Department of Mathematical Sciences
The PhD School of Science
Faculty of Science
University of Copenhagen - Denmark

PhD Thesis

Phan Thành Nam

Contributions to the rigorous study of the structure of atoms

Thesis Advisor:	Jan Philip Solovej University of Copenhagen
Assessment Committee:	Jan Dereziński University of Warsaw
	Maria J. Esteban CNRS and Université Paris-Dauphine
	Enno Lenzmann (Chairman) University of Copenhagen
Date of Submission:	14 September 2011
Date of Defense:	28 October 2011

Phan Thành Nam
Department of Mathematical Sciences
University of Copenhagen
Universitetsparken 5
DK-2100 Copenhagen Ø
Denmark
ptnam@math.ku.dk
ptnam373@yahoo.com

DOI 10.1007/s00023-011-0123-2
ISBN 978-87-91927-66-9

Contents

Contents i

Acknowledgments ii

Summary iii

1 Introduction 1

1 Born-Oppenheimer approximation . . . 1
2 Existence of ground states . . . 2
3 Ground state energy . . . 4
4 Radius of atom . . . 9

2 Overview of the results 10

1 Overview of Paper I. New bounds on the maximum ionization of atoms . . . 10
2 Overview of Paper II. Asymptotic for two-dimensional atoms 16
3 Overview of Paper III. Bogoliubov theory and bosonic atoms 20

3 Conclusions and perspectives 29

Bibliography 31

Annexes: Manuscripts 37

Paper I. New bounds on the maximum ionization of atoms, Preprint 2010. . . . 37
Paper II. Joint with F. Portmann and J.P. Solovej, Asymptotics for two dimensional atoms, Annales Henri Poincaré (2011). . 59
Paper III. Bogoliubov theory and bosonic atoms, Preprint 2011. 91

Acknowledgments

I deeply thank my advisor Jan Philip Solovej for taking care me so nicely and always opening the door for any of my stupid questions. With his patience, humor and inspiration, I really learn how to enjoy mathematics rather than how to do mathematics.

It has been a fantastic period of my life when being a PhD student at Department of Mathematical Sciences, University of Copenhagen. I thank everybody at the Department for creating the great environment to work in, and for various mathematical and friendly discussions.

I had an exciting summer at the Département de Mathématiques, Université de Cergy-Pontoise in 2010. I am grateful to Mathieu Lewin for the warm hospitality and many helpful discussions, and to Séverine Paul for her enthusiastic help in practical issues.

Parts of the thesis are joint work with Fabian Portmann and Jan Philip Solovej, to whom I always enjoy to discuss with.

I would like to take this opportunity to express my gratitude to my former teachers Pham Ngoc Dinh Alain, Duong Minh Duc and Dang Duc Trong, for all of their time and patience invested in building my mathematical background.

Last, but certainly not least, I thank my family and my friends for their constant support in all of these years.

Summary

The thesis is concerned to some mathematical problems on the structure of atoms within the Born-Oppenheimer approximation: the existence and nonexistence of ground states; the asymptotics of the ground state energy of large atoms; and the asymptotics of the radius of large atoms.

In Paper I we provide a new upper bound on the maximum number of electrons that a nucleus can bind. The bound is first proved for non-relativistic atoms without magnetic field, but it can be also extended to non-relativistic atoms in magnetic field and to pseudo-relativistic atoms.

In Paper II we consider large atoms confined to two dimensions. We compute the ground state energy of the atoms up the the leading order and the first correction. Moreover, we show that in two dimensions, the radius of a neutral atom is unbounded when the nuclear charge tends to infinity, which is contrary to the expected behavior of three-dimensional atoms.

In Paper III we consider the ground state energy of bosonic atoms, namely the atoms with "bosonic electrons". It is well-known that the leading order of the ground state energy is determined by the Hartree model, and we expect that the first correction is given by the Bogoliubov approximation. We first formulate the general Bogoliubov theory as a variational model, and then we study the Bogoliubov theory for bosonic atoms in details. The comparison between the Bogoliubov ground state energy and the quantum ground state energy up to the second order, however, is still heuristic, and some further works are required to make everything rigorous.

Resumé

Denne afhandling drejer sig om matematiske problemer vedrrende strukturen af atomer i Born-Oppenheimer tilnærmelsen: Eksistens og ikke-eksistens af grundtilstande; Asymptotik af grundtilstandsenergien for store atomer; Asymptotik af atomradius af store atomer.

I artikel I giver vi en ny vre grnse pådet maksimale antal elektroner en kerne kan binde. Begrnsningen vises først for ikke-relativistiske atomer uden

magnetfelter, men kan udvides til ikke-relativistiske atomer i magnetfelter og til pseudo-relativistiske atomer.

I artikel II studeres store atomer begrænset til to dimensioner. Vi beregner grundtilstandsenergien til ledende orden samt første korrektion. Desuden viser vi, at i to dimensioner er atomets radius ubegrnset når kerneladningen går mod uendelig, hvilket er i kontrast til den forventede opførsel af tre-dimensionelle atomer.

I artikel III betragter vi grundtilstandsenergien af bosoniske atomer, nemlig atomer med "bosoniske elektroner". Det er velkendt, at grundtilstandsenergien til ledende orden er bestemt af Hartree-modellen og vi forventer, at den første korrektion er givet ved Bogolubov tilnærmelsen. Vi formulerer først Bogolubovteori som en variationel model og studerer Bogolubovteorien for bosoniske atomer i detaljer. Sammenligningen op til anden orden mellem grundtilstandsenergien i Bogolubovteori og grundtilstandsenergien i kvantemekanik er kun heuristisk og kræver yderligere arbejde for at være stringent.

Abstract

The thesis is concerned to some mathematical problems on the structure of atoms. We provide a new upper bound on the maximum number of electrons that a nucleus can bind, consider the ground state energy and the radius of a large atom confined to two dimensions, and study the Bogoliubov approximation for bosonic atoms.

Chapter 1

Introduction

1 Born-Oppenheimer approximation

Let us consider an atom with an infinitely heavy nucleus of charge $Z > 0$ and N non-relativistic quantum electrons in $\mathbb{R}^3$. The nucleus is fixed at the origin and the N-electron system is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}.$$

An N-electron wave function Ψ is a normalized function in $L^2((\mathbb{R}^3)^N)$ which is antisymmetric, namely

$$\Psi(x_1, ..., x_i, ..., x_j, ..., x_N) = -\Psi(x_1, ..., x_j, ..., x_i, ..., x_N)$$

for any $x_i \in \mathbb{R}^3$. Here $L^2((\mathbb{R}^3)^N)$ is a Hilbert space with the inner product

$$\langle \Psi_1, \Psi_2 \rangle = \int_{(\mathbb{R}^3)^{2N}} \overline{\Psi_1(x_1, ..., x_N)} \Psi_2(y_1, ..., y_N) dx_1 ... dx_N dy_1 ... dy_N.$$

The Hamiltonian $H_{N,Z}$ consists of the electron kinetic operators and the electron-nucleus and electron-electron Coulomb interactions. The anti-symmetry of the wave function is the condition to take the Pauli exclusion principle into account. Because the spin number plays no important role in our analysis here, for simplicity we may take $q = 1$ (spinless). The nuclear charge Z is allowed to be any positive number, although it is an integer in the physical case.

Here we choose the units such that all of the reduced Plancks constant, the mass of the electron and $(-1)\times$ the charge of the electron are equal to

1. The factor 1/2 in front of the kinetic operators $-\Delta_i := -\Delta_{x_i}$ can be replaced by any positive constant, by changing the units.

The ground state energy of the N electrons is the bottom of the spectrum of $H_{N,Z}$,

$$E(N,Z) = \inf \operatorname{spec} H_{N,Z} = \inf_{||\Psi||_{L^2}=1} \langle \Psi, H_{N,Z}\Psi \rangle .$$

A ground state $\Psi_{N,Z}$ is a wave function with the lowest energy, i.e.

$$(\Psi_{N,Z}, H_{N,Z}\Psi_{N,Z}) = E(N,Z).$$

By the standard variational calculation, we may see that $\Psi_{N,Z}$ is a ground state if and only if it is a solution to the Schrödinger equation

$$H_{N,Z}\Psi_{N,Z} = E_{N,Z}\Psi_{N,Z}.$$

Of our interests are the properties of the ground state energy and the ground states (if exist) of $H_{N,Z}$. Among other things, there are three important questions which we shall discuss in details below: the existence (or nonexistence) of ground states; the asymptotics of the ground state energy of large atoms; and the asymptotics of the radius of large atoms.

2 Existence of ground states

It is well known that $H_{N,Z}$ is bounded from below and its essential spectrum is given by the HVZ Theorem (see e.g. Theorem 11.2 in [73] or Theorem 2.1 in [27] for a proof)

$$\text{ess-spec } H_{N,Z} = [E(N-1), \infty).$$

As a consequence, if $E(N,Z) < E(N-1,Z)$ then $E(N,Z)$ is an isolated eigenvalue of $H_{N,Z}$ and hence there exists a ground state $\Psi_{N,Z}$. In this case, we say that the N electrons can be *bound* and the wave function $\Psi_{N,Z}$ is called a *bound state*. Physically, the binding inequality $E(N,Z) < E(N-1,Z)$ means that one cannot remove any electron without paying some positive energy.

Zhislin (1960) [77] showed that the binding inequality $E(N,Z) < E(N-1,Z)$ occurs provided that $N < Z+1$. It is a very interesting open problem, sometimes referred to as the *ionization conjecture*, that the maximum number $N_c = N_c(Z)$ of electrons that can be bound is either $Z+1$ or $Z+2$ (see [62, 63, 65, 67, 35]). Because $N_c \geq Z$ due to Zhislin's Theorem, it remains to find an upper bound on N_c.

Sigal (1982, 1984) [60, 61] and Ruskai (1982) [54] were the first ones proving that N_c is not too large. In fact, Ruskai [54] showed that $N_c =$

$O(Z^{6/5})$ and Sigal [61] proved that $N_c \leq 18Z$ and $\liminf_{Z\to\infty} N_c/Z \leq 2$. Then Lieb (1984) [32] proved that $N_c < 2Z+1$ for all $Z > 0$.

In fact, Lieb's result is a slightly stronger, which says that if $N \geq 2Z+1$ then the Schrödinger equation

$$(H_{N,Z} - E(N,Z))\Psi = 0$$

has no solution. Because his proof is very simple and elegant, let us revisit it below.

Proof of Lieb's upper bound. Multiplying the Schrödinger equation

$$(H_{N,Z} - E(N,Z))\Psi = 0 \tag{1.1}$$

by $|x_N|\overline{\Psi}$ and then integrating, one gets

$$\begin{aligned} 0 &= \langle |x_N|\Psi, (H_{N-1,Z} - E(N,Z))\Psi\rangle + \frac{1}{2}\langle |x_N|\Psi, -\Delta_N \Psi\rangle \\ &\quad + \left\langle \Psi, \left[-Z + \sum_{i=1}^{N-1} \frac{|x_N|}{|x_i - x_N|}\right]\Psi \right\rangle. \end{aligned} \tag{1.2}$$

The first term in the right hand side of (1.2) is non-negative since

$$H_{N-1,Z} \geq E(N-1,Z) \geq E(N,Z)$$

in the space of $(N-1)$ particles x_1,...,x_{N-1}. The second term is also non-negative due to the inequality

$$\operatorname{Re}\langle |x|f, -\Delta f\rangle \geq 0 \text{ for all } f \in H^1(\mathbb{R}^3). \tag{1.3}$$

Thus the third term in (1.2) must be non-positive. Using the antisymmetry and the triangle inequality $|x_i| + |x_j| \geq |x_i - x_j|$ we arrive at

$$0 \geq \left\langle \Psi_{N,Z}, \left(-Z + \frac{1}{N}\sum_{1\leq i<j\leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|}\right)\Psi_{N,Z}\right\rangle > -Z + \frac{N-1}{2}.$$

The inequality is strict since the triangle inequality is strict almost everywhere. □

Lieb's upper bound settles the conjecture for hydrogen but it is around twice of the conjectured bound for large Z.

