25/11})$ followed by an optimization in $\epsilon_2$ yielding $O(Z^{53/3})$ we get

$$E^S(Z, Z) \geq E^{TF}(Z) - CZ^{25/11}$$

(4.75)

which is the missing lower bound.

There are various extensions and related results to the above asymptotic exactness:

**Scott and Schwinger corrections:** The next order term in the asymptotic (4.50) is known. The energy with leading correction is

$$E^S(Z) = E^{TF}(Z) + \frac{Z^2}{2} + O(Z^{25/11}),$$

(4.76)

i.e., there is a correction term of order $Z^2$ predicted by and named after Scott [59]. There are various proofs of this result. One [50, 53] that is close to the proof of the leading order uses Macke orbitals [3.10] instead of coherent states leading to the Hellmann–Weizsäcker functional (3.9) but replaced by hydrogenic orbitals for small angular momenta both for the upper and the lower bound.

The method was actually carried through in the noninteracting setting earlier [51]. There were also earlier results on the lower bound using a WKB-type analysis (54), Hughes [55, 56]. Moreover the result was extended to ions (Bach [57]) and to molecules (Ivrii and Sigal [58], Solovej and Spitzer [59], Balodis [60]).

As Scott conjectured the correction is generated by the Coulomb singularity. A nonsingular potential has no correction up to order $O(Z^{25/11})$.

In fact even the subleading correction $-\gamma_S Z^{3/2}$ was predicted by Schwinger [61] yielding

$$E^S(Z) = E^{TF}(Z) + \frac{Z^2}{2} - \gamma_S Z^{3/2} + o(Z^{3/2})$$

(4.77)

and established in a series of papers by Fefferman and Seco [62, 68]. Unfortunately we cannot present any of those results here as their size — in particular the latter one — transcends the limitations of a proceedings contribution.
The convergence of the density on the Thomas–Fermi scale:

Hand in hand with the asymptotic energetic exactness there is also convergence of the quantum density. Suppose that $\rho_S^Z$ is a sequence of reduced one-particle densities of ground states of $H - \frac{Z}{|\cdot|}, Z$ as $Z \to \infty$. Then

$$\int_M dx Z^{-2} \rho_S^Z(Z^{-\frac{1}{2}}x) \to \int_M dx \rho_1(x) \quad (4.78)$$

for every bounded measurable set $M$ where $\rho_1$ is the minimizer of the Thomas–Fermi functional for $Z = 1$ (Baumgartner [69] and Lieb and Simon [34]). This weak convergence with a large set of test function can be actually supplemented by a convergence in Coulomb norm (see Merz et al. [70] in the context of relativistic quantum mechanics which, however, holds also in the nonrelativistic context).

We conclude with another apparently strange fact besides the nonexistence of negative ions. It concerns the molecular Thomas–Fermi functional which is like (4.1) but with $Z/|x|$ replaced by the potential of all $K$ nuclei $\sum_{k=1}^{K} Z_k/|x - R_k|$ and the nuclear-nuclear repulsion $\sum_{1 \leq k < l \leq K} Z_k Z_l/|R_k - R_l|$ added. Teller [71] showed that the molecular Thomas–Fermi functional is for all $\rho \in \mathcal{I}$ and all pairwise different nuclear positions $R_1, \ldots, R_K \in \mathbb{R}^3$ always bigger than the sum of the atomic energies $E^\text{TF}(Z_1) + \cdots + E^\text{TF}(Z_K)$. (For a detailed proof see Lieb and Simon [34].)

Although this looks at first sight completely unphysical, it expresses an important fact: the energy is bounded from below by a linear quantity in the number of particles involved. Together with the Lieb–Thirring inequality this is an essential input for showing that the thermodynamic limit of Coulomb systems exists (Lieb and Lebowitz [72]), since the energy is an extensive quantity, i.e., it is proportional to the amount of matter.

4.2. The Thomas–Fermi–Weizsäcker functional

Already the heuristic derivation of the Thomas–Fermi functional suggests that the Thomas–Fermi approximation might fail when the potential does change rapidly. This is also reflected in the proof of Theorem 4.11 where the leading error term occurs because of the nuclear singularity. Weizsäcker realized this problem in the context of nuclear physics and suggested to add a term which scales like the kinetic energy, is rotational and translation invariant, and penalizes changes of the density, i.e., is nonnegative and
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vanishes where the density is constant. He suggested the following functional

\[ E_{\text{TFW}}^{\lambda} (\rho) := \frac{\lambda}{2} \int_{\mathbb{R}^3} \text{d}x |\nabla \sqrt{\rho}|^2 + E_{\text{TF}}^{\lambda} (\rho), \]  

(4.79)

known as the Thomas–Fermi–Weizsäcker functional, defined on \( \mathcal{A} \). Weizsäcker’s original choice was \( \lambda = 1 \). A derivation by the gradient expansion of the Hohenberg–Kohn functional yields \( \lambda = \frac{1}{9} \) (Kirzhnits [73]) whereas adaptation to numerical computations yields \( \frac{1}{5} \) (Yonei and Tomishima [74]).

We will comment on yet another adaptation in the context of the Scott correction.

Benguria [75] pioneered the mathematical investigation of the TFW-functional. We will follow — with minor modifications — Benguria et al. [76] for the basic results: We remark that \( \nabla \sqrt{\rho} \in L^2 (\mathbb{R}^3) \) (and \( \rho \in L^1 (\mathbb{R}^3) \)) by the Sobolev inequality. Since \( \rho \in L^1 (\mathbb{R}^3) \), it follows by interpolation that \( \rho \in L^{\frac{5}{3}} (\mathbb{R}^3) \). By the same argument \( \rho \in L^{\frac{6}{5}} (\mathbb{R}^3) \) and therefore by the Hardy–Littlewood–Sobolev inequality

\[ D[\rho] \leq C \|\rho\|_{\frac{6}{5}}^2 < \infty. \]

Thus \( \rho \in I \).

This implies that all the terms are well defined and, moreover,

\[ \inf \{ E_{\text{TFW}}^{\lambda} (\mathcal{A}) \} \geq \inf \{ E_{\text{TF}}^{\lambda} (I) \} > -\infty. \]  

(4.80)

**Lemma 4.12:** The Thomas–Fermi–Weizsäcker functional and its restrictions to \( \mathcal{A}_N \) and \( \mathcal{A}_{\partial N} \) are strictly convex.

