Asymptotics of the ground state energy of heavy molecules and related topics

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Abstract

We consider asymptotics of the ground state energy of heavy atoms and molecules and derive it including Schwinger and Dirac corrections. We consider also related topics: an excessive negative charge, ionization energy and excessive negative charge when atoms can still bind into molecules.

Contents

Contents 1

0 Introduction 2
  0.1 Framework 3
  0.2 Problems to consider 4
  0.3 Thomas-Fermi theory 6
  0.4 Main results sketched and plan of the chapter 7

1 Reduction to semiclassical theory 9
  1.1 Lower estimate 9
  1.2 Upper estimate 12
  1.3 Remarks and Dirac correction 14
The purpose of this paper and several which will follow it is to apply semiclassical methods developed in the Book of the author [I7] to the theory of heavy atoms and molecules. Because of this we combine our semiclassical methods with the traditional methods of that theory, mainly function-analytic.

In this paper we consider the case without magnetic field. Next papers will be devoted to the cases of the self-generated magnetic field, strong external magnetic field and hyperstrong external magnetic field and combined external and self-generated fields. Basically this paper should be considered
as an introduction. This paper is a revitalization of [Ivr1] but in the case without magnetic field.

We explore the ground state energy, an excessive negative charge, ionization energy and excessive negative charge when atoms can still bind into molecules.

I learned all I know about Multiparticle Quantum Theory from Michael Sigal, Elliott Lieb, Philip Solovej. Some remarks of Volker Bach were very useful for the beginner in the field. I am extremely thankful to all of them.

## 0.1 Framework

Let us consider the following operator (quantum Hamiltonian)

\[ H = H_N := \sum_{1 \leq j \leq N} H_{V, x_j} + \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1} \]  

on

\[ \mathcal{F} = \bigwedge_{1 \leq n \leq N} \mathcal{H}, \quad \mathcal{H} = L^2(\mathbb{R}^d, \mathbb{C}^q) \]  

with

\[ H_V = D^2 - V(x) \]

describing \( N \) same type particles in the external field with the scalar potential \(-V\) (it is more convenient but contradicts notations of the previous chapters), and repulsing one another according to the Coulomb law.

Here \( x_j \in \mathbb{R}^d \) and \((x_1, ..., x_N) \in \mathbb{R}^{Nd}\), potential \( V(x) \) is assumed to be real-valued. Except when specifically mentioned we assume that

\[ V(x) = \sum_{1 \leq k \leq M} \frac{Z_m}{|x - y_m|} \]

where \( Z_k > 0 \) and \( y_k \) are charges and locations of nuclei.

Mass is equal to \( \frac{1}{2} \) and the Plank constant and a charge are equal to 1 here. The crucial question is the quantum statistics.

(0.1.5) We assume that the particles (electrons) are fermions. This means that the Hamiltonian should be considered on the Fock space \( \mathcal{F} \) defined by (0.1.2) of the functions antisymmetric with respect to all variables \((x_1, s_1), ..., (x_N, s_N)\).
Here \( \varsigma \in \{1, \ldots, q\} \) is a spin variable.

Remark 0.1.1. (i) Meanwhile for bosons one should consider this operator on the space of symmetric functions. The results would be very different from what we will get here. Since our methods fail in that framework, we consider only fermions here.

(ii) In this Chapter we do not have magnetic field and we can assume that \( q = 1 \); for \( q \geq 1 \) no modifications of our arguments is required and results are the same albeit with different numerical coefficients. In the next chapters we introduce magnetic field (external or self-generated) we will be interested in \( d = 3, q = 2 \) and

\[
H_{V,A} = ((i\nabla - A) \cdot \sigma)^2 - V(x)
\]

where \( \sigma = (\sigma_1, \sigma_2, \sigma_3) \), \( \sigma_k \) are Pauli matrices.

Let us assume that

\[
\text{(0.1.7) Operator } \mathcal{H} \text{ is self-adjoint on } \mathcal{H}.
\]

As usual we will never discuss this assumption.

0.2 Problems to consider

We are interested in the ground state energy \( E = E_N \) of our system i.e. in the lowest eigenvalue of the operator \( H = H_N \) on \( \mathcal{H} \):

\[
\text{(0.2.1) } E := \inf \text{ Spec } H \quad \text{on } \mathcal{H},
\]

more precisely we are interested in the asymptotics of \( E_N = E(y; Z; N) \) as \( V \) is defined by (0.1.4) and \( N \asymp Z := Z_1 + Z_2 + \ldots + Z_M \to \infty \) and we are going to prove that\(^1\) \( E \) is equal to Thomas-Fermi energy \( \mathcal{E}^{\text{TF}} \) with Scott and Dirac-Schwinger corrections and with \( o(Z^\frac{3}{2}) \) error.

Here we use notations \( y = (y_1, \ldots, y_M), Z = (Z_1, \ldots, Z_M). \)

We are also interested in the asymptotics for the ionization energy

\[
\text{(0.2.2) } I_N := -E_N + E_{N-1}.
\]

\(^1\) Under reasonable assumption \( |y_m - y_{m'}| \gg Z^{-\frac{1}{2}} \) for all \( m \neq m' \).
It is well-known (see G. Zhislin [Zh]) that $I_N > 0$ as $N \leq Z$ (i.e. molecule can bind at least $Z$ electrons) and we are interested in the following question: estimate maximal excessive negative charge

$$\max_{N: I_N > 0} N - Z$$

i.e. how many extra electrons can bind a molecule?

All these questions so far were considered in the framework of the fixed positions $y_1, ..., y_M$ but we can also consider

$$\widehat{E} = \widehat{E}_N = \widehat{E}(y; Z; N) = E + U(y; Z)$$

with

$$\sum_{1 \leq m < m' \leq M} \frac{Z_m Z_{m'}}{|y_m - y_{m'}|}$$

and

$$\widehat{E}(Z; N) = \inf_{y_1, ..., y_M} \widehat{E}(y; Z; N)$$

and replace $I_N$ by $\widehat{I}_N = -\widehat{E}_N + \widehat{E}_{N-1}$ and modify all our questions accordingly. We call these frameworks fixed nuclei model and free nuclei model respectively.

In the free nuclei model we can consider two other problems:

- Estimate from below minimal distance between nuclei i.e.

$$\min_{1 \leq m < m' \leq M} |y_m - y_{m'}|$$

for which such minimum is achieved;

- Estimate maximal excessive positive charge

$$\max_N \{ Z - N : \widehat{E} < \min_{N_1, ..., N_M: N_1 + ... + N_M = N} \sum_{1 \leq m \leq M} E(Z_m; N_m) \}$$

for which molecule does not disintegrates into atoms\textsuperscript{2).}

\textsuperscript{2) One can ask the same question about disintegration into smaller molecules but our methods are too crude to distinguish between such questions.}
0.3 Thomas-Fermi theory

The first approximation is the Thomas-Fermi theory. Let us introduce the spacial density of the particle with the state \( \Psi \in \mathcal{H} \):

\begin{equation}
\rho(x) = \rho_{\Psi}(x) = N \int |\Psi(x, x_2, ..., x_N)|^2 \, dx_2 \cdots dx_N
\end{equation}

where \( | \cdot | \) means a norm in \( \mathbb{C}^{Nq} \) and antisymmetricity of \( \Psi \) implies that it does not matter what variable \( x_j \) is replaced by \( x \) while in the general case one should sum on \( j = 1, ..., N \). Let us write the Hamiltonian, describing the corresponding “quantum liquid”:

\begin{equation}
\mathcal{E}(\rho) = \int \tau(\rho(x)) \, dx - \int V(x)\rho(x) \, dx + \frac{1}{2} D(\rho, \rho),
\end{equation}

with

\begin{equation}
D(\rho, \rho) = \iint |x - y|^{-1} \rho(x)\rho(y) \, dxdy
\end{equation}

where \( \tau \) is the energy density of a gas of noninteracting electrons. Namely,

\begin{equation}
\tau(\rho) = \sup_{w \geq 0} (\rho w - P(w))
\end{equation}

is the Legendre transform of the pressure \( P(w) \) given by the formula

\begin{equation}
P(w) = \kappa_1 w^{\frac{d+1}{d}}, \quad \kappa_1 = 2(2\pi)^{-d}(d + 2)^{-1} \omega_d.
\end{equation}

The classical sense of the second and the third terms in the right-hand expression of (0.3.2) is clear and the density of the kinetic energy is given by \( \tau(\rho) \) in the semiclassical approximation (see remark 0.3.1). So, the problem is

\begin{equation}
\text{(0.3.6) Minimize functional } \mathcal{E}(\rho) \text{ defined by (0.3.2) under restrictions:}
\end{equation}

\begin{equation}
\text{(0.3.7)}_{1,2} \quad \rho \geq 0, \quad \int \rho \, dx \leq N.
\end{equation}

The solution if exists is unique because functional \( \mathcal{E}(\rho) \) is strictly convex (see below). The existence and the property of this solution denoted further by \( \rho^{TF} \) is known in the series of physically important cases.
Remark 0.3.1. If $w$ is the negative potential then

\begin{equation}
(0.3.8) \quad \text{tr } e(x, x, 0) \approx P'(w)
\end{equation}

defines the density of all non-interacting particles with negative energies at point $x$ and

\begin{equation}
(0.3.9) \quad \int_{-\infty}^{0} \tau \, d\tau \, \text{tr } e(x, x, \tau) dx \approx -\int P(w) \, dx
\end{equation}

is the total energy of these particles; here $\approx$ means “in the semiclassical approximation”.

We consider in the case of $d = 3$ a large (heavy) molecule with potential (0.1.4). It is well-known\(^3\) that

**Proposition 0.3.2.** (i) For $V(x)$ given by (0.1.4) minimization problem (0.3.6) has a unique solution $\rho = \rho_{\mathrm{TF}}$; then denote $E_{\mathrm{TF}} := E(\rho_{\mathrm{TF}})$;

(ii) Equality in (0.3.7) holds if and only if $N \leq Z := \sum_{m} Z_{m}$;

(iii) Further, $\rho_{\mathrm{TF}}$ does not depend on $N$ as $N \geq Z$;

(iv) Thus

\begin{equation}
(0.3.10) \quad \int \rho_{\mathrm{TF}} \, dx = \min(N, Z), \quad Z := \sum_{1 \leq m \leq M} Z_{m}.
\end{equation}

### 0.4 Main results sketched and plan of the chapter

In the first half of the Chapter we derive asymptotics for ground state energy and justify Thomas-Fermi theory.

First of all, in Section 1 we reduce the calculation of $E$ to calculation of $N_{1}(H_{W} - \nu)$ and to estimate for $D(e(x, x, \nu) - \rho, e(x, x, \nu) - \rho)$ where $N_{1}(H_{W} - \nu) = \text{Tr}(H_{W} - \nu)^{-}$ is the sum of the negative eigenvalues of operator $H_{W} - \nu \ H_{W} = D^{2} - W$, $W = W_{\mathrm{TF}}$, $\rho = \rho_{\mathrm{TF}}$ are Thomas-Fermi potential and $\rho_{\mathrm{TF}}$

\(^3\) E. Lieb, “Thomas-fermi and related theories of atoms and molecules”, [L2], pp. 263–301.
Thomas-Fermi density respectively (or their appropriate approximations), \( \nu \) is either \( \lambda_N \) \((N\text{-th eigenvalue of } H_W)\) or its appropriate approximation and \( e(x, y, \nu) \) is the Schwartz kernel of \( E(\nu) \) which is the spectral projector of \( H_W \).

Section 2 is devoted to the systematic presentation of the Thomas-Fermi theory.

Further, in Section 3 we apply our semiclassical methods and calculate \( N_1(H_W - \nu) \) and estimate \( D(e(x, x, \nu) - \rho, e(x, x, \nu) - \rho) \) and also \( |\lambda_N - \nu| \) where now \( \nu \) is the chemical potential (which is the Thomas-Fermi approximation to \( \lambda_N \)). As a result under appropriate restrictions to \( N, Z \) and

\[
a := \min_{j \neq k} |y_j - y_k| \gg Z^{-\frac{1}{3}}
\]
we prove that

\[
E = \mathcal{E}^{\text{TF}} + \text{Scott} + \text{Dirac} + \text{Schwinger} + o(Z^{\frac{5}{3}})
\]
and

\[
D(\rho - \rho^{\text{TF}}, \rho - \rho^{\text{TF}}) = o(Z^{\frac{5}{3}})
\]
where

\[
\text{Scott} = q \sum_{1 \leq m \leq M} Z_m^2
\]

\[
\text{Dirac} = -\frac{9}{2}(36\pi)^{\frac{5}{3}}q^{\frac{5}{3}} \int (\rho^{\text{TF}})^{\frac{4}{3}} dx,
\]

\[
\text{Schwinger} = (36\pi)^{\frac{5}{3}}q^{\frac{5}{3}} \int (\rho^{\text{TF}})^{\frac{4}{3}} dx
\]
and \( \Psi \) is the ground state.

**Remark 0.4.1.** (i) Actually we will recover even slightly better remainder estimate \( O(Z^{\frac{5}{3} - \delta}) \) in (0.4.2) and (0.4.3) as \( a \geq Z^{-\frac{1}{3} + \delta} \).

(ii) Condition \( a \geq Z^{-\frac{1}{3}} \) bans nuclei to be so close that the repulsion energy between them be much larger than the total energy of all the electrons. Estimates in case when this condition is violated will be also proven;

(iii) Keeping in mind that there is no binding in Thomas-Fermi theory (and this statement could be quantified) one gets immediately that in the free nuclei model \( a \geq Z^{-\frac{5}{3}} \) and therefore remainder estimate \( O(Z^{\frac{5}{3} - \delta}) \) holds.
Due to scaling in the Thomas-Fermi theory (see proposition 2.2.1) \( \mathcal{E}^{\text{TF}} \sim q^\frac{2}{3} \overline{Z}^\frac{2}{3} = q^3 (q^{-1} Z)^\frac{2}{3} \), Scott \( q Z^2 = q^3 (q^{-1} Z)^2 \), and both Dirac and Schwinger are \( \sim q^\frac{1}{3} \overline{Z}^\frac{1}{3} = q^3 (q^{-1} Z)^\frac{1}{3} \).

In the second half of the Chapter we apply estimate (0.4.3) to investigate negatively and positively charged systems. In Section 4 we consider negatively charged systems and derive an upper estimate for the excessive negative charge \( (N - Z) \) such that \( Z > 0 \) and ionization energy \( \mathcal{I}_N \) itself.

In Section 5 we derive upper and lower estimates for \( \mathcal{I}_N + \nu \) and an upper estimate for the excessive positive charge for which in the framework of the free nuclei model \( a < \infty \).

1 Reduction to semiclassical theory

To justify the heuristic formula \( E \sim \mathcal{E}^{\text{TF}} = \mathcal{E}(\rho^{\text{TF}}) \) and to find an error estimate let us deduce the lower and upper estimates for \( E \).

1.1 Lower estimate

For the lower estimate we apply the electrostatic inequality due to E. H. Lieb:

\[
\sum_{1 \leq j < k \leq N} \int |x_j - x_k|^{-1} |\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \geq \frac{1}{2} D(\rho_\Psi, \rho_\Psi) - C \int \rho_\Psi^\frac{4}{3}(x) \, dx
\]

with \( \rho_\Psi \) defined by (0.3.1). This inequality holds for all (not necessarily antisymmetric) functions \( \Psi \) with \( \|\Psi\|_{L^2(\mathbb{R}^3)} = 1 \). Therefore

\[
\langle H\Psi, \Psi \rangle \geq \sum_{1 \leq j \leq N} \langle H_{V,x_j} \Psi, \Psi \rangle + \frac{1}{2} D(\rho_\Psi, \rho_\Psi) - C \int \rho_\Psi^\frac{4}{3}(x) \, dx =
\]

\[
\sum_{1 \leq j \leq N} \langle H_{V,x_j} \Psi, \Psi \rangle + \frac{1}{2} D(\rho_\Psi - \rho, \rho_\Psi - \rho) - \frac{1}{2} D(\rho, \rho) - C \int \rho_\Psi^\frac{4}{3}(x) \, dx
\]

where \( \langle \cdot, \cdot \rangle \) means the inner product in \( \mathcal{H} \) and \( H_{V} \) is one-particle Schrödinger operator with the potential

\[
W = V - |x|^{-1} \ast \rho,
\]
where \( \rho \) is an arbitrary chosen real-valued non-negative function.

The physical sense of the second term in \( W \) is transparent: it is a potential created by a charge \(-\rho\). Skipping the positive second term in the right-hand expression of (1.1.2) and believing that the last term is not very important for the ground state function \( \Psi \) we see that we need to estimate from below the first term.

Here assumption that \( \Psi \) is antisymmetric is crucial. Namely, for general (or symmetric—does not matter) \( \Psi \) the best possible estimate is \( N\lambda_1 \) where \( \lambda_1 \) is the lowest eigenvalue of \( H_W \) (we always assume that there is sufficiently many eigenvalues under the bottom of the essential spectrum of \( H_W \)) and we cannot apply semiclassical theory. However, for antisymmetric \( \Psi \) situation is rather different.

Namely, let \( \lambda_1 \leq \lambda_2 \leq \lambda_3 \leq \ldots \) be negative eigenvalues of \( H_W \) (on \( \mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^q) \)). Then the first term in the right-hand expression of (1.1.2) is bounded from below by

\[
\sum_{1 \leq j \leq N} \lambda_j = N_1(H_W - \bar{\lambda}) + \bar{\lambda}N
\]

where \( N(B), N_1(B) = \text{Tr } B^- \) are the number and the sum of all the negative eigenvalues of operator \( B \) respectively such that \( \text{Spec}_{\text{ess}}(B) \subset \mathbb{R}^+ \) provided \( \bar{\lambda} = \lambda_N < 0 \); the latter assumption is equivalent to

\[
N(H_W) \geq N.
\]

Applying the semiclassical approximation (which needs to be justified!) one gets

\[
N_1(H_W - \bar{\lambda}) = N_1(H_W - \bar{\lambda}) + \text{error}_1
\]

with

\[
N_1(H_W - \bar{\lambda}) := -\int P(W(x) + \bar{\lambda}) \, dx
\]

and therefore the lower estimate for the ground state energy is

\[
E \geq -\int P(W + \bar{\lambda}) \, dx + \bar{\lambda}N - \frac{1}{2}D(\rho, \rho) - \text{error}
\]

---

\textsuperscript{4)} As we derive also an upper estimate for \( E \) we will get an upper estimate for this term as a bonus.
where error now includes both an estimate for $\int \rho^2 \psi^4 \, dx$ and the semiclassical remainder estimate.

Furthermore, applying a semiclassical approximation for the number $N(H - \bar{\lambda})$ of eigenvalues below $\bar{\lambda}$ (and this number should be approximately $N$) one gets an equality

$$N = \mathcal{N}(H_W - \bar{\lambda}) + \text{error}_0$$

with

$$\mathcal{N}(A - \bar{\lambda}) := \int P'(W(x) + \bar{\lambda}) \, dx$$

where error$_0$ is a semiclassical approximation here.

To get the best possible lower estimate one should pick up $\rho$ delivering maximum to the functional

$$(1.1.11) \quad - \int P(W(x) + \nu) \, dx + \nu N - \frac{1}{2} D(\rho, \rho)$$

($\nu = \bar{\lambda}$ here) under assumptions $(0.3.7)_{1,2}$ and $(1.1.3)$ as we skip all the errors.

One can see that the optimal choice is the Thomas-Fermi potential and density. The above arguments are very standard in MQT with $\rho = \rho^{TF}$, $W = W^{TF}$ from the very beginning.

On the other hand, let us consider the Euler-Lagrange equation for $\rho = \rho^{TF}$ under condition $\int \rho \, dx = N$:

$$(1.1.12) \quad \tau'(\rho) - W = \nu \quad (\rho > 0), \quad W = V - |x|^{-1} * \rho$$

with the Lagrange factor $\nu$ $^6)$. Expressing $\rho$ and integrating we get

$$(1.1.13) \quad N = \mathcal{N}(H_W - \nu) = \int P'(W(x) + \nu) \, dx.$$ 

Comparing $(1.1.12)$ and $(1.1.13)$ we get that with some error $\bar{\lambda} \sim \nu$. Substituting to the first term in $(1.1.6)$ $\bar{\lambda} = \nu$ and $\nu - W = -\tau'_B(\rho)$ we get the lower estimate $E \geq E^{TF} - \text{error}.$

$^5)$ Or some their close approximations.

$^6)$ Called chemical potential and in contrast to $\bar{\lambda}$ belonging to Thomas-Fermi theory.
Remark 1.1.1. (i) Instead of (1.1.6) we will use a better estimate\(^7\):

\[
\sum_{1 \leq j \leq N} \lambda_j = \sum_{1 \leq j \leq N} (\lambda_j - \nu) + \nu N \geq N_1 (H_W - \nu) + \nu N.
\]

The advantage is that we even do not mess up with the semiclassical asymptotics for \(N(H_W - \nu)\). Further, one can replace here \(N\) by \(\int \rho^{\text{TF}} dx\):

(1.1.14) \(\sum_{1 \leq j \leq N} \lambda_j \leq \sum_{1 \leq j \leq N} (\lambda_j - \nu) + \nu N \geq \mathcal{N}_1 (H_W - \nu) + \nu N\).