For large atoms, the asymptotic neutrality $\lim_{Z\to\infty} N_c/Z = 1$ was first proved by Lieb, Sigal, Simon and Thirring (1988) [36]. Later, it was improved to $N_c \leq Z + O(Z^{5/7})$ by Seco, Sigal and Solovej (1990) [57] and by Fefferman and Seco (1990) [18]. The bound $N_c \leq Z + \text{const}$, for some Z-independent constant, is still unknown, although it holds true for some important approximation models such as the Thomas-Fermi and related theories [30, 8] and the Hartree-Fock theory [65, 67]. The Thomas-Fermi and the Hartree-Fock theories will be recalled below.

The main result in Paper I is to improve Lieb's upper bound for small Z.

3 Ground state energy

To discuss about the ground state energy, let us for simplicity consider only neutral atoms ($N = Z$). It was already known that

$$E(Z,Z) = c^{\mathrm{TF}} Z^{7/3} + c^{\mathrm{S}} Z^2 + c^{\mathrm{DS}} Z^{5/3} + o(Z^{5/3}) \tag{1.4}$$

where the leading (Thomas-Fermi [75, 20]) term was established in [37], the second (Scott [56]) term was proved in [24, 59], and the third (Dirac-Schwinger [12, 55]) term was shown in [19]. In the following, we shall explain heuristically these terms, and we will see that the asymptotic energy (1.4) is still correct with $E(Z,Z)$ replaced by $E(N,Z)$ for any $N \geq Z$.

Thomas-Fermi term

The Thomas-Fermi term of order $Z^{7/3}$ may be understood entirely from semiclassics. The Thomas-Fermi theory involves two approximations. First, the semiclassical approximation for the kinetic energy is (see [43, 37])

$$\frac{1}{2}\left\langle \Psi, \sum_{i=1}^{N} \Delta_i \Psi \right\rangle = \frac{1}{2}\operatorname{Tr}(-\Delta\gamma_\Psi) \approx \frac{1}{2} K_{\mathrm{sc}} \int\limits_{\mathbb{R}^3} [\rho_\Psi(x)]^{5/3} dx \text{ with } K_{\mathrm{sc}} = \frac{3}{5}\left(3\pi^2\right)^{2/3}.$$

Here γ_Ψ is the one-body density matrix of Ψ, which is an operator on $L^2(\mathbb{R}^3)$ with the kernel given by

$$\gamma_\Psi(x,y) := N \int_{\mathbb{R}^{3(N-1)}} \Psi(x, x_2, ..., x_N, \sigma_N) \overline{\Psi(y, x_2, ..., x_N, \sigma_N)} dx_2 ... dx_N$$

and $\rho_\Psi(x) = \gamma_\Psi(x,x)$. Note that $0 \leq \gamma_\Psi \leq 1$ and $\operatorname{Tr}(\gamma_\Psi) = \int_{\mathbb{R}^3} \rho = N$. In fact, Lieb and Thirring [43] showed the rigorous lower bound, for any density matrix $0 \leq \gamma \leq 1$,

$$\operatorname{Tr}(-\Delta\gamma) \geq R_{LT} K_{\mathrm{sc}} \int\limits_{\mathbb{R}^3} [\rho_\gamma(x)]^{5/3} dx$$

with $R_{LT} = 0.185$ and they conjectured that we can take $R_{LT} = 1$. Currently, the best constant is given by Dolbeault, Laptev and Loss [13] that we can take $R_{LT} = 0.672$.

The second estimate we need in the Thomas-Fermi Theory is the approximation between the electron-electron interaction and the self-electrostatic energy

$$\left\langle \Psi, \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\Psi \right\rangle \approx \frac{1}{2} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\Psi(x)\rho_\Psi(y)}{|x-y|} dxdy =: D(\rho_\Psi, \rho_\Psi).$$

Lieb and Oxford [29, 34] verified this approximation by the lower bound

$$\left\langle \Psi, \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\Psi \right\rangle \ge D(\rho_\Psi, \rho_\Psi) - 1.68 \int\limits_{\mathbb{R}^3} [\rho_\Psi(x)]^{4/3} dx.$$

Put these above approximation together, we obtain the Thomas-Fermi functional

$$\mathcal{E}^{\mathrm{TF}}(\rho, Z) := \frac{K_{\mathrm{sc}}}{2} \int\limits_{\mathbb{R}^3} [\rho(x)]^{5/3} dx - Z \int\limits_{\mathbb{R}^3} \frac{\rho(x)}{|x|} dx + D(\rho, \rho)$$

and the Thomas-Fermi energy

$$E^{\mathrm{TF}}(N, Z) := \inf \left\{ E^{\mathrm{TF}}(Z, \rho) : \rho \ge 0, \int \rho = N \right\}.$$

By the scaling $\rho(x) = Z^2 \widetilde{\rho}(Z^{1/3}x)$ we obtain

$$E^{\mathrm{TF}}(Z, Z) = c^{\mathrm{TF}} Z^{7/3} \text{ where } c^{\mathrm{TF}} = E^{\mathrm{TF}}(N = Z = 1).$$

This is the leading term in (1.4). The above scaling and the properties of the Thomas-Fermi minimizer also suggest that almost of electrons are located mainly at a distance of order $Z^{-1/3}$ from the nucleus and they are the source of the leading term of the ground state energy.

Scott term

The Scott term of order Z^2 is a pure quantum correction coming from the essentially finitely many inner most electrons at a distance of order Z^{-1} from the nucleus. To see it, let us assume that the Thomas-Fermi minimizer ρ_Z^{TF} is a good approximation to the density ρ_Ψ of the ground state (at least at the small distance) and arrive at the following estimate on the electron-electron interaction

$$\left\langle \Psi, \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\Psi \right\rangle \approx D(\rho_\Psi, \rho_\Psi) \approx D(\rho_\Psi, \rho_Z^{\mathrm{TF}}).$$

Putting this into the Hamiltonian $H_{N,Z}$ we get

$$\langle \Psi, H_{N,Z}\Psi\rangle \approx \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left[\left(-\frac{1}{2}\Delta - V_Z^{\mathrm{TF}}(x)\right)\rho_\Psi\right],$$

where

$$V_Z^{\mathrm{TF}}(x) = \frac{Z}{|x|} - \rho_Z^{\mathrm{TF}} * |x|^{-1}.$$

If we allow ρ_Ψ to be any density matrix and take the infimum both sides, we arive at the asymptotic estimate

$$E(Z,Z) = \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - {V_Z}^{\mathrm{TF}}(x)\right)_-\right] + o(Z^2),$$

where $\mathrm{Tr}[H_-]$ means the sum of all of negative eigenvalues of H.

Note that we may recover the leading term by the semiclassical approximation

$$\begin{aligned}\mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - {V_Z}^{\mathrm{TF}}(x)\right)_-\right] &= \iint_{\mathbb{R}^3\times\mathbb{R}^3}\left(\frac{1}{2}(2\pi p)^2 - {V_Z}^{\mathrm{TF}}(x)\right)_- dp dx + o(Z^3)\\ &= c^{\mathrm{TF}} Z^{7/3} + o(Z^3).\end{aligned}$$

Moreover, observe that the most singular part of the Thomas-Fermi potential V_Z^{TF} comes from the region near the origin, where $V_Z^{\mathrm{TF}} \approx Z|x|^{-1}$ if $|x| \in O(|Z|^{-1})$. By comparing $(-\frac{1}{2}\Delta - {V_Z}^{\mathrm{TF}}(x))$ to the hydrogen Hamiltonian $H_Z^{\mathrm{hyd}} = -\frac{1}{2}\Delta - Z|x|^{-1}$ in this region, ones can obtain the first correction to the semiclassics (see [71], Theorem 16)

$$\mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - {V_Z}^{\mathrm{TF}}(x)\right)_-\right] = \iint_{\mathbb{R}^3\times\mathbb{R}^3}\left(\frac{1}{2}(2\pi p)^2 - {V_Z}^{\mathrm{TF}}(x)\right)_- dp dx + \frac{1}{2}Z^2 + o(Z^2).$$

This explains the Scott term $c^{\mathrm{S}}Z^2 = (1/2)Z^2$ in the asymptotic energy (1.4).

Dirac-Schwinger term

Finally, to reach at the Dirac-Schwinger term $c^{\mathrm{DS}}Z^{5/3}$ in (1.4), we can not simply replace the electron-electron interaction by the direct term $D(\rho_\Psi,\rho_\Psi)$, but we have to also take the electron correlation into account. The Hartree-Fock theory does this job by restricting the wave functions among the forms $\Psi = u_1 \wedge u_2 \wedge ... \wedge u_N$, where $\{u_i\}_{i=1}^N$ is any orthonormal family in $L^2(\mathbb{R}^3 \times \{1,...,q\})$. Such a wave function is called a Slater determinant because it can be rewritten as

$$\Psi(z_1,...,z_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_1(z_1) & u_1(z_2)\dots & u_1(z_N) \\ u_2(z_1) & u_2(z_2)\dots & u_2(z_N) \\ \vdots & \vdots & \vdots \\ a_N(z_1) & u_N(z_2)\cdots & u_N(z_N) \end{pmatrix}.$$

It is straightforward to see that if $\Psi = u_1 \wedge u_2 \wedge ... \wedge u_N$ then $\gamma_\Psi(x,y) = \sum\limits_{i=1}^N u_i(x)\overline{u_i(y)}$ and the energy $\langle \Psi, H_{N,Z}\Psi\rangle$ is equal to

$$\mathcal{E}^{\mathrm{HF}}(Z,\gamma_\Psi) := \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\gamma_\Psi\right] + D(\rho_\Psi,\rho_\Psi) - \frac{1}{2}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma_\Psi(x,y)|^2}{|x-y|}dxdy.$$

Thus the Hartree-Fock theory involves the one-body density matrices of the wave functions while the Thomas-Fermi theory involves only the density functionals. The Hartree-Fock energy is

$$\begin{aligned} E^{\mathrm{HF}}(N,Z) &:= \inf\{(\Psi, H_{N,Z}\Psi)|\Psi \text{ is a Slater determinant}\} \\ &= \inf\{\mathcal{E}^{\mathrm{HF}}(Z,\gamma) : 0 \le \gamma \le 1, \mathrm{Tr}(\gamma) = N\} \end{aligned}$$

where the second identity is due to Lieb's variational principle [31]. Note that by the definition, the Hartree-Fock energy is always an upper bound to the quantum ground state energy.

It is widely believed by the chemists and physicists that the ground state energy $E(N,Z)$ can be approximated very precisely by $(\Psi, H_{N,Z}\Psi)$ when Ψ is the Slater determinant made up by the first N negative eigenfunctions of $(-\frac{1}{2}\Delta - V_Z^{\mathrm{TF}})$, the Schrödinger operator with the Thomas-Fermi potential. Starting by verifying this experience, Fefferman and Seco [19] showed that the absolute ground state energy

$$E(Z) = \inf_N E(N,Z) = E(N_c(Z),Z)$$

obeys the asymptotics

$$E(N_c(Z),Z) = c^{\mathrm{TF}}Z^{7/3} + c^{\mathrm{S}}Z^2 + c^{\mathrm{DS}}Z^{5/3} + o(Z^{5/3-\varepsilon}). \tag{1.5}$$

for some universal constant $\varepsilon > 0$. In fact, (1.5) is still slightly different from (1.4) because the neutral atom ($N = Z$) is replaced by the maximum negative ionization ($N = N_c(Z)$). However, with the help from the knowledge of the Hartree-Fock theory, we can obtain (1.4) from (1.5) as follows.

An implicit consequence of Fefferman and Seco's approach is that the Hartree-Fock ground state energy $E^{\mathrm{HF}}(N_c(Z), Z)$ agrees with the quantum ground state energy $E(N_c(Z), Z)$ up to an error of order $o(Z^{5/3})$. Bach [3] generalized this result by proving that the same estimate is correct for all N near Z, namely if $Z - O(Z^{1/3}) \le N \le Z + O(Z^{5/7})$ then

$$0 \le E^{\mathrm{HF}}(N, Z) - E(N, Z) \le o(Z^{5/3-\varepsilon}).$$

Note that $N_c(Z) \le Z + O(Z^{5/7})$ [57, 18].