**Proof:** Obviously the sets \( \mathcal{A}, \mathcal{A}_N, \) and \( \mathcal{A}_{\partial N} \) are convex. Moreover, the Thomas–Fermi functional is strictly convex by Lemma [4.13]. Thus it suffices to show convexity of the Weizsäcker term. To this end pick \( \alpha \in (0, 1) \) and \( \rho, \sigma \in \mathcal{A} \). We set \( \psi_1 := \sqrt{\rho}, \psi_2 := \sqrt{\sigma}, \) and \( \psi_3 := \sqrt{\alpha \rho + (1 - \alpha)\sigma} \). Then

\[ \begin{align*}
\psi_3 \nabla \psi_3 &= \sqrt{\alpha} \psi_1 \sqrt{\alpha} \nabla \psi_1 + \sqrt{1 - \alpha} \psi_2 \sqrt{1 - \alpha} \nabla \psi_2 \\
&\leq \sqrt{\alpha \rho + (1 - \alpha)\sigma} \sqrt{\alpha |\nabla \psi_1|^2 + (1 - \alpha) |\nabla \psi_2|^2}
\end{align*} \]

by the Schwarz inequality. Thus, we have after integration

\[ \int_{\mathbb{R}^3} |\nabla \sqrt{\alpha \rho + (1 - \alpha)\sigma}|^2 \leq \alpha \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + (1 - \alpha) \int_{\mathbb{R}^3} |\nabla \sqrt{\sigma}|^2 \]  

(4.81)

which is the convexity of the Weizsäcker term.

As usual, the strict convexity implies that there is at most one minimizer of the functional. The existence of the minimizer is shown again by weak
compactness. The argument is more elaborate but in spirit similar to the Thomas–Fermi case. We skip the proof and merely report the result:

**Theorem 4.13:** The Thomas–Fermi–Weizsäcker functional has a unique minimizer $\rho_Z$ on $A$ with $N_c := \int_{\mathbb{R}^3} \rho_Z > Z$. Moreover, for $N \leq N_c$ it has a unique minimizer $\rho_{Z,N}$ on $A_{\partial N}$ whereas for $N > N_c$ there is no minimizer on $A_{\partial N}$. The minimizers fulfill the Euler equations

$$
\left( -\frac{\lambda}{2} \Delta + \gamma_{TF} \rho_Z^{\frac{4}{3}} - \phi \rho_Z \right) \sqrt{\rho_Z} = 0,
$$

$$
\left( -\frac{\lambda}{2} \Delta + \gamma_{TF} \rho_{Z,N}^{\frac{4}{3}} - \phi \rho_{Z,N} \right) \sqrt{\rho_{Z,N}} = -\mu_{Z,N} \sqrt{\rho_{Z,N}} \tag{4.83}
$$

with some $\mu_{Z,N} > 0$.

Thus, in contrast to Thomas–Fermi theory, there are negative ions in Thomas–Fermi–Weizsäcker theory. Benguria and Lieb [77] gave an estimate on the maximal negative ionization. They show

$$
N_c \leq Z + 270.74 \left( \frac{\lambda}{2\gamma_{TF}} \right)^{\frac{2}{3}} \tag{4.84}
$$

(actually times the number of of nuclei in the molecular case). Using $\lambda = \frac{1}{5}$ as suggested by Yonei and Tomishima [74] becomes $N_c \leq Z + 0.82$ which is not far from the physical fact that there are no doubly or higher charged negative ions (Massey [42]).

We do not prove the bound (4.84) here. Instead, we offer the famous — again unpublished — argument of Benguria developed in Thomas–Fermi theory. It gives a worse bound, but is relatively short and widely used, e.g., it generalizes to the Hartree–Fock and quantum case where it has been used by Lieb [13].

**Theorem 4.14:**

$$
N_c < 2Z. \tag{4.85}
$$

**Proof:** We first we note an observation by Lieb [14], namely

$$
-\Delta | \cdot | + | \cdot |(-\Delta) > 0. \tag{4.86}
$$

We prove this inequality by recognizing that it is merely a recast of Hardy’s
inequality. For, say, $f \in C_0^\infty(\mathbb{R}^3)$, we have

$$-(f, (\Delta |x| + |x| \Delta)f) = (f, \left\{ \sqrt{\cdot}(-\Delta)\sqrt{\cdot} + \left[ \sqrt{\cdot}, [\sqrt{\cdot}, -\Delta] \right] \right\}f) = \left(\sqrt{\cdot}f, \left(\Delta - \frac{1}{4}|\cdot|^2\right)\sqrt{\cdot}f \right) > 0 \quad (4.87)$$

unless $f = 0$. (Here $[A, B] := A \circ B - B \circ A$ denotes the commutator.)

In passing we note that (4.86) can be generalized to the relativistic case, i.e., $\sqrt{-\Delta}$ instead of $-\Delta$ (see Lieb [14] for a restricted validity, Dall’Acqua and Solovej [78] for the full inequality and Handrek et al. [79] for an extension to the two-dimensional case.) In fact a much larger class of such anticommutator inequalities is true (Chen et al. [80]).

We prove (4.85) by multiplying (4.83) by $\sqrt{\rho Z}(x)|x|$ followed by integration:

$$0 = \int_{\mathbb{R}^3} \rho Z \left( -|x|\sqrt{\rho Z}(x)\frac{\lambda}{2}\Delta\sqrt{\rho Z}(x) + \gamma_{TF}|x|\rho Z(x)^{\frac{3}{2}} - |x|\rho Z(x)\varphi_{\rho Z}(x) \right)$$

$$> -Z \int_{\mathbb{R}^3} \rho Z + \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{|x|}{|x - y|}\rho Z(x)\rho Z(y)$$

$$= -Z \int_{\mathbb{R}^3} \rho Z + \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{|x| + |y|}{|x - y|}\rho Z(x)\rho Z(y) \geq -ZN_c + \frac{1}{2}N_c^2 \quad (4.88)$$

where we have used that the first summand is real allowing to replace $|\cdot|(-\Delta)$ by half of its anticommutator, and then use the inequality (4.86). In the last step, we used the triangle inequality and $\int_{\mathbb{R}^3} \rho Z = N_c$. Rearranging terms gives the desired inequality.

To conclude this section we expand on the above remark about the wide applicability of Benguria’s idea: a similar type of argument shows that any minimizer $\gamma$ of the Hartree–Fock functional on $D$ (see Section 5.1) fulfills the inequality

$$\text{tr}(\gamma) < 2Z + 1 \quad (4.89)$$

and that the Hamiltonian $H_{-Z/||\cdot||}$ has no bound states, if $N \geq 2Z + 1$ (Lieb [14]). The latter implies that there is no doubly charged negative hydrogen.