(1.1.15) \(N(H_W) < N\).

we estimate the first term in the right-hand expression of (1.1.2) from below by \(N_1(H_W)\) i.e. we will get the same formula but with \(\nu = 0\).

1.2 Upper estimate

To get the upper estimate one takes a test function \(\Psi(x_1, \ldots, x_N)\) which is not a ground state here but an antisymmetrization with respect to \((x_1, \ldots, x_N)\) of the product \(\phi_1(x_1) \cdots \phi_N(x_N)\) where \(\phi_1, \ldots, \phi_N\) are orthonormal eigenfunctions of \(H_W\) corresponding to eigenvalues \(\lambda_1, \ldots, \lambda_N\), provided \(\lambda_N < 0\). Namely this function minimizes the first term in the right-hand expression of (1.1.2).

One can write

\[
\Psi = \frac{1}{N!} \det(\phi_i(x_j))_{i,j=1,\ldots,N}
\]

and it is called Slater determinant. Obviously, \(\|\Psi\| = 1\) and

\[
\rho_\Psi(x) = \text{tr} e_N(x, x)
\]

where

\[
e_N(x, y) = \sum_{1 \leq j \leq N} \phi_j(x)\phi_j^\dagger(y)
\]

is the Schwartz kernel of the projector to the subspace spanned on \(\{\phi_j\}_{1 \leq j \leq N}\).

\(\Psi\) is the Slater determinant. Obviously, \(\|\Psi\| = 1\) and

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\]

where

\[
e_N(x, y) = \sum_{1 \leq j \leq N} \phi_j(x)\phi_j^\dagger(y)
\]

is the Schwartz kernel of the projector to the subspace spanned on \(\{\phi_j\}_{1 \leq j \leq N}\).
Remark 1.2.1. If \( q \geq 2 \) then \( \phi_j = \phi_j(x, \varsigma) \) and \( \Psi(x_1, \varsigma_1; \ldots; x_N, \varsigma_N) \) is an anti-symmetrization with respect to \( (x_1, \varsigma_1; \ldots; x_N, \varsigma_N) \) of the product \( \phi_1(x_1, \varsigma_1) \cdots \phi_N(x_N, \varsigma_N) \).

Easy calculations show that

\[
\langle H \Psi, \Psi \rangle = \sum_{1 \leq j \leq N} \lambda_j + \frac{1}{2} D(\rho_\Psi - \rho, \rho_\Psi - \rho) - \frac{1}{2} D(\rho, \rho) - \frac{1}{2} \int |x - y|^{-1} \text{tr} e^+_n(x, y)e_n(x, y) \, dx \, dy.
\]

The first term in the right-hand expression again is equal to the middle expression in (1.1.4) which does not exceed

\[
N_1(H_W - \nu) + \nu N + |\lambda_N - \nu| \cdot |N(H_W - \nu) - N|.
\]

Really, we need to consider (non-zero) terms which do not cancel in

\[
\sum_{j \leq N} (\lambda_j - \nu) - \sum_{\lambda_j < \nu} (\lambda_j - \nu)
\]

and their absolute value does not exceed \( |\lambda_N - \nu| \) while their number does not exceed \( |N(H_W - \nu) - N| \).

Again, discounting all the errors and considering semiclassical approximation (including \( \rho_\Psi(x) \sim P'(W(x) + \nu) \)) we arrive to a functional

\[
-\int P(W(x) + \nu) \, dx + \nu N - \frac{1}{2} D(\rho, \rho) + \frac{1}{2} D(P'(W + \nu) - \rho, P'(W + \nu) - \rho)
\]

which needs to be minimized under assumptions (0.3.7)_{1,2} and (1.1.3). This functional differs from (1.1.11) which was minimized by the last term. One can prove that (1.2.6) minimizes as \( \rho = \rho^\text{TF} \), \( W = W^\text{TF} \) and \( \nu \) is a chemical potential. So again we may pick them (or their appropriate approximations) up from the very beginning.

Therefore in addition to a semiclassical error of the previous subsection we need to consider also semiclassical errors

\[
\begin{align*}
(1.2.7) & \quad D(\text{tr} \, e(x, x, \nu) - P'(W + \nu), \text{tr} \, e(x, x, \nu) - P'(W + \nu)), \\
(1.2.8) & \quad D(e(x, x, \nu) - e_N(x, x), e(x, x, \nu) - e_N(x, x))
\end{align*}
\]
where \( e(x, y, \nu) \) is the Schwartz kernel of the spectral projector \( \theta(\tau - H_W) \) of \( H_W \),

(1.2.9) \[ N(H_W - \nu) - \int P'(W + \nu) \, dx \]

and

(1.2.10) \[ \lambda_N - \nu. \]

**Remark 1.2.2.** (i) Recall that we assumed that \( \lambda_N < 0 \) i.e. (1.1.5) holds. In the opposite case (1.1.15) selecting appropriate \( \phi_j(x) \) with \( j = N(H_W) + 1, \ldots, N \) we with arbitrarily small error estimate the first term in the right-hand expression of (1.1.2) from above by \( N_1(H_W) \) as i.e. we will get the same formula but with \( \nu = 0 \) and we also will need to estimate (1.2.7) with \( \nu = 0 \).

(ii) To make this case compatible with the case (1.1.5) we will need to estimate \( |\nu| \) (and \( |N - Z| \)) under assumption (1.1.15); we will also compare \( \mathcal{E}_{TF} \) calculated for such \( \nu \) (or, equivalently, \( N \) as they are connected) and \( \nu = 0 \) (and \( N = Z \)).

(iii) Sure \( \rho_{TF} \) and \( W_{TF} \) depend on \( \nu \) (or \( N \)) but we will prove that for \( N - Z \) relatively small we can do all calculations as \( \nu = 0 \) (and \( N = Z \)).

(iv) If we are interested in the estimate for \( D(\rho_{\Psi} - \rho_{TF}, \rho_{\Psi} - \rho_{TF}) \) where \( \Psi \) is the ground state, we do not need to calculate a semiclassical error in \( N_1(H_W - \nu) \); in fact we can simply stick with \( N_1(H_W - \tilde{\lambda}) \) with \( \tilde{\lambda} = \lambda_N \) under assumption (1.1.5) and \( \tilde{\lambda} = 0 \) otherwise. As a result in certain cases our estimate for \( D(\rho_{\Psi} - \rho_{TF}, \rho_{\Psi} - \rho_{TF}) \) will be better than the error in an approximation for \( \Psi \) and we need the former rather than the latter for the results of the second half of this Chapter. Especially significant the difference will be when we introduce magnetic field.

### 1.3 Remarks and Dirac correction

Now almost everything is in framework of the theory we developed; the only missing is an estimate

(1.3.1) \[ \int \rho_{\Psi}^{\frac{4}{3}} \, dx \leq CZ^{\frac{5}{3}} \]
for a reasonable candidate $\Psi$ to the ground state; one can find it in E. Lieb’s Selecta$^3$.

However if we want a more sharp asymptotics with Dirac–Schwinger terms, we need a remainder estimate $o(Z^{\frac{5}{2}})$ or better; luckily there is improved electrostatic inequality due to Theorem 1, G. Graf and J. P. Solovej [GS] (see also V. Bach [Ba]).

**Theorem 1.3.1.** Let $N \geq \epsilon Z$. Then for the ground state $\Psi$

\begin{align}
E_{HF} & \geq E \geq E_{HF} - CZ^{\frac{5}{2} - \delta} \\
E & \geq E_{DS} - CZ^{\frac{5}{2} - \delta}
\end{align}

with some exponent $\delta > 0$ where

\begin{equation}
E_{HF} := \inf_{\Psi} E_{HF}(\Psi),
\end{equation}

where in (1.3.4) $\Psi$ runs through Slater determinants$^8$) and

\begin{equation}
E_{HF}(\Psi) := \sum_{1 \leq j \leq N} \langle H_{V,x_j} \Psi, \Psi \rangle + \frac{1}{2} D(\rho_\Psi, \rho_\Psi) -
\frac{1}{2} \int \int |x - y|^{-1} \text{tr} e_N^1(x, y)e_N(x, y) \text{d}x \text{d}y,
\end{equation}

\begin{equation}
E_{DS} := \sum_{j: 1 \leq j \leq N; \lambda_j < 0} \lambda_j - \frac{1}{2} D(\rho^{TF}, \rho^{TF}) - \kappa_{\text{Dirac}} \rho^{TF}^{\frac{4}{7}} \text{d}x,
\end{equation}

$\kappa_{\text{Dirac}} = (2\pi)^{-3} q c_{TF}^2$, $c_{TF} = (6\pi^2 / q^2)^{\frac{3}{2}}$ is a Dirac constant.

Here (1.3.2)–(1.3.5) are (1.15), (1.16), (1.8), (1.6) respectively and (1.3.6) is a combination of (1.12) and (2.2.12) of this paper$^9)$. Actually we need only (1.3.3) and (1.3.6).

$^8)$ Albeit not necessarily of eigenfunctions of $H_W$.

$^9)$ We do not have a coefficient $\frac{1}{2}$ in the definition of $D(., .)$ but G. Graf and J. P. Solovej [GS] have.
As we are going to prove that the last terms in (1.3.5) and (1.2.4) coincide modulo $O(Z^{\frac{5}{2}-\delta})$ we made a necessary step completely.

2 Thomas-Fermi theory

Thomas-Fermi theory is well-developed in the no-magnetic-field case. We cannot suggest any better reading than E. Lieb’s Selecta\(^3\).

In the Thomas-Fermi theory $N$ is a real nonnegative number (not necessarily an integer).

2.1 Existence

Let us recall that in order to get the best lower estimate (neglecting semiclassical errors) one needs to maximize

$$\Phi_*(W + \nu) := -\int P(W + \nu) \, dx - \frac{1}{8\pi} \| \nabla (W - V) \|^2$$

given by (1.1.11) where we used equalities

$$D(\rho, \rho) = -(\rho, W - V) = \frac{1}{4\pi} \| \nabla (W - V) \|^2,$$

(2.1.3)  \[ \rho := \frac{1}{4\pi} \Delta (W - V), \]

$\| . \|$ means $L^2$-norm and $W \to 0$ as $|x| \to \infty$.

On the other hand, to get the best possible upper estimate (neglecting semiclassical errors) one needs to minimize

$$\Phi^*(\rho', \nu) := \int (\tau(\rho') - \nu \rho') \, dx + \frac{1}{2} D(\rho', \rho') - \nu \int \rho' \, dx$$

where

(2.1.5)  \[ \rho' := P'(W + \nu) \]

and $\tau(\rho)$ the Legendre transformation (0.3.4) of $P$. Recall that according to (0.3.5)

$$P(w) = \frac{q}{15\pi^2} w^5_+, \quad P'(w) = \frac{q}{6\pi^2} w^3_+$$

16
and therefore
\[ \tau(\rho) = \frac{3}{5} (6\pi^2 q^{-1})^{\frac{3}{2}} \rho^\frac{5}{3}. \] (2.1.7)

**Proposition 2.1.1.** In our assumptions for any fixed \( \nu \leq 0 \)

(i) \( \Phi_*(W + \nu) \) is a strictly concave functional;

(ii) \( \Phi^*(\rho) \) is a strictly convex functional;

(iii) \( \Phi_*(W + \nu) \leq \Phi^*(\rho, \nu) \) for any \( \rho \geq 0 \) and \( W \),

(iv) These extremal problems have a common solution \( W \) and \( \rho \) and

\[ \rho = \frac{1}{4\pi} \Delta(W - V) = P'(W + \nu), \] (2.1.8)

\[ W = o(1) \quad \text{as} \quad |x| \to \infty; \] (2.1.9)

(v) On the other hand, solution of (2.1.8)–(2.1.9) is the solution of the both extremal problems;

(vi) Neither of these problem has a solution for \( \nu > 0 \);

(vii) Function

\[ N(\nu) = \int P'(W + \nu) dx \] (2.1.10)

is continuous and monotone increasing at \( (-\infty, 0] \) with \( N(\nu) \to 0 \) as \( \nu \to -\infty \) and \( N(0) = Z \);

(viii) For \( \nu \) and \( N \) linked by \( N = N(\nu) \) solutions of the problem above coincide with \( \rho^{TF}, W^{TF} \) of the problem (0.3.6) and one can skip condition (0.3.6)$_2$ for \( N \geq Z \) and

\[ \mathcal{E}^{TF} = \Phi(W^{TF} + \nu) + \nu N = \Phi^*(\rho^{TF}, \nu) + \nu N. \] (2.1.11)

**Proof.** The proof of statements (i),(ii) is obvious; therefore both problems have unique solutions. Comparing Euler-Lagrange equations we get that these solutions coincide which yields (iv) and (iii). Proof of (v)–(vii) is also rather obvious. \( \Box \)
Proposition 2.1.2. For arbitrary $W$ the following estimates hold with absolute constants $\epsilon_0 > 0$ and $C_0$:

\[
(2.1.12) \quad \epsilon_0 D(\rho - \rho^{\text{TF}}, \rho - \rho^{\text{TF}}) \leq \Phi_*(W^{\text{TF}} + \nu) - \Phi_*(W + \nu) \leq C_0 D(\rho - \rho', \rho - \rho')
\]

and

\[
(2.1.13) \quad \epsilon_0 D(\rho' - \rho^{\text{TF}}, \rho' - \rho^{\text{TF}}) \leq \Phi^*(\rho, \nu) - \Phi^*(\rho^{\text{TF}}, \nu) \leq C_0 D(\rho - \rho', \rho - \rho')
\]

with $\rho = \frac{1}{4\pi} \Delta(W - V)$, $\rho' = P'(W + \nu)$.

Proof. This proof is rather obvious as well. \qed

2.2 Properties

Proposition 2.2.1. The solution of the Thomas-Fermi problem has following scaling properties

\[
(2.2.1) \quad W^{\text{TF}}(x; Z; y; N; q) = q^\frac{3}{2} N^\frac{1}{4} W^{\text{TF}}(q^\frac{3}{2} Z^\frac{1}{2} x; N^{-1} Z; q^\frac{1}{2} N^\frac{1}{2} y; 1; 1),
\]

\[
(2.2.2) \quad \rho^{\text{TF}}(x; Z; y; N; q) = N^2 q^2 \rho^{\text{TF}}(q^\frac{3}{2} Z^\frac{1}{2} x; N^{-1} Z; q^\frac{1}{2} N^\frac{1}{2} y; 1; 1),
\]

\[
(2.2.3) \quad \mathcal{E}^{\text{TF}}(Z; y; N; q) = q^\frac{3}{2} N^\frac{1}{2} \mathcal{E}^{\text{TF}}(N^{-1} Z; q^\frac{1}{2} N^\frac{1}{2} y; 1; 1),
\]

\[
(2.2.4) \quad \nu^{\text{TF}}(Z; y; N; q) = q^\frac{3}{2} N^\frac{1}{2} \nu^{\text{TF}}(N^{-1} Z; q^\frac{1}{2} N^\frac{1}{2} y; 1; 1)
\]

where $\nu^{\text{TF}} = \nu$ is the chemical potential; recall that $Z = (Z_1, \ldots, Z_M)$ and $y = (y_1, \ldots, y_M)$ are arrays and parameter $q$ also enters into Thomas-Fermi theory.

Proof. Proof is trivial by scaling. \qed

As we can exclude $q$ by scaling we do not indicate dependence on it anymore.

Proposition 2.2.2. Let $M = 1$. Then the solution of the Thomas-Fermi problem has the following properties:
(i) \( W^{TF}(x; Z_m, y_m; N) \) and \( \rho^{TF}(x; Z_m, x_m; N) \) are spherically symmetric (with respect to \( y_m \)) and are non-increasing convex functions of \( |x - y_m| \);

(ii) As \( N = Z_m \)

\[
W^{TF} \propto \min(Z_m|x - y_m|^{-1}, |x - y_m|^{-4}),
\]

\[
\rho^{TF} \propto \min(Z^3_m|x - y_m|^{-\frac{3}{2}}, |x - y_m|^{-6})
\]

with the threshold at \( |x - x_m| \approx r^*_m = Z^{-\frac{1}{3}}_m \) when \( W^{TF} \approx Z^4_m \) and \( \rho^{TF} \approx Z^2_m \).

(iii) As \( \epsilon Z_m \leq N < Z_m \)

\[
- \nu \propto |Z_m - N|^{\frac{1}{3}}
\]

and (2.2.5) holds as \( |x - y_m| \leq \bar{r}_m \propto -\nu|Z_m - N|^{-1} \) while

\[
W^{TF} \propto (Z_m - N)|x - y_m|^{-1} \quad \text{as} \quad |x - y_m| \geq |Z_m - N|^{-\frac{1}{3}};
\]

(iv) Meanwhile \( \rho^{TF} = 0 \) as \( |x - y_m| \geq \bar{r}_m \) and \( \rho^{TF} = O(|Z_m - N|^2) \) as \( |x - y_m| \leq \bar{r}_m \).

For atoms let \( \bar{r}_m \) denote the exact radius of support of \( \rho^{TF} \).

**Proposition 2.2.3.** As \( M \geq 2 \)

\[
\sum_m \epsilon W_m^{TF}(C(x - y_m)) \leq W^{TF} \leq C \sum_m W_m^{TF}(\epsilon(x - y_m))
\]

where \( W_m^{TF} \) stays for an atomic solution with the charge \( Z_m \) located at \( y_m \) and the same chemical potential \( \nu \).

**Proof.** Proof is due to comparison arguments of E. Lieb, J. P. Solovej and J. Yngvarsson [LSY1, LSY2]. \( \square \)

**Proposition 2.2.4.** (i) Let \( N \leq Z \) and

\[
l(x) = \frac{1}{2} \min_m |x - y_m|,
\]

\[
\zeta(x) = (W^{TF}(x))^\frac{1}{2};
\]
Then

$$(2.2.12) \quad \zeta(x) \leq \tilde{\zeta}(x) = \begin{cases} Z^\frac{1}{2} \ell(x)^{-\frac{1}{2}} & \text{as } \ell(x) \leq Z^{-\frac{1}{2}}, \\ \ell(x)^{-2} & \text{as } Z^{-\frac{1}{2}} \leq \ell(x) \leq |Z - N|^{-\frac{1}{2}}, \\ |Z - N|^\frac{1}{2} \ell(x)^{-\frac{1}{2}} & \text{as } \ell(x) \geq |Z - N|^{-\frac{1}{2}}; \end{cases}$$

$\zeta(x)$ and $\tilde{\zeta}(x)$ are both $\ell$-admissible and

$$(2.2.13) \quad |D^\alpha W^{TF}(x)| \leq C_\alpha \zeta(x)^2 \ell(x)^{-|\alpha|} \quad \forall \alpha : |\alpha| \leq 3,$$

and

$$(2.2.14) \quad |D^\alpha W^{TF}(x) - D^\alpha W^{TF}(y)| \leq C_\alpha \zeta(x)^2 \ell(x)^{-\frac{1}{2}} |x - y|^\frac{1}{2} \quad \forall x, y : |x - y| \leq \varepsilon \ell(x)$$

(ii) Unless $\zeta(x) \asymp (-\nu)^\frac{1}{2}$ estimates (2.2.14) hold for all $\alpha$.

**Proof.** This proof is rather obvious corollary of the Euler-Lagrange equation. \(\square\)

**Remark 2.2.5.** Let

$$(2.2.15) \quad Z_m \asymp N \quad \forall m.$$ 

Then $\zeta(x) \asymp \tilde{\zeta}(x)$.

**Theorem 2.2.6.** 10) Consider $\mathcal{E}^{TF}$ and

$$(2.2.16) \quad \mathcal{E}^{TF} := \mathcal{E}^{TF} + U,$$

$$(2.2.17) \quad U = U(Z_1, \ldots, Z_M; y_1, \ldots, y_M) = \sum_{1 \leq m < m' \leq M} \frac{Z_m Z_{m'}}{|x_m - x_{m'}|}.$$ 

Select a nucleus $y_m$ and a unit vector $n$ such that

$$(2.2.18) \quad \langle y_k - y_m, n \rangle \leq 0 \quad \forall k$$

and plug $y_m + \alpha n$ instead of $x_m$ into $\mathcal{E}^{TF}$ and into $\mathcal{E}^{TF}$ 11). Then

---

10) Theorem 1 of R. Benguria [Be].

11) So all other nuclei are confined in half-space and $y_m$ moves away outside
(i) $\mathcal{E}^\text{TF}_\alpha$ is a non-increasing function of $\alpha \geq 0$;

(ii) $\mathcal{E}^\text{TF}_\alpha$ is a non-increasing function of $\alpha \geq 0$;

(iii)–(iv) For fixed $\alpha > 0$ both $\mathcal{E}^\text{TF}_\alpha - \mathcal{E}^\text{TF}_0$ and $\mathcal{E}^\text{TF}_\alpha - \mathcal{E}^\text{TF}_0$ are non-decreasing functions of $N$.