On the other hand, Solovej [67] showed that within the Hartree-Fock theory, the maximum negative ionization and the ionization energy are bounded by some universal constants, namely there exist C_1 and C_2 such that

$$E^{\mathrm{HF}}(N, Z) = E^{\mathrm{HF}}(Z + C_1, Z)$$

for any $N \ge Z + C_1$ and

$$0 \le E^{\mathrm{HF}}(N-1, Z) - E^{\mathrm{HF}}(N, Z) \le C_2$$

for any $N \ge Z$. (In fact, it was just stated explicitly in [67] that $0 \le E^{\mathrm{HF}}(Z-1, Z) - E^{\mathrm{HF}}(Z, Z) \le C_2$, but the approach in [67] indeed gives the stronger bound as we stated above.)

Thus putting the above estimates together, we find that for any $N \ge Z$ one has

$$\begin{aligned} & |E(N,Z) - E(N_c(Z), Z)| \\ \le\ & |E(N,Z) - E^{\mathrm{HF}}(N,Z)| + |E^{\mathrm{HF}}(N,Z) - E^{\mathrm{HF}}(N_c(Z), Z)| \\ & + |E(N_c(Z), Z) - E^{\mathrm{HF}}(N_c(Z), Z)| \\ \le\ & O(Z^{5/3-\varepsilon}) + O(1) + O(Z^{5/3-\varepsilon}) = O(Z^{5/3-\varepsilon}). \end{aligned}$$

Therefore, (1.5) implies that for any $N \ge Z$,

$$E(N, Z) = c^{\mathrm{TF}} Z^{7/3} + c^{\mathrm{S}} Z^2 + c^{\mathrm{DS}} Z^{5/3} + o(Z^{5/3-\varepsilon}).$$

In the case $N = Z$ we obtain (1.4).

In Paper II, we compute the ground state energy of a large atoms confined in two dimensions; and in Paper III we consider the ground state energy of bosonic atoms.

4 Radius of atom

It is an interesting fact from the periodic table that the neutral atoms in the same group often have comparable radii, even if their nuclear charge are very different. So people may conjecture that the radii of atoms are bounded by some universal constant [62, 63, 65, 67].

To state the conjecture rigorously, let us assume that the Hamiltonian $H_{Z,Z}$ has a ground state Ψ_Z. The radius R_Z is the distance from the nucleus to the outermost surface of the atom, such that outside the ball $B(0, R_Z)$ the expectation number of electron is 1. Thus R_Z satisfies

$$\int_{|x|\geq R_Z} \rho_{\Psi_Z}(x)dx = 1. \tag{1.6}$$

where ρ_{Ψ_Z} is the density of the wave function Ψ_Z. Note that both of the wave function Ψ_Z and the radius R_Z maybe not unique. The conjecture is that there exist universal constant $0 < c < C < \infty$ (independent of Z) such that

$$c \leq R_Z \leq C \tag{1.7}$$

for all $Z > 0$ and for all R_Z satisfying (1.6).

As we discussed before, it is suggested from the Thomas-Fermi theory that almost of electrons live in the distance of order $Z^{-1/3}$ from the nucleus. In fact, it is well-known that

$$\int_{\mathbb{R}^3} |x|\rho_{\Psi_Z}(x)dx \geq C_0 Z^{2/3}$$

for some universal constant $C_0 > 0$ (see e.g. Lemma 2 in [48] for an explicit constant). Consequently, we obtain the lower bound $R_Z \geq CZ^{-1/3}$.

By a more careful analysis in comparison with the Thomas-Fermi theory, Seco, Sigal and Solovej [57] proved the improved lower bound $R_Z \geq C_2 Z^{-5/21}$. Solovej [67] also showed the bound (1.7) within the Hartree-Fock theory. However, it is still an open problem to prove the universal bound in the quantum theory.

In Paper II, we show that the conjecture fails in two dimensions. More precisely, if a neutral atom is confined in two dimensions then its radius is unbounded when the nuclear charge tends to infinity.

Chapter 2

Overview of the results

1 Overview of Paper I. New bounds on the maximum ionization of atoms

In this paper we give an explicit upper bound to the maximum number of electrons that a nucleus can bind. Because one of our constants depends on the spin number (as we shall explain below), let us include the physical spin $q = 2$ and consider the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$

on the antisymmetric space $\bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$. We denote by $E(N, Z)$ the ground state energy of $H_{N,Z}$ and we say that N electrons can be bound if $E(N, Z) < E(N-1, Z)$. As discussed in the Introduction, by HVZ Theorem the binding condition means that $E(N, Z)$ is an isolated eigevalue of $H_{N,Z}$.

Of our interest is the maximum number $N_c = N_c(Z)$ of electrons that can be bound. It is an interesting conjecture that N_c is either $N+1$ or $N+2$. Note that the ionization conjecture only concerns fermions since for bosonic atoms it was shown that $\lim_{Z\to\infty} N_c/Z \approx 1.21$ by Benguria and Lieb [7] and Solovej [66] (the numerical value 1.21 is taken from [6]).

In spite of the asymptotic neutrality $\lim_{Z\to\infty} N_c/Z = 1$ [36, 57, 18], Lieb's upper bound $N_c < 2Z + 1$ [32] is still the best one for realistic atoms (corresponding to the range $1 \le Z \le 118$ in the current periodic table). The purpose in our work is to find an improved upper bound for all $Z > 0$. As in [32], we do not need the binding inequality; more precisely, that $E(N, Z)$ is an eigenvalue of $H_{N,Z}$ is sufficient for our analysis. Our main result is the following.

Theorem 1.1 (Bound on maximum ionization of non-relativistic atoms). *Let $Z > 0$ (not necessarily an integer). If $E(N, Z)$ is an eigenvalue of $H_{N,Z}$ then either $N = 1$ or*

$$N < 1.22Z + 3Z^{1/3}.$$

The factor 1.22 can be replaced by β^{-1} with β being defined by (2.1).

Remark. (i) The bound $1.22Z + 3Z^{1/3}$ is less than Lieb's bound $2Z + 1$ when $Z \geq 6$.

(ii) It can be seen from our proof that the factor 3 in front of the second term of order $Z^{1/3}$ in our bound is proportional to $q^{2/3}$ where q is the spin number. Therefore, our result only holds for fermions. For bosonic atoms, one may take $q = N$ and hence our bound becomes CZ, which is worse than Lieb's one. In our proof, the Pauli exclusion principle hides in the fact that we use the Lieb-Thirring inequality to show that the average distance from the electrons to the nucleus of charge Z is at least of order $Z^{-1/3}$. In contrast, the corresponding distance in the bosonic atoms is of order Z^{-1}.

(iii) Although Lieb's method [32] can be generalized to molecules, we have not yet been able to adapt our method to this case.

Let us discuss briefly the strategy of proof of Theorem 1.1. As the first step, we modify Lieb's proof in [32] by multiplying the Schrödinger equation $(H_{N,Z} - E(N, Z))\Psi = 0$ by $|x_N|\overline{\Psi}$. Then employing the Lieb-Thirring inequality to control error terms, we arrive at the bound

$$\alpha_N(N - 1) < Z(1 + 0.83\ N^{-2/3}),$$

where

$$\alpha_N := \inf_{x_1,\ldots,x_N \in \mathbb{R}^3} \frac{\sum\limits_{1\leq i<j\leq N} \frac{|x_i|^2+|x_j|^2}{|x_i-x_j|}}{(N-1)\sum\limits_{i=1}^{N} |x_i|}.$$

Roughly speaking, the number α_N^{-1} yields an upper bound on N/Z. This bound improves previous results since α_N is bigger than $1/2$. To derive some effective estimates on α_N, we may think of α_N as the lowest energy of N classical particles acting on $\mathbb{R}^3$ via the potential $V(x, y) = \frac{x^2+y^2}{|x-y|}$, under some normalizing condition. It is natural to believe that if N becomes large then α_N converges to the statistical limit

$$\beta := \inf \left\{ \frac{\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{2|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)}{\int\limits_{\mathbb{R}^3} |x|\,\mathrm{d}\rho(x) \int\limits_{\mathbb{R}^3} \mathrm{d}\rho(x)} : \rho \text{ a positive measure in } \mathbb{R}^3 \right\}. \quad (2.1)$$

Results of this form in bounded domain have already appeared in [47]. In our case, we can show the explicit estimate

$$\alpha_N \geq \frac{N}{N-1}[\beta - 3(\beta/6)^{1/3}N^{-2/3}],$$

with β being defined by (2.1). Thus we get

$$N[\beta - 3(\beta/6)^{1/3}N^{-2/3}] < Z(1 + 0.83\ N^{-2/3}).$$

This inequality gives an upper bound of N in terms of Z and β. We can show that $\beta \geq 0.8218$ and this lower bound ensures the inequality $N < 1.22\ Z + 3\ Z^{1/3}$ in Theorem 1.1 (here $1.22 \approx 1/0.8218$).

Remark. We do not know the exact numerical value of β, but if in the variational definition we restrict ρ to radially symmetric measures in (2.1) then we obtain the upper bound $\beta \leq 0.8705$. Therefore, the lower bound $\beta \geq 0.8218$ is already rather precise, although there is of course still room for improvement.

Now we explain the lower bound $\beta \geq 0.8218$. We need to use the following inequalities (see [48] Lemma 5)

$$\begin{aligned}
&\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \\
\geq &\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \left(\max\{|x|,|y|\} + \frac{(\min\{|x|,|y|\})^2}{|x-y|}\right)\mathrm{d}\rho(x)\,\mathrm{d}\rho(y), \qquad (2.2)
\end{aligned}$$

and

$$\begin{aligned}
&\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|}\,\mathrm{d}\,\rho(x)\,\mathrm{d}\rho(y) \\
\geq &\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \left(|x-y| + \frac{2}{3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\right)\mathrm{d}\rho(x)\,\mathrm{d}\rho(y). \qquad (2.3)
\end{aligned}$$

Note that both of (2.2) and (2.3) will become identities if the measure ρ is radially symmetric. The inequality (2.2) follows from a key result of the original proof of the asymptotic neutrality in [36] (Theorem 3.1), that for any $\varepsilon > 0$, if N large enough then for all $\{x_i\}_{i=1}^N \subset \mathbb{R}^3$,

$$\max_{1\leq j\leq N}\left\{\sum_{1\leq i\leq N, i\neq j} \frac{1}{|x_i - x_j|} - \frac{N(1-\varepsilon)}{|x_j|}\right\} \geq 0.$$

The inequality (2.3) is a consequence of the kernel expression

$$\frac{x^2+y^2}{|x-y|} = |x-y| + \frac{2x.y}{|x-y|}$$

and the observation that $2x.y/|x-y|$ is a positive kernel.

Using a convex combination of (2.2) and (2.3), we arrive at

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} W_\lambda(x,y)\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)$$

for any positive measure ρ on $\mathbb{R}^3$ and $\lambda\in[0,1]$, where

$$\begin{aligned} W_\lambda(x,y) \quad := \quad & \lambda\left(\max\{|x|,|y|\} + \frac{(\min\{|x|,|y|\})^2}{|x-y|}\right) \\ & +(1-\lambda)\left(|x-y| + \frac{2}{3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\right). \end{aligned} \tag{2.4}$$

It turns out that

$$\beta \geq \sup_{\lambda\in[0,1]} \inf_{x,y\in\mathbb{R}^3} \frac{W_\lambda(x,y)}{|x|+|y|} \approx 0.8218$$

Note that our method also applies to other models of atoms, such as the non-relativistic atoms in magnetic fields and the relativistic atoms.