4.3. The Engel–Dreizler functional

The known limiting theorem, as well as the heuristic derivation, of Thomas–Fermi and related theories assume large particle numbers. This, in turn
requires for atoms also large atomic number $Z$, since, as we saw, only large $Z$ atoms allow for large number $N$ of electrons to be bound. However, this renders a nonrelativistic treatment physically questionable: Using $\frac{m^2 v^2}{2} = -E$ and using $E = -Z^2/2$, i.e., the hydrogenic ground state energy, yields an estimated speed of $Z$ for the innermost electrons. This compares with the speed of light $c = 137.037$ in Hartree units (Michelson [81]). Thus, for uranium, $Z = 92$, the innermost electrons reach roughly $0.67$ of the speed of light. This suggests that relativistic effects should be taken into account which has been realized early. However, the heuristic derivation along the lines of the derivation of the nonrelativistic Thomas–Fermi functional yields an atomic functional which is unbounded from below. The semiclassical relativistic kinetic energy term is not strong enough to prevent collapse of electrons into the nucleus. A review of these facts and various ad hoc attempts to cure this problem can be found in Gombas’s classical book [10] and encyclopedia article [82].

Engel and Dreizler [83] offered a systematic solution to the problem. The functional which they propose reads in the atomic case

$E_{ED}^\text{Z}(\rho) := T^W(\rho) + T^\text{TF}(\rho) - X(\rho) + V(\rho).$ (4.90)

The first summand on the right is an inhomogeneity correction of the kinetic energy generalizing the Weizsäcker correction. Using the abbreviation $p(x) := (3\pi^2 \rho(x))^{1/3}$,

$T^W(\rho) := \int_{\mathbb{R}^3} dx \frac{3\lambda}{8\pi^2} \left(\nabla p(x)\right)^2 f\left(p(x)/c\right)^2$ (4.91)

with $f(t)^2 := t(t^2 + 1)^{-1} + 2t^2(t^2 + 1)^{-1}\text{arsinh}(t)$ where $\text{arsinh}$ is the inverse function of the hyperbolic sine and $\lambda \in \mathbb{R}_+$ is given by the gradient expansion as $\frac{1}{9}$ but in the nonrelativistic analog sometimes taken as an adjustable parameter (Weizsäcker [9], Yonei and Tomishima [74], Lieb and Lieberman [54], Lieb [55]). The second summand is the relativistic generalization of the Thomas–Fermi kinetic energy. It is

$T^\text{TF}(\rho) := \int_{\mathbb{R}^3} dx \frac{c^5}{8\pi^2} T^\text{TF}\left(p(x)/c\right)$ (4.92)

with $T^\text{TF}(t) := t(t^2 + 1)^{3/2} + t^3(t^2 + 1)^{1/2} - \text{arsinh}(t) - \frac{8}{3}t^3$. The third summand is a relativistic generalization of the exchange energy. It is

$X(\rho) := \int_{\mathbb{R}^3} dx \frac{c^4}{8\pi^3} X\left(p(x)/c\right)$ (4.93)
with \( X(t) := 2t^4 - 3[t^2 + 1]^{1/2} - \text{arsinh}(t)^2 \), and, eventually, the last summand is the potential energy, namely the sum of the electron-nucleus energy and the electron-electron energy. It is

\[
V(\rho) := -Z \int_{\mathbb{R}^3} d\mathbf{x} \rho(\mathbf{x})|\mathbf{x}|^{-1} + D[\rho].
\] (4.94)

The Engel–Dreizler functional is defined on

\[
P := \{ \rho \in L^2(\mathbb{R}^3) \mid \rho \geq 0, \ D[\rho] < \infty, \ F \circ p \in D^1(\mathbb{R}^3) \}. \quad (4.95)
\]

Initial steps analyzing the functional have been carried out by Chen et al. [86] and refined in [87] (in these proceedings). It is bounded from below for all nuclear charges – a surprising fact which is not even true for various quantum models –, it yields in first order for \( c/Z \) fixed the Thomas–Fermi theory, and is stable in the sense of stability of matter [88]. A relativistic correction is expected for the Scott correction of the functional.

### 4.4. Density functionals in phase space

The functionals of the one-particle density \( \rho \) in position space which we have considered so far can be generalized to functionals of the one-particle density \( f \) in phase space. They are of particular interest, if the Hamiltonian of the system is no longer a sum of terms which depend either on momentum or on position but a sum that also contains mixed terms. Densities depending on both momentum and position are also important, if the time dependence of the density is of interest.

The set of measurable functions \( f : \mathbb{R}^6 \rightarrow \mathbb{R}_+ \) is the set of (semiclassical) densities in phase space. For a system of identical fermions of \( q \) spin states each the Pauli principle is implemented by requiring the additional constraint \( f \leq q \). The integral \( \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{\xi} f(\mathbf{x}, \mathbf{\xi}) \) is the particle number of \( f \). The fermionic phase space energy functional of an atom of a fermionic quantum system with kinetic energy \( T \), external potential \( V \), additional momentum dependent external potential \( \tilde{V} \), and interaction \( W \) is

\[
\mathcal{E}(f) := \int_{\mathbb{R}^6} d\mathbf{\xi} d\mathbf{x} \left[ T(\mathbf{\xi}) + V(\mathbf{x}) + \tilde{V}(\mathbf{\xi}) \right] f(\mathbf{\xi}, \mathbf{x}) + \frac{1}{2} \int_{\mathbb{R}^6} d\mathbf{\xi} d\mathbf{x} \int_{\mathbb{R}^6} d\mathbf{\eta} d\mathbf{y} \ W(\mathbf{x}, \mathbf{y}) f(\mathbf{\xi}, \mathbf{x}) f(\mathbf{\eta}, \mathbf{y}) \] (4.96)

with \( f : \mathbb{R}^6 \rightarrow [0, q] \). We call \( \rho_f(\mathbf{x}) := \int_{\mathbb{R}^3} d\mathbf{\xi} f(\mathbf{\xi}, \mathbf{x}) \) the position density at \( \mathbf{x} \) and \( \tau_f(\mathbf{\xi}) := \int_{\mathbb{R}^3} d\mathbf{x} f(\mathbf{\xi}, \mathbf{x}) \) the momentum density at \( \mathbf{\xi} \).
This is, of course, formal only as long as we do not specify the various terms and the allowed densities and show that all terms are well defined. For definiteness and simplicity we will again consider a generic choice only, namely an atom, i.e., we choose
\[
T(\xi) := \frac{\xi^2}{2}, \quad V(x) := -Z/|x|, \quad \tilde{V} = 0, \quad W(x, y) = 1/|x - y|, \quad q = 2,
\]
and the domain of definition
\[
P := \left\{ f : \mathbb{R}^6 \to [0, 2] \left| \int_{\mathbb{R}^6} d\xi \int_{\mathbb{R}^6} dx \left( 1 + |\xi|^2 \right) f(\xi, x) < \infty, \quad \rho_f \in \mathcal{C} \right\}. \quad (4.97)
\]