Equality

\begin{equation}
\nu = \frac{\partial \mathcal{E}^\text{TF}}{\partial N}
\end{equation}

implies that (iii)–(iv) is equivalent to

\begin{equation}
\nu_\alpha \geq \nu_0.
\end{equation}

**Theorem 2.2.7.**

(i) For fixed $Z_1, \ldots, Z_M; y_1, \ldots, y_M$ and $N = Z$

\begin{equation}
\lambda^7 \mathcal{E}^\text{TF}(Z; \lambda y; N) = \mathcal{E}^\text{TF}(\lambda^3 Z; \lambda y^3; \lambda^3 N)
\end{equation}

is positive non-decreasing function of $\lambda > 0$ and has a finite limit as $\lambda \to +\infty$;

(ii) This limit does not depend on $Z_1, \ldots, Z_M$. 

Scaling property without assumption $N = Z$ holds for $\mathcal{E}^\text{TF}$ and $U$ as well. These two theorems imply immediately

**Proposition 2.2.8.** Let (2.2.15) be fulfilled. Then

\begin{equation}
\mathcal{E}^\text{TF}(Z; y; N) - \min_{N_1, \ldots, N_M} \sum_{1 \leq m \leq M} \mathcal{E}^\text{TF}(Z_m; N_m) \geq \epsilon \min(a^{-7}, Z^2)
\end{equation}

where

\begin{equation}
a = \frac{1}{2} \min_{m < m'} |y_m - y_{m'}|.
\end{equation}

---

12) (1.8)–(1.9) of H. Brezis and E. Lieb [BrL].
**Proof.** In virtue of theorem 2.2.6(i) it suffices to prove proposition for \( M = 2 \) (all other nuclei could be pulled to infinity), and in virtue of theorem 2.2.6(iii) it suffices to prove proposition for \( Z = N \).

Then the proof is due to theorem 2.2.7(i) and (2.2.15), which provides uniformity.

**Remark 2.2.9.** In virtue of (2.2.19) the minimum (with respect to \( N_1, \ldots, N_M \)) in the sum in the right hand expression is reached when \( \nu_j = \nu_k \) for all \( j, k \). The same is true for a system of isolated molecules.

**Proposition 2.2.10.** Let \( \mathcal{Q} \) denote Thomas-Fermi excess energy which is the left-hand expression of (2.2.22). Then

\[
(2.2.24) \quad D(\rho^{\text{TF}} - \bar{\rho}^{\text{TF}}, \rho^{\text{TF}} - \bar{\rho}^{\text{TF}}) \leq C \mathcal{Q}, \quad \bar{\rho}^{\text{TF}} := \sum_{1 \leq m \leq M} \rho_m^{\text{TF}}.
\]

**Proof.** We follow “non-binding” proof due to Baxter (see E. Lieb *Selecta*3).

According to Baxter lemma there exist \( g, 0 \leq g \leq \rho^{\text{TF}} \) and \( h = \rho^{\text{TF}} - g \) such that \( g * |x|^{-1} = V_1 \) a.e. when \( h > 0 \) and \( g * |x|^{-1} \leq V_1 \) a.e. when \( h = 0 \). Here \( V_m = Z_m|x - y_m|^{-1} \).

Let \( \alpha = \int g \, dx, \beta = \int h \, dx \) and let \( \mathcal{E}_1^{\text{TF}}, \mathcal{E}^{\text{TF}}' \) be Thomas-Fermi energies for the first atom and for the rest of molecule respectively and \( \rho_1^{\text{TF}}, \rho^{\text{TF}}' \) be corresponding Thomas-Fermi densities. Then

\[
(2.2.25) \quad \min_{N_1 + N' \leq N} \left( \mathcal{E}_1^{\text{TF}}(N_1) + \mathcal{E}^{\text{TF}}'(N') \right) \leq \mathcal{E}_1(\alpha) + \mathcal{E}^'(\beta) \leq \\
\mathcal{E}(g) + \mathcal{E}'(h) - \varepsilon D(g - \rho_1^{\text{TF}}, g - \rho_1^{\text{TF}}) - \varepsilon D(\rho^{\text{TF}} - \rho' , h - \rho') \leq \\
\mathcal{E}(g + h) + \int h(V_1 - g * |x|^{-1}) \, dx - \int (V_1 - |g * |x|^{-1}) \, d\mu' \\
- \varepsilon D(g - \rho_1^{\text{TF}}, g - \rho_1^{\text{TF}}) - \varepsilon D(\rho^{\text{TF}} - \rho'^{\text{TF}}, h - \rho'^{\text{TF}})
\]

where \( \mu_1, \mu' \) are measures with densities \( Z_1 \delta(x - y_1) \) and \( \sum_{2 \leq m \leq M} Z_m \delta(x - y_m) \) and we used the superadditivity of \( \tau(\rho) = \rho^{\frac{3}{2}} \). The last expression doesn’t exceed

\[
(2.2.26) \quad \mathcal{E}^{\text{TF}} - \varepsilon D(g - \rho_1^{\text{TF}}, g - \rho_1^{\text{TF}}) - \varepsilon D(h - \rho'^{\text{TF}}, h - \rho'^{\text{TF}}).
\]
Using induction with respect to $M$ we arrive to

\[(2.2.27) \quad D(\rho^{TF} - \rho_1^{TF} - \rho^{TF}, \rho^{TF} - \rho_1^{TF} - \rho^{TF}) \leq 2D(g - \rho_1^{TF}, g - \rho_1^{TF}) + 2D(h - \rho^{TF}, h - \rho^{TF}) \leq CQ\]

and finally to (2.2.24).

\[\text{Problem 2.2.11.} \quad \text{Find the stronger lower bound in (2.2.22) as } N < Z. \quad \text{Would be the left-hand expression } \preceq \min(a^{-7} + |Z - N|^2a^{-1}, Z^\frac{1}{2})?\]

3 Application of semiclassical methods

3.1 Asymptotics of the trace

In this subsection we calculate asymptotics of $\text{Tr}(H_W - \nu)^-$. Here we need to consider both inner and outer zones.

An inner zone (near nucleus $x_m$) is a ball where $V_j = Z_m|x - y_m|^{-1}$ dominates $W - V_m$. For a single nucleus ($M = 1$) it is defined by

\[|x - y_m| \leq \epsilon Z_m^{-\frac{1}{2}}\]  

(3.1.1)

but in the case $M \geq 2$ there are another restrictions

\[|x - y_m| \leq \epsilon \min_{m' \neq m}(Z_m(Z_m + Z_{m'})^{-1}|y_m - y_{m'}|)\]  

(3.1.2)

and

\[|x - y_m| \leq Z_m^{\nu^{-1}}\]  

(3.1.3)

but we shrink this zone to

\[|x - y_m| \leq r_m := \epsilon \min(Z_mZ^{-1}a, Z_m^{-\frac{1}{2}}).\]  

(3.1.4)

Let us consider contribution of the zone $X_m$ described by (3.1.4) to $N_1(H_W - \nu) = \text{Tr}(H_W - \nu)^-$, both into the principal part of asymptotics and
the remainder. Let \( \psi_m \) be a partition element concentrated in \( \mathcal{X}_m \) and equal to 1 in \( \{ x : |x - y_m| \leq \frac{1}{2} r_m \} \). Then according to Theorem 12.5.8 of [I7]

\[
\text{Tr}((H_W - \nu)^{-1}\psi_m) = \int \text{Weyl}_1(x) \psi_m(x) \, dx + \text{Scott}_m + O(R_m)
\]

where \( \text{Weyl}_1(x) \) and \( \text{Scott}_m \) are calculated for the case \( q = 1 \) and then multiplied by \( q^{13} \):

\[
\text{Weyl}_1(x) := -\frac{q}{15\pi^2} (W(x) + \nu)^{\frac{5}{2}}
\]

while \( R_m \) is \( C\zeta^2(\zeta \ell) = C\zeta^3 \ell \) calculated on its border i.e.

\[
R_m = CZ_m^2 + CZ_m r_m^{-1} \leq CZ_m^3 + CZ^3 a^{-\frac{1}{2}}.
\]

Really, one needs just to rescale \( x \mapsto (x - y_m)r_m^{-1} \) and \( \tau \mapsto \tau Z_m^{-1} r_m \) and introduce a semiclassical parameter \( h = Z_m r_m \).

**Remark 3.1.1.** (i) These arguments work only as \( r_m \geq Z_m^{-1} \) (i.e. \( Z_m^2 \geq a^{-1}Z \));

(ii) As \( Z_m^2 \geq a^{-1}Z \) but \( a \geq Z^{-1} \) we define \( r_m = a^{\frac{1}{2}}Z^{-\frac{1}{2}} \) and we do not include \( \text{Scott}_m^{14} \) into the principal expression; moreover, in this case we include \( \mathcal{X}_m \) into a singular zone and use variational methods to estimate its contribution into the principal part of asymptotics; it will not exceed \( CZa^{-1} \leq CZ^3 a^{-\frac{1}{2}} \);

(iii) Furthermore, as \( a \leq Z^{-1} \) we set \( r_m = Z^{-1} \) and we do not include any \( \text{Scott}_m^{14} \) into the principal part of asymptotics and include all \( \mathcal{X}_m \) into singular zones; using variational methods we estimate their contributions into the principal part of asymptotics by \( CZ^2 \).

Therefore

\[
\text{(3.1.8)} \text{ The total contribution of all inner zones into remainder does not exceed the right-hand expression of (3.1.7) as } a \geq Z^{-1} \text{ and } CZ^2 \text{ as } a \leq Z^{-1}.
\]

---

13) As operator \( H_w - \nu \) is nothing but \( q \) copies of \( \Delta - (W + \nu) \).

14) However it will be less than the remainder estimate, so we can include it into the principal part of asymptotics anyway.
Let us consider contributions of the outer zone $\mathcal{X}_0$ which is complimentary to the union of inner zones. Then

\begin{equation}
(3.1.9) \quad \text{Tr}((H_W - \nu)^-\psi_0) = \int \text{Weyl}_1(x)\psi_0(x) \, dx + O(R_0)
\end{equation}

with $\text{Weyl}_1(x)$ defined by (3.1.6) where

\begin{equation}
(3.1.10) \quad R_0 = \int_{\mathcal{X}_0} C\tilde{\zeta}(x)^3\ell^{-2} \, dx
\end{equation}

and

\begin{equation}
(3.1.11) \quad \tilde{\zeta} = \begin{cases}
Z^{\frac{3}{2}}\ell^{-\frac{1}{2}} & \text{as } \ell \leq Z^{-\frac{1}{2}}, \\
\ell^{-2} & \text{as } \ell \geq Z^{-\frac{1}{2}}.
\end{cases}
\end{equation}

We justify (3.1.9)–(3.1.11) a bit later by an appropriate partition of unity. One can see easily that contribution of $\{x: \ell(x) \leq Z^{-\frac{1}{2}}\}$ into expression (3.1.10) does not exceed the same expression as in (3.1.8) and that contribution of $\{x: \ell(x) \geq Z^{-\frac{1}{2}}\}$ into (3.1.10) does not exceed $CZ^\frac{5}{2}$. Then we arrive to

**Theorem 3.1.2.** Let $W = W^{\text{TF}}, N \asymp Z, W = W^{\text{TF}}$. Then

\begin{equation}
(3.1.12) \quad \text{Tr}(H_W - \nu)^- = \int \text{Weyl}_1(x) \, dx + \sum_{1 \leq m \leq M} \text{Scott}_m + O(R),
\end{equation}

with

\begin{equation}
(3.1.13) \quad R := \begin{cases}
CZ^\frac{5}{2} + CZ^\frac{3}{2}a^{-\frac{1}{2}} & \text{as } a \geq Z^{-1}, \\
CZ^2 & \text{as } a \leq Z^{-1}.
\end{cases}
\end{equation}

**Proof.** (i) Consider $\nu = 0$ first. Then we just apply $\ell$-admissible partition of unity. Sure, $\zeta \ell \leq 1$ as $\ell \geq 1$ but we can deal with it either by taking $\zeta = \ell^{-1}$ here or considering it as a singular zone and applying here variational estimate as well.

(ii) Variational estimate works for $\nu < 0$ as well; furthermore, zone $\{x: W(x) \leq (1 - \epsilon)\nu, \ell \geq |\nu|^{-\frac{1}{2}}\}$ is classically forbidden.

(iii) However as $\nu \leq -c$ we have a little problem as $W^{\text{TF}}$ is not very smooth, it is only $C^{\frac{7}{2}}$ as $W \asymp -\nu$. The best\footnote{From the point of view of generalization to the case when magnetic field is present and it is not too weak, so magnetic version of $W^{\text{TF}}$ has multiple singularities.} way to deal with it is to take...
\( \varepsilon \ell \)-mollification with \( \varepsilon = h^{1-\delta} \), \( h = (\zeta \ell)^{-1} \), use rough microlocal analysis of Section 4.5 of [I7] and framing; it will bring an approximation error not exceeding \( C\varepsilon^{\frac{3}{2}}h^{-3}|\nu| \) which does not exceed \( |\nu| = O(|Z - N|^\frac{3}{2}) \). We leave easy details to the reader.

Now we arrive to the lower estimate for \( E \):

**Corollary 3.1.3.** As \( N \asymp Z \)

\[(3.1.14) \quad E \geq \mathcal{E}^{TF} + \text{Scott} - CR \]

with \( R \) defined by (3.1.13).

**Proof.** We know from subsection 1.1 that

\[(3.1.15) \quad E \geq N_1(H_W - \nu) + \nu N - \frac{1}{2}D(\rho, \rho) - CZ^{\frac{3}{2}} \]

as \( W \) is given by (1.1.3). In virtue of theorem 3.1.2

\[(3.1.16) \quad E \geq \int \text{Weyl}_1(x) \, dx + \nu \int \text{Weyl}(x) \, dx - \frac{1}{2}D(\rho, \rho) + \text{Scott} - CR \]

where we also plugged instead of \( N \) as \( N < Z \) (and \( \nu < 0 \))

\[(3.1.17) \quad N = \int \text{Weyl}(x) \, dx \]

with

\[(3.1.18) \quad \text{Weyl}(x) = \frac{q}{6\pi^2} (W(x) + \nu)^{\frac{3}{2}}. \]

One can check easily that three first terms in the right-hand expression of (3.1.18) constitute exactly \( \Phi_s(W + \nu) \) coinciding with \( \mathcal{E}^{TF} \) as \( W = W^{TF} \).\( \Box \)

**Remark 3.1.4.** (i) As \( a \leq Z^{-\frac{1}{2}} \) using the same method one can prove a slightly better remainder estimate–with \( Z^{\frac{3}{2}}a^{-\frac{3}{2}} \) replaced by

\[(3.1.19) \quad \sum_{1 \leq m < m' \leq M} \min\left( \left( Z_m + Z_{m'} \right)^{\frac{3}{2}}|x_m - x_{m'}|^{-\frac{3}{2}}, (Z_m + Z_{m'})^2 \right) \]

allowing to lighter nuclei to be closer one to another.

(ii) To improve it further allowing lighter nuclei to be closer to heavier ones one needs to improve Theorem 12.5.8 of [I7] which seems to be too difficult task for a such little gain.

26
3.2 Upper estimate for $E$

Recall that in virtue of subsection 1.2

\[ E \leq N_1(H_W - \nu) + \nu N - \frac{1}{2}D(\rho, \rho) + |\lambda_N - \nu| \cdot |N(H_W - \nu) - N| + \frac{1}{2}D(\text{tr} e_N(x, x) - \rho, \text{tr} e_N(x, x) - \rho) \]

and thus we need to estimate two last terms in the right-hand expression.

3.2.1 Estimating $|\lambda_N - \nu|$

First we need to estimate $|\lambda_N - \nu|$. We will use the heuristic equality $N(H_W - \lambda_N) \approx N$ or more precisely

\[ (3.2.2)_{1,2} \quad N(H_W - \lambda_N - 0) \leq N \leq N(H_W - \lambda_N + 0) \]

and equality

\[ (3.2.3) \quad \int \text{Weyl}(x) \, dx = \text{min}(N, Z) \]

where the $(3.2.2)_{2}$ is valid only if $\lambda_N < 0$ i.e. $N(H_W) \geq N$.

Case $\lambda_N < \nu$.

Then we will use $(3.2.2)_{2}$ and to calculate $N(H_W - \lambda_N + 0)$ we will use semiclassical approximation:

\[ (3.2.4) \quad N(H_W - \lambda_N + 0) = \int \text{Weyl}(x, \lambda_N) \, dx + O(R_0) \]

with the semiclassical error

\[ (3.2.5) \quad R_0 = \int \zeta^2 \ell^{-1} \, dx \]

with integral not exceeding

\[ CZ \int_{\{|x| \leq Z^{-\frac{1}{3}}\}} |x|^{-2} \, dx + C \int_{\{|x| \geq Z^{-\frac{1}{3}}\}} |x|^{-5} \, dx \sim CZ^\frac{2}{3}; \]
again we need to consider separately cases of $N \geq Z$ and $\nu = 0$ when integral (3.2.5) is taken over $\mathbb{R}^3$ and $N < Z$ and $\nu < 0$ when it should be taken over $\{\ell(x) \leq C(Z - N)^{-\frac{1}{2}}\}$; in the latter case to cover non-smoothness we consider an approximation (mollification) of $W$ and an approximation error $\varepsilon^\frac{1}{2} h^{-3} \ll 1$. Therefore

(3.2.6) \[ \int \text{Weyl}(x, \lambda_N) \, dx \geq N - CZ^\frac{3}{2} \]

comparing with (3.2.3) we conclude that

(3.2.7) \[ \int \left( (W(x) + \nu)^\frac{3}{2} - (W(x) + \lambda_N)^\frac{3}{2} \right) \, dx \leq CZ^\frac{2}{3} \]

Here an integrand is non-negative (since $\lambda_N < \nu$) and one can see easily that the main contribution to integral is delivered by zone $\{x : \ell(x) \simeq |\lambda_N|^{-\frac{1}{2}}\}$ and the whole integral is $\simeq |\lambda_N|^{-\frac{1}{2}} |\nu - \lambda_N|$. Therefore (3.2.7) yields

\[ |\lambda_N - \nu| \leq C(|\nu| + |\lambda_N - \nu|)^\frac{1}{2} Z^\frac{3}{2} \]

which is equivalent to

(3.2.8) \[ |\lambda_N - \nu| \leq CZ^\frac{1}{2} + C|\nu|^{\frac{1}{2}} Z^\frac{3}{2} \simeq CZ^\frac{3}{2} + C(Z - N)^{\frac{1}{2}} Z^\frac{3}{2} \leq CZ. \]

In particular

(3.2.9) If $|\nu| \leq c_0 Z^\frac{3}{2}$ (i.e. $(Z - N)_+ \leq c_1 Z^\frac{3}{2}$) then $|\lambda_N| \leq C_0 Z^\frac{3}{2}$

and

(3.2.10) \[ |\lambda_N - \nu| \cdot |N(H_W - \nu) - N| \leq CZ \cdot Z^\frac{3}{2} = CZ^\frac{3}{2}. \]

**Case** $\lambda_N \geq \nu$.

Then we will use (3.2.2) but if $N(H_W) < N$ then integral (3.2.5) is diverging.

To avoid all related difficulties we will consider first the case when we necessarily conclude that $|\lambda_N| \geq (1 - \epsilon)|\nu|$. To do so note that even

\[ |\lambda_N| \leq C_0 Z^\frac{3}{2}. \]

On the other hand, if $|\lambda_N| \geq C_0 Z^\frac{3}{2}$ one can see easily that (3.2.7) is $\simeq Z$ because $|\nu| \leq c_0 Z^\frac{3}{2}$ due to $N \simeq Z$. 

28
if the main contribution to integral (3.2.7)\(^{17}\) is delivered by zone \(\{x : \ell \propto (Z - N)|\lambda_N|^{-1} \gg |\nu|^\frac{2}{3}|\lambda_N|^{-1}\}\), we will ignore it considering a zone \(\{x : \ell(x) \leq C_0|\nu|^\frac{2}{3}\}\) instead of \(\{x : \ell(x) \leq C_0|\nu|^\frac{2}{3}|\lambda_N|^{-1}\}\)\(^{18}\).

One can prove easily that

(3.2.11) The contribution of zone \(\{\ell \leq C_0|\nu|^\frac{2}{3}\}\) to the semiclassical remainder when calculating \(N(H_W - \lambda_N)\) does not exceed \(CZ^\frac{2}{3}\).

Therefore we arrive to

(3.2.12) \(|\lambda_N - \nu| \leq C|\nu|^\frac{1}{2}Z^\frac{1}{3} \cong C(Z - N)^\frac{1}{3}Z^\frac{1}{3} \leq CZ\)

(cf. (3.2.8)). In particular

(3.2.13) If \(|\nu| \geq CZ^\frac{2}{3}\) (i.e. \((Z - N) \geq CZ^\frac{2}{3}\)) then \(|\lambda_N| \approx |\nu|\)

(cf. (3.2.9)). Then one can easily recover (3.2.8) completely. Since \(|N(H_W - \nu) - N| \leq CZ^\frac{2}{3}\) we arrive to (3.2.10).

**Case** \(|\nu| \leq \eta = CZ^\frac{2}{3}\).

This case (i.e. \((Z - N) \leq \eta^\frac{2}{3} = CZ^\frac{2}{3}\)) is the most important one. The easiest way to tackle it is to pick up \(\rho^{TF}\) and \(W^{TF}\) calculated as if \(\nu = 0\) i.e. \(Z = N\); that means the change of the test function \(\Psi\) in the upper estimate.