With the presence of a magnetic field, the atoms are described by the Hamiltonian

$$H_{N,Z,\mathcal{A}} = \sum_{i=1}^N \left(T_{\mathcal{A}}^{(i)} - \frac{Z}{|x_i|}\right) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i-x_j|}$$

acting on the fermionic space $\bigwedge^N (L^2(\mathbb{R}^3)\otimes\mathbb{C}^2)$. The kinetic operator is the Pauli operator

$$T_{\mathcal{A}} = |\sigma\cdot(-i\nabla+\mathcal{A}(x))|^2 = (-i\nabla+\mathcal{A}(x))^2 + \sigma\cdot\mathcal{B},$$

where $\mathcal{A}$ is the magnetic potential, $\mathcal{B}=\mathrm{curl}(A)$ is the magnetic field and $\sigma=(\sigma^1,\sigma^2,\sigma^3)$ are the Pauli matrices

$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

For simplicity we shall always assume that $\mathcal{A}\in L^4_{\rm loc}(\mathbb{R}^3,\mathbb{R}^3)$, $\nabla\cdot A\in L^2_{\rm loc}(\mathbb{R}^3)$ and $|\mathcal{B}|\in L^{3/2}(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$. Under these assumptions, it is well known that $(-i\nabla + \mathcal{A}(x))^2$ is essentially selfadjoint on $L^2(\mathbb{R}^3)$ with core $C_c^\infty(\mathbb{R}^3)$ [45], and $|\mathcal{B}| + Z/|x|$ is infinitesimally bounded with respect to $(-i\nabla + \mathcal{A}(x))^2$ (see e.g. [58, 46]). In particular, the ground state energy

$$E(N, Z, \mathcal{B}) = \inf \text{spec } H_{N,Z,\mathcal{A}}$$

is finite. We shall also assume that $N \mapsto E(N, Z, \mathcal{B})$ is non-increasing (for example, this is the case if $\mathcal{B} = (0, 0, B)$ is a constant magnetic field [40]). Note that the ground state energy depends on $\mathcal{A}$ only through $\mathcal{B}$ by *gauge invariance* (see e.g. [35] p. 21).

Of our interest is the maximum number N_c such that $E(N_c, Z, \mathcal{B})$ is an eigenvalue of $H_{N,Z,\mathcal{A}}$. Seiringer (2001) [58] showed that

$$N_c < 2Z + 1 + \frac{1}{2} \frac{E(N_c, Z, \mathcal{B}) - E(N_c, Z, \mathcal{B})}{N_c Z(k-1)} \tag{2.5}$$

for all $k > 1$. In the homogeneous case, $\mathcal{B} = (0, 0, B)$, his bound yields

$$N_c < 2Z + 1 + C_1 Z^{1/3} + C_2 Z \min\left\{(B/Z^3)^{2/5}, 1 + |\ln(B/Z^3)|^2\right\}. \tag{2.6}$$

This improves the earlier bound $N_c < 2Z+1+cB^{1/2}$ in [9] (where the Hamiltonian $H_{N,Z,\mathcal{A}}$ is restricted to a small class of wavefunctions in the lowest Landau band). In particular, in the semiclassical regime $\lim_{Z\to\infty}(B/Z^3) = 0$, Seiringer's bound implies that

$$\limsup_{Z\to\infty} \frac{N_c}{Z} \leq 2.$$

In contrast, it was shown by Lieb, Solovej and Yngvason (1994) [40] that if $\lim_{Z\to\infty}(B/Z^3) = \infty$, then

$$\liminf_{Z\to\infty} \frac{N_c}{Z} \geq 2.$$

We can improve these bounds as follows.

Theorem 1.2 (Bounds on maximum ionization of atoms in magnetic fields)**.** *Let $Z > 0$ and let $\mathcal{B}$ satisfy the assumption stated above. Then we have, for every $k > 1$,*

$$N_c < (1.22Z + 3Z^{1/3}) \left(1 + \frac{E(N_c, Z, \mathcal{B}) - E(N_c, kZ, \mathcal{B})}{N_c Z^2 (k-1)}\right). \tag{2.7}$$

If $\mathcal{B} = (0, 0, B)$ is a constant magnetic field then

$$N_c < (1.22\ Z + 3Z^{1/3}) \quad \times \quad \Big(1 + 11.8\ Z^{-2/3} + \\ + \min\left\{0.42\left(B/Z^3\right)^{2/5}, C(1 + |\ln(B/Z^3)|^2)\right\}\Big)$$

for some universal constant C (independent of Z and B). In particular, if $\lim_{Z\to\infty}(B/Z^3) = 0$ *then*

$$\liminf_{Z\to\infty} \frac{N_c}{Z} \leq 1.22.$$

The number 1.22 *in all bounds can be replaced by β^{-1} with β being defined by (2.1).*

Remark. As shown in [46], one can make a slight improvement on our bounds by using the Hardy-type inequality $T_{\mathcal{A}} \geq (d_{\mathcal{B}}/4)|x|^{-2}$ instead of $T_{\mathcal{A}} \geq 0$, for some $0 < d_{\mathcal{B}} \leq 1$. It allows us to include a factor $(1 - d_{\mathcal{B}})$ in front of the term involved to $E(N, Z, \mathcal{B}) - E(N, kZ, \mathcal{B})$ in (2.7).

Now we consider the pseudo-relativistic atoms, which are described by the Hamiltonian

$$H^{\rm rel}_{N,Z} = \sum_{i=1}^{N} \left(\alpha^{-1}(\sqrt{-\Delta_i + \alpha^{-1}} - \alpha^{-1}) - \frac{Z}{|x_i|} \right) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|}$$

acting on the fermionic space $\bigwedge^N (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$. Here $\alpha > 0$ is the *fine-structure constant.* It is well known that the ground state energy $E^{\rm rel}(N, Z) := \inf \operatorname{spec} H^{\rm rel}_{N,Z}$ is finite if and only if $Z\alpha \leq 2/\pi$ (see e.g. [35]). The physical value is $\alpha = e^2/(\hbar c) \approx 1/137$ and hence $Z < 87.22$. However, in our mathematical setting we allow α and Z to be any positive numbers as long as $Z\alpha \leq 2/\pi$.

As in the previous dicussions, we are also interested in the maximum number N_c such that the ground state energy $E^{\rm rel}(N_c, Z)$ is an eigenvalue of $H^{\rm rel}_{N_c,Z}$. Note that Lieb's bound $N_c < 2Z + 1$ still holds in this case. In fact, due to a technical gap the original proof of Lieb in [32] works properly only when $Z\alpha < 1/2$. However, it is posible to fill this gap to obtain the bound up to $Z\alpha < 2/\pi$ [11]. On the other hand, up to our knowledge, no result about asymptotic behavior of N_c/Z is available for the pseudo-relativistic model, although within pseudo-relativistic Hartree-Fock theory it was recently shown by Dall'Acqua and Solovej (2010) [10] that $N_c \leq Z + \text{const}$.

We have the following result.

Theorem 1.3 (Bound on maximum ionization of pseudo-relativistic atoms)**.** *For every $Z > 0$ such that $Z\alpha \leq \kappa < 2/\pi$ we have either $N_c = 1$ or*

$$N_c < 1.22Z + C_\kappa Z^{1/3}$$

for some constant C_κ depending only on κ. The number 1.22 *can be replaced by β^{-1} with β being defined by (2.1).*

2 Overview of Paper II. Asymptotic for two-dimensional atoms

In this joint work with Fabian Portmann and Jan Philip Solovej, we consider atoms confined to two dimensions with particles interacting via the three-dimensional Coulomb potential. The atom with a fixed nucleus of charge $Z > 0$ and N non-relativistic quantum electrons of charge -1 is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$

acting on the antisymmetric space $\bigwedge_{i=1}^{N} L^2(\mathbb{R}^2)$. Here for simplicity we shall assume that electrons are spinless because the spin only complicates the notation and our coefficients in an obvious way.

One possible approach to obtain the above Hamiltonian is to consider a three-dimensional atom confined to a thin layer $\mathbb{R}^2 \times (-a, a)$ in the limit $a \to 0^+$ (see [14], Section 3, for a detailed discussion on the hydrogen case).

To the best of our knowledge, there is no existing result on the ground state energy and the ground states of the system, except for the case of hydrogen [76, 52]. The purpose of this article is to give a rigorous analysis for large Z-atom asymptotics.

Theorem 2.1 (Ground state energy). *Fix $\lambda > 0$. When $Z \to \infty$ and $N/Z \to \lambda$, the ground state energy $E(N, Z)$ of $H_{N,Z}$ is*

$$E(N, Z) = -\frac{1}{2} Z^2 \ln Z + \left(E^{\mathrm{TF}}(\lambda) + \frac{1}{2} c^{\mathrm{H}} \right) Z^2 + o(Z^2)$$

where $E^{\mathrm{TF}}(\lambda)$ is the Thomas-Fermi energy (defined below) and $c^{\mathrm{H}} = -3\ln(2) - 2\gamma_E + 1 \approx -2.2339$ with $\gamma_E \approx 0.5772$ being Euler's constant [16]. In particular, $\lambda \mapsto E^{\mathrm{TF}}(\lambda)$ is strictly convex and decreasing on $(0, 1]$ and $E^{\mathrm{TF}}(\lambda) = E^{\mathrm{TF}}(1)$ if $\lambda \ge 1$.

Remark. (i) The two-dimensional atom has two regions. The innermost region of size Z^{-1} contains a finite number of electrons and contributes with Z^2 to the total energy. The outer region from Z^{-1} to order 1 has a high density of electrons and can be understood semiclassically. It contributes to the energy $Z^2 \ln(Z)$ from the short distance divergence and Z^2 from the bulk at distance 1.

(ii) By considering the hydrogen semiclassics we conjecture that the next term of $E(\lambda Z, Z)$ is of order $Z^{3/2}$.

Theorem 2.2 (Extensivity of neutral atoms)**.** *Assume that $N/Z \to 1$ and $\Psi_{N,Z}$ is a ground state of $H_{N,Z}$. Then, for any $R > 0$ there exists $C_R > 0$ such that*

$$\int_{|x|\geq R} \rho_{\Psi_{N,Z}}(x)dx \geq C_R Z + o(Z).$$

Remark. If we define the radius R_Z of a neutral atom ($N = Z$) by

$$\int_{|x|\geq R_Z} \rho_{\Psi_{Z,Z}}(x)dx = 1$$

then Theorem 2.2 implies that $\lim_{Z\to\infty} R_Z = \infty$. In three dimensions, however, the radius is expected to be bounded independently of Z (see [57, 67]).

Our main tool to understand the ground state energy and the ground states is the two-dimensional Thomas-Fermi (TF) theory below. In this theory, the Z-ground state scales as $Z\rho^{\mathrm{TF}}_{N/Z}(x)$ and it suffices to introduce only the Z-independent theory (the Z-dependent TF theory can be defined from the TF theory below by scaling $\rho \mapsto Z\rho$). The three-dimensional TF theory was studied in great mathematical detail by Lieb-Simon [37, 30] (see also [33], Chap. 11 for the the simplest version of the TF theory).

Definition (Thomas-Fermi functional)**.** For any nonnegative function $\rho \in L^1(\mathbb{R}^2)$ we define the *TF functional* as

$$\mathcal{E}^{\mathrm{TF}}(\rho) \;:=\; \int\limits_{\mathbb{R}^2} \left(\pi\rho^2(x) - \frac{\rho(x)}{|x|} + (4\pi)^{-1}[|x|^{-1}-1]_+^2\right)dx + D(\rho,\rho).$$

For any $\lambda > 0$ we define the *TF energy* as

$$E^{\mathrm{TF}}(\lambda) := \inf\left\{\mathcal{E}^{\mathrm{TF}}(\rho) | \rho \geq 0, \|\rho\|_{L^1(\mathbb{R}^2)} \leq \lambda\right\}. \tag{2.8}$$

Let us explain the terms in the TF functional. The term $\pi\rho^2$ comes from the semiclassics of the kinetic energy while $-\int \rho(x)|x|^{-1}$ and the direct term

$$D(\rho,\rho) = \frac{1}{2}\iint \rho(x)\rho(y)|x-y|^{-1}dxdy$$

stands for the Coulomb interactions. The appearance of $(4\pi)^{-1}[|x|^{-1}-1]_+^2$ ensures that the TF functional is bounded from below,

$$\begin{aligned}
\mathcal{E}^{\mathrm{TF}}(\rho) \;&=\; \int\limits_{|x|\leq 1} \pi\left(\rho(x) - \frac{1}{2\pi|x|}\right)^2 dx + \int\limits_{|x|>1} \left(\pi\rho^2(x) - \frac{\rho(x)}{|x|}\right)dx \\
&\quad + D(\rho,\rho) - \frac{3}{4} \\
&\geq\; -\int \rho - \frac{3}{4}.
\end{aligned}$$

Basic information about the TF theory is collected in the following theorem.