The kinetic energy term is finite by definition as well as the electron-electron repulsion, since it is equal to \(D[\rho_f]\). We decompose the electron-nucleus attraction as in (4.22). The long-range part \(V_l\) is dominated as in Thomas–Fermi theory by \(D[\rho_f]\). It remains to control the short-range part:
\[
\int_{|x| < R} \frac{d\xi}{|x|} \int_{\mathbb{R}^3} \frac{d\xi}{(1 + |\xi|^2)^{\alpha q}} \left( \int_{\mathbb{R}^6} d\xi \int_{\mathbb{R}^6} dx \left( 1 + |\xi|^2 \right)^{\alpha q} f(\xi, x) \right)^{\frac{1}{q}} \leq 2^{\frac{q}{10}} \left( \int_{|x| < R} \frac{d\xi}{|x|} \int_{\mathbb{R}^3} \frac{d\xi}{(1 + |\xi|^2)^{\alpha q}} \right)^{\frac{10}{q}} \left( \int_{\mathbb{R}^6} d\xi \int_{\mathbb{R}^6} dx \left( 1 + |\xi|^2 \right)^{\alpha q} f(\xi, x) \right)^{\frac{1}{q}} < \infty \quad (4.98)
\]
with \( p = \frac{3q}{10}, \quad q = \frac{2}{10}, \quad \text{and} \quad \alpha = \frac{1}{q} \). This shows that all the terms are well defined.

4.4.1. Marginal functionals: The position space
One possibility to minimize \(E\) is to split the minimization into two steps. The classical way is to fix \(x\) and to minimize — in a first step — over the functions \(f(\cdot, x)\). Any minimizer can obviously be picked such that it takes the values 0 and 2 only and because of the symmetry and the monotonity of the Coulomb potential they can be picked as characteristic functions (times 2) of balls \(B_{R(x)}(0)\) centered at the origin with radius \(R(x)\) aka Fermi balls and Fermi radius. The relation between the radii and the density is
\[
R(x) = \frac{3}{\sqrt{\pi}} \rho_f(x). \quad (4.99)
\]
The second step consists in minimizing the Thomas–Fermi functional as described in Sec. 4.11. Thus, the minimizer \(f_{\text{min}}\) of \(E\) on \(\mathcal{P}\) is — apart from
the factor 2 — the characteristic function of the the classical allowed phase space

$$\{(\xi, x) \in \mathbb{R}^6 \mid \xi^2/2 - \varphi_{\rho_2}(x) < 0\}$$

(4.100)

for the Thomas–Fermi potential $\varphi_{\rho_2}$, i.e.,

$$f_{\text{min}}(\xi, x) := 2\theta\left(-\left[\xi^2/2 - \varphi_{\rho_2}(x)\right]\right).$$

(4.101)

This shows that the infimum of the phase space functional $E$ is equal to the infimum of the Thomas–Fermi functional. Thus $E$ is not only well defined but also bounded from below yielding the same energy.

4.4.2. Marginal functions: The momentum space

A less obvious way to minimize $E$ is to reverse the order, i.e., to fix $\xi$ in the first step and to minimize $E$ over the functions $f(\xi, \cdot)$. Again those minimizers take only the values 0 and 2 and are characteristic functions of balls $B_{\tilde{R}(\xi)}(0)$ centered at the origin with a now $\xi$-dependent radius $\tilde{R}(\xi)$ with the relation $\tilde{R}(\xi) = \frac{\sqrt{3\pi^2\tau(\xi)}}{3\sqrt{Z}}$ to the momentum density $\tau$. The result is Englert’s momentum space semiclassical functional [89]

$$E_E^Z(\tau) := \int_{\mathbb{R}^3} d\xi \xi^2\tau(\xi) - \frac{Z}{2} \frac{1}{\sqrt{3\pi^2}} \int_{\mathbb{R}^3} d\xi \tau(\xi)^{2/3}$$

$$+ \frac{3}{4} \frac{1}{\sqrt{3\pi^2}} \int_{\mathbb{R}^3} d\xi \int_{\mathbb{R}^3} d\eta \left(\tau_{\leq}(\xi, \eta)\tau_{\geq}(\xi, \eta)\right)^{2/3} - \frac{1}{5} \tau_{\leq}(\xi, \eta)$$

(4.102)

where $\tau_{\leq}(\xi, \eta) := \min\{\tau(\xi), \tau(\eta)\}$ and $\tau_{\geq}(\xi, \eta) := \max\{\tau(\xi), \tau(\eta)\}$.

The second step is the minimization of $E_E^Z$. As to be expected it yields the same energy as the Thomas–Fermi functional.

A mathematical analysis of $E_E^Z$ including the convergence of the one-particle reduced momentum density of an atom described by the Schrödinger equation to the minimizer of the hydrogenic Englert functional has been carried through by Conta et al. [90].

At first sight $E_E^Z$ might look repelling: whereas the kinetic energy term is simple, the two potential terms, in particular the electron-electron repulsion term look unfamiliar. However, when momentum-dependent potentials are present like for the Compton profile, it simplifies the treatment. Another application is an alternate investigation of the Scott correction (Cinal and Englert [91, 92]).
4.4.3. Time-dependent equations

Runge and Gross [93] argued for the existence of a time-dependent analog of the stationary density functional formalism. In particular they derived an Euler-type equation for the density and the current. Fournais et al. [94] analyzed the argument pointing out various problems with singular potentials, in particular Coulomb potentials. Nevertheless an equation of Runge–Gross type generalizing Thomas–Fermi theory is known in the literature since long — although to some extent ignored by the density functional community, e.g., Runge and Gross do not reference it: Bloch [95] (see also Gombas [10; §20]) introduced the following Euler-type equation

\[ \partial_t \varphi_t = \frac{1}{2} (\nabla \varphi_t)^2 + \int \frac{dp}{\rho_t} - \frac{Z}{|\cdot|} + \rho_t \ast |\cdot|^{-1} \]  

(4.103)

supplemented by the continuity equation

\[ \partial_t \rho_t = \nabla \cdot (\rho_t \nabla \varphi_t). \]  

(4.104)

Here \( \varphi \) is the potential of the velocity field \( u \), i.e., \( u = -\nabla \varphi \), \( \rho \) is the density of electrons, and \( p \) is the pressure as a function of \( \rho \). The Thomas–Fermi choice for \( p \) is \( p(\rho) := \frac{1}{5} \gamma_{TF} \rho^{5/3} \), i.e., we have

\[ \partial_t \varphi_t = \frac{1}{2} (\nabla \varphi_t)^2 + \gamma_{TF} \rho_t^{2/3} - \frac{Z}{|\cdot|} + \rho_t \ast |\cdot|^{-1} \]  

(4.105)

which reduces to the stationary Thomas–Fermi equation (4.26) when \( \varphi \) is constant.