We need to modify an upper estimate of \(\sum_{1 \leq j \leq N} \lambda_j\). To do this we note that

(3.2.14) \(\lambda_N \geq -\eta\)

and

(3.2.15) A number of eigenvalues between \(\lambda_N\) (if \(\lambda_N < 0\)) and 0 does not exceed \(CZ^\frac{2}{3} + C\eta^\frac{2}{3}\)

which can be proven easily by our standard methods. Therefore

(3.2.16) \(\sum_{1 \leq j \leq N} \lambda_j \leq \text{Tr} H_W + C\eta(Z^\frac{2}{3} + \eta^\frac{2}{3})\)

and the last term is less than \(CZ^\frac{5}{3}\) as long as \(\eta \leq CZ^\frac{20}{11}\) which is fulfilled.

In this last case\(^{19}\) we arrive to an upper estimate with \(\mathcal{E}^{TF}\) calculated

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\(^{17}\) Now an integrand is non-positive.

\(^{18}\) Obviously these zones coincides as \(|\nu| \approx |\lambda_N|\).

\(^{19}\) Pending an analysis of the next subsubsection.
as if \( \nu = 0 \) i.e. \( \mathcal{E}^{TF}(Z; y; Z) \) which is less than \( \mathcal{E}^{TF}(Z; y; N) \). Actually the difference between these two is \( \simeq |\nu|^\frac{2}{3} \leq |\eta|^\frac{2}{3} \).

### 3.2.2 Estimating D-term

We need to estimate the last term in the right-hand expression of (3.2.1); we estimate it by

\[
\begin{align*}
C_0 D(\operatorname{tr} e(x, x, \nu) - P'(W + \nu), \operatorname{tr} e(x, x, \nu) - P'(W + \nu)) \\
+ C_0 D(\operatorname{tr} e(x, x, \nu) - \operatorname{tr} e_N(x, x), \operatorname{tr} e(x, x, \nu) - \operatorname{tr} e_N(x, x)) \\
+ C_0 D(\rho - P'(W + \nu), \rho - P'(W + \nu))
\end{align*}
\]

where the last term vanishes as \( \rho = \rho^{TF}, W = W^{TF} \); however for technical reasons we want to avoid this assumption.

#### Estimating the first term.

To estimate the first term in (3.2.17) we apply semiclassical asymptotics

\[
\operatorname{tr} e(x, x, \nu) = \text{Weyl}(x) + O(\zeta^2 \ell^{-1})
\]

where \( \text{Weyl}(x) = P'(W(x) + \nu) \) and therefore this term does not exceed

\[
\int \int \zeta(x)^2 \zeta(y)^2 \ell(x)^{-1} \ell(y)^{-1} |x - y|^{-1} \, dx \, dy.
\]

Estimating this integral by the double sum of integrals over domains \( \{(x, y) : \ell(x) \leq Z^{-\frac{1}{3}}, \ell(y) \leq Z^{-\frac{1}{3}} \} \) and \( \{(x, y) : \ell(x) \geq Z^{-\frac{1}{3}}, \ell(y) \geq Z^{-\frac{1}{3}} \} \) we get

\[
CZ^2 \int \int_{\{|x| \leq Z^{-\frac{1}{3}}, |y| \leq Z^{-\frac{1}{3}} \}} |x|^{-2} |y|^{-2} |x - y|^{-1} \, dx \, dy
\]

and

\[
C \int \int_{\{|x| \geq Z^{-\frac{1}{3}}, |y| \geq Z^{-\frac{1}{3}} \}} |x|^{-3} |y|^{-3} |x - y|^{-1} \, dx \, dy
\]

respectively and rescaling we get the same integrals but both with the “threshold” \( \frac{1}{3} \) rather than \( Z^{-\frac{1}{3}} \) and both with factor \( Z^\frac{2}{3} \) rather than \( Z^2 \) or 1 respectively; one can see easily that both integrals (without factor \( Z^\frac{2}{3} \)) are \( \asymp 1 \) and then (3.2.19) is \( O(Z^\frac{2}{3}) \).

Therefore we proved
Proposition 3.2.1. As $W = W^{\text{TF}}$ the first term in (3.2.17) does not exceed $CZ^{\frac{3}{2}}$.

Remark 3.2.2. (i) For $N \geq Z$ and $\nu = 0$ we used that $\zeta \leq C_1 \ell^{-2}$ for $\ell \geq Z^{-\frac{1}{2}}$;

(ii) for $N < Z$ and $\nu < 0$ we used that zone $\{x : \ell \geq C(Z - N)^{-\frac{1}{2}}\}$ is classically forbidden ($W + \nu < 0$ there) and therefore integral is taken over zone $\{x : \ell \leq C(Z - N)^{-\frac{1}{2}}\}$ where $\zeta \leq C_1 \ell^{-2}$;

(iii) As $N < Z$ $W^{\text{TF}}$ is not very smooth near $W + \nu = 0$ but one can handle it by rescaling arguments;

(iv) Alternatively (preferably\textsuperscript{15}) one can replace $W^{\text{TF}}$ by its mollification $W^{\text{TF}}_{\varepsilon}$.

Estimating the second term.

Consider now the second term in (3.2.17). Due to arguments of the previous paragraph modulo $O(Z^{\frac{3}{2}})$ one can rewrite it as

\begin{equation}
C_1 D(P'(W + \lambda_N) - P'(W + \nu), P'(W + \lambda_N) - P'(W + \nu)).
\end{equation}

Really, if we replace $\text{tr} e(x, x, \nu)$ and $\text{tr} e_N(x, x)$ by Weyl$(x, \nu)$ and Weyl$(x, \lambda_N)$ respectively we make a semiclassical errors estimated by $Z^{\frac{3}{2}}$ provided either $\lambda_N < \nu$ or $\lambda_N \asymp \nu$ which is always the case unless $|\nu| \leq CZ^{\frac{3}{2}}$ but in this case we just “cheat” resetting everything to the case $\nu = 0$.

Let us estimate (3.2.22). According to the previous subsubsection there are two cases:

(i) $N \geq Z - CZ^{\frac{3}{2}}$, in which case $|\nu| \leq CZ^{\frac{3}{2}}$ and $|\lambda_N| \leq CZ^{\frac{3}{2}}$, and (3.2.22) does not exceed

\begin{align*}
C|\nu - \lambda_N|^2 \int_{\{\ell(x) \leq L, \ell(y) \leq L\}} |x - y|^{-1} \zeta(x) \zeta(y) \, dxdy \\
+ C \int_{\{\ell(x) \geq L, \ell(y) \geq L\}} |x - y|^{-1} \zeta(x) \zeta(y)^3 \, dxdy
\end{align*}

with $L = |\lambda_N - \nu|^{-\frac{1}{4}}$; one can calculate easily that both terms are $\asymp C|\lambda_N - \nu|^2 \leq CZ^{\frac{3}{2}} \ll Z^{\frac{3}{2}}$.
(ii) $N \leq Z - CZ^{\frac{2}{3}}$, in which case (3.2.22) does not exceed
\[
C|\nu - \lambda_N|^2 \int \int_{\{\ell(x) \leq L, \ell(y) \leq L\}} |x - y|^{-1} \zeta(x) \zeta(y) \, dx \, dy
\]
with $L = |\nu|^{-\frac{1}{2}}$ and this integral does not exceed $|\lambda_N - \nu|^2 |\nu|^{-\frac{1}{2}}$ which due to (3.2.8) does not exceed $C(Z - N)^{\frac{1}{2}} Z^{\frac{5}{3}} \leq CZ^{\frac{5}{3}}$.

**Estimating the third term.**

The third term in (3.2.17) does not exceed
\[
C_1 D(\rho - \rho^{TF}, \rho - \rho^{TF}) + C_1 D(P'(W + \nu) - P'(W^{TF} + \nu), P'(W + \nu) - P'(W^{TF} + \nu))
\]
and we leave to the reader an easy proof that both terms here are $O(Z^{\frac{5}{3} - \delta})$ as $W$ is a described mollification of $W^{TF}$.

### 3.2.3 Finally, a theorem

As we finished an upper estimate for $E$ we arrive to

**Theorem 3.2.3.** Let $N \ll Z$ and let $\Psi$ be a ground state. Then

\[
(E - \mathcal{E}^{TF} - \text{Scott}) \leq C \begin{cases} Z^{\frac{5}{3}} + Ca^{-\frac{1}{2}} Z^{\frac{5}{3}} & \text{as } a \geq Z^{-1}, \\ Z^2 & \text{as } a \leq Z^{-1} \end{cases}
\]

where $a$ is the minimal distance between nuclei.

### 3.3 Improved asymptotics

So far as $a \geq Z^{-\frac{1}{3}}$ we recovered only $O(Z^{\frac{5}{3}})$ for both error estimate in $E$ and (as a coproduct, see subsection 3.4) for $D(\rho_\psi - \rho^{TF}, \rho_\psi - \rho^{TF})$.

Our purpose is to improve them to $o(Z^{\frac{5}{3}})$ (or slightly better) as $a \geq Z^{-\frac{1}{3}}$ and recover Schwinger and Dirac terms. To do so in the lower estimate for $E$ one just need an improved electrostatic inequality (see Theorem 1.3.1) and also improved semiclassical estimates in $\text{Tr}(H_W - \nu)^-$ and $N(H_W - \nu)$. 

32
For improved upper estimate we will need also to improve estimate
\[ \frac{1}{2} \mathcal{D}(\rho_\Psi - \rho_T, D(\rho_\Psi - \rho_T^T)) \] for the test function \( \Psi \) and apply an estimate
\[
\int |x - y|^{-1} \text{tr} e^i_N(x, y) e^i_N(x, y) \, dx \, dy + \kappa_{\text{Dirac}} \int \rho_T^T(x) \, dx \leq Z^{\frac{5}{3} - \delta}
\]
which is due to Theorem 6.3.17\(^{20}\) of [I7].

**Remark 3.3.1.** (i) Only contribution of zones
\[
\{ x : Z^{-\frac{1}{2} - \delta_1} \leq |x - y_m| \leq Z^{-\frac{1}{2} b^{\delta_1}} \}
\]
with \( b := \min(aZ^{\frac{1}{2}}, Z) \) should be considered as contribution of both zones \( \{ x : \ell(x) \leq Z^{-\frac{1}{2} b^{\delta_1}} \} \) and \( \{ x : \ell(x) \leq Z^{-\frac{1}{2} b^{\delta}} \} \) are \( O(Z^{\frac{5}{6} b^{-\delta}}) \).

(ii) Only \( m \) with \( Z_m \geq Z b^{-\delta_2} \) should be considered as contribution of others is lesser than the remainder estimate.

**Proposition 3.3.2.** Let \( \vartheta \) be a (small) parameter such that \( b^{-\delta_2} \leq \vartheta \leq 1 \); consider \( m \) with \( Z_m \geq Z \vartheta^{\delta_1} \). Let \( \phi(x) = \psi(r^{-1}(x - y_m)) \) with \( \psi \in C^\infty_0(B(0, 1)) \) and \( r \) defined below.

(i) Further, let \( (Z - N)^{-1} \geq r = Z^{-\frac{1}{2}} \vartheta^{-1} \). Then inequalities
\[
| \int \phi(x) \int_{-\infty}^\lambda (e(x, x, \lambda') - \text{Weyl}(x, \lambda')) \, dx \, d\lambda' - \text{Scott – Schwinger} | \leq CZ^{\frac{2}{3}} \vartheta^\delta,
\]
\[
| \int \phi(x) (e(x, x, \lambda) - \text{Weyl}(x, \lambda)) \, dx | \leq CZ^2 \vartheta^\delta
\]
and
\[
D\left( \phi(e(x, x, \lambda) - \text{Weyl}(x, \lambda)), \phi(e(x, x, \lambda) - \text{Weyl}(x, \lambda)) \right) \leq CZ^{\frac{5}{6}} \vartheta^\delta
\]
hold with some exponent \( \delta > 0 \) for all \( \lambda \leq 0 \) and for \( \phi \) which is \( r \)-admissible.

\(^{20}\) This theorem implies the above estimate with \( \delta = 1 \) which is definitely overkill for our purposes.
(ii) On the other hand, let \((Z - N)^{-\frac{1}{3}} \leq r\). Let \(W\) be a constructed above mollification of \(W^{TF}\). Then

(a) Estimates (3.3.3)–(3.3.5) hold for all \(\lambda \leq \nu\);
(b) Further, estimates (3.3.4), (3.3.5) hold for \(\lambda \in [\nu, 0]\) such that \(N(H - \lambda) \leq N\).
(c) Furthermore, in this last case

\[
(3.3.6) \quad |\lambda - \nu| \leq CZ^{\frac{2}{3}}(Z - N)^{\frac{1}{3}}\vartheta^\delta.
\]

To prove these statements we need to study behavior of the Hamiltonian trajectories. First we want to prove that in the indicated zone \(W^{TF}\) is a weak perturbation of \(W_m^{TF}\) which is a single atom Thomas-Fermi potential with \(Z_m\) and with \(\nu_m = \nu\).

**Proposition 3.3.3.** In the framework of proposition 3.3.2 in \(B(y_m, r)\)

\[
(3.3.7) \quad |D^\alpha(W^{TF} - W_m^{TF})| \leq c_\alpha W_m^{TF} |x - y_m|^{-|\alpha|} \vartheta^\delta.
\]

This estimate holds for all \(\alpha\) as \(W^{TF}/(-\nu)\) is disjoint from 1; otherwise it holds for \(|\alpha| \leq 3\) and

\[
(3.3.8) \quad |D^\alpha(W^{TF} - W_m^{TF}) (x) - D^\alpha(W^{TF} - W_m^{TF})(y)| \leq cW_m^{TF} [x - x_m]^{-\frac{\vartheta}{2}} |x - y|^{\frac{1}{2}} \vartheta^\delta
\]

as \(|\alpha| = 3\) and \(|x - x_m| \asymp |y - y_m| \asymp (Z - N)^{-\frac{1}{3}}\).

**Proof.** An easy proof based on variational approach is left to the reader. \(\square\)

Next let us consider manifold \(\Sigma_\lambda = \{(x, \xi) : H(x, \xi) = \lambda\}\) with \(H(x, \xi) = |\xi|^2 - W(x)\), and let us introduce a measure \(\mu_\lambda\) with the density \(dx d\xi : dH\) on \(\Sigma_\lambda\); this measure is invariant with respect to the Hamiltonian flow with the Hamiltonian \(H(x, \xi)\). Note that \(\mu_\lambda(\Sigma_\lambda) \asymp Z\).

**Proposition 3.3.4.** In the framework of proposition 3.3.2 there exists a set \(\Sigma'_{\lambda, \vartheta} \subset \Sigma_\lambda\) such that

\[
(3.3.9) \quad \mu_\lambda(\Sigma'_{\lambda, \vartheta}) \leq C \vartheta^\delta Z
\]

34
and through each point \((x, \xi)\) belonging to \(\vartheta(Z^{-\frac{1}{2}}, Z^{-\frac{3}{2}})\)-vicinity of \(\Sigma \setminus \sum_{\lambda, \delta}'\) there passes a Hamiltonian trajectory \((x(t), \xi(t))\) of \(H\) of the length \(T = Z^{-\frac{1}{2}}\vartheta^{-\delta}\) along which

\[
(D_{(xZ^{\frac{1}{2}}, \xiZ^{-\frac{3}{2}})}^\alpha(x(t)Z^{\frac{1}{2}}, \xi(t)Z^{-\frac{3}{2}})) \leq C\vartheta^{-K} \quad \forall \alpha : |\alpha| \leq m
\]

and

\[
|x(t) - x(0)|Z^{\frac{1}{2}} + |\xi(t) - \xi(0)|Z^{-\frac{3}{2}} \geq \vartheta^K |t|Z
\]

where \(m\) is arbitrary and \(K, \delta\) depend on \(m\).

**Proof.** We will just sketch it. First, let us consider the case \(M = 1\). In this case we first include into \(\sum_{\lambda, \delta}'\) all the points \((x, \xi)\) with trajectories not residing over \(\{\vartheta^\delta Z^{-\frac{1}{2}} \leq \ell(x) \leq Z^{-\frac{1}{2}}\vartheta^{-\delta}\} \) for all \(t : |t| \leq T^{21})\).

Further, if \((Z - N)_+ \geq Z^{9\vartheta}\) we also include into \(\sum_{\lambda, \delta}'\) all the points \((x, \xi)\) with trajectories not residing over \(B(x_1, (1 - \vartheta^\delta)\bar{r})\); here \(\bar{r}\) is an exact radius of \(\text{supp} \rho^{TF}\). Then (3.3.9)–(3.3.10) hold and we reduce \(\delta, \delta'\) if necessary.

It is known that not all the Hamiltonian trajectories are closed (see Appendix 6.B). Then one can prove easily that adding to \(\sum_{\lambda, \delta}'\) the set satisfying (3.3.9) we can fulfill (3.3.11) as well. One can find the similar arguments in the proof of Theorem 7.4.12 of [I7].

The general case is due of this particular one, proposition 3.3.3 and trivial perturbation arguments.

**Proof of proposition 3.3.2.** Now statements (i), (ii) follow from propositions 3.3.3 and 3.3.4 and the standard arguments; as \((Z - N)_+ \geq Z^{9\vartheta}\) we need to mollify \(W^{TF}\) in the standard way.

To prove statement (iii) we can use decomposition (16.3.1) of [I7] and apply to the contribution of zone \(\{(x, y) : |x - y| \geq Z^{-\frac{1}{2}}\vartheta^\delta\}\) the same standard arguments. Meanwhile one can notice that contribution of zone \(\{(x, y) : |x - y| \geq Z^{-\frac{1}{2}}\vartheta^\delta\}\) is \(O(Z^{\frac{3}{2} - \delta})\).

Combining all these improvements we arrive to

**Theorem 3.3.5.** Let \(N \asymp Z\). Let \(a \geq Z^{-\frac{1}{2}}\) and let \(\Psi\) be a ground state. Then

\[
|E - E^{TF} - \text{Scott} - \text{Dirac} - \text{Schwinger}| \leq CZ^{\frac{5}{2}}(Z^{-\delta} + (aZ^{\frac{1}{2}})^{-\delta})
\]

21) i.e. trajectories, leaving this “comfort zone” for some \(t : |t| \leq T\).
3.4 Corollaries

3.4.1 Estimates for $D(\rho_\Psi - \rho^{TF}, \rho_\Psi - \rho^{TF})$

Recall that in the lower estimate there was in the left-hand expression a non-negative term $\frac{1}{2}D(\rho_\Psi - \rho^{TF}, \rho_\Psi - \rho^{TF})$ which we so far just dropped. Also recall that the term $a^{-\frac{1}{2}}Z^\frac{3}{2}$ in the remainder estimate appeared only because we replaced $\text{Tr}(H_\Psi - \nu)^-$ by its Weyl approximation (with correction terms) which we by no means need for estimating this term as $\text{Tr}(H_\Psi - \nu)^-$ was present in both lower and upper estimates. Then we arrive to

**Theorem 3.4.1.** Let $N \asymp Z$ and let $\Psi$ be a ground state. Then

\[(3.4.1)\quad D(\rho_\Psi - \rho^{TF}, \rho_\Psi - \rho^{TF}) \leq CQ := \left\{ \begin{array}{ll} Z^\frac{3}{2} & \text{as } a \leq Z^{-\frac{1}{3}}, \\ Z^\frac{3}{2}(Z^{-\delta} + (aZ^\frac{3}{2})^{-\delta}) & \text{as } a \geq Z^{-\frac{1}{3}}. \end{array} \right.\]

3.4.2 Estimates for distance between nuclei in the free nuclei model

Let us estimate from below the distance between nuclei in the stable molecule in the free nuclei model (with the full energy optimized with respect to the position of the nuclei).

**Theorem 3.4.2.** Let $M \geq 2$ and let $Z_m \asymp Z$ for all $m$ be fulfilled. Assume that

\[(3.4.2)\quad E(Z; N) + \sum_{1 \leq m < m' \leq M} Z_j Z_k |y_m - y_{m'}|^{-1} \leq \min_{N_1, \ldots, N_M: N_1 + \ldots + N_M = N} \sum_{1 \leq m \leq M} E(Z_m; N_m)\]

Then

\[(3.4.3)\quad |y_m - y_{m'}| \geq Z^{-\frac{5}{3} + \delta_1} \quad \forall m \neq m'\]

and

\[(3.4.4)\quad |\hat{E}^{TF}(Z; N) - \hat{E}^{TF}(Z; N) - \text{Scott - Dirac - Schwinger}| \leq CZ^\frac{5}{2} - \delta.\]
Proof. Note first that \(|E| \leq CZ^{\frac{2}{3}}\) and in virtue of theorem 3.2.3 we can replace \(E\) by \(E^{\text{TF}}\) with \(O(Z^2)\) error:

\[
E^{\text{TF}}(Z; y; N) = \sum_{1 \leq m < m' \leq M} Z_j Z_k |y_m - y_{m'}|^{-1} \leq \min_{N_1, \ldots, N_M} \sum_{1 \leq m \leq M} E^{\text{TF}}(Z_m; N_m) - CZ^2;
\]

which in virtue of proposition 2.2.8 is impossible unless \(a^{-7} \leq CZ^2\) i.e. \(a \geq \epsilon Z^{-\frac{2}{3}}\).