Theorem 2.3 (Thomas-Fermi theory)**.** *Let $\lambda > 0$.*

(i) *(Existence) The variational problem* (2.8) *has a unique minimizer $\rho_\lambda^{\mathrm{TF}}$. Moreover, the functional $\lambda \mapsto E^{\mathrm{TF}}(\lambda)$ is strictly convex, decreasing on* $(0, 1]$ *and $E^{\mathrm{TF}}(\lambda) = E^{\mathrm{TF}}(1)$ if $\lambda \geq 1$.*

(ii) *(*TF *equation) The TF minimizer $\rho_\lambda^{\mathrm{TF}}$ satisfies the TF equation*

$$2\pi\rho_\lambda^{\mathrm{TF}}(x) = \left[V_\lambda^{\mathrm{TF}}\right]_+$$

where $V_\lambda^{\mathrm{TF}}(x)$ is the TF potential defined by

$$V_\lambda^{\mathrm{TF}}(x) := |x|^{-1} - (\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1})(x) - \mu_\lambda^{\mathrm{TF}}.$$

Here $\mu_\lambda^{\mathrm{TF}}$ is a constant satisfying $\mu_\lambda^{\mathrm{TF}} > 0$ if $\lambda < 1$ and $\mu_\lambda^{\mathrm{TF}} = 0$ if $\lambda \geq 1$.

(iii) *(*TF *minimizer) $\rho_\lambda^{\mathrm{TF}}$ is radially symmetric; $\int \rho_\lambda^{\mathrm{TF}} = \min\{\lambda, 1\}$ and*

$$0 \leq |x|^{-1} - 2\pi\rho_\lambda^{\mathrm{TF}} \leq C|x|^{-1/2} \text{ for all } x \neq 0.$$

Moreover, $\operatorname{supp} \rho_\lambda^{\mathrm{TF}}$ *is compact if and only if $\lambda < 1$.*

By using the standard strategy in three dimensions, we can show that if Ψ is a ground state for $H_{N,Z}$ with $N \approx \lambda Z$ then we have the density approximations $\rho_\Psi \approx Z\rho_\lambda^{\mathrm{TF}}$ (in some appropriate sense) and the energy approximation

$$\begin{aligned} E(N, Z) &= \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma_\Psi\right] + D(\rho_\Psi, \rho_\Psi) + o(Z^2) \\ &= Z\,\mathrm{Tr}\left[\left(-(2Z)^{-1}\Delta - V_\lambda^{\mathrm{TF}}\right)_-\right] - Z^2\left[\mu_\lambda^{\mathrm{TF}}(N/Z) + D(\rho_\lambda^{\mathrm{TF}})\right] + o(Z^2). \end{aligned}$$

However, there are two important differences from the three-dimensional case. First, recall that the TF theory has the Z-ground state $Z\rho_{N/Z}^{\mathrm{TF}}(x)$ and ρ_1^{TF} has unbounded support. Roughly speaking, the extensivity of the TF ground state implies the extensivity of neutral atoms (in contrast, the three-dimensional TF Z-ground state scales as $Z^2\rho^{\mathrm{TF}}(Z^{1/3}x)$, i.e. its core *shrinks* as $Z^{-1/3}$). Second, the two-dimensional TF potential $V_\lambda^{\mathrm{TF}}(x)$ is *not* in $L^2_{loc}(\mathbb{R}^2)$ (it behaves like $|x|^{-1}$ near the origin). Consequently, one *cannot* write the semiclassics of $\mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}\right]_-$ in the usual way because

$$(2\pi)^{-2}\iint [h^2p^2 - V^{\mathrm{TF}}(x)]_- dp dx = -(8\pi h^2)^{-1}\int [V^{\mathrm{TF}}(x)]_+^2 dx = -\infty.$$

In contrast, the three-dimensional semiclassical approximation leads to the behavior

$$-(15\pi^2h^3)^{-1}\int_{\mathbb{R}^3}[V^{\mathrm{TF}}(x)]_+^{5/2}dx$$

which is finite for the Coulomb singularity $V^{\mathrm{TF}}(x) \sim |x|^{-1} \in L^{5/2}_{\mathrm{loc}}(\mathbb{R}^3)$.

To deal with the singularity near the origin, we shall follow the strategy of proving the Scott's correction given by Solovej and Spitzer [71] (see also [70]), that is to compare the semiclassics of TF-type potentials with hydrogen. More precisely, in the region close to the origin we shall compare directly with hydrogen, whereas in the exterior region we can employ the coherent state approach. We do not use the new coherent state approach introduced in [71], since the usual one [30, 74] is sufficient for our calculations. In fact, we can prove the following semiclassical estimate for potentials with Coulomb singularities in two dimensions.

Theorem 2.4 (Semiclassics for Coulomb singular potentials)**.** *Let $V \in L^2_{\mathrm{loc}}(\mathbb{R}^2\backslash\{0\})$ be a real-valued potential such that $1_{\{|x|\geq 1\}}V_+ \in L^2(\mathbb{R}^2)$ and*

$$|V(x)-\kappa|x|^{-1}| \leq C|x|^{-\theta} \text{ for all } |x|\leq \delta,$$

where $\kappa>0$, $\delta>0$, $1>\theta>0$ and $C>0$ are universal constants. Then, as $h\to 0^+$,

$$\begin{aligned}\mathrm{Tr}\left[-h^2\Delta - V\right]_- &= -(8\pi h^2)^{-1}\int_{\mathbb{R}^2}\left([V(x)]_+^2-\kappa^2[|x|^{-1}-1]_+^2\right)dx\\ &\quad +\kappa^2(4h^2)^{-1}\left[\ln(2\kappa^{-1}h^2)+c^{\mathrm{H}}\right]+o(h^{-2}),\end{aligned}$$

where $c^{\mathrm{H}} = -3\ln(2)-2\gamma_E+1 \approx -2.2339$ with $\gamma_E\approx 0.5772$ being Euler's constant [16].

The Thomas-Fermi potential $V^{\mathrm{TF}}_\lambda(x)$ is a special case of the Coulomb singular potential in Theorem 2.4. In fact, it satisfies that $[V^{\mathrm{TF}}_\lambda]_+ \in L^1(\mathbb{R}^2)$ and

$$|V^{\mathrm{TF}}_\lambda(x)-|x|^{-1}| \leq C(|x|^{-1/2}+1) \text{ for all } x\neq 0.$$

The following theorem will turn out to be the main ingredient to prove Theorems 2.1 and 2.2. The parameter h will eventually be replaced by $(2Z)^{-1/2}$ in our application.

Theorem 2.5 (Semiclassics for Thomas-Fermi potential)**.** *When $h\to 0^+$ one has*

$$\begin{aligned}\mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}_\lambda\right]_- &= -(8\pi h^2)^{-1}\int_{\mathbb{R}^2}\left([V^{\mathrm{TF}}_\lambda(x)]_+^2-[|x|^{-1}-1]_+^2\right)dx\\ &\quad +(4h^2)^{-1}\left[\ln(2h^2)+c^{\mathrm{H}}\right]+o(h^{-2}).\end{aligned}$$

where $c^{\mathrm{H}} = -3\ln(2) - 2\gamma_E + 1 \approx -2.2339$.

Moreover, there is a density matrix γ_h *such that*

$$\mathrm{Tr}\left[(-h^2\Delta - V_\lambda^{\mathrm{TF}})\gamma_h\right] = \mathrm{Tr}\left[-h^2\Delta - V_\lambda^{\mathrm{TF}}\right]_- + o(h^{-2})$$

and

$$2h^2\,\mathrm{Tr}(\gamma_h) \le \int \rho_\lambda^{\mathrm{TF}}, \quad D((2h^2)\rho_{\gamma_h} - \rho_\lambda^{\mathrm{TF}}) = o(1).$$

3 Overview of Paper III. Bogoliubov theory and bosonic atoms

In this paper we formulate the Bogoliubov variational principle in the same spirit of the generalized Hartree-Fock theory [5]. Our formulation bases on the earlier discussions in [67, 69]. Then we analyze the Bogoliubov approximation for bososnic atoms.

We start by introducing some conventional notations. Let $\mathfrak{h}$ be a complex separable Hilbert space with the inner product $(.,.)$ and let $\mathcal{F} = \mathcal{F}(\mathfrak{h}) := \bigoplus_{N=0}^{\infty} \mathfrak{h}_N$ be the bosonic Fock space. We denote by $a(f)$ and $a^*(f)$ the usual annihilation and creation operators and denote by $\mathcal{N} := \sum_{N=0}^{\infty} N 1_{\mathfrak{h}_N}$ the number particle operator on $\mathcal{F}$.

Let $J : \mathfrak{h} \to \mathfrak{h}^*$ be the *anti-unitary* defined by

$$J(x)(y) = (x, y)_{\mathfrak{h}}, \text{ for all } x, y \in \mathfrak{h}.$$

We can define the *generalized annihilation* and *creation* operators

$$\begin{aligned} A(f \oplus Jg) &= a(f) + a^*(g), \\ A^*(f \oplus Jg) &= a^*(f) + a(g), \text{ for all } f, g \in \mathfrak{h}. \end{aligned}$$

It is straightforward to check the conjugate relation

$$A^*(F) = A(\mathcal{J}F) \text{ for all } F \in \mathfrak{h} \oplus \mathfrak{h}^*$$

and the canonical commutation relation (CCR)

$$[A(F_1), A^*(F_2)] = (F_1, \mathcal{S}F_2) \text{ for all } F_1, F_2 \in \mathfrak{h} \oplus \mathfrak{h}^*$$

where

$$\mathcal{S} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \; \mathcal{J} = \begin{pmatrix} 0 & J^* \\ J & 0 \end{pmatrix}.$$

Definition (Bogoliubov transformations)**.** A bosonic *Bogoliubov transformation* is a linear bounded isomorphism $\mathcal{V} : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ satisfying

$$\mathcal{J}\mathcal{V}\mathcal{J} = \mathcal{V} \text{ and } \mathcal{V}^*\mathcal{S}\mathcal{V} = \mathcal{S}.$$

The Bogoliubov transformations form a subgroup of the isomorphisms in $\mathfrak{h} \oplus \mathfrak{h}^*$ which preserve the conjugate relation and the canonical commutation relation. We say that a Bogoliubov transformation $\mathcal{V}$ is *unitarily implementable* if it is implemented by a unitary mapping $\mathbb{U}_{\mathcal{V}} : \mathcal{F} \to \mathcal{F}$, namely

$$A(\mathcal{V}F) = \mathbb{U}_{\mathcal{V}} A(F) \mathbb{U}_{\mathcal{V}}^* \text{ for all } F \in \mathfrak{h} \oplus \mathfrak{h}^*. \tag{2.9}$$

Because the Bogoliubov transformation $\mathcal{V}$ satisfies $\mathcal{J}\mathcal{V}\mathcal{J} = \mathcal{V}$, it must have the form

$$\mathcal{V} = \begin{pmatrix} U & V \\ JVJ & JUJ^* \end{pmatrix} \tag{2.10}$$

for some linear operators $U : \mathfrak{h} \to \mathfrak{h}$, $V : \mathfrak{h}^* \to \mathfrak{h}$. It is well-known that $\mathcal{V}$ is unitarily implementable if and only if it satisfies Shale's condition [64] $\mathrm{Tr}(VV^*) < \infty$ (see [5], Theorem 2.2 for the fermionic analogue, the Shale-Stinespring condition).