There are existence results for such Euler equations with regular potentials. The Coulomb case, however, seems to be still open. There are, however, nonexistence results for highly charged negative ions. Chen et al. [96], following a strategy developed by Lenzmann and Lewin [97], showed

**Theorem 4.15:** Assume that \( \varphi_t \) and \( \rho_t \) is a weak solution of (4.105) and (4.104) with \( \int_{\mathbb{R}^3} dx \frac{1}{Z} \rho_0(x) |\nabla \varphi_0(x)|^2 + E_{TF}(\rho_0) < \infty \), assume \( B \subset \mathbb{R}^3 \) bounded and measurable, and set

\[ N_{TF}(t, B) := \int_B dx \rho_t(x) \]  

(4.106)

which is the number of electrons in \( B \). Then, in temporal average for large time, \( N_{TF}(t, B) \) does not exceed 4\( Z \), i.e.,

\[ \lim \sup_{T \to \infty} \frac{1}{T} \int_0^T dt N_{TF}(t, B) \leq 4Z. \]  

(4.107)
This shows that the number of electrons that an atom can acquire is bounded by $4Z$ generalizing the bound of the time-independent setting. There is, however, a price paid: the generalization yields a worse constant.

Whereas the generalization of the Thomas–Fermi equation to the time-dependent case requires the introduction of the velocity field of the matter, the transfer of the phase space theory as condensed in the variational principle \cite{196} depending on the phase space density does not require any extra functions. The natural generalizations is the Vlasov equation (Vlasov \cite{98, 99}). We formulate it — for notational simplicity — in the atomic case only. We write

$$K(x) := -\nabla V_{\text{tot}}(x) = -Z \frac{x}{|x|^3} + \int_{\mathbb{R}^3} dy \rho_t(y) \frac{x - y}{|x - y|^3} \quad \text{(4.108)}$$

for the force of the nucleus and the electron cloud exerted on an electron. With this notation the Vlasov equation reads

$$\partial_t f_t + \xi \cdot \nabla_x f_t + K \cdot \nabla_\xi f_t = 0. \quad \text{(4.109)}$$

Suppose that $f_t$ is a weak solution of the Vlasov equation. Then

$$\mathcal{E}_V(f_t) := \int_{\mathbb{R}^6} d\xi dx \frac{1}{2} \xi^2 f_t(\xi, x) - \int_{\mathbb{R}^3} dx V(x) \rho_t(x) + D[\rho] \quad \text{(4.110)}$$

is called the energy. It is a conserved quantity.

As in the case of the time-dependent Thomas–Fermi theory Chen et al. \cite{96, Theorem 1} proved — again following \cite{97} — an upper bound on the charge that can remain in any fixed ball:

**Theorem 4.16:** Assume $f_t$ to be a weak solution of the Vlasov equation \textbf{(4.109)} of finite energy \textbf{(4.110)}, assume $B \subset \mathbb{R}^3$ bounded and measurable, and set

$$N_V(t, B) := \int_{\mathbb{R}^3} d\xi \int_B dx f_t(\xi, x) \quad \text{(4.111)}$$

which is the number of electrons in $B$. Then in temporal average for large time $N_V(t, B)$ does not exceed $4Z$, i.e.,

$$\limsup_{T \to \infty} \frac{1}{T} \int_0^T dt N_V(t, B) \leq 4Z. \quad \text{(4.112)}$$

Actually, the solution of the Vlasov equation, if existing, can be compared with with the solution of the Schrödinger equation when the external potential is not too singular. (See, e.g., Petrat and Pickl \cite{100} and the references given there.)
5. Functionals of the one-particle density matrix

5.1. The Hartree–Fock functional

We call
\[ D := \{ \gamma \in \mathfrak{S}^1(L^2(\Gamma)) \mid 0 \leq \gamma \leq 1, (-\Delta + 1)\gamma \in \mathfrak{S}^1(L^2(\Gamma)) \}, \]
\[ D_N := \{ \gamma \in D \mid \text{tr}(\gamma) \leq N \}, \]
\[ D_{\partial N} := \{ \gamma \in D \mid \text{tr}(\gamma) = N \} \] (5.1)
the set of one-particle reduced density matrices with finite kinetic energy, those with particle number not exceeding \( N \), and those with particle number equal to \( N \).

We call
\[ E_{\text{HF}} : D \to \mathbb{R}, \gamma \mapsto \text{tr}\left( -\frac{1}{2}\Delta \gamma \right) - \int_{\mathbb{R}^3} dx \frac{Z \rho_\gamma(x)}{|x|} + D[\rho_\gamma] - \frac{1}{2} \int_{\Gamma} dx \int_{\Gamma} dy \frac{|\gamma(x, y)|^2}{|x - y|} =: X[\gamma] \] (5.2)
the Hartree–Fock functional where \( \rho_\gamma \) is the one-particle density of \( \gamma \) defined as in (2.20) and \( \gamma(x, y) \) is the density matrix’s \( \gamma \) integral kernel. The first summand is the kinetic energy, the second is the attraction potential of the nucleus, the third is the classical Coulomb potential of the charge density \( \rho_\gamma \), aka direct or Hartree term, the last term is called the exchange energy of \( \gamma \).

The functional is well defined which is obvious for the kinetic energy by definition. For the second term we use the variational principle for hydrogenic atoms: for every \( \xi \in H^1(\Gamma) \), \( a \in \mathbb{R}^3 \) and \( \zeta \in (0, \infty) \), we have
\[ \int_{\Gamma} dx \frac{|\xi(x)|^2}{|x - a|} \leq \frac{1}{2} \left( \zeta^{-1} \int_{\Gamma} dx |\nabla \xi(x)|^2 + \zeta \int_{\Gamma} dx |\xi(x)|^2 \right) \] (5.3)
and thus with \( \zeta = 1 \)
\[ 0 \leq \int_{\mathbb{R}^3} dx \frac{\rho_\gamma(x)}{|x|} \leq \sum_{\alpha} \lambda_{\alpha} \int_{\Gamma} dx \frac{|\xi_\alpha(x)|^2}{|x|} \leq \frac{1}{2} (\text{tr}(\Delta \gamma) + \text{tr}(\gamma)) < \infty \] (5.4)
rendering the attraction potential finite. For the third term — using again (5.3) with \( \zeta = 1 \) and \( a = y \) — we have
\[ D[\rho_\gamma] \leq \frac{1}{2} \text{tr}(\gamma) \frac{1}{2} (\text{tr}(\Delta \gamma) + \text{tr}(\gamma)) < \infty. \] (5.5)
Eventually we remark that the exchange term is bounded by the direct term using Schwarz’s inequality in the summation over \( n \) and \( m \):

\[
0 \leq X[\gamma] = \frac{1}{2} \int_{\Gamma} \int_{\Gamma} dx \int_{\Gamma} dy \frac{\sum_{n,m} \lambda_n \lambda_m \xi_n(x) \xi_n(y) \xi_m(x) \xi_m(y)}{|x - y|} \\
\leq \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho_n(x) \rho_m(y)}{|x - y|} = D[\rho_\gamma] \tag{5.6}
\]

which shows that also the exchange term is finite.