Then, again in virtue of theorem 3.2.3 we can replace \(E\) by \(E^{\text{TF}} + \text{Scott}\) with \(O(Z^{\frac{3}{2}})\) error. Let us take into account that for molecule \(\text{Scott}\) equals the sum of \(\text{Scot}^{m}_{m}\). Therefore in (3.4.5) we can replace \(CZ^2\) by \(CZ^{\frac{3}{2}}\). Applying again proposition 2.2.8 we conclude that \(a \geq \epsilon Z^{-\frac{3}{4}}\).

Let us improve this estimate further. In virtue of theorem 3.3.5 again we can replace \(E\) by \(E^{\text{TF}} + \text{Scott} + \text{Dirac} + \text{Schwinger}\) with \(O(Z^{\frac{5}{2}-\delta_2})\) error. However one needs to compare Dirac–Schwinger correction for molecule with the sums of such corrections for separate atoms:

**Proposition 3.4.3.** If \(a \geq Z^{-\frac{1}{2}+\delta_1}\) and

\[
E^{\text{TF}}(Z; y; N) = \sum_{1 \leq m \leq M} E^{\text{TF}}(Z_m; N_m) + O(Z^{\frac{5}{2}-\delta_1})
\]

where \(N = N_1 + \ldots + N_M\) then

\[
\int (\rho^{\text{TF}})^{\frac{1}{2}} \, dx = \sum_{1 \leq m \leq M} \int (\rho^{\text{TF}}_m)^{\frac{1}{2}} \, dx + O(Z^{\frac{5}{2}-\delta_2})
\]

where \(\rho^{\text{TF}}_m = \rho^{\text{TF}}(x - y_m; Z_m; N_m)\) are atomic Thomas-Fermi densities.

Proof of proposition 3.4.3 will be provided immediately. Therefore \(\text{Dirac}\) and \(\text{Schwinger}\) correction terms for molecule are equal to the sums of \(\text{Dirac}^{m}_{m}\) and \(\text{Schwinger}^{m}_{m}\) correction terms respectively with \(O(Z^{\frac{5}{2}-\delta_2})\) error and in (3.4.5) we can replace \(CZ^2\) by \(CZ^{\frac{3}{2}-\delta_2}\). Applying proposition 2.2.8 again we conclude that \(a \geq Z^{\frac{5}{2}-\delta}\).
Proof of proposition 3.4.3. Note that the left-hand expression of (2.2.24) is equal to

\begin{equation}
\|\nabla (W_{\text{TF}} - \bar{W}_{\text{TF}})\|^2,
\bar{W}_{\text{TF}} := \sum_{1 \leq m \leq M} W_{m,\text{TF}}^T
\end{equation}

and therefore this expression is less than \(CQ \leq CZ^2\) as well. Then as \(a \geq Z^{-\frac{1}{2}+\delta}\) we conclude that if we restrict norm to zone \(\{x : |x - y_m| \leq Z^{-\frac{1}{2}+\delta}\}\) we can replace \(\tilde{\rho}_{\text{TF}}^T\) and \(\bar{W}_{\text{TF}}^T\) by \(\rho_m^T\) and \(W_m^T\) respectively in (2.2.24), (3.4.8).

Using Thomas-Fermi equations we conclude that in this zone

\begin{equation}
|D^\alpha (W_{\text{TF}}^T - W_m^T)| \leq C_\alpha W_m^T \ell^{-|\alpha|} Z^{-\delta_2} \quad \forall \alpha : |\alpha| \leq 2
\end{equation}

and then \(|(\rho_{m,\text{TF}}^T)^{\frac{1}{2}} - (\rho_m^T)^{\frac{1}{2}}| \leq C(\rho_m^T)^{\frac{1}{2}} Z^{-\delta_2}\) which implies (3.4.7) because \(\int (\rho_m^T)^{\frac{1}{2}} dx \asymp Z^\frac{1}{2}\) and contributions of zone \(\{x : \ell(x) \geq Z^{-\frac{1}{2}+\delta}\}\) to each integral is \(O(Z^{\frac{1}{2}-\delta})\).

\[\square\]

4 Negatively charged systems

In this section we consider the case \(N \geq Z\) and provide upper estimates for excessive negative charge \((N - Z)\) as \(l_N > 0\) and for ionization energy \(l_N\).

4.1 Estimates of the correlation function

First of all we provide some estimates which will be used for both negatively and positively charged systems. Let us consider the ground-state function \(\Psi(x_1, \xi_1; \ldots; x_N, \xi_N)\) and the corresponding density \(\rho_{\Psi}(x)\).

The crucial role plays estimate (3.4.1) \(D(\rho_{\Psi} - \rho_{\text{TF}}^T, \rho_{\Psi}^T - \rho_{\text{TF}}^T) \leq CQ\) of theorem 3.4.1 and the difference between upper and lower bounds for \(E_N\) (with \(N_1(H_{W} - \nu) + \nu N\) not replaced by its semiclassical approximation).

Let us consider the classical density of the electron system

\begin{equation}
\varphi_\varepsilon(x) = \sum_{1 \leq j \leq N} \delta(x - x_j)
\end{equation}

and the smeared classical density

\begin{equation}
\varphi_{\varepsilon, \varepsilon}(x) = \varphi_\varepsilon * \varphi_\varepsilon = \sum_{1 \leq j \leq N} \varphi_\varepsilon(x - x_j)
\end{equation}
where \( \varepsilon \) will be chosen later; here \((\mathbf{x}, \mathbf{z}) = (x_1, z_1; \ldots, x_N, z_N) \in (\mathbb{R}^3 \times \mathbb{C}^q)^N\).

(4.1.3) \( \phi_\varepsilon(z) = \varepsilon^{-3} \phi(z \varepsilon^{-1})\), \( \phi \in \mathcal{C}_0^\infty(B(0, \frac{1}{2})) \) is a spherically symmetric, non-negative function such that \( \int \phi(x) \, dx = 1 \).

Then \( \int \phi_\varepsilon(x) f(x) \, dx = f(0) + O(\varepsilon^2) \) for any \( f \in \mathcal{C}^2 \). Let us consider

\[
(4.1.4) \quad K_N(x) := \frac{1}{2} D(\phi_\varepsilon(\cdot) - \rho(\cdot), \phi_\varepsilon(\cdot) - \rho(\cdot))
\]

where \( \rho = \frac{1}{4\pi} \Delta (W - V) \), \( W \) is either \( W^{\text{TF}} \) if \( \nu = 0 \) or a “good” approximation for it, constructed in the previous section.

Using Newton’s screening theorem\(^{22}\) we conclude that

\[
(4.1.5) \quad \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1} \geq \frac{1}{2} D(\phi_\varepsilon(\cdot), \phi_\varepsilon(\cdot)) - C \varepsilon^{-1} N
\]

where the last term estimates

\[
\sum_{1 \leq j \leq N} D(\phi_\varepsilon(x - x_j), \phi_\varepsilon(x - x_j)) .
\]

On the other hand,

\[
(4.1.6) \quad \frac{1}{2} D(\phi_\varepsilon(\cdot), \phi_\varepsilon(\cdot)) = \int \phi_\varepsilon(|x|^{-1} * \rho) \, dx + K_N(x) - \frac{1}{2} D(\rho, \rho)
\]

and therefore

\[
(4.1.7) \quad H_N \geq \sum_{1 \leq j \leq N} H_{W_\varepsilon}(x_j) + K_N(x) - \frac{1}{2} D(\rho, \rho) - C \varepsilon^{-1} N
\]

on \( (\mathcal{L}_2^2(\mathbb{R}^3, \mathbb{C}^q))^N \) where \( W_\varepsilon \) is the “smeared” potential:

\[
(4.1.8) \quad W_\varepsilon(x) = V(x) - \phi_\varepsilon * |x|^{-1} * \rho.
\]

Note, that the smeared potential doesn’t depend on \( \mathbf{x} \) and is defined via \( \rho \) rather than \( \rho_\Psi \).

\(^{22}\) That uniformly charged sphere \( S(0, r) \) creates potential \( v(x) = -q \min(|x|^{-1}, r^{-1}) \) where \( q \) is the total charge of the sphere.
Also let us define
\[ N_x(x_2, \ldots, x_N) := \sum_{2 \leq j \leq N} (\chi_x * \phi_\varepsilon)(x_j) \]
and
\[ \tilde{N}_x := \int \rho(y) \chi_x(y) dy \]
with \( \chi_x(y) := \chi(x, y), \chi \in \mathcal{C}^\infty(\mathbb{R}^6) \).

Furthermore, let us consider function \( \theta \in \mathcal{C}^\infty(\mathbb{R}^3) \) such that
\[ 0 \leq \theta \leq 1, \quad |\nabla^\alpha \theta^\frac{1}{2}| \leq c_\alpha b^{-|\alpha|} \quad \forall \alpha. \]

Consider
\[ J := |\int \left( \rho_\psi^{(2)}(x, y) - \rho(y) \rho_\psi(x) \right) \theta(x) \chi(x, y) dx dy|. \]

Obviously
\[ J \leq \int \rho_\psi^{(2)}(x, y) |\chi_x * \phi_\varepsilon - \chi_x(y)| \theta(x) dx dy \]
\[ + N \int |\Psi(x, x_2, \ldots, x_N)|^2 |N_x(x_2, \ldots, x_N) - \tilde{N}_x| \theta(x) dx dx_2 \cdots dx_N \]
\[ \leq CN\varepsilon^5 \|
abla^\frac{s+1}{2} \chi \|_{L^\infty} \Theta \]
\[ + \left( N \int |\Psi(x, x_2, \ldots, x_N)|^2 |N_x - \tilde{N}_x|^2 \theta(x) dx dx_2 \cdots dx_N \right)^\frac{1}{2} \Theta^\frac{1}{2} \]
where \( \rho_\psi^{(2)}(\cdot, \cdot) \) is the quantum correlation function,
\[ \rho_\psi^{(2)}(x, y) := N(N - 1) \int |\Psi(x, y, x_3, \ldots, x_N)|^2 dx_3 \cdots dx_N, \]
\[ \int \rho_\psi^{(2)}(x, y) dy = (N - 1) \rho_\psi(x), \]
\[ \Theta = \Theta_\psi := \int \theta(x) \rho_\psi(x) dx \]
and we used Cauchy-Schwartz inequality.
Since
\[
N_x(x_2, \ldots, x_N) - \bar{N}_x = \int (\sum_{2 \leq j \leq N} \phi_\varepsilon(y - x_j) - \rho(y)) \chi(x, y) \, dxdy,
\]
we again from Cauchy-Schwartz inequality conclude that
\[
|N_x - \bar{N}_x|^2 \leq C \|\nabla_y \chi\|_{L^2}^2 \cdot K_{N-1}(x_2, \ldots, x_N).
\]
Note that
\[
\sum_{1 \leq j \leq N} \langle H_N \theta^\frac{1}{2}(x_j) \Psi, \theta^\frac{1}{2}(x_j) \Psi \rangle =
\]
\[E_N \int \int \theta(x) \rho_\Psi(x) \, dx + \int |\nabla \theta^\frac{1}{2}|^2(x) \rho_\Psi(x) \, dx\]
and then (4.1.7) yields that
\[
E_N \int \theta(x) \rho_\Psi(x) \, dx \geq - \int |\nabla \theta^\frac{1}{2}|^2(x) \rho_\Psi(x) \, dx + \frac{1}{2} D(\rho, \rho) \Theta - C \varepsilon^{-1} N \Theta.
\]
Also note that
\[
\sum_{1 \leq j \leq N} \langle H_{N_1} \theta^\frac{1}{2}(x_j) \Psi, \theta^\frac{1}{2}(x_j) \Psi \rangle
\]
\[+ \int K_N(x) \theta(x) |\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots \, dx_N - \frac{1}{2} D(\rho, \rho) \Theta - C \varepsilon^{-1} N \Theta.
\]
Then the second term in the right-hand expression of (4.1.19) is bounded from below by \((\nu N + N_1(H_{N^1} - \nu))\) \(\Theta\), while the left-hand expression is \(E_N \Theta\). Therefore assembling terms proportional to \(\Theta\) we conclude that
\[
S \Theta + \int |\nabla \theta^\frac{1}{2}|^2 \rho_{\Psi} \, dx \geq \sum_j \langle H_{N_1, x_j} \theta^\frac{1}{2}(x_j) \Psi, \theta^\frac{1}{2}(x_j) \Psi \rangle
\]
\[+ \int K_N(x_1, \ldots, x_N) \theta(x_1) |\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots \, dx_N.
\]
with
\[ S := E_N - \nu N - N_1(H_{W_\varepsilon} - \nu) + \frac{1}{2}D(\rho, \rho). \]

Due to non-negativity of operator $D_x^2$, the last term in (4.1.21) is greater than $-CT\Theta$ with
\[ T = \sup_{\text{supp } \theta} W; \]
so we arrive to
\[ N \int K_N(x_1, \ldots, x_N)\theta(x_1)|\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \leq C(S + T + \varepsilon^{-1}N)\Theta + P \]
with
\[ P = \int |\nabla \theta|^{\frac{1}{2}}|\rho\psi| \, dx. \]

Combining this with (4.1.13), (4.1.17) we conclude that
\[ \mathcal{J} \leq C \sup_x \|\nabla_y \chi\|_{L^2(\mathbb{R}^3)} \left( (S + \varepsilon^{-1}N + T)\Theta + P \right)^{\frac{1}{2}} \Theta^{\frac{1}{2}} + C\varepsilon N \|\nabla_y \chi\|_{L^\infty} \Theta \]
due to obvious estimate
\[ K_{N-1}(x_2, \ldots, x_N) \leq 2K_N(x_1, \ldots, x_N) + \varepsilon^{-1}N. \]

Now we want to estimate $S$ from above and for this we need an upper estimate for $E_N$. Recall that due to arguments of subsection 1.2 $S \leq CQ$ provided we manage to prove that expressions (1.2.7)–(1.2.10) satisfy the same estimates as before if we plug $W_{\varepsilon}$ instead of $W$.

So we need to calculate both semiclassical errors (which are calculated exactly as for $W = W^{TF}$) and the principal parts, and in calculations of $D(P'(W_{\varepsilon} + \nu) - \rho^{TF}, P'(W_{\varepsilon} + \nu) - \rho^{TF})$ and $D(\rho_{\varepsilon} - \rho^{TF}, \rho_{\varepsilon} - \rho^{TF})$ an error is $O(\varepsilon^2 Z^3)$ due to estimates
\[ |D^\alpha(W - W_{\varepsilon})| \leq C \begin{cases} Z\ell^{-1-|\alpha|}(1 + \ell\varepsilon^{-1})^{-2} & \forall \alpha \quad \text{as } \ell \leq \varepsilon Z^{-\frac{1}{2}} \\ \varepsilon^2\ell^{-6-|\alpha|} & \forall \alpha \quad \text{as } \ell \geq \varepsilon Z^{-\frac{1}{2}}, \ell \neq \tilde{r}, \\ \varepsilon^2\ell^{-6-|\alpha|} & \forall \alpha : |\alpha| \leq \frac{3}{2} \quad \text{as } \ell \approx \tilde{r}. \end{cases} \]
Then one can prove easily that the sum of these two expressions does not exceed $CQ + CZ^2\varepsilon^2 + CZ^2\varepsilon$, and this estimate cannot be improved. Choosing $\varepsilon \leq Z^{-\frac{3}{2}}$ we estimate these two terms by $CZ^\frac{3}{2}$.

Under this restriction an error in the principal part of asymptotics of $\int e(x, x, \lambda) \, dx$ does not exceed $CZ\varepsilon^2$ which is less than the semiclassical error. Then $S \leq CQ$.

So, the following proposition is proven:

**Proposition 4.1.1.** If $\theta, \chi$ are as above then

\[(4.1.29) \quad J = | \int \left( \rho^{(2)}_\psi(x, y) - \rho(y)\rho_\psi(x) \right) \theta(x)\chi(x, y) \, dx\,dy| \leq \]

\[C \sup_x \| \nabla_y \chi_x \|_{L^2(\mathbb{R}^3)} \left( (Q + \varepsilon^{-1}N + T)\frac{1}{2} \Theta + \rho^{\frac{1}{2}} \Theta^{\frac{1}{2}} \right) + C\varepsilon N \| \nabla_y \chi \|_{L^\infty} \Theta \]

with $\Theta = \Theta_\psi$ defined by (4.1.15) and $T, P$ defined by (4.1.23), (4.1.25) and arbitrary $\varepsilon \leq Z^{-\frac{3}{2}}$.

### 4.2 Excessive negative charge

Let us select $\theta = \theta_b$ 

\[(4.2.1) \quad \text{supp} \theta \subset \{x : \ell(x) \geq b\}.\]

Note that $H_N \psi = E_N \psi$ yields

\[(4.2.2) \quad E_N \int \rho_\psi(x)\ell(x)\theta(x) \, dx = \sum_j \langle \psi, \ell(x_j)\theta(x_j)H_N \psi \rangle = \]

\[\sum_j \langle \ell(x_j)\frac{1}{2} \theta^{\frac{1}{2}}(x_j)\psi, \ell(x_j)\frac{1}{2} \theta^{\frac{1}{2}}(x_j)H_N \psi \rangle - \sum_j \| \nabla \left( \theta^{\frac{1}{2}}(x_j)\ell(x_j)\frac{1}{2} \right) \psi \|^2\]

and isolating the contribution of $j$-th electron in $j$-th term we get

\[(4.2.3) \quad E_N \int \rho_\psi(x)\ell(x)\theta \, dx \geq E_{N-1} \int \rho_\psi(x)\ell(x)\theta \, dx + \]

\[\sum_j \langle \psi, \ell(x_j)\theta(x_j) \left( -V(x_j) + \sum_{k : k \neq j} |x_j - x_k|^{-1} \right) \psi \rangle - \sum_j \| \nabla \left( \theta^{\frac{1}{2}}(x_j)\ell(x_j)\frac{1}{2} \right) \psi \|^2\]
due to non-negativity of operator $D_x^2$.

Now let us select $b$ to be able to calculate the magnitude of $\Theta$. Note that

$$\left| \int \theta(x)(\rho(x) - \rho(x)) \, dx \right| \leq CD(\rho_\infty - \rho, \rho_\infty - \rho) \frac{1}{2} \| \nabla \theta \| \approx CD(\rho_\infty - \rho, \rho_\infty - \rho)^{\frac{1}{2}} b^{\frac{1}{2}} \leq CQ b^{\frac{1}{2}}$$

and

$$\int \theta(x) \rho(x) \, dx \approx b^{-3}$$

as long as

$$Z^{-\frac{1}{3}} \leq b \leq C(Z - N)^{-\frac{1}{3}}$$

because $\rho \approx |x|^{-6}$ as $Z^{-\frac{1}{3}} \leq |x| \leq c_0(Z - N)^{-\frac{1}{3}}$. Note that the right-hand expression of (4.2.5) is larger than the right-hand expression of (4.2.5) as $b \geq C_0 Q^{-\frac{1}{2}}$. Therefore let us pick up

$$b := \epsilon_0 Q^{-\frac{1}{2}};$$

it does not conflict with (4.2.6) provided

$$N \geq Z - C_0 Q^2$$

and then

$$\Theta \approx Q^2.$$

Then the same arguments imply that the last term in the right-hand expression of (4.2.3) does not exceed $Cb^{-1} \Theta$; using inequality

$$\int \rho_\infty(x) \ell(x) \theta(x) \, dx \geq b \Theta$$
we conclude that

\[
\text{(4.2.11)} \quad b \mathcal{W}_b \leq \int \theta(x) V(x) \ell(x) \rho_\psi(x) \, dx \\
- \int \varrho_\psi^{(2)}(x, y) \ell(x) \rho_\psi(x) \, dx dy + C b^{-1} \Theta = \\
\int \theta(x) V(x) \ell(x) \rho_\psi(x) \, dx \\
- \int \varrho_\psi^{(2)}(x, y) \ell(x) \rho_\psi(x) \, dx dy \\
- \int \varrho_\psi^{(2)}(x, y) \ell(x) \rho_\psi(x) \, dx dy + C b^{-1} \Theta. 
\]

Denote by \( I_1, I_2, \) and \( I_3 \) the first, second and third terms in the right-hand expression of (4.2.11) respectively. Symmetrizing \( I_3 \) in the right-hand expression of (4.2.11) with respect to \( x \) and \( y \)

\[
I_3 = -\frac{1}{2} \int \varrho_\psi^{(2)}(x, y) \theta(y) \theta(x) \, dx dy
\]

and using inequality \( \ell(x) + \ell(y) \geq \min_j (|x - x_j| + |y - x_j|) \geq |x - y| \) we conclude that this term is less than

\[
\text{(4.2.12)} \quad -\frac{1}{2} \int \varrho_\psi^{(2)}(x, y) \theta(y) \theta(x) \, dx dy = \\
- \frac{1}{2} (N - 1) \int \rho_\psi(x) \theta(x) \, dx + \frac{1}{2} \int \rho_\psi^{(2)}(x, y) (1 - \theta(y)) \theta(x) \, dx dy.
\]

Here the first term is exactly \(-\frac{1}{2} (N - 1) \Theta\); replacing \( \varrho_\psi^{(2)}(x, y) \) by \( \rho(y) \rho_\psi(x) \) we get

\[
\text{(4.2.13)} \quad \frac{1}{2} \int (1 - \theta(y)) \rho(y) \, dy \times \Theta
\]

with an error

\[
\text{(4.2.14)} \quad \frac{1}{2} \int (\varrho_\psi^{(2)}(x, y) - \rho(y) \rho_\psi(x)) (1 - \theta(y)) \theta(x) \, dx dy
\]

which we estimate using proposition 4.1.1 with \( \chi(x, y) = 1 - \theta(y) \). Then \( \|
\nabla_y \chi \|_{L^2} \asymp b^\frac{3}{2}, \|
\nabla_y \chi \|_{L^\infty} \asymp b^{-1}, T \asymp b^{-4}, P \asymp b^{-1} \Theta \) and picking up
\[ \varepsilon = Z^{-\frac{3}{2}} \] we conclude that an error (4.2.14) is less than \( Cb^{\frac{1}{2}} \Theta \approx CQ^{\frac{3}{2}} \Theta \) and we conclude that

\[
(4.2.15) \quad I_3 \leq -\frac{1}{2} (N - Z)_+ \Theta + CQ^{\frac{3}{2}} \Theta
\]

because \( \int \rho \theta \, dy \approx Q^{\frac{3}{2}} \) and \( \int \rho(y) \, dy = \min(Z, N) \).