We call a mapping ρ on $\mathcal{B}(\mathcal{F})$, the space of bounded operators on the Fock space, is a state if $\rho \geq 0$ and $\mathrm{Tr}\,\rho = 1$. We can define the *one-particle density matrix* (*1-pdm* for short) $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ of a state ρ by

$$(F_1, \Gamma F_2) = \rho(A^*(F_2)A(F_1)) \text{ for all } F_1, F_2 \in \mathfrak{h} \oplus \mathfrak{h}^*.$$

Note that if Γ is 1-pdm then $\Gamma \geq 0$ and

$$\Gamma = \begin{pmatrix} \gamma & \alpha \\ J\alpha J & 1 + J\gamma J^* \end{pmatrix} \tag{2.11}$$

where $\gamma : \mathfrak{h} \to \mathfrak{h}$ and $\alpha : \mathfrak{h}^* \to \mathfrak{h}$ are linear bounded operators defined by

$$(f, \gamma g) = \rho(a^*(g)a(f)),\ (f, \alpha J g) = \rho(a(g)a(f)) \text{ for all } f, g \in \mathfrak{h}.$$

Moreover, if Γ has the form (2.11) then $\Gamma \geq 0$ if and only if $\gamma \geq 0$, $\alpha^* = J\alpha J$ and $\gamma \geq \alpha J(1+\gamma)^{-1}J^*\alpha^*$ (see [49], Lemma 1.1).

If a state ρ has the 1-pdm of the form (2.11) then its particle number expectation is $\rho(\mathcal{N}) = \mathrm{Tr}(\gamma)$. Of primary physical interest are the states with *finite particle number expectation*. Note that any 1-dpm with finite particle number expectation can be diagonalized by a unitarily implementable Bogoliubov transformation. The finite-dimensional case of the following theorem was already proved in [69] (Theorem 9.8). For the fermionic analogue, see [5] (the proof of Theorem 2.3).

Theorem 3.1 (Diagonalization 1-dpm's by Bogoliubov transformations)**.** *If Γ has the form (2.11) with $\Gamma \geq 0$ and $Tr(\gamma) < \infty$ then there is a Bogoliubov unitarily implementable transformation $\mathcal{V} : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ and a trace class operator $\xi : \mathfrak{h} \to \mathfrak{h}$ such that*

$$\mathcal{V}^*\Gamma\mathcal{V} = \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}.$$

Similarly to generalized Hartree-Fock theory [5], of our particular interest are the quasi-free states, which satisfy Wick's Theorem, namely

$$\rho[A(F_1)...A(F_{2m-1})] = 0 \text{ for all } m \geq 1$$

and

$$\rho[A(F_1)...A(F_{2m})] = \sum_{\sigma \in P_{2m}} \rho[A(F_{\sigma(1)})A(F_{\sigma(2)})]...\rho[A(F_{\sigma(2m-1)})A(F_{\sigma(2m)})]$$

where P_{2m} is the set of pairings

$$P_{2m} = \{\sigma \in S_{2m} \mid \sigma(2j-1) < \sigma(2j+1), j = 1, \ldots, m-1, \\ \sigma(2j-1) < \sigma(2j),\ j = 1, \ldots, m\}.$$

It is obvious that a quasi-free state is determined completely from its 1-dpm. The crucial point is that among all states having the same 1-pdm (with finite particle number), there exists a unique quasi-free state. See [5] for fermionic analogue.

Theorem 3.2 (Quasi-free states and quasi-free pure states)**.**

(i) Any operator $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ of the form (2.11) satisfying $\Gamma \geq 0$ and $\mathrm{Tr}(\gamma) < \infty$ is the 1-pdm of a quasi-free state with finite particle number expectation.

(ii) A pure state $|\Psi\rangle\langle\Psi|$ with finite particle number expectation is a quasi-free state if and only if $\Psi = \mathbb{U}_{\mathcal{V}}|0\rangle$ for some Bogoliubov unitary mapping $\mathbb{U}_{\mathcal{V}}$ as in (2.9).

Any operator $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ of the form (2.11) satisfying $\Gamma \geq 0$ and $\mathrm{Tr}(\gamma) < \infty$ is the 1-pdm of a quasi-free pure state if and only if $\Gamma\mathcal{S}\Gamma = -\Gamma$.

One of the motivation of considering the quasi-free pure states is that they minimize the quadratic Hamiltonians. For a positive semi-definite operator $\mathcal{A}$ on $\mathfrak{h} \oplus \mathfrak{h}^*$ such that $\mathcal{J}\mathcal{A}\mathcal{J} = \mathcal{A}$, the operator

$$H_{\mathcal{A}} = \sum_{i,j=1} (F_i, \mathcal{A}F_j)A^*(F_i)A(F_j),$$

acting on $\mathcal{F}$ is called a *quadratic Hamiltonian* corresponding to $\mathcal{A}$. Here $\{F_i\}_{i\ge1}$ is an orthonormal basis for $\mathfrak{h}\oplus\mathfrak{h}^*$ (the sum is independent of the choice of $\{F_i\}_{i\ge1}$).

We consider ground state energy of $H_{\mathcal{A}}$,

$$E(H_{\mathcal{A}}) \;:=\; \inf\{\rho(H_{\mathcal{A}})|\rho \text{ is a state with } \rho(\mathcal{N})<\infty\} \tag{2.12}$$

Theorem 3.3 (Minimizing quadratic Hamiltonians)**.** *Let $\mathcal{A}$, $H_{\mathcal{A}}$ and $E(H_{\mathcal{A}})$ as above.*

(i) *We have* $E(H_{\mathcal{A}})=\inf\{\rho(H_{\mathcal{A}})|\rho$ is a quasi-free pure state$\}$.

(ii) *If there is a unitarily implementable Bogoliubov transformation $\mathcal{V}_{\mathcal{A}}$ such that $\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}}$ is diagonal then there is a quasi-free pure state ρ_0 such that $\rho_0(H_{\mathcal{A}})=E(H_{\mathcal{A}})$. Moreover, if $\mathcal{A}$ is positive definite then ρ_0 is unique.*

(iii) *If the variational problem (2.12) has a minimizer then $\mathcal{A}$ is diagonalized by a unitarily implementable Bogoliubov transformation $\mathcal{V}_{\mathcal{A}}$. Moreover, if Γ is the 1-pdm of the minimizer then we have*

$$\mathcal{A}\Gamma=-\mathcal{A}\mathcal{S}1_{(-\infty,0)}[\mathcal{A}\mathcal{S}].$$

In particular, $\mathcal{A}\Gamma\mathcal{S}=\mathcal{S}\Gamma\mathcal{A}\le 0$.

Remark. If an operator W is not self-adjoint but $U^{-1}WU$ is self-adjoint for some invertible operator U then we can still define the projection $1_{(-\infty,0)}[W]$ by

$$1_{(-\infty,0)}[W]:=U1_{(-\infty,0)}[U^{-1}WU]U^{-1}.$$

It is easy to check that the definition is independent on the choice of U. In particular, we can define

$$1_{(-\infty,0)}[\mathcal{A}\mathcal{S}]:=(\mathcal{V}_{\mathcal{A}}^*)^{-1}1_{(-\infty,0)}[\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{S}(\mathcal{V}_{\mathcal{A}}^*)^{-1}]\mathcal{V}_{\mathcal{A}}^*$$

where $\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{S}(\mathcal{V}_{\mathcal{A}}^*)^{-1}$ is self-adjoint.

The Bogoliubov variational states should include not only the quasi-free states but also the coherent states, which correspond to the condensations. Recall that (see [69], or [49] for a proof) for every $\phi\in\mathfrak{h}$, there exists (uniquely up to a complex phase) a *coherent unitary* (or a *Weyl operator*) $\mathbb{U}_\phi:\mathcal{F}\to\mathcal{F}$ such that

$$\mathbb{U}_\phi^*a(f)\mathbb{U}_\phi=a(f)+(f,\phi) \text{ for all } f\in\mathfrak{h}.$$

A *Bogoliubov variational state* is a triple $(\gamma, \alpha, \phi) \in \mathcal{G}^{\mathrm{B}} \times \mathfrak{h}$ where

$$\mathcal{G}^{\mathrm{B}} := \left\{ (\gamma, \alpha) | \Gamma_{\gamma,\alpha} = \left(\begin{array}{cc} \gamma & \alpha \\ J\alpha J & 1 + J\gamma J^* \end{array} \right) \geq 0, \mathrm{Tr}(\gamma) < \infty \right\}.$$

Given a Hamiltonian $\mathbb{H} : \mathcal{F} \to \mathcal{F}$, we can define the *Bogoliubov energy functional*

$$\mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi) := \rho_{\gamma,\alpha}(\mathbb{U}_\phi^* \mathbb{H} \mathbb{U}_\phi)$$

where $\rho_{\gamma,\alpha}$ is the quasi-free state with the 1-dpm $\Gamma_{\gamma,\alpha}$. The *Bogoliubov ground state energy* is

$$E^{\mathrm{B}}(\lambda) = \inf \left\{ \mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi) | (\gamma, \alpha, \phi) \in \mathcal{G}^{\mathrm{B}} \times \mathfrak{h}, \mathrm{Tr}(\gamma) + ||\phi||^2 = \lambda \right\}$$

where λ stands for the total particle number of the system.

We now concentrate on the case of *bosonic atoms*. For a bosonic atom we mean a system including a nucleus fixed at the origin in $\mathbb{R}^3$ with nucleus charge $Z > 0$ and N "bosonic electrons" with charge -1. The system is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\Delta_i - \frac{Z}{|x|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$$

acting on the symmetric space $\mathcal{H}_N = \bigotimes_{\mathrm{sym}}^N L^2(\mathbb{R}^3)$. The ground state energy of the system is given by

$$E(N, Z) = \inf\{(\Psi, H_{N,Z}\Psi) | \Psi \in \mathcal{H}_N, ||\Psi||_{L^2} = 1\}.$$

Due to the HVZ Theorem (see e.g. [35] Lemma 12.1), $E(N, Z) \leq E(N-1, Z)$ and if $E(N, Z) < E(N-1, Z)$ then $E(N, Z)$ is an isolated eigenvalue of $H_{N,Z}$. Unlike the asymptotic neutrality of fermionic atoms, in the bosonic case the binding $E(N, Z) < E(N-1, Z)$ holds for all $0 \leq N \leq N_c(Z)$ with $\lim_{Z\to\infty} N_c(Z)/Z = t_{\mathrm{c}} \approx 1.21$ (see [7, 66, 6, 2]).

The leading term of the ground state energy $E(N, Z)$ is given by the *Hartree theory* [7]. In the Hartree theory, the ground state energy is

$$E^{\mathrm{H}}(N, Z) = \inf\{\mathcal{E}^{\mathrm{H}}(u, Z) : ||u||_{L^2}^2 = N\}$$

where

$$\mathcal{E}^{\mathrm{H}}(u, Z) = \int_{\mathbb{R}^3} |\nabla u(x)|^2 \, dx - \int_{\mathbb{R}^3} \frac{Z|u(x)|^2}{|x|} + \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|u(x)|^2 |u(y)|^2}{|x - y|} dxdy.$$

By the scaling $u(x) = Z^2 u_1(Zx)$ we have

$$\mathcal{E}^{\mathrm{H}}(u, Z) = Z^3 \mathcal{E}^{\mathrm{H}}(u_1, 1).$$

Therefore,

$$E^{\mathrm{H}}(N, Z) = Z^3 e(N/Z, 1) \text{ where } e(t) = E^{\mathrm{H}}(t, 1).$$

It is well-known (see [6, 30]) that $e(t)$ is convex, $e(t)' < 0$ when $t < t_c \approx 1.21$ and $e'(t) = 0$ when $t \geq t_c$. Moreover, for any $0 < t < t_c \approx 1.21$, $e(t)$ has a unique minimizer ϕ_t, which is positive, radially-symmetric and it is the unique solution to the nonlinear equation $h_t \phi_t = 0$ where

$$h_t = -\Delta - \frac{1}{|x|} + |\phi_t|^2 * \frac{1}{|x|} - e'(t).$$

As a consequence, $h_t \geq 0$. Moreover, since $\sigma_{\mathrm{ess}}(h_t) = [-e'(t), 0]$, there is a gap $\Delta_t > 0$ if $t < t_c$ such that $(h_t - \Delta_t) P_t^{\perp} \geq 0$ where $P_{\phi_t}^{\perp} = 1 - P_t$ with P_t being the one-dimensional projection onto $\mathrm{Span}\{\phi_t\}$.