We will now exhibit some properties of the Hartree–Fock theory and begin with a theorem by Lieb \cite{101} but will present Bach’s \cite{102, Section 3} version of the proof.

**Theorem 5.1:** Suppose \( N \in \mathbb{N} \), \( \gamma \in D_{\partial N} \), and \( \gamma \neq \gamma^2 \). Then there exists \( \gamma' \in D_{\partial N} \) such that

\[
E_{HF}(\gamma') < E_{HF}(\gamma). \quad \text{In particular, any minimizer of } E_{HF} \text{ on } D_{\partial N} \text{ is a projection.}
\]

**Proof:** Since \( \gamma \) is not a projection there is at least one eigenvalue, say \( \lambda_1 \in (0, 1) \). Then, since \( N \) is an integer, there is also a second eigenvalue \( \lambda_2 \in (0, 1) \). We write \( \xi_1 \) and \( \xi_2 \) for two corresponding orthonormal eigenvectors and set

\[
\gamma_\epsilon := \gamma + \epsilon \left( |\xi_1\rangle\langle\xi_1| - |\xi_2\rangle\langle\xi_2| \right) \tag{5.7}
\]

which is in \( D_{\partial N} \) as long as \( \epsilon + \lambda_1, -\epsilon + \lambda_2 \in [0, 1], \epsilon \in \mathbb{R} \). We compute

\[
D[\rho_\delta] - X[\delta] = \int_{\mathbb{R}^2} \frac{dx \, dy}{|x - y|} \left( |\xi_1(x)|^2 |\xi_2(y)|^2 - |\xi_2(x)|^2 |\xi_1(y)|^2 \right) \\
- \left| \xi_1(x) \xi_1(y) - \xi_2(x) \xi_2(y) \right|^2 \\
= -2 \int_{\mathbb{R}^2} dx \, dy \frac{|\xi_1(x)|^2 |\xi_2(y)|^2 - |\xi_1(x)\xi_2(x)\xi_1(y)|^2 |\xi_2(y)|^2}{|x - y|} < 0 \tag{5.8}
\]

where, in the last step, we have used the Schwarz inequality and the fact that equality in the Schwarz inequality can only hold when \( \xi_1 \otimes \xi_1 \) and \( \xi_2 \otimes \xi_2 \) are linearly dependent which, however, is definitely not the case, since \( \xi_1 \) is orthogonal to \( \xi_2 \). Thus

\[
E_{HF}(\gamma_\epsilon) - E_{HF}(\gamma) = \epsilon \left[ \text{tr} \left( \frac{-\frac{1}{2} \Delta - Z}{|x|} \delta \right) + 2D(\rho_\gamma, \rho_\delta) - 2X(\gamma, \delta) \right] \\
+ \epsilon^2 \left( D[\rho_\delta] - X[\delta] \right) < 0 \tag{5.9}
\]
where we choose the sign of $\epsilon$ equal to minus the sign of the bracket in (5.9), use (5.8), and decrease or increase $\epsilon$, depending on our choice of the sign of $\epsilon$ until $\epsilon + \lambda_1$ or $-\epsilon + \lambda_2$ become 0 or 1 for the first time. This does not only prove the theorem but it even shows that we can choose $\gamma'$ such that it has at least one less eigenvalue in the open interval $(0, 1)$. Of course this argument can be iterated as long as there are eigenvalues that are not equal to 0 or 1.

This result can be used to show that the particle number of minimizers is an integer, poetically speaking, is quantized (Friesecke [103]). Writing $G_Z$ for the set of all minimizers of $E_{HF}^Z$ on $D$, we have

**Theorem 5.2:** For any $Z > 0$ the set of minimizers $G_Z$ contains a projection. Moreover, if for all $\gamma \in G_Z$ the operator $h_{Z,\gamma}^{HF}$ has no zero eigenvalue, then $G_Z$ consists of projections only.

**Proof:** Running through the proof of Theorem 5.1 again shows that a minimizer $\gamma$ can have at most one eigenvalue, say $\lambda$, which is strictly between zero and one. Write $\xi$ for a corresponding normalized eigenfunction which is also an eigenfunction of $h_{Z,\gamma}^{HF}$. Such a choice is possible, since the Hartree–Fock equations (5.12) ensure that the Hartree–Fock operator $h_{Z,\gamma}^{HF}$ commutes with the $\gamma$.

We set $\gamma_\epsilon := \gamma + \epsilon |\xi\rangle \langle \xi|$ and write

$$h_{Z,\gamma}^{TF} f(x) := \left( -\frac{1}{2} \Delta - \frac{Z}{|x|} - \int_{R^3} \frac{dy \rho_\gamma(y)}{|x - y|} \right) f(x) - \int_{\Gamma} dy \frac{\gamma(x, y)}{|x - y|} f(y).$$

(5.10)

Now, we compute

$$\mathcal{E}_Z^{HF}(\gamma_\epsilon) - \mathcal{E}_Z^{HF}(\gamma) = \epsilon \langle \xi, h_{Z,\gamma}^{HF} \xi \rangle \leq 0$$

(5.11)

by choosing the appropriate sign of $\epsilon$. By choosing $\epsilon + \lambda = 1$, if the expectation is negative and $\epsilon + \lambda = 0$ gives a projection that has an energy which is at least as low as the energy of $\gamma$. Thus, we do not increase the energy – in fact we strictly decrease the energy unless $\xi$ is a zero energy eigenvalue of Hartree–Fock operator $h_{Z,\gamma}^{HF}$ — by replacing the eigenvalue $\lambda$ by 0 or 1 depending on the sign of $\langle \xi, h_{Z,\gamma}^{HF} \xi \rangle$. However, the strict decrease would imply that $\gamma$ cannot be a minimizer. Thus, we are left with the case of an zero energy eigenvalue, the change in the energy is indifferent towards the $\epsilon$. By construction $\gamma_\epsilon$ is a minimizer and a projection.
The Euler equation, i.e., the equation that a minimizer $\gamma$ of the Hartree–Fock functional $E_{HF}$ fulfills, reads
\[
[h_{HF}, \gamma] = 0 \quad (5.12)
\]
or in orbital form
\[
h_{HF} \xi_n = -\mu_n \xi_n \quad (5.13)
\]
with Lagrange parameters $\mu_1, \ldots, \mu_N \in \mathbb{R}_+$, $\xi_1, \ldots, \xi_N$ orthonormal spinors, and $\gamma = |\xi_1\rangle\langle \xi_1| + \cdots + |\xi_N\rangle\langle \xi_N|$. The existence of minimizers, and thus the existence of solutions of the Hartree–Fock equations, has been shown for $N < Z + 1$ by Lieb and Simon [104]. Note, however, that, in general, one cannot expect uniqueness of the solution because of the lack of convexity of the exchange term.