On the other hand,

\[
(4.2.16) \quad I_2 \leq -\int \varrho^{(2)}_{\psi}(x, y) \ell(x) |x - y|^{-1} (1 - \bar{\theta}(y)) \theta(x) \, dxdy
\]

with \( \bar{\theta} = \theta_{b(1-\varepsilon)} \) and replacing \( \varrho^{(2)}_{\psi}(x, y) \) by \( \rho(y) \rho_{\psi}(x) \) we get

\[
(4.2.17) \quad -\int \rho_{\psi}(x) \rho(y) \ell(x) |x - y|^{-1} (1 - \bar{\theta}(y)) \theta(x) \, dxdy
\]

and we estimate an error in the same way by \( CQ^{\frac{3}{2}} \Theta \).

Therefore

\[
I_1 + I_2 \leq \int \theta(x) V(x) \ell(x) \rho_{\psi}(x) \, dx - \int \rho_{\psi}(x) \ell(x) \rho(y) |x - y|^{-1} (1 - \bar{\theta}(y)) \theta(x) \, dxdy + CQ^{\frac{3}{2}} \Theta =
\]

\[
\int \theta(x) W(x) \ell(x) \rho_{\psi}(x) \, dx + \int \rho(y) \rho_{\psi}(x) \ell(x) |x - y|^{-1} \bar{\theta}(y) \theta(x) \, dxdy + CQ^{\frac{3}{2}} \Theta
\]

due to \( V - W = |x|^{-1} * \rho \); since \( W\ell \leq Cb^{-3} \) we can skip the first term in the right-hand expression. Furthermore, as

\[
\int \rho(y) |x - y|^{-1} \bar{\theta}(y) \, dy \approx \Theta \approx Q^{\frac{3}{2}}
\]

we can skip the second term as well.

Adding \( I_3 \) and multiplying by \( \Theta^{-1} \) we arrive to

\[
(4.2.18) \quad b|_{\mathcal{N}} \leq -\frac{1}{2} (N - Z)_+ + CQ^{\frac{3}{2}}
\]

which implies immediately
**Theorem 4.2.1.** Let condition (2.2.15) be fulfilled.

(i) In the fixed nuclei model let $N > Z$. Then

\[
(N - Z)^+ \leq C |Z| = CZ^\delta \left\{ \begin{array}{ll}
1 & \text{as } a \leq Z^{-\frac{1}{4}}, \\
N^{-\delta} + (aZ^\frac{1}{2})^{-\delta} & \text{as } a \geq Z^{-\frac{1}{8}}; 
\end{array} \right.
\]

(ii) In particular for a single atom and for molecule with $a \geq Z^{-\frac{1}{16}}$

\[
(N - Z)^+ \leq Z^\frac{5}{7};
\]

(iii) In the free nuclei model let $\hat{I}_N > 0$. Then estimate (4.2.20) holds.

### 4.2.1 Estimate for ionization energy

Recall that as $N < Z$ we assumed that $N \geq Z - C |Z|$ (see (4.2.8)) and $b = Q^{-\frac{1}{6}}$. Then (4.2.18) also implies $I_N \leq C |Z|$ and we arrive to

**Theorem 4.2.2.** Let condition (2.2.15) be fulfilled and let $N \geq Z - C_0 Z^\delta$.

Then

(i) In the framework of fixed nuclei model

\[
I_N \leq CZ^\frac{3}{2}.
\]

(ii) In the framework of free nuclei model

\[
\hat{I}_N \leq Z^\frac{3}{2} - \delta'.
\]

**Remark 4.2.3.** (i) Classical theorem of G. Zhislin [Zh] implies that the system can bind at least $Z$ electrons; the proof is based on the demonstration that the energy of the system with $N < Z$ electrons plus one electron on the distance $r$ is increasing as $r \to +\infty$ because potential created by the system with $N < Z$ electrons behaves as $(Z - N)|x|^{-1}$ as $|x| \to \infty$.

(ii) In the proof of theorem 4.2.1(iii) and 4.2.2(ii) we note that tearing off one electron in free nuclei model is easier than in the fixed nuclei model.

The following problem looks relatively easy:

47
Problem 4.2.4. In statements (i), (ii) of theorems 4.2.1 and 4.2.2 get rid off condition (2.2.15).

5 Positively charged systems

In this section we consider the case of positively charged system with $Z - N \geq C_0 Q^2$ with sufficiently large $C_0$.

First let us find asymptotics of the ionization energy; the principal term will be $-\nu$ but we need to estimate a remainder.

5.1 Estimate from above for ionization energy

As $M = 1$ construction is well-known: let us pick up function $\theta$ such that $\theta = 1$ as $|x - y_m| \geq \tilde{r} - b$ and $\theta = 0$ as $|x - y_m| \leq \tilde{r} - 2b$ where $\tilde{r}$ is an exact radius of support $\rho_{\text{TF}}$. Here $b \ll \tilde{r}$. As $M \geq 1$ let us pick instead

$$\theta(x) = \mathcal{F}^2(\nu^{-1}[W(x) + \nu])$$

where $f \in C^\infty(\mathbb{R})$, supported in $(-\infty, 2)$ and equal 1 in $(-\infty, 1)$, $\nu \leq \nu$.

We will assume that

$$\nu \geq \tilde{r} \asymp C_1 (Z - N)^{-\frac{1}{2}}$$

with sufficiently large $C_1$; we will discuss dropping this assumption later. Then as we know that $\rho_{\text{TF}}$ is supported in $c\tilde{r}$-vicinity of nuclei, we conclude that “atoms” are rather disjoint.

One can see easily that then as $W + \nu \approx 0$,

$$|\nabla W| \asymp \tilde{r}^{-5};$$

then the width of the zone $\{x : 0 \leq W(x) + \nu \leq 2\nu\}$ is $\asymp \nu|\nabla W|^{-1} \asymp b = \nu \tilde{r}^5$ and

$$\Theta_{\text{TF}} := \int \theta(x) \rho_{\text{TF}} \, dx \asymp \nu^\frac{3}{2} \times b\tilde{r}^2 = \nu^\frac{5}{2} \tilde{r}^7$$
while $\|\nabla \theta\| \asymp b^{-\frac{1}{2}} \bar{r} = v^{-\frac{1}{2}} \bar{r}^{-\frac{1}{2}}$ and therefore to ensure that $\Theta$ has the same magnitude (5.1.4) we pick up the smallest $v$ such that $v^{\frac{3}{2}} \bar{r}^2 \geq C v^{-\frac{3}{2}} \bar{r}^{\frac{3}{2}} Q^\frac{3}{2}$
i.e.

\begin{equation}
(5.1.5) \quad v := C_2 \bar{r}^{-\frac{17}{2}} Q^\frac{1}{2} \quad (\iff b = C_2 \bar{r}^\frac{13}{2} Q^\frac{1}{2});
\end{equation}

then

\begin{equation}
(5.1.6) \quad \Theta \asymp \bar{r}^{-\frac{1}{2}} Q^\frac{3}{2}
\end{equation}

Then (4.1.15) is fulfilled. Note that $v \leq \nu = \bar{r}^{-4}$ iff $(Z - N) \geq Q^3$ exactly as we assumed.

Then (4.2.11) is replaced by

\begin{equation}
(5.1.8) \quad 1_N \int \ell(x) \rho \psi(x) \theta(x) \, dx \leq \int \theta(x) V(x) \ell(x) \rho \psi(x) \, dx
\end{equation}

\begin{equation*}
- \int \left( \phi_\psi^{(2)}(x, y) - \rho \psi(x) \rho(y) \right) \ell(x) |x - y|^{-1} \theta(x) \, dxdy + Cb^{-2} \bar{r} \Theta
\end{equation*}

where $Cb^{-2} \bar{r} \Theta$ estimates the last term in the right-hand expression of (4.2.3). Then

\begin{equation}
(5.1.9) \quad - \int \left( \phi_\psi^{(2)}(x, y) - \rho \psi(x) \rho(y) \right) \ell(x) |x - y|^{-1} \theta(x) \, dxdy \leq
\end{equation}

\begin{equation*}
- \int \left( \phi_\psi^{(2)}(x, y) - \rho \psi(x) \rho(y) \right) (1 - \omega(x, y)) \ell(x) |x - y|^{-1} \theta(x) \, dxdy
\end{equation*}

\begin{equation*}
+ \int \rho \psi(x) \rho(y) \omega(x, y) \ell(x) |x - y|^{-1} \theta(x) \, dxdy
\end{equation*}

with $\omega = \omega_\gamma$: $\omega = 0$ as $|x - y| \geq 2 \gamma$ and $\omega = 1$ as $|x - y| \leq \gamma, \gamma \geq b$.

To estimate the first term in the right-hand expression one can apply proposition 4.1.1. In this case $\|\nabla_\gamma \chi\|_{L^2} \asymp C \bar{r} \gamma^{-\frac{1}{2}}, \|\nabla_\gamma \chi\|_{L^\infty} \asymp \bar{r} \gamma^{-2}$ and
plugging $P = b^{-2} \Theta$ and $T = \nu, \varepsilon = Z^{-\frac{2}{3}}$ we conclude that this term does not exceed

$$C \bar{r}(\gamma^{-\frac{1}{2}} \bar{Q}^{\frac{1}{2}} + CZ^{\frac{1}{2}} \gamma^{-2}) \Theta, \quad \bar{Q} = \max(Q, Z^{\frac{1}{3}}).$$

Consider the second term in the right-hand expression of (5.1.9). Note that

$$\int \rho(y) \omega(x, y)|x - y|^{-1} dy \leq C(\bar{r}^{-\frac{15}{2}} \gamma^{\frac{7}{2}} + \nu^{\frac{5}{2}} \gamma^{2})$$

since $\rho(y) \approx (W(y) + \nu)^{\frac{3}{2}}$ and $|\nabla W| \approx \bar{r}^{-5}$; then this term does not exceed $C(\bar{r}^{-\frac{15}{2}} \gamma^{\frac{7}{2}} + \nu^{\frac{5}{2}} \gamma^{2}) \bar{r} \Theta$.

Adding to (5.1.10) we get

$$C \left(\gamma^{-\frac{1}{2}} \bar{Q}^{\frac{1}{2}} + CZ^{\frac{1}{2}} \gamma^{-2} + \bar{r}^{-\frac{15}{2}} \gamma^{\frac{7}{2}} + \nu^{\frac{5}{2}} \gamma^{2}\right) \bar{r} \Theta.$$ 

Optimizing with respect to $\gamma = \bar{Q}^{\frac{1}{2}} \nu^{-\frac{1}{2}}$ we get $C \nu^{\frac{3}{3}} \bar{Q}^{\frac{3}{2}} \bar{r} \Theta$ and (5.1.8) becomes

$$\int \rho(x) \omega(x, y) |x - y|^\varepsilon dy \leq C(\bar{r}^{-\frac{15}{2}} \gamma^{\frac{7}{2}} + \nu^{\frac{5}{2}} \gamma^{2})$$

where we took into account that $V - |x|^{-1} \rho = W$, and that $W + \nu \nu$ on $\text{supp} \theta$.

Since a factor at $(I_N + \nu)$ in the left-hand expression of (5.1.11) is obviously $\approx \bar{r} \Theta$ we arrive to $(I_N + \nu) \leq C \nu + \nu^{\frac{3}{3}} \bar{Q}^{\frac{3}{2}}$.

Recalling definition (5.1.4) of $\nu$ we arrive to an upper estimate in Theorem 5.2.1 below:

$$I_N + \nu \leq C \nu = CQ^{\frac{1}{2}}(Z - N)^{\frac{17}{16}}.$$ 

Really, this is true if $Q \geq Z^{\frac{3}{3}}$ (we are interested in the general approach) and in this case $\nu \geq \nu^{\frac{3}{3}} Q^{\frac{3}{2}}$. On the other hand, if $Q = Z^{\frac{1}{8}}(aZ^{\frac{1}{2}})^{-\delta}, aZ^{\frac{1}{2}} \geq 1$, then we get an extra term $CQ^{\frac{1}{2}}(Z - N)^{\frac{1}{2}} Z^{\frac{3}{3}}$ but we can skip it decreasing unspecified exponent $\delta > 0$ in the definition of $Q$. 50
Remark 5.1.1. (i) We will prove the same estimate from below in the next subsection.

(ii) Note that the relative error in the estimates is \( \frac{v}{\nu} = (Z - N)^{-\frac{1}{2}} Q^{\frac{1}{6}} \).

(iii) In the proof we used not assumption (5.1.2) itself but its corollary (5.1.3). If we do not have such assumption instead of equality (5.1.4) we have a problem to estimate \( |\nabla \theta^2| \) : namely we need estimate the first factor in the product \( \|\nabla \theta^2\|D(\rho - \rho^{TF}, \rho - \rho^{TF})^{\frac{1}{2}} \).

Let us select \( f \) in (5.1.1) such that \( |f'| \leq cf^{1-\delta/2} \) with arbitrarily small \( \delta > 0 \). Then

\[
\begin{align*}
\frac{b^2}{\theta^2} \leq C \int_{\mathcal{Z}} \theta^{1-\delta} \, dx \leq C \left( \int_{\mathcal{Z}} \theta \, dx \right)^{1-\delta} C \left( \int_{\mathcal{Z}} 1 \, dx \right)^{\delta} \leq C \left( \Theta^{TF} \right)^{1-\delta} v^{-\frac{3}{2}(1-\delta)} Q^{3\delta}
\end{align*}
\]

with \( \mathcal{Z} = \text{supp} \nabla \theta \) and \( b = \tilde{r}^{\frac{11}{6}} Q^{\frac{1}{6}} \) and an error is less than \( \epsilon \Theta^{TF} \) provided

\[
v = C_2 \tilde{r}^{-\frac{12}{5}} Q^{\frac{1}{6}} \times (\tilde{T} Q)^{-\delta_1}
\]

which leads to a marginally larger error.

Estimate \( P \) could be done in the same manner but here slight increase of it does not matter.

(iv) The same arguments of (iii) could be applied to the proof of the lower estimate in the next subsection despite rather different definition of \( \Theta_{\Psi} \) by (5.2.6).

(v) In view of Theorem 5.3.1 stable molecules do not exist in the free nuclei model as \( Z - N \geq CQ^{\frac{3}{7}} \) and in atomic case \( \hat{l}_N = l_N \).

Problem 5.1.2. Consider \( f \) such that \( |f'| \leq f g^{-1}(f) \) where \( g^{-1}(t) \in L^1 \) and further improve remainder estimate without assumption (5.1.3).
5.2 Estimate from below for ionization energy

Now let us prove estimate \( I_N + \nu \) from below. Let \( \Psi = \Psi_N(x_1, \ldots, x_N) \) be the ground state for \( N \) electrons, \( \|\Psi\| = 1 \); consider an antisymmetric test function

\[
\tilde{\Psi} = \tilde{\Psi}(x_1, \ldots, x_{N+1}) = \Psi(x_1, \ldots, x_N)u(x_{N+1}) - \sum_{1 \leq j \leq N} \Psi(x_1, \ldots, x_{j-1}, x_{N+1}, x_{j+1}, \ldots, x_N)u(x_j)
\]

Then

\[
E_{N+1}|\tilde{\Psi}|^2 \leq \langle H_{N+1}\tilde{\Psi}, \tilde{\Psi} \rangle = N\langle H_{N+1}\Psi u, \tilde{\Psi} \rangle = N\langle H_N\Psi u, \tilde{\Psi} \rangle + N\langle H_{V,N+1}\Psi u, \tilde{\Psi} \rangle + N\sum_{1 \leq i \leq N} |x_i - x_{N+1}|^{-1}\Psi u, \tilde{\Psi} \rangle = (E_N - \nu')|\tilde{\Psi}|^2 + N\langle H_{W+\nu',N+1}\Psi u, \tilde{\Psi} \rangle
\]

and therefore

\[
N^{-1}(I_N + \nu')|\tilde{\Psi}|^2 \geq \langle H_{W+\nu',N+1}\Psi u, \tilde{\Psi} \rangle - \langle (\sum_{1 \leq i \leq N} |x_i - x_{N+1}|^{-1} - (V - W)(x_{N+1}))\Psi u, \tilde{\Psi} \rangle
\]

with \( \nu' \geq \nu \) to be chosen later. One can see easily that

\[
N^{-1}|\tilde{\Psi}|^2 = \|\Psi\|^2 \cdot \|u\|^2 - N \int \Psi(x_1, \ldots, x_{N-1}, x)\Psi^\dagger(x_1, \ldots, x_{N-1}, x)u(y)u^\dagger(y) \, dx_1 \cdots dx_{N-1} \, dx \, dy
\]

where \( \dagger \) means a complex or Hermitian conjugation.

Note that every term in the right-hand expression in (5.2.2) is the sum of two terms: one with \( \tilde{\Psi} \) replaced by \( \Psi(x_1, \ldots, x_N)u(x_{N+1}) \) and another with \( \tilde{\Psi} \) replaced by \( -N\Psi(x_1, \ldots, x_{N-1}, x_{N+1})u(x_N) \). We call these terms direct and indirect respectively.

Obviously, in the direct and indirect terms \( u \) appears as \( |u(x)|^2 \, dx \) and as \( u(x)u^\dagger(y) \, dx \, dy \) respectively multiplied by some kernels.
Recall that $u$ is an arbitrary function. Let us take $u(x) = \theta^\frac{1}{2}(x)\phi_j(x)$ where $\phi_j$ are orthonormal eigenfunctions of $H_{W+\nu}$ and $\theta(x)$ is $b$-admissible function supported in \{ $x : -\nu \geq W(x) + \nu \geq \frac{2}{3}\nu$ \} and equal 1 in \{ $x : | -2\nu \geq W(x) + \nu \geq \frac{1}{3}\nu$ \}, satisfying (4.1.11), and $b = \nu^5$.

Let us substitute it into (5.2.2), multiply by $\varphi(\lambda L^{-1})$ and take sum with respect to $j$ we get the same expressions with $|u(x)|^2 \, dx$ and $u(x)u^\dagger(y) \, dxdy$ replaced by $F(x, x) \, dx$ and $F(x, y) \, dxdy$ respectively with

(5.2.4) \[ F(x, y) = \int \varphi(\lambda L^{-1}) \, d_\lambda e(x, y, \lambda). \]

Here $\varphi(\tau)$ is a fixed $C^\infty$ non-negative function equal to 1 as $\tau \leq \frac{1}{2}$ and equal to 0 as $\tau \geq 1$ and $L = \nu' - \nu = 6\nu$.

Under described construction and procedures the direct term generated by $N^{-1}\|\Psi\|^2$ is

(5.2.5) \[ \int \theta(x)\varphi(\lambda L^{-1}) \, d_\lambda e(x, x, \lambda) \, dx \]

and applying semiclassical approximation we get

(5.2.6) \[ \Theta_\Psi := \int \varphi(\lambda L^{-1}) \, d_\lambda P_B'(W + \nu - \lambda) \, dx \]

and under assumptions (2.2.15) and (5.1.2) the remainder estimate is $C\hbar^{-1}\tau^2 b^{-2} = C\nu^5\tau^2 b^{-1} = C\nu^{-\frac{1}{3}}\tau^{-3}$; one can prove it easily by partition of unity on $\text{supp } \theta$ and applying semiclassical asymptotics with effective semiclassical parameter $\hbar = 1/(v^\frac{1}{2}b) = v^{-\frac{1}{3}}\tau^{-5}$.