By scaling back, we conclude that $E^{\mathrm{H}}(tZ, Z)$ has the unique minimizer and the operator

$$h_{t,Z} = -\Delta - \frac{Z}{|x|} + |\phi_{t,Z}|^2 * \frac{1}{|x|} - Z^2 e'(t)$$

satisfies $h_{t,Z} \phi_{t,Z} = 0$ and $(h_{t,Z} - Z^2 \Delta_t) P_{\phi_{t,Z}}^{\perp} \geq 0$ when $t < t_c$.

Our aim is to investigate the first correction to the ground state energy $E(tZ, Z)$. We shall analyze the Bogoliubov variational model for bosonic atoms and compare to the full quantum theory. From the general discussion on the Bogoliubov theory, we have the Bogoliubov variational problem

$$E^{\mathrm{B}}(N, Z) \quad = \quad \inf \left\{ \mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi, Z) | (\gamma, \alpha, \phi) \in \mathcal{G}^{\mathrm{B}}, \mathrm{Tr}(\gamma) + ||\phi||^2 = N \right\} \tag{2.13}$$

where

$$\begin{aligned} \mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi, Z) = {} & \mathrm{Tr}(-[\Delta - Z|x|^{-1}]\widetilde{\gamma}) + D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + X(\gamma, \gamma) + X(\alpha, \alpha) \\ & + \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\gamma(x,y) \overline{\phi(x)} \phi(y)}{|x - y|} dx dy + \mathrm{Re} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\alpha(x,y) \overline{\phi(x) \phi(y)}}{|x - y|} dx dy. \end{aligned}$$

Here we are using the notations $\widetilde{\gamma} := \gamma + |\phi\rangle \langle \phi|$ and

$$D(f, g) = \frac{1}{2} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\overline{f(x)} g(y)}{|x - y|} dx dy, \;\; X(\gamma, \gamma') = \frac{1}{2} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\overline{\gamma(x,y)} \gamma'(x,y)}{|x - y|} dx dy.$$

The properties of the Bogoliubov theory for bosonic atoms are the following.

Theorem 3.4 (Existence of minimizers)**.** *Let the nucleus charge Z and the electron number N be any positive numbers (not necessarily integers).*

(i) If the binding inequality

$$E^{\mathrm{B}}(N,Z) < E^{\mathrm{B}}(N',Z) \text{ for all } 0 < N' < N$$

holds then $E^B(N,Z)$ has a minimizer.

(ii) The energy $E^{\mathrm{B}}(N,Z)$ is strictly decreasing on $N \in [0, N_c(Z)]$ with $N_c(Z) \geq Z$ for all Z and

$$\liminf_{Z\to\infty} \frac{N_c(Z)}{Z} \geq t_c \approx 1.21.$$

Theorem 3.5 (Bogoliubov ground state energy)**.** *If $Z \to \infty$ and $N/Z = t \in (0, t_c)$ then*

$$E^{\mathrm{B}}(N,Z) = Z^3 e(t) + Z^2 \mu(t) + o(Z^2)$$

where

$$\mu(t) := \inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} \left[\mathrm{Tr}[h_t\gamma] + \mathrm{Re} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma(x,y)+\alpha(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} dxdy \right]. \tag{2.14}$$

The coefficient $\mu(t)$ is finite and satisfies the lower bound

$$\mu(t) \leq t^{-1}e(t) - e'(t) + \widetilde{\mu}(t) < t^{-1}e(t) - e'(t) < 0,$$

where

$$\widetilde{\mu}(t) := \min_{(\gamma',\alpha')\in G^B, \gamma'\phi_t = 0} \left\{ \mathrm{Tr}[h_t\gamma'] + \mathrm{Re} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma'(x,y)+\alpha'(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} \right\}.$$

Note that if we restrict the Hamiltonian $H_{N,Z}$ into the class of N-particle product functions $\Psi_u = u \otimes u \otimes ... \otimes u$ then by scaling $u(x) = (N-1)^{-1/2} Z^2 u_0(Zx)$ we have

$$\inf_{||u||=1} \langle \Psi_u, H_{N,Z}\Psi_u\rangle = Z^3 e(t) + Z^2[t^{-1}e(t) - e'(t)] + o(Z^2).$$

Because $\mu(t) < t^{-1}e(t) - e'(t)$, the Bogoliubov ground state energy is strictly lower than the lowest energy of the product wave functions at the second oder.

We conjecture that the Bogoliubov theory determines the first correction to the leading term of the quantum energy.

Conjecture 3.6 (First correction to the leading energy)**.** *If $Z \to \infty$ and $N/Z = t \in (0, t_c)$ then*

$$E(N,Z) = E^{\mathrm{B}}(N,Z) + o(Z^2) = Z^3 e(t) + Z^2 \mu(t) + o(Z^2).$$

Now we give a heuristic discussion supporting the conjecture. While the picture is rather clear, some technical work is still needed to make the argument rigorous.

First at all, due to the variational principle, the Bogoliubov energy $E^{\mathrm{B}}(N,Z)$ is a rigorous upper bound to the quantum grand canonical energy

$$E^{\mathrm{g}}(N,Z) = \inf\{(\Psi, \bigoplus_{N=0}^{\infty} H_{N,Z}\Psi), \Psi \in \mathcal{F}, ||\Psi|| = 1\}.$$

On the other hand, if the conjecture on the convexity of function $N \mapsto E(N,Z)$ (see [35], p. 229) is correct then $E^{\mathrm{g}}(N,Z) = E(N,Z)$, and hence $E^{\mathrm{B}}(N,Z)$ is an upper bound to $E(N,Z)$.

To see the lower bound, let us choose an orthonormal basis $\{u_n\}_{n=0}^{\infty}$ for $\mathfrak{h}$ with $u_0 = \phi_{t,Z}/||\phi_{t,Z}||$ and represent the Hamiltonian $\mathbb{H}_Z = \bigoplus_{N=0}^{\infty} H_{N,Z}$ in the second quantization

$$\mathbb{H}_Z = \sum_{m,n\geq 0} h_{m,n} a_m^* a_n + \frac{1}{2} \sum_{m,n,p,q \geq 0} W_{m,n,p,q} a_m^* a_n^* a_p a_q$$

where $a_n = a(u_n)$ and

$$h_{m,n} = (u_m, (-\Delta - Z|x|^{-1})u_n), W_{m,n,p,q} = \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\overline{u_m(x) u_n(y)} u_p(x) u_q(y)}{|x-y|}.$$

Assume that Ψ is a ground state for $E(N,Z)$. We shall denote by $\langle \mathbb{H}_Z \rangle_\Psi$ the expectation $\langle \Psi, \mathbb{H}_Z \Psi \rangle$. As in [4] we have the condensation $\mathrm{Tr}(P^\perp \gamma_\Psi) \leq C$ where P is the one-dimensional projection onto u_0. If we denote $\gamma = P^\perp \gamma_\Psi P^\perp$ and $\alpha = P^\perp \alpha_\Psi P^\perp$ then $(\gamma, \alpha) \in \mathcal{G}^{\mathrm{B}}$ and $\mathrm{Tr}(\gamma) \leq C$. We now consider the terms in $\mathbb{H}_Z$.

The leading term $Z^3 e(t)$ of the ground state energy $E(N,Z)$ comes from the terms of full condensation

$$\begin{aligned} & h_{00} \langle a_0^* a_0 \rangle_\Psi + W_{0000} \langle a_0^* a_0^* a_0 a_0 \rangle_\Psi \\ \geq \; & Z^3 e(t) - Z^2 e'(t) \,\mathrm{Tr}(\gamma) + Z^2 [t^{-1} e(t) - e'(t)] + o(Z^2). \end{aligned}$$

Because almost of particles live in the condensation u_0, we may ignore all terms in the two-body interaction with 0 or 1 operators $a_0^\#$ (where $a_0^\#$ is either a_0 or a_0^*). Moreover, we apply the Bogoliubov principle in which we replace any $a_0^\#$ by $\sqrt{N_0} \approx \sqrt{N}$. A direct computation shows that the terms with 1 and 3 operators $a_0^\#$ should be canceled together, and the terms with 0 and 2 operator $a_0^\#$ contribute the energy

$$\mathrm{Tr}\left[\left(-\Delta - Z|x|^{-1} + N|u_0|^2 * |.|^{-1}\right)\gamma\right] + \mathrm{Re} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\gamma(x,y)+\alpha(x,y))\phi_{t,Z}(x)\phi_{t,Z}(y)}{|x-y|} dxdy.$$

Putting the above approximation together we arrive at the desired lower bound

$$\begin{aligned} \langle \mathbb{H}_Z \rangle_\Psi \ &\geq \ Z^3 e'(t) + Z^2[t^{-1}e(t) - e'(t)] \\ &\quad + \mathrm{Tr}[h_{t,Z}\gamma] + \mathrm{Re} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma(x,y)+\alpha(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} + o(Z^2) \\ &\geq \ Z^3 e'(t) + Z^2[t^{-1}e(t) - e'(t) + \widetilde{\mu}(t)] + o(Z^2) \\ &\geq \ Z^3 e'(t) + Z^2 \mu(t) + o(Z^2). \end{aligned}$$

Note that this estimate also implies the identity $\mu(t) = t^{-1}e(t) - e'(t) + \widetilde{\mu}(t)$ (thus $Z^2\widetilde{\mu}(t) < 0$ is the difference between the Bogoliubov energy and the lowest energy of product functions).

Chapter 3

Conclusions and perspectives

In this chapter, we describe some problems for future research, which are related to the subject represented in the thesis.

Problem 1. The ionization conjecture.

A very interesting open problem is to understand the experimental fact that a neutral atom can bind at most one or two extra electrons (see e.g. [32]). Rigorously, if we denote by $E(N,Z)$ the ground state energy of the atoms with a fixed nucleus and N electrons, and denote by $N_c = N_c(Z)$ the largest number such that N_c electrons can be *bound*, namely $E(N_c,Z) < E(N_c-1,Z)$, then the conjecture says that $N_c \le Z+2$.

It is well-known that $Z \le N_c < 2Z+1$ [32] and $N_c/Z \to 1$ as $Z \to \infty$ [36]. We proved that $N_c < 1.22\ Z + 3\ Z^{1/3}$, which improves Lieb's upper bound $2Z+1$ when $Z \ge 6$ [48]. In the next step, we expect to prove the asymptotic neutrality $N_c/Z \to 1$ for some other models, such as the non-relativistic atoms with magnetic-fields and pseudo-relativistic atoms. The further step, which may be very difficult, is to prove the universal bound $N_c \le N + C$.

Problem 2. Energy of 2-dimensional atoms.

In the joint work with F. Portmann and J.P. Solovej [50] we showed that the ground state energy of a two-dimensional atom with the nuclear charge Z and N electrons is given by

$$E(N,Z) = -\frac{1}{2}Z^2\ln(Z) + e(\lambda)Z^2 + o(Z^2)$$

when $Z \to \infty$ and $N/Z = \lambda + o(|\ln Z|^{-1})$. Unlike what ones expect on the the usual 3-dimensional atoms, the 2-dimensional atom is extensive, which in particular implies that the radius of the atom is unbounded when $Z \to \infty$.

By observing the spectrum of the hydrogen, we expect the next term is of order $Z^{3/2}$. To understand this term, we need to improve the error of the semiclassical approximation for the Thomas-Fermi potential to $o(h^{-2+1})$, instead of $o(h^{-2})$. However, the challenging point in two dimension is that the TF potential is not in $L^2_{\rm loc}(\mathbb{R}^2)$ (it behaves like $|x|^{-1}$ near the origin).

Problem 3. The first correction to the energy of bosonic atoms.

We consider the Bogoliubov theory for bosonic atoms. In [49] we showed that within the Bogoliubov approximation, the ground state energy of an atom with a fixed nucleaus with charge Z and $N = tZ$ non-relativistic electrons is

$$E^{\rm B}(N,Z) = Z^3 e(t) + Z^2 \mu(t) + o(Z^2)$$

as $Z \to \infty$. The leading term is determined by the Hartree theory, which is already known to be correct to the ground state energy $E(N,Z)$ in the full quantum theory [7]. The next step is to verify the conjecture that the second term is also correct to the quantum theory, namely

$$E(N,Z) = E^{\rm B}(N,Z) + o(Z^2).$$

Problem 4. Bogoliubov ground state for two-component charged Bose gases.