Next we turn to a result that is well known for the traditional Hartree–Fock functional, i.e., the one with all the $\lambda_n$ equal to either 0 or 1.

**Theorem 5.3:** Pick $N \in \mathbb{N}$. If the infimum of $E_{HF}(D_{\partial N})$ is assumed, then we have for any $\gamma \in D_N$
\[
E^S(Z, N) \leq E_{HF}^H(\gamma). \quad (5.14)
\]

**Proof:** By Theorem 5.1 we know that $E_{HF}(\gamma)$ can be lowered unless $\gamma$ is a projection and $\inf \{E_{HF}(D_{\partial N})\}$ is assumed by a projection. Thus, we can assume $\gamma$ to be a projection in $D_{\partial N}$. Thus
\[
\gamma = |\xi_1\rangle\langle \xi_1| + \cdots + |\xi_N\rangle\langle \xi_N| \quad (5.15)
\]
for orthonormal $\xi_1, \ldots, \xi_N$ each in $H^1(\Gamma)$. We write
\[
\Psi := \sqrt{\frac{1}{N!}} |\xi_1(x_1) \cdots \xi_N(x_N)| \quad (5.16)
\]
for the Slater determinant of these orbitals. A straightforward computation shows
\[
E^S(Z, N) \leq \langle \Psi, H_{Z/|x|, N}\Psi \rangle = E_{Z}^{\text{classical}}_{HF}(\xi_1, \ldots, \xi_N)
\]
\[
= \sum_{n=1}^N \int_{\Gamma} dx \left( |\nabla \xi_n(x)|^2 - \frac{Z}{|x|} |\xi(x)|^2 \right) + \frac{1}{2} \int_{\Gamma^2} dx \, dy \sum_{n=1}^N |\xi_n(x)|^2 \sum_{m=1}^N |\xi_m(y)|^2 - \sum_{n=1}^N |\xi_n(x)\xi_n(y)|^2 \frac{|x - y|}{|x - y|}
\]
\[
= E_{Z}^{HF}(\gamma) \quad (5.17)
\]
where we used the Ritz variational principle [105] in the first step. \qed
In fact, Bach [102] proved a correlation bound that allows to prove also the reverse inequality (for suitable choice of $N$ that includes $N = Z$) up to errors yielding
\[
E_{\text{HF}}(Z) = E_{\text{TF}}(Z) + \frac{Z^2}{2} - \gamma_S Z^5 + o(Z^5).
\] (5.18)

As mentioned already in (4.89) the maximal number of electrons of any Hartree–Fock minimizer is bounded by $2Z + 1$. Solovej [44] has improved this by the following asymptotic bound.

**Theorem 5.4:** There exists a constant $C$ such for all $Z$ any minimizer of $E_{\text{HF}}^Z$ on $\mathcal{D}$ fulfills
\[
\text{tr}(\gamma) - Z \leq C,
\] (5.19)
i.e., the charge in excess of neutrality is bounded uniformly in the atomic number $Z$.

The method is to use Thomas–Fermi theory successively to screen the nucleus.

5.2. The Müller functional

Comparing with (2.31), the Hartree–Fock functional can be viewed as the full quantum functional with an ansatz for the two particle density
\[
\rho^{(2)}(x, y) := \frac{1}{2} \sum_{\sigma, \tau = 1}^{2} (\gamma(x, x)\gamma(y, y) - |\gamma(x, y)|^2).
\] (5.20)

This ansatz keeps the property that $\rho^{(2)} \geq 0$, which we showed in fact in (5.6) when we dominated the exchange term by the classical electron-electron interaction. However, it does, in general, not keep the normalization, since
\[
\int_{\mathbb{R}^6} \rho^{(2)} = \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{1}{2} \sum_{\sigma, \tau = 1}^{2} (\gamma(x, x)\gamma(y, y) - |\gamma(x, y)|^2)
\]
\[= \frac{1}{2} \left( N^2 - \text{tr}(\gamma^2) \right) \geq \left( \frac{N}{2} \right),
\] (5.21)
where equality holds if and only if $\gamma$ is a projection.

Müller [106] also makes an ansatz for the two-particle density, however reversing the situation. He keeps the normalization condition and gives up
the positivity. His ansatz is

$$\rho^{(2)}(x, y) := \frac{1}{2} \sum_{\sigma, \tau = 1}^{2} (\gamma(x, x)\gamma(y, y) - |\gamma^{\frac{1}{2}}(x, y)|^2)$$

(5.22)

where the root denotes the operator root, i.e., the eigenvalues of \( \gamma \) are replaced by their roots. (Actually Müller considered a family of functionals with the exchange part of the two-particle density depending on parameter \( p \in [0, \frac{1}{2}] \). The functional considered here is the case \( p = 0 \).) Thus the Müller functional reads

$$\mathcal{E}_Z^M : \mathcal{D} \rightarrow \mathbb{R},$$

$$\gamma \mapsto \text{tr} \left( -\frac{1}{2} \Delta \gamma \right) - \int_{\mathbb{R}^3} dx \frac{Z \rho_{\gamma}(x)}{|x|} + D[\rho_{\gamma}] - X[\gamma^{\frac{1}{2}}].$$

(5.23)

To show that the functional is well defined it suffices to show that \( X[\gamma^{\frac{1}{2}}] \) is finite, since the first three terms are identical with the first three terms of the Hartree–Fock functional.

$$X[\gamma^{\frac{1}{2}}] \leq \frac{1}{2} \int_{\Gamma} dy \, dx \frac{|\gamma^{\frac{1}{2}}(x, y)|^2}{|x - y|}$$

\[\leq \frac{1}{2} \sqrt{\int_{\Gamma^2} dy \, dx \, |\gamma^{\frac{1}{2}}(x, y)|^2} \sqrt{\int_{\Gamma^2} dy \, dx \, |\gamma^{\frac{1}{2}}(x, y)|^2} \]

\[\leq \sqrt{\text{tr}(\gamma)} \sqrt{\text{tr}(-\Delta \gamma)} < \infty \]

(5.24)

using the Schwarz inequality first and then, in the last step, Hardy’s inequality and the fact that \( \int_{\Gamma^2} dy \, dx \, |\gamma^{\frac{1}{2}}(x, y)|^2 = \text{tr}(\gamma) \). The functional has been analyzed by Frank et al. [107]. One of the interesting properties of the functional is its convexity which follows from an entropy inequality of Wigner and Yanase [108]. On the other hand it suffers from the same defect as the Thomas–Fermi–Dirac functional, the TF functional minus a \( \int \rho^{\frac{3}{2}} \)-term: Even if \( Z = 0 \) the infimum of the Müller functional is negative. Thus the binding energy of the electrons is not just the infimum of the Müller functional but the infimum at \( Z = 0 \), which turns out to be \( \text{tr}(\gamma)/8 \), has to be subtracted. We write \( \hat{\mathcal{E}}_Z^M \) for the correspondingly modified functional.