On the other hand, indirect term generated by $N^{-1}\|\Psi\|^2$ is

(5.2.7) \[ -N \int \theta^\frac{1}{2}(x)\theta^\frac{1}{2}(y)\Psi(x_1, ..., x_{N-1}, x)\Psi^\dagger(x_1, ..., x_{N-1}, y) \times \]

\[ F(x, y) \, dxdydx_1 \cdots dx_{N-1} \]

\[ 23^\text{rd} \text{Or rather its corollary (5.1.3).} \]
and since the operator norm of $F(.,.,.)$ is 1 the absolute value of this term doesn’t exceed

$$
(5.2.8) \quad N \int \theta(x)|\Psi(x_1, \ldots, x_{N-1}, x)|^2 \, dx = \int \theta(x) \rho \psi(x) \, dx \leq \int \theta(x) \rho(x) \, dx + CQ \frac{1}{2} \| \nabla \theta \|^2
$$

where $\rho^{TF} = 0$ on $\text{supp} \, \theta$ and under assumption (5.1.2) $\| \nabla \theta \|^2 \asymp b^{-\frac{1}{2}} r \asymp \zeta^{-\frac{1}{2}} r^{-\frac{3}{2}}$.

Recall that $P'(W^{TF} + \nu) = \rho^{TF}$. We will take $\nu' = \nu + L$ large enough to keep $\Theta_{\psi}$ larger than all the remainders including those due to replacement $W$ by $W^{TF}$ and $\rho$ by $\rho^{TF}$ in the expression above. One can note easily that

$$
(5.2.9) \quad \Theta_{\psi} \asymp h^{-3} \times b^{-2} r^2 \asymp v^2 b r^2 \asymp v^2 r^7.
$$

Therefore

$$
(5.2.10) \quad \text{As } \nu = C_0 \tilde{r}^{-\frac{13}{6}} Q^\frac{1}{3} \text{ and } Z - N \geq C_0 Z^\frac{5}{7} \text{ the total expression generated by } N^{-1} \| \Psi \|^2 \text{ is greater than } c \Theta \text{ with } \Theta = v^2 r^7.
$$

Now let us consider direct terms in the right-hand expression of (5.2.2). The first of them is

$$
(5.2.11) \quad - \int \theta^{\frac{1}{2}}(x) \varphi(\lambda L^{-1}) d_\lambda (H_{W+\nu',x} \theta^{\frac{1}{2}}(x) e(x,y,\lambda))_{y=x} \, dx =
$$

$$
- \int \theta(x) \varphi(\lambda L^{-1}) d_\lambda (H_{W+\nu',x} e(x,y,\lambda))_{y=x} \, dx
$$

$$
- \frac{1}{2} \int \varphi(\lambda L^{-1})[[H_{W}, \theta^{\frac{1}{2}}], \theta^{\frac{1}{2}}] d_\lambda e(x,x,\lambda) \geq
$$

$$
\int \theta(x)(\nu' - \nu - \lambda) \varphi(\lambda L^{-1}) d_\lambda e(x,x,\lambda) \, dx - C \int |\nabla \theta^{\frac{1}{2}}|^2 e(x,x,\nu') \, dx.
$$

Note that the absolute value of last term in the right-hand expression of (5.2.11) does not exceed $C b^{-1} r^2 L^\frac{5}{2} \asymp C v^2 r^{-3} \ll C v \Theta$.

The second direct term in the right-hand expression is

$$
(5.2.12) \quad - \int \theta(x) \left( \rho \psi * |x|^{-1} - (V - W)(x) \right) F(x,x) \, dx =
$$

$$
- D(\rho \psi - \bar{\rho}, \theta(x) F(x,x)) \geq
$$

$$
- CD(\rho \psi - \rho, \rho \psi - \bar{\rho})^{\frac{1}{2}} \cdot D\left( \theta^{\frac{1}{2}} F(x,x), \theta^{\frac{1}{2}} F(x,x) \right)^{\frac{1}{2}} \geq - CQ \frac{1}{2} \frac{r^2}{r^2} v^2
$$
provided $V - W = |x|^{-1} * \rho$ with $D(\rho - \rho^{TF}, \rho - \rho^{TF}) \leq CQ$; the absolute value of this term is $\ll \nu \Theta$.

Further, the first indirect term in the right-hand expression of (5.2.2) is

$$(5.2.13) \quad -N \int \theta^{\frac{1}{2}}(y) \psi(x_1, ..., x_{N-1}, x) \psi^\dagger(x_1, ..., x_{N-1}, y) \times$$

$$\varphi(\lambda L^{-1}) d_\lambda(H_{W+y, x} \theta^{\frac{1}{2}}(x) e(x, y, \lambda)) \ dx dy dx_1 \cdots dx_{N-1} =$$

$$-N \int \theta^{\frac{1}{2}}(y) \theta^{\frac{1}{2}}(x) \psi(x_1, ..., x_{N-1}, x) \psi^\dagger(x_1, ..., x_{N-1}, y) \times$$

$$\varphi(\lambda L^{-1})(\nu' - \nu - \lambda) d_\lambda e(x, y, \lambda) \ dx dy dx_1 \cdots dx_{N-1}$$

Note that one can rewrite the sum of the first terms in the right-hand expressions in (5.2.11) and (5.2.13) as

$$\sum_j \hat{\psi}_j(x_1, ..., x_{N-1}) := \int \psi(x_1, ..., x_{N-1}) \hat{\theta}^{\frac{1}{2}}(x) \phi_j(x) \ dx$$

and therefore this sum is non-negative.

One can prove easily that the absolute value of the second term in (5.2.13) is less than

$$Cv^{\frac{1}{2}} b^{-1} \int \rho \varphi(y) \theta^{\frac{1}{2}}(y) \ dy \leq Cv - \frac{1}{2} \tilde{r}^{-5} \Theta \ll \nu \Theta.$$
\[-\int (|y|^{-1} \ast \rho_\lambda(y) - (V - \mathcal{W})(y)) \Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \times \]
\[\theta^\frac{1}{2}(x_N) \theta^\frac{1}{2}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy \]
\[-\int \left( \sum_{1 \leq i \leq N} |y-x_i|^{-1} - |y|^{-1} \ast \rho_\lambda(y) \right) \Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \times \]
\[\theta^\frac{1}{2}(x_N) \theta^\frac{1}{2}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy;\]

recall that \(\rho_\lambda\) is a smeared density, \(x = (x_1, \ldots, x_N)\).

Since \(|y|^{-1} \ast \rho_\lambda(y) - (V - \mathcal{W})(y) = |y|^{-1} \ast (\rho_\lambda - \rho)\), the first term in the right-hand expression is equal to

\[(5.2.16) \quad \int \theta^\frac{1}{2}(x_N) \Psi(x_1, \ldots, x_N) \times \]
\[D_y \left( \rho_\lambda(y) - \rho(y), F(x_N, y, \lambda) \theta^\frac{1}{2}(y) \Psi(x_1, \ldots, x_{N-1}, y) \right) \, dx_1 \cdots dx_N;\]

and its absolute value does not exceed

\[(5.2.17) \quad \left( N \int D(\rho_\lambda(\cdot) - \rho(\cdot), \rho_\lambda(\cdot) - \rho(\cdot)) |\Psi(x_1, \ldots, x_N)|^2 \theta(x_N) \, dx_1 \cdots dx_N \right)^\frac{1}{2} \times \]
\[N^{-\frac{1}{2}} \left( D_y \left( F(x_N, y, \lambda) \theta^\frac{1}{2}(y) \Psi(x_1, \ldots, x_{N-1}, y), \right. \right. \]
\[\left. \left. F(x_N, y, \lambda) \theta^\frac{1}{2}(y) \Psi(x_1, \ldots, x_{N-1}, y) \right) \, dx_1 \cdots dx_N \right)^\frac{1}{2}.\]

Due to estimate (4.1.24) and definition (4.1.4) as the first factor in (5.2.17) does not exceed \(\left( (Q + T + \varepsilon^{-1} N) \Theta + P \right)^{\frac{1}{2}}\) where we assume that \(\varepsilon \leq \varepsilon^{-\frac{1}{2}}\) and \(\Theta \approx b^{-\frac{1}{2}} Q^{\frac{1}{2}} t\) is now an upper estimate for \(\int \theta(y) \rho(y) \, dy\)-like expressions; due to our choice of \(v\) it coincides with \(\Theta = v^{-\frac{1}{2}} t^7\).

Then according to (4.1.25) \(P \approx C b^{-2} \Theta \ll Q \Theta\) and according to (4.1.23) \(T \ll Q\) and therefore in all such inequalities we may skip \(P\) and \(T\) terms; so we get \(C(Q + \varepsilon^{-1} N)^{\frac{1}{2}} \Theta^\frac{3}{2}\).

Meanwhile the second factor in (5.2.17) (without square root) is equal to

\[N^{-1} \int L^{-2} \tilde{\varphi}^\prime(\lambda L^{-1}) \varphi^\prime(\lambda L^{-1}) |y - z|^{-1} e(x_N, y, \lambda) \theta^\frac{1}{2}(y) \Psi(x_1, \ldots, x_{N-1}, y) \times \]
\[e(x_N, z, \lambda') \theta^\frac{1}{2}(z) \Psi^\dagger(x_1, \ldots, x_{N-1}, z) \, dydz \, dx_1 \cdots dx_{N-1} \, dx_N \, d\lambda d\lambda'.\]
after integration to \( x_N \) we get instead of marked terms \( e(y, z, \lambda) \) (recall that \( e(., ., .) \) is the Schwartz kernel of projector and we keep \( \lambda < \lambda' \)) and then integrating with respect to \( \lambda' \) we arrive to

\[
N^{-1} \int |y - z|^{-1} F(y, z) \theta^{\frac{1}{2}}(y) \Psi(x_1, \ldots, x_{N-1}, y) \times \\
\theta^{\frac{1}{2}}(z) \Psi^{\dagger}(x_1, \ldots, x_{N-1}, z) \, dy \, dz \, dx_1 \cdots dx_{N-1};
\]

where now \( F \) is defined by (5.2.4) albeit with \( \varphi^2 \) instead of \( \varphi \). This latter expression does not exceed

(5.2.18) \[
N^{-1} \int \int |y - z|^{-1} |F(y, z)||\theta^{\frac{1}{2}}(y)||\Psi(x_1, \ldots, x_{N-1}, y)||^2 \times \\
dy \, dz \, dx_1 \cdots dx_{N-1}.
\]

Then due to proposition 6.C.1 \( \int |y - z|^{-1}|F(y, z)| \, dz \) does not exceed \( Cb^{-1}h^{-1} \approx v^{\frac{1}{2}}, \) and thus expression (5.2.18) does not exceed \( CZ^{-2}v^{\frac{1}{2}}\Theta \) and therefore the second factor in (5.2.17) does not exceed \( CN^{-1}v^{\frac{1}{2}}\Theta^{\frac{1}{2}} \) and the whole expression (5.2.17) does not exceed

\[
C(Q + \varepsilon^{-1}N)^{\frac{1}{2}}\Theta^{\frac{1}{2}} \times N^{-1}v^{\frac{1}{2}}\Theta^{\frac{1}{2}} = CN^{-1}(Q + \varepsilon^{-1}N)^{\frac{1}{2}}v^{\frac{1}{2}}\Theta
\]

and then

(5.2.19) As \( \varepsilon \geq Z^{-1}v^{-\frac{3}{2}} \) the first term in the right-hand expression of (5.2.15) does not exceed \( Cv\Theta. \)

Further, we need to estimate the second term in the right-hand expression of (5.2.15). It can be rewritten in the form

(5.2.20) \[
\sum_{1 \leq i \leq N} \int U(x_i, y) \Psi(x_i, \ldots, x_N) \Psi^{\dagger}(x_1, \ldots, x_{N-1}, y) \theta^{\frac{1}{2}}(x_N) \theta^{\frac{1}{2}}(y) \times \\
F(x_N, y) \, dx_1 \cdots dx_N \, dy
\]

where \( U(x_i, y) \) is the difference between potential generated by the charge \( \delta(x - x_i) \) and the same charge smeared; note that \( U(x_i, y) \) is supported in
{(x_i, y) : |x_i - y| \leq \varepsilon}. Let us estimate the \(i\)-th term in this sum with \(i < N\) first; multiplied by \(N(N - 1)\), it doesn’t exceed

\[(5.2.21)\]

\[
N\left(\int |U(x_i, y)|^2|\psi(x_1, \ldots, x_N)|^2\theta^\frac{1}{2}(x_N)\theta^\frac{1}{2}(y)|F(x_N, y)|\;dx_1 \cdots dx_N\;dy\right)^{\frac{1}{2}}
\]

here \(\omega\) is \(\varepsilon\)-admissible and supported in \{((x_i, y) : |x_i - y| \leq 2\varepsilon\} function. Due to proposition 6.C.1 in the second factor \(\int \theta^\frac{1}{2}(x_N)|F(x_N, y)|\;dx_N \leq C\) and therefore the whole second factor doesn’t exceed

\[(5.2.22)\]

\[
C\left(\int \theta^\frac{1}{2}(x)\omega(x, y)\phi^{(2)}_\psi(x, y)\;dxdy\right)^{\frac{1}{2}}
\]

where we replaced \(x_i\) by \(x\). According to Proposition 4.1.1 in the selected expression one can replace \(\phi^{(2)}_\psi(x, y)\) by \(\rho(x)\rho(y)\) with an error which does not exceed

\[
C\left(\sup_x \|\nabla y \chi_x\|_{L^2(\mathbb{R}^N)}(Q + \varepsilon^{-1}N)^{\frac{1}{2}} + C\varepsilon N\|\nabla y \chi\|_{L^\infty}\right)\Theta
\]

which as we plug \(\sup_x \|\nabla y \chi_x\|_{L^2(\mathbb{R}^N)} \asymp \varepsilon^{\frac{3}{2}},\|\nabla y \chi\|_{L^\infty} \asymp \varepsilon^{-1}\) becomes \(CN\Theta\). Meanwhile, consider

\[(5.2.23)\]

\[
\int |U(x_i, y)|^2\theta^\frac{1}{2}(y)|F(x_N, y)|\;dy.
\]

Again due to proposition 6.C.1 it does not exceed

\[
Cv^\frac{3}{2}\int |U(x_i, y)|^2\theta^\frac{1}{2}(y)(|x_N - y|^v + 1)^{-s}\;dy
\]

and this integral should be taken over \(B(x_i, \varepsilon)\), with \(|U(x_i, y)| \leq |x_i - y|^{-1}\), so (5.2.23) does not exceed \(C\varepsilon v^\frac{3}{2}\omega'(x_i, x_N)\) with \(\omega'(x, y) = (1 + v^\frac{1}{2}|x - y|)^{-s}\) (provided \(\varepsilon \leq v^{-\frac{1}{2}}\) which will be the case). Therefore the first factor in (5.2.21) doesn’t exceed

\[(5.2.24)\]

\[
C\varepsilon^{\frac{1}{2}}v^\frac{3}{2}\left(\int \theta^\frac{1}{2}(x)\omega'(x, y)\phi^{(2)}_\psi(x, y)\;dxdy\right)^{\frac{1}{2}}.
\]
Therefore in selected expression one can replace $\phi^{(2)}_\psi(x, y)$ by $\rho \psi(x) \rho(y)$ with an error which does not exceed what we got before but with $\varepsilon$ replaced by $v^{-\frac{1}{2}}$, i.e. also $C N \Theta$.

However in both selected expressions replacing $\phi^{(2)}_\psi(x, y)$ by $\rho \psi(x) \rho(y)$ we get just $0$. Therefore expression (5.2.21) does not exceed $C \varepsilon^{\frac{1}{2}} v^{\frac{1}{2}} Z \Theta$ which does not exceed $C v \Theta$ provided $\varepsilon \leq C v^{\frac{1}{2}} Z^{-2}$.

So, we have two restrictions to $\varepsilon$ from above: the last one and $\varepsilon \leq Z^{-\frac{2}{3}}$, and one can see easily that both of them are compatible with with restriction to $\varepsilon$ in (5.2.19).

Finally, consider term in (5.2.20) with $i = N$ (multiplied by $N$);

\begin{equation}
(5.2.25) \quad N \int U(x_N, y) |\Psi(x_1, \ldots, x_N)|^2 \theta^\frac{1}{2} (x_N) \theta^\frac{1}{2} (y) F(x_N, y) \, dx_1 \cdots dx_N \, dy
\end{equation}
due to Cauchy inequality it does not exceed

\begin{equation}
(5.2.26) \quad N \left( \int |x_N - y|^{-2} |\Psi(x_1, \ldots, x_N)|^2 \theta^\frac{1}{2} (x_N) \theta^\frac{1}{2} (y) \, dx_1 \cdots dx_N \, dy \right)^{\frac{1}{2}} \times
\end{equation}

\begin{equation}
N \left( \int |F(x_N, y)|^2 |\Psi(x_1, \ldots, x_N)|^2 \theta^\frac{1}{2} (x_N) \theta^\frac{1}{2} (y) \, dx_1 \cdots dx_N \, dy \right)^{\frac{1}{2}}
\end{equation}

where both integrals are taken over $\{|x_N - y| \leq \varepsilon\}$ and integrating with respect to $y$ there we get that it

\begin{equation}
C \varepsilon^{\frac{1}{2}} \Theta^{\frac{1}{2}} \times v^{\frac{1}{2}} \varepsilon^{\frac{3}{2}} \Theta^{\frac{1}{2}} = C v^{\frac{3}{2}} \varepsilon^2 \Theta \ll v \Theta.
\end{equation}

Therefore the right-hand expression in (5.2.2) is $\geq -C v \Theta$ and recalling that $\nu' - \nu = O(v)$ we recover an lower estimate in Theorem 5.2.1 below:

\begin{equation}
(5.2.27) \quad I_N + \nu \geq -C v = C Q^{\frac{1}{2}} (Z - N)^{\frac{1}{2}}.
\end{equation}

Combining with a lower estimate (5.1.12) and recalling estimate (3.1.5) for $Q$ we arrive to

**Theorem 5.2.1.** Let conditions (2.2.15) and (5.1.2) be fulfilled and let $N \leq Z - C_0 Q^{\frac{1}{2}}$ with $Q \leq C_1 Z^{\frac{3}{2}}$. Then

In the framework of fixed nuclei model under assumption (5.1.2)

\begin{equation}
(5.2.28) \quad |I_N + \nu| \leq C (Z - N)^{\frac{12}{7}} Z^{-\frac{\delta}{3}} \begin{cases} 1 & \text{as } a \leq Z^{-\frac{1}{3}}, \\ N^{-\delta} + (a Z^{\frac{1}{2}})^{-\delta} & \text{as } a \geq Z^{-\frac{1}{3}}. \end{cases}
\end{equation}

59
5.3 Estimate for excessive positive charge

To estimate excessive positive charge when molecules can still exist in free nuclei model we apply arguments of section 5 of B. Ruskai and J. P. Solovej [RS]. In view of Theorem 3.4.2 it is sufficient to consider the case

\[ a = \min_{j < k} |x_j - x_k| \geq C_0 \bar{r}. \]

Therefore in Thomas-Fermi theory \( \rho^{\text{TF}} \) is supported in separate “atoms”.

Consider \( a \)-admissible functions \( \theta_m(x) \), supported in \( B(y_m, \frac{1}{3} a) \) as \( k = 1, \ldots, M \) and in \( \{|x - y_m| \geq \frac{1}{4} a \ \forall \ m = 1, \ldots, M\} \) as \( k = 0 \), such that

\[ \theta_0^2 + \ldots + \theta_M^2 = 1. \]

Then for the ground state \( \Psi \)

\[ E_N = \langle H \Psi, \Psi \rangle = \sum_\alpha \langle \theta_\alpha H \theta_\alpha \Psi, \Psi \rangle - \sum_\alpha \| \nabla_k \theta_\alpha \Psi \|^2 \]

with the sum over of \((M + 1)\)-cluster decompositions \( \alpha = (\alpha_0, \ldots, \alpha_M) \) of \( \{1, \ldots, N\} \) and \( \theta_\alpha(x) = \prod_{0 \leq k \leq M} \prod_{i \in \alpha_k} \theta_k(x_i) \). Then for any given \( \alpha \)

\[ H = \sum_{0 \leq k \leq M} H_{\alpha_k} + J_\alpha \]

with the cluster Hamiltonians \( H_{\alpha_k} \) involving only potential of \( k \)-th nucleus (no nucleus potential as \( k = 0 \)) and only electrons belonging to \( \alpha_k \) and such that

\[ H_{\alpha_k} \geq E_{\text{at}}(N_k(\alpha), Z_k), \quad H_{\alpha_0} \geq 0 \]

and with the intercluster Hamiltonian

\[ J_\alpha = \sum_{1 \leq k \leq M} \sum_{i \notin \alpha_k} -Z_k |x_i - y_k|^{-1} \]

\[ + \sum_{k < l} \sum_{i \in \alpha_k, j \in \alpha_j} |x_i - x_j|^{-1} + \sum_{k < l} Z_k Z_l |y_l - y_k|^{-1}. \]

Let us note that

\[ \sum_\alpha \theta_\alpha^2 J_\alpha = \sum_{0 \leq k < l \leq M} J_{kl} \]
with \( J_{kl} \) given by (32)–(33) of Ruskai–Solovej [RS] as \( k, l > 0 \) and \( k = 0 \) respectively:

\[
(5.3.8) \quad J_{kl} = Z_k Z_l |y_k - y_l|^{-1} - Z_k \sum_i \theta_i(x_i)^2 |x_i - y_k|^{-1} - Z_l \sum_i \theta_i(x_i)^2 |x_i - y_l|^{-1} + \sum_{i \neq j} \theta_k(x_i)^2 \theta_l(x_j)^2 |x_i - x_j|^{-1},
\]

and

\[
(5.3.9) \quad J_{0l} = \sum_i \theta_0(x_i)^2 \left( -Z_l |x_i - y_l|^{-1} + \sum_j \theta_l(x_j)^2 |x_i - x_j|^{-1} \right).
\]

Then we recover (35) Ruskai–Solovej [RS]

\[
(5.3.10) \quad \langle J_{kl} \Psi, \Psi \rangle = Z_k Z_l |y_k - y_l|^{-1} - Z_k \int \rho(x) \theta_k(x)^2 |x - y_l|^{-1} dx - Z_l \int \rho(x) \theta_l(x)^2 |x - y_k|^{-1} dx + \int 2\Theta^{(2)}(x, y) \theta_k(x) \theta_l(y) dx dy.
\]

Applying proposition 4.1.1 and estimate (3.4.1) (replacing first \( \theta_k \) with \( k = 1, \ldots, M \) by \( \bar{\theta}_k \) supported in \( B(x_k, c \bar{r}) \) and estimating an error), we conclude that

\[
(5.3.11) \quad \int \rho(x) \theta_k(x)^2 |x - y_l|^{-1} dx = \left( \int \rho^{TF}(x) \theta_k(x)^2 |x - y_l|^{-1} dx + O(Y) \right) |y_k - y_l|^{-1},
\]

\[
(5.3.12) \quad \int \rho(x) \bar{\theta}(x)^2 dx = N_k^{TF} + O(Y),
\]

with

\[
(5.3.13) \quad N_k^{TF} = \int \rho^{TF}(x) \theta_k(x)^2 dx, \quad Y := Q^{1 \over 2} F^{1 \over 2}
\]

(compare with (36)–(37) of Ruskai–Solovej [RS]) which yields

\[
(5.3.14) \quad \int \rho(x) \left( 1 - \sum_{1 \leq k \leq M} \bar{\theta}_k(x) \right) dx \leq CY
\]

61
and we prove that (5.3.12) holds for \( \theta_k \) as well (of Ruskai–Solovej [RS]).