It is a remarkable fact that the matter made of two-component charged bosons is *not* stable in the second kind. More precisely, the ground state energy of the Hamiltonian

$$H_N = -\frac{1}{2}\sum_{i=1}^{N} \Delta_i + \sum_{1\le i<j\le N} \frac{e_i e_j}{|x_i - x_j|}$$

acting on the symmetric subspace of $L^2((\mathbb{R}^3 \times \{\pm 1\})^N)$ is of order $N^{7/5}$ (instead of N in fermionic matter).

The correct leading term $-AZ^{7/5}$ was predicted by F. Dyson in 1967 and then proved Lieb and Solovej [39] (lower bound) and Solovej [68] (upper bound) using the argument of the Bogoliubov approximation. We may put the question on the existence of Bogoliubov ground states for this model. Moreover, Groh [23] proved that if we allow the charged bosons have different masses then the Bogoliubov approximation still gives the upper bound to the ground state energy. It would be nice if ones can show the same thing for the lower bound, and hence validate the Bogoliubov theory in this case.

Bibliography

[1] M. Abramowitz and I.A. Stegun (eds.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, New York: Dover Publications, 9th-Printing (1970).

[2] V. Bach, Ionization energies of bosonic coulomb systems, *Lett. Math. Phys.*, **21**, 139-149 (1991).

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

[4] V. Bach, R. Lewis, E.H. Lieb and H. Siedentop, On the number of bound states of a bosonic N-particle Coulomb system, *Math. Z.* **214**, 441-460 (1993)

[5] V. Bach, E.H. Lieb and J.P. Solovej, Generalized Hartree-Fock theory and the Hubbard model, *J. Stat. Phys.* Vol. 76, No. 1-2, 3-89 (1994)

[6] B. Baumgartner, On the Thomas-Fermi-von Weizäcker and Hartree energies as functions of the degree of ionization, *J. Phys. A* **17**, 1593-1602 (1984).

[7] R. Benguria and E.H. Lieb, Proof of stability of highly negative ions in the absence of the Pauli principle, *Phys. Rev. Lett.* **50**, 1771-1774 (1983).

[8] R. Benguria and E.H. Lieb, The most negative ion in the Thomas-Fermi-von Weizsäcker theory of atoms and molecules, *J. Phys. B* **18**, 1045-1059 (1985).

[9] R. Brummelhuis and M.B. Ruskai, A one-dimensional model for many-electron atoms in extremely strong magnetic fields: maximum negative ionization, *J. Phys. A: Math. Gen.* **32** 2567-82 (1999).

[10] A. Dall'Acqua and J.P. Solovej, Excess charge for pseudo-relativistic atoms in Hartree-Fock theory, *Documenta Mathematica*, to appear (2010).

[11] A. Dall'Acqua, T. Østergaard Sørensen and E. Stockmeyer, private communication.

[12] P.A.M. Dirac, Note on exchange phenomena in the Thomas-Fermi atom, *Proc. Cambridge Phil. Soc.*, **26**, 376-385 (1930).

[13] J. Dolbeault, A. Laptev, and M. Loss, Lieb-Thirring inequalities with improved constants, *J. Eur. Math. Soc.* **10**, 1121-1126 (2008).

[14] P. Duclos, P. Štoviček and M. Tušek, On the two-dimensional Coulomb-like potential with a central point interaction, *J. Phys. A: Math. Theor.* **43**, 474020 (2010).

[15] F.J. Dyson, Ground State Energy of a Finite System of Charged Particles. *J. Math. Phys.* **8**, 1538–1545 (1967).

[16] L. Euler, *Inventio summae cuiusque seriei ex dato termino generali*, St. Petersbourg, (1736).

[17] C.L. Fefferman and R. de la Llave, Relativistic stability of matter, *I. Rev. Mat. Iberoam.* **2**(1,2), 119-161 (1986).

[18] C. Fefferman and L. A. Seco, Asymptotic neutrality of large ions, *Commun. Math. Phys.* **128**, 109-130 (1990).

[19] C.L. Fefferman and L. Seco, On the energy of a large atom, *Bulletin of the A.M.S.*, **23**, 525-530 (1990).

[20] E. Fermi, Un Metodo Statistico per la Determinazione di alcune Priopritetà dell'Atomo. *Rend. Accad. Naz. Lincei* **6**, 602-607 (1927).

[21] R. L. Frank, E. H. Lieb, R. Seiringer, and H. Siedentop, Müller exchange-correlation energy in density-matrix-functional theory, *Phys. Rev. A* **76**, 052517 (2007).

[22] M. Gaudin, Une démonstartion simpliflée du théorème de Wick en méchanique statistique. *Nucl. Phys.* **15** (1960)

[23] A. Groh, Upper bound to the ground state energy of the two-component charged Bose gas with arbitrary masses, *Diploma Thesis*, Ludwig-Maximilians-Universität Mn̈chen (2010)

[24] W. Hughes, An atomic energy bound that gives Scott's correction, *Adv. Math.*, **79**, 213-270 (1990)

[25] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, "Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules, *Phys. Rev. A* **16**, 1782-1785 (1977).

[26] E. Lenzmann and M. Lewin, Minimizers for the Hartree-Fock-Bogoliubov theory of neutron stars and white dwarfs, *Duke Math. Journal*, **152**, no. 2, 257–315 (2010).

[27] M. Lewin, Geometric methods for nonlinear many-body quantum systems, *J. Funct. Anal.*, **260**, 3535-3595 (2011).

[28] E.H. Lieb, The stability of matter, *Rev. Mod. Phys.* **48**, 553-569 (1976).

[29] E. H. Lieb, A lower bound for Coulomb energies, *Phys. Lett. A* **70**, 444-446 (1979).

[30] E.H. Lieb, Thomas-Fermi and related theories of atoms and molecules, *Rev. Mod. Phys.* **53**, 603-641 (1981).

[31] E.H. Lieb, Variational principle for many-fermion systems, *Phys. Rev. Lett.* **46**, 457-459 (1981).

[32] E.H. Lieb, Bound on the maximum negative ionization of atoms and molecules, *Phys. Rev. A* **29**, 3018-3028 (1984).

[33] E.H. Lieb and M. Loss, *Analysis*, 2nd Ed., AMS., Providence, Rhode Island (2001).

[34] E.H. Lieb and S. Oxford, An improved lower bound on the indirect Coulomb energy, *Internat. J. Quantum Chem.* **19**, 427-439 (1981).

[35] E. H. Lieb and R. Seiringer, The stability of matter in quantum mechanics, Cambridge University Press, 2009.

[36] E.H. Lieb, I. M. Sigal, B. Simon and W. Thirring, Asymptotic neutrality of large-Z ions, *Commun. Math. Phys.* **116**, 635-644 (1988).

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

[38] E.H. Lieb and B. Simon, The Hartree-Fock theory for Coulomb systems, *Commun. Math. Phys.* **53** (3), 185-194 (1977).

[39] E.H. Lieb and J.P. Solovej, Ground State Energy of the Two-Component Charged Bose Gas. *Commun. Math. Phys.* **252**, 485–534 (2004)

[40] E.H. Lieb, J.P. Solovej and J. Yngvason, Asymptotics of heavy atoms in high magnetic fields: I. Lowest Landau band regions, *Commun. Pure Appl. Math.* **47** 513-91 (1994).

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

[42] E.H. Lieb, J. P. Solovej, J. Yngvason, Ground States of Large Quantum Dots in Magnetic Fields, *Phys. Rev. B.* **51**, no. 16, 10646-10666 (1995).

[43] E.H. Lieb and W. Thirring, Bound for the Kinetic Energy of Fermions which Proves the Stability of Matter, *Phys. Rev. Lett.* **35**, 687-689 (1975).

[44] E.H. Lieb and H.-T. Yau, The Chandrasekhar theory of stellar collapse as the limit of quantum mechanics, *Commun. Math. Phys.* 112 (1987), 147-174.

[45] H. Leinfelder and C.G. Simader, Schrödinger operators with singular magnetic vector potentials, *Math. Z.* **176**, 1-19 (1981).

[46] M. Melgaard and T. Johnson, On the maximal ionization for the atomic Pauli operator, *Proc. R. Soc. A* **461**, 3355-3364, (2005).

[47] J. Messer and H. Spohn, Statistical mechanics of the isothermal Lane-Emden equation, *J. Stat. Phys.*, Vol. 29, No. 3, 561-578 (1982).

[48] P.T. Nam, New bounds on the maximum ionization of atoms, Preprint 2010, arXiv:1009.2367.

[49] P.T. Nam, Bogoliubov theory and bosonic atoms, Preprint 2011, arXiv:1109.2875.

[50] P.T. Nam, F. Portmann and J.P. Solovej, Asymptotics for two dimensional atoms, *Ann. Henri Poincaré* (2011), in press, DOI: 10.1007/s00023-011-0123-2.

[51] I. P. Natanson, *Theory of Functions of a Real Variable*, Frederick Ungar, New York, 1965.

[52] D. G. W. Parfitt and M. E. Portnoia, The two-dimensional hydrogen atom revisited, *J. Math. Phys.* **43**, no. 10 (2002).

[53] S.N.M. Ruijsenaars, On Bogoliubov transformations for systems of relativistic charged particles, *J. Math. Phys.*, vol. 18, No. 3 (1977).

[54] M.B. Ruskai, Absence of discrete spectrum in highly negative ions, II. Extension to Fermions, *Commun. Math. Phys.* **82**, 325 327 (1982).

[55] J. Schwinger, Thomas-Fermi model: The second correction, *Phys. Rev. A*, **24**, vol. 5, 2353-2361 (1981).

[56] J.M.C. Scott, The binding energy of the Thomas-Fermi atom, *Phys. Rev.* **43**, no. 343, 859-867 (1952).

[57] L. A. Seco, I. M. Sigal, and J. P. Solovej, Bound on the ionization energy of large atoms, *Commun. Math. Phys.* **131**, 307-315 (1990).

[58] R. Seiringer, On the maximal ionization of atoms in strong magnetic fields, *J. Phys. A: Math. Gen.* **34**, 1943-1948 (2001).

[59] 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).

[60] I.M. Sigal, Geometric methods in the quantum many-body problem. Nonexistence of very negative ions, *Commun. Math. Phys.* **85**, 309-324 (1982).

[61] I.M. Sigal, How many electrons can a nucleus bind? *Ann. Phys.* **157**, 307-320 (1984).

[62] B. Simon, Fifteen problems in mathematical physics, in *Perspectives in Mathematics*, 423454, Anniversary of Oberwolfach 1984 (W. Jger, J. Moser and R. Remmert, eds.), Birkhuser Verlag, Basel (1984). [23]

[63] B. Simon, Schrödinger operators in the twenty-first century, in *Mathematical Physics 2000* (A. Fokas, A. Grigoryan, T. Kibble, and B. Zegarlinski, eds.), Imperial College Press, 283288 (2000).

[64] D. Shale, Linear Symmetries of Free Boson Fields, *Trans. Amer. Math. Soc.* **103**, 149-167 (1962).

[65] J. P. Solovej, Proof of the ionization conjecture in a reduced Hartree-Fock model, *Invent. Math.* **104**, 291-311 (1991).

[66] J.P. Solovej, Asymptotics for bosonic atoms, *Lett. Math. Phys.* **20**, 165-172 (1990)

[67] J.P. Solovej, The ionization conjecture in Hartree-Fock theory. *Annals of Math.* **158**, 509-576 (2003).

[68] J.P. Solovej, Upper Bounds to the Ground State Energies of the One- and Two-Component Charged Bose Gases, *Commun. Math. Phys.* **266**, 797–818 (2006)

[69] J.P. Solovej, Many body quantum mechanics, Lectures notes at LMU Münich, 2007. Online available at `http://www.mathematik.uni-muenchen.de/~lerdos/WS08/QM/solovejnotes.pdf`

[70] J.P. Solovej, T. Ø. Sørensen, W. Spitzer, The relativistic Scott correction for atoms and molecules, *Comm. Pure Appl. Math.* Vol. **LXIII**, 39-118 (2010).

[71] J.P. Solovej and W. Spitzer, A new coherent