It is \( \hat{\mathcal{E}}_Z^M \) that determines the maximal number of electrons that can be bound. The critical electron number \( N_c^M \) — defined as the largest electron number \( N \) for which \( \hat{\mathcal{E}}_Z^M \) ceases to have a minimizer on \( \mathcal{D} \partial N \) — is at least \( Z \). On the other hand Frank et al. [109] showed that, like in the Hartree–Fock case, there is a constant \( C \) such that

$$N_c^M - Z \leq C$$

(5.25)
uniformly in $Z$. They use a different technique from the one used in (4.88) to obtain the necessary a priori bound followed by a variation of Solovej’s successive screening. The technique works also in the case of exchange terms that are not dominated by the classical electron-electron interaction like the Thomas–Fermi–Dirac–Weizsäcker functional where they developed their technique (Frank et al. [110]) (see also Chen et al. [87] for the a priori bound for the relativistic density functional of Engel and Dreizler). The bound (5.25) on the excess charge has been generalized by Kehle [111] to a functional of Sharma et al. [112] with $X[\gamma_1^2]$ replaced by $X[\gamma^p]$ with $p \in \left[\frac{1}{2}, 1\right]$ which interpolates between the Müller and the Hartree–Fock functional.

Energetically the same accuracy as for the Hartree–Fock functional in (5.18) is known, i.e.,

$$E^M(Z) = E^{TF}(Z) + \frac{Z^2}{2} - \gamma S Z^\frac{5}{3} + o(Z^\frac{5}{3})$$  \hspace{1cm} (5.26)

which is shown by proving $E^M(Z) = E^{HF} + o(Z^\frac{5}{3})$ (see [113, 114]).

Thus, as far as the current knowledge of the asymptotics of the ground-state energy is concerned, the Müller functional yields the Hartree–Fock functional accuracy. There are however indications that the two complement each other also in a different way: while the Hartree–Fock functional is known to yield an upper bound on the true quantum energy, it is conjectured that the ground-state energy of the Müller functional is a lower bound to the quantum molecular ground-state energy. Frank et al. [107, Section V] proved this for $N = 2$. Moreover, numerical evidence suggests that it might be true for all $N$. A positive answer to this question would give an even more advanced tool to estimate the energy of Coulomb systems from below than the Lieb–Thirring inequality with the conjectured classical constant.

Appendix: Maximal functions of powers and Thomas–Fermi energy of exchange holes

First we show that inverse powers $|x|^{-\alpha}$ are eigenfunctions of the maximal operator with eigenvalue $C_{\alpha,d} := M(|\cdot|^{-\alpha})(0, 0, 1)$ or less poetical

Lemma A.1: Assume $\alpha \in [0,d)$. Then

$$M(|\cdot|^{-\alpha}) = C_{\alpha,d} \cdot |\cdot|^{-\alpha}.$$  \hspace{1cm} (A.1)
Proof: We write $\omega_d$ for the volume of the unit ball in $d$ dimensions, pick $x \in S^2$, and compute

$$M(|\cdot|^\alpha)(x) := \sup_{R > 0} \frac{\int_{|x-y| < R} |y|^{-\alpha} \, dy}{\omega_d R^d} = \sup_{R > 0} \frac{\int_{|y| > R} |x-y|^{-\alpha} \, dy}{\omega_d R^d}$$

$$= \sup_{R > 0} \frac{|x|^{d-\alpha} \int_{|y| > |x|} \int_{|y| < |x|} |y|^{-\alpha} \, dy}{\omega_d |x|^d R^d} = |x|^{-\alpha} \sup_{R > 0} \frac{\int_{|y| > R} |y|^{-\alpha} \, dy}{\omega_d R^d}$$

(A.2)

where we observe in the first step that the integral does not depend on the direction of $x$, and in the second step we scale $y \rightarrow |x|^{-1} y$ and $R \rightarrow |x|^1 R$.

Next we turn to the infimum of the Thomas–Fermi functional with root of the Coulomb potential $(Z/|x|)^{\frac{1}{2}}$, arbitrary positive Thomas–Fermi constant $\gamma$, and constraint $\int \rho \leq Z$ on the electron number.

**Lemma A.2:** For $\gamma, Z, C \in \mathbb{R}_+$ and $M_Z := \{\rho \in L^\frac{2}{d}(\mathbb{R}^3) | \rho \geq 0, \int_{\mathbb{R}^3} \rho \leq Z\}$ set

$$I_{\gamma,Z} := \inf_{\rho \in M_Z} \int_{\mathbb{R}^3} \left( \frac{3}{5} \gamma \rho(x)^{\frac{5}{2}} - C \sqrt{\frac{Z}{|x|}} \rho(x) \right).$$

(A.3)

Then

$$I_{\gamma,Z} = \frac{Z^{\frac{4\gamma}{\gamma + 2}}}{\gamma + 2} I_{1,1}. \quad \text{(A.4)}$$

**Proof:** By scaling $\rho \rightarrow Z^\frac{1}{2} \rho(\alpha \cdot)$ we get

$$I_{\gamma,Z} = \frac{1}{\alpha^\frac{d}{2}} \inf_{\rho \in M_{1,1}} \int_{\mathbb{R}^3} \left( \frac{3}{5} \gamma Z^{\frac{1}{2}} \alpha^\frac{5}{2} \rho(x)^{\frac{5}{2}} - CZ^{\frac{1}{2}} \alpha^\frac{3}{2} Z \alpha^\frac{1}{2} \sqrt{\frac{1}{|x|}} \rho(x) \right).$$

(A.5)

Picking $\alpha := \gamma^{\frac{2}{7}} Z^{-\frac{3}{7}}$ implies $\gamma Z^{\frac{1}{7}} \alpha^\frac{5}{2} = Z^{\frac{1}{7}} \alpha^\frac{7}{2}$ which allows to take this common factor in front of the infimum yielding eventually

$$I_{\gamma,Z} = \frac{Z^{\frac{4\gamma}{\gamma + 2}}}{\gamma + 2} \inf_{\rho \in M_{1,1}} \int_{\mathbb{R}^3} \left( \frac{3}{5} \rho(x)^{\frac{5}{2}} - C \frac{1}{|x|^\frac{1}{2}} \rho(x) \right); \quad \text{(A.6)}$$

quod erat demonstrandum. \qed
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