The last term in (5.3.11) is estimated by proposition 4.1.1 and estimate (3.4.1) and the same replacement trick:

\[
\int \phi^{(2)}(x, y) \theta_k(x)^2 \theta_l(y)^2 |x - y|^{-1} \, dx \, dy \geq \\
\int \phi^{(2)}(x, y) \tilde{\theta}_k(x)^2 \theta_l(y)^2 |x - y|^{-1} \, dx \, dy \geq \\
\int \rho_{TF}(x) \rho_{TF}(y) \tilde{\theta}_k(x)^2 \theta_l(y)^2 |x - y|^{-1} \, dx \, dy - \\
C \left( Q_1 \int \rho_{TF}(x) \theta_l(x)^2 \, dx + Ya^{-1} \right) |y_k - y_l|^{-1}
\]

and repeating the same trick we get that it is larger than

\[
\int \rho_{TF}(x) \rho_{TF}(y) |x - y|^{-1} \, dx \, dy - C(Z - N) Ya^{-1} - CY^2 a^{-1}.
\]

Then we conclude that

\[
\langle J_{kl}, \Psi \rangle \geq J_{kl}^{TF} - CNTa^{-1}
\]

with

\[
J_{kl}^{TF} = \int \rho_{TF}(x) \rho_{TF}(y) \theta_k(x) \theta_l(y) |x - y|^{-1} \, dx \, dy \\
- Z_k \int \rho_{TF}(x) \theta_l(y) |x - y_k|^{-1} \, dx - Z_l \int \rho_{TF}(x) \theta_k(y) |x - y_l|^{-1} \, dx \\
+ Z_k Z_l |x_k - x_l|^{-1}
\]

and

\[
|\langle J_{0l}, \Psi \rangle| \leq C(Z - N) Ya^{-1} + CY^2 a^{-1}
\]

(compare with (39)–(40) of Ruskai–Solovej [RS]) provided

\[
\int \rho_{TF}(y) |x - y|^{-1} \tilde{\theta}_k(x) \, dy - N_k^{TF} |x - y_k|^{-1} \leq \\
C(Z - N) |x - x_k|^{-1}
\]
as $|x - y_k| \geq C\bar{r}$.

Let us note that the absolute value of the last term in the right-hand expression of (5.3.3) doesn’t exceed $Ca^{-2}Y$ due to (5.3.12). Now stability condition yields

$$J = \sum_{k<l} l_{kl} \leq CYa^{-2} + C(Z - N)Ya^{-1} + CY^2a^{-1}. \quad (5.3.21)$$

This inequality, (5.3.1) and proposition 5.3.3 below yield that $Z - N \leq CY = C\bar{r}^\frac{1}{2}Q^\frac{1}{2}$. Since $\bar{r} \simeq (Z - N)^{-\frac{1}{2}}$ we arrive to $(Z - N) \leq CQ^\frac{1}{2}$:

**Theorem 5.3.1.** Let condition (2.2.15) be fulfilled. Then in the framework of free nuclei model with $M \geq 2$ the stable molecule does not exist unless

$$Z - N \leq Z^\frac{1}{2} - \delta. \quad (5.3.22)$$

**Remark 5.3.2.** Unfortunately, we don’t prove that molecules exist. We are not aware of any rigorous result of this type in frames of our models.

**Proposition 5.3.3.** Let (5.3.1) be fulfilled. Then inequality (5.3.20) holds and

$$J \geq \epsilon(Z - N)^2a^{-1}. \quad (5.3.23)$$

**Proof.** Proof Note first that

$$E^{TF} \leq E(\bar{\rho}) = \sum_j E(\rho_j^{TF}) + J^{TF}(\bar{\rho}) \leq \sum_j E^{TF}(\rho_j^{TF}) + C(Z - N)^2a^{-1} \quad (5.3.24)$$

with $\bar{\rho} = \sum_j \rho_j^{TF}$ while

$$\sum_j E(\rho_j^{TF}) \leq \sum_j E(\theta_j\rho_j^{TF}); \quad (5.3.25)$$

then

$$J^{TF}(\rho^{TF}) \leq C(Z - N)^2a^{-1} \quad (5.3.26)$$
and using (5.3.22) we conclude that

\begin{equation}
D(\rho^{\text{TF}} - \bar{\rho}, \rho^{\text{TF}} - \bar{\rho}) \leq C(Z - N)^2 a^{-1}.
\end{equation}

Further,

\begin{equation}
\Delta := \sum_j D(\rho^{\text{TF}} \theta_j - \rho^{\text{TF}}_j, \rho^{\text{TF}} \theta_j - \rho^{\text{TF}}_j) \leq D(\rho^{\text{TF}} - \bar{\rho}, \rho^{\text{TF}} - \bar{\rho}) + C r a^{-1} \Delta
\end{equation}

and combining with (5.3.26) we conclude that

\begin{equation}
\Delta \leq C(Z - N)^2 a^{-1}
\end{equation}

due to (5.3.1). Combining with $\rho_j^{\text{TF}} \ast |x|^{-1} = N_j^{\text{TF}} |x - x_j|^{-1}$ for $|x - x_j| \geq r_s$ we arrive to (5.3.20). Further,

\begin{equation}
J^{\text{TF}}(\rho^{\text{TF}}) \geq J^{\text{TF}}(\bar{\rho}) - C \Delta^{\frac{1}{2}} r a^{-\frac{3}{2}} (Z - N) a^{-\frac{3}{2}} - C \Delta r^{-1}
\end{equation}

which together with (5.3.28) and (5.3.29) yields (5.3.23).

\section{Appendices}

\subsection{Electrostatic inequalities}

We know already that there are two sources of errors in the lower estimate: due to electrostatic inequality (1.1.1) and semiclassical errors. For the first error in the case $\vec{B} = \text{const}$ E. Lieb, J. P. Solovej and J. Yngvarsson [LSY2] provide the (almost) perfect estimate; the reader can find the proof based on magnetic Lieb-Thirring inequality (and this inequality as well) in that paper (p. 122) which in the case of $\vec{B} = 0$ becomes

\begin{theorem}
For the ground state $\Psi$ of (0.1.1) with potential (0.1.4)

\begin{equation}
\int \rho_\Psi^{\frac{1}{2}} dx \leq CZ^{\frac{2}{5}} N^{\frac{1}{2}} (Z + N)^{\frac{1}{3}}
\end{equation}

otherwise.

In particular for $c^{-1}N \leq Z \leq cN$ the right-hand expression doesn’t exceed $CZ^{\frac{5}{7}}$.
\end{theorem}
On the other hand, for $B = 0$ there is a more precise inequality due to V. Bach [Ba] and G. Graf and J. P. Solovej [GS]:

**Theorem 6.A.2.** For the ground state $\Psi$ of (0.1.1) with potential (0.1.4)

\[ \langle H\Psi, \Psi \rangle \geq N_1(A - \nu) + \nu N - \frac{1}{2} \int \int |x - y|^{-1}|e(x, y, \nu)|^2 \, dx \, dy - CN^{\frac{5}{3} - \delta} \]

with some exponent $\delta > 0$.

We will discuss magnetic field case in more details in the Appendix to the next Chapter.

### 6.B Hamiltonian trajectories

We are going to prove that for $W = W_{TF}$ in $M = 1$ case the generic trajectory on the energy level $\nu$ is not periodic. We use some ideas from V. Arnold [A], pages 37–38. Recall that in this case $W = W(r)$ ($r = |x - x_1|$) and angular momentum $\vec{M}$ is a motion integral. Then any trajectory lies on some plane and if $M = |\vec{M}| > 0$ it lies in $\{0 < r < \bar{r}\}$ where $W$ is analytic and $W(\bar{r}) = -\nu$.

(6.B.1) Let us assume that all the trajectories on the energy level $\nu$ are periodic.

Then the rotation number

\[ \Phi = \int_{r_1}^{r_2} \frac{M \, dr}{r^2 \sqrt{2(W(r) + \nu) - M^2 r^{-2}}} \]

showing the increment of the polar angle over a half-trajectory should be $\pi k^{-1}$ with $k \in \mathbb{N}$ and should not depend on $M$ where $r_1 \leq r_2$ are roots of $(W(r) + \nu) - M^2 r^{-2} = \nu$. So, $\Phi$ should be the same for all trajectories on the energy level $\nu$. One can see easily that for $M \to 0$ $\Phi$ tends to those of the Coulomb potential. So, $\Phi = 2\pi$ for all trajectories on the energy level $\nu$.

Let $r_0$ be a root of $F(r) = 2(W(r) + \nu) + r^4(W'(r))^2 = 0$. One can see easily that $F(\bar{r}) > 0$, $F(r) \to \infty$ as $r \to 0$ and $F'(r) < 0$ because

\[ W' < 0, \quad W'' + 2rW' = r^{-1}(r^2W'(r))' = r\Delta W > 0. \]
So, the unique root exists. Then \( r = r_0 \) is a circular motion with \( M = -r_0^2 W'(r_0) \).

Then (V. Arnold [A], problem 2 at page 37)

\[
\Phi \to \pi \sqrt{W'/(3W + rW'')}^{-1}|_{r=r_0} = \Phi_0
\]

for trajectories tending to circular. However, \( 3W' + rW'' > W' \) due to (6.B.3) and then \( \Phi_0 > \pi \). Contradiction to assumption (6.B.1).

### 6.C Some spectral function estimates

**Proposition 6.C.1.** For Schrödinger operator \( W \in C^\infty \) and for \( \phi \in C^\infty_0([-1,1]) \) the following estimate holds for any \( s \):

\[
(6.C.1) \quad |F(x, y)| \leq C h^{-3} (1 + h^{-1}|x - y|)^{-s},
\]

\[
(6.C.2) \quad F(x, y) := \int \phi(\lambda) \, d\lambda e(x, y, \lambda).
\]

**Remark 6.C.2.** Surely, \( WL^{-1} \) is not \( C^\infty \) even after rescaling but the proof works for it after rescaling.

**Proof.** Let \( u(x, y, t) = \int e^{-ih^{-1}\lambda t} \, d\lambda e(x, y, \lambda) \) be the Schwartz’s kernel of \( e^{-ih^{-1}Ht} \).

Fix \( y \). Note first that \( L^2 \)-norm\(^{24)} \) of \( \phi(hD_t)\chi(t)\omega(x)u(x, y, t) \) is less than \( Ch^s \) as \( \chi \in C^\infty_0([-\epsilon, \epsilon]) \) and \( \omega \in C^\infty \) supported in \( \{|x - y| \geq \epsilon_1\} \) \( (\epsilon_1 = C\epsilon) \) due to the finite speed of propagation of singularities.

We conclude then that \( L^2 \)-norm of \( \phi(hD_t)\chi(t)\omega(x)u(x, y, t) \) is less than \( Ch^s \) for \( \omega \in C^\infty \) supported in \( \{|x - y| \geq C\} \).

Then \( L^2 \)-norm of \( \partial_t \nabla \phi(hD_t)\chi(t)\omega(x)u \) doesn’t exceed \( Ch^s \). Then due to imbedding inequality \( L^\infty \)-norm of \( \phi(hD_t)\chi(t)\omega(x)u \) doesn’t exceed \( Ch^s \).

Setting \( t = 0 \) and using this inequality and \( |F(x, y)| \leq Ch^{-3} \) (due to Chapter 4) of [I7] we get that \( |F(x, y)| \leq Ch^s \) for \( |x - y| \geq \epsilon_0 \).

Now let us consider general \( |x - y| = r \geq Ch \). Rescaling \( x - y \mapsto (x - y)r^{-1} \) we need to rescale \( h \mapsto hr^{-1} \) and rescaling above inequality and keeping in mind that \( F(x, y) \) is a density with respect to \( x \) we get \( |F(x, y)| \leq Ch^s r^{-3-s} \) which is equivalent to (6.C.1)–(6.C.2).

\(^{24)} \) With respect to \( x, t \) here and below.
Bibliography

[A] V. I. Arnold: *Mathematical Methods of Classical Mechanics*. Springer-Verlag (1990).

[Ba] V. Bach: *Error bound for the Hartree-Fock energy of atoms and molecules*, Commun. Math. Phys. 147:527–548 (1992).

[Be] R. Benguria: *Dependence of the Thomas-Fermi energy on the nuclear coordinates*, Commun. Math. Phys., 81:419–428 (1981).

[BeL] R. Benguria and E. H. Lieb: *The positivity of the pressure in Thomas-Fermi theory*, Commun. Math. Phys., 63:193–218 (1978).

[BrL] H. Brezis and E. H. Lieb: *Long range potentials in Thomas-Fermi theory*, Commun. Math. Phys. 65, 231-246 (1979).

[E] L. Erdős, *Magnetic Lieb-Thirring inequalities*. Commun. Math. Phys., 170:629–668 (1995).

[ES3] L. Erdős, J.P. Solovej, *Ground state energy of large atoms in a self-generated magnetic field*. Commun. Math. Phys. 294, No. 1, 229-249 (2009) arXiv:0903.1816

[EFS1] L. Erdős, S. Fournais, J.P. Solovej: *Stability and semiclassics in self-generated fields*. arXiv:1105.0506

[EFS2] L. Erdős, S. Fournais, J.P. Solovej: *Second order semiclassics with self-generated magnetic fields*. arXiv:http://arxiv.org/abs/1105.0512

[EFS3] L. Erdős, S. Fournais, J.P. Solovej: *Scott correction for large atoms and molecules in a self-generated magnetic field* arXiv:1105.0521

[FS] C. Fefferman and L.A. Seco: *On the energy of a large atom*, Bull. AMS 23, 2, 525–530 (1990).

[FSW1] R. L. Frank, H. Siedentop, S. Warzel: *The ground state energy of heavy atoms: relativistic lowering of the leading energy correction*. Commun. Math. Phys. 278 no. 2, 549–566 (2008)

[FSW2] R. L. Frank, H. Siedentop, S. Warzel: *The energy of heavy atoms according to Brown and Ravenhall: the Scott correction*. Doc. Math. 14, 463–516 (2009).
[FLL] J. Fröhlich, E. H. Lieb, and M. Loss: *Stability of Coulomb systems with magnetic fields. I. The one-electron atom.* Commun. Math. Phys. 104 251–270 (1986)

[GS] G. M. Graf and J. P. Solovej: *A correlation estimate with applications to quantum systems with Coulomb interactions,* Rev. Math. Phys., 6(5a):977–997 (1994). Reprinted in The state of matter a volume dedicated to E. H. Lieb, Advanced series in mathematical physics, 20, M. Aizenman and H. Araki (Eds.), 142–166, World Scientific 1994.

[H] W. Hughes: *An atomic energy bound that gives Scott’s correction,* Adv. Math. 79, 213–270 (1990).

[Ivr1] V. Ivrii, *Asymptotics of the ground state energy of heavy molecules in the strong magnetic field. I.* Russian Journal of Mathematical Physics, 4(1):29–74 (1996).

[Ivr2] *Asymptotics of the ground state energy of heavy molecules in the strong magnetic field. II.* Russian Journal of Mathematical Physics, 5(3):321–354 (1997).

[Ivr3] V. Ivrii, *Heavy molecules in the strong magnetic field.* Russian Journal of Math. Phys. 4(1):29–74 (1996).

[Ivr4] V. Ivrii, *Heavy molecules in the strong magnetic field. Estimates for ionization energy and excessive charge* 6(1):56–85 (1999).

[Ivr5] Sharp spectral asymptotics for operators with irregular coefficients. *Pushing the limits. II.* Comm. Part. Diff. Equats., 28 (1&2):125–156, (2003).

[Ivr6] V. Ivrii *Sharp spectral asymptotics for operators with irregular coefficients. III.* Schrödinger operator with a strong magnetic field, arXiv:math/0510326 (Aug. 27, 2003), 81pp.

[I7] V. Ivrii *Microlocal Analysis and Sharp Spectral Asymptotics,* in progress: available online at http://www.math.toronto.edu/ivrii/futurebook.pdf

[IS] Ivrii, V. and Sigal, I. M *Asymptotics of the ground state energies of large Coulomb systems.* Ann. of Math., 138:243–335 (1993).
[L] E. H. Lieb: *Thomas-Fermi and related theories of atoms and molecules*, Rev. Mod. Phys. **65**, No. 4, 603-641 (1981)

[L2] E. H. Lieb: *Variational principle for many-fermion systems*, Phys. Rev. Lett. **46**, 457–459 (1981) and **47** 69(E) (1981)

[L2] *The stability of matter: from atoms to stars* (Selecta). Springer-Verlag (1991).

[LLS] E. H. Lieb, M. Loss and J. P. Solovej: *Stability of Matter in Magnetic Fields*, Phys. Rev. Lett. **75**, 985–989 (1995)

[LO] E. H. Lieb and S. Oxford: *Improved Lower Bound on the Indirect Coulomb Energy*, Int. J. Quant. Chem. **19**, 427–439, (1981)

[LS] E. H. Lieb and B. Simon: *The Thomas-Fermi theory of atoms, molecules and solids*, Adv. Math. **23**, 22-116 (1977)

[LSY1] E. H. Lieb, J. P. Solovej and J. Yngvarsson: *Asymptotics of heavy atoms in high magnetic fields: I. Lowest Landau band regions*, Comm. Pure Appl. Math. 47:513–591 (1994).

[LSY2] E. H. Lieb, J. P. Solovej and J. Yngvarsson: *Asymptotics of heavy atoms in high magnetic fields: II. Semiclassical regions*, Comm. Math. Phys., 161: 77–124 (1994).

[RS] M. B. Ruskai, M. B. and J. P. Solovej: *Asymptotic neutrality of polyatomic molecules*. In Schrödinger Operators, Springer Lecture Notes in Physics 403, E. Balslev (Ed.), 153–174, Springer Verlag (1992).

[SW1] H. Siedentop and R. Weikard: *On the leading energy correction for the statistical model of an atom: interacting case*, Commun. Math. Phys. **112**, 471–490 (1987)

[SW2] H. Siedentop and R. Weikard: *On the leading correction of the Thomas-Fermi model: lower bound*, Invent. Math. **97**, 159–193 (1990)

[SW3] H. Siedentop and R. Weikard: *A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators*, Ann. Sci. École Norm. Sup. (4), **24**, no. 2, 215–225 (1991).
[Sob1] A. V. Sobolev: *Quasi-classical asymptotics of local Riesz means for the Schrödinger operator in a moderate magnetic field*. Ann. Inst. H. Poincaré, 62 no. 4, 325-360, (1995)

[Sob] A. V. Sobolev: *Discrete spectrum asymptotics for the Schrödinger operator with a singular potential and a magnetic field*, Rev. Math. Phys 8 (1996) no. 6, 861–903.

[SS] J. P. Solovej, W. Spitzer: *A new coherent states approach to semiclassics which gives Scott’s correction*. Comm. Math. Phys. 241 (2003), no. 2-3, 383–420.

[SSS] J. P. Solovej, T.O. Sørensen, W. Spitzer: *Relativistic Scott correction for atoms and molecules*. Comm. Pure Appl. Math. Vol. LXIII. 39-118 (2010).

[Zh] G. Zhislin, *Discussion of the spectrum of Schrödinger operator for systems of many particles*. Tr. Mosk. Mat. Obs., 9, 81–128 (1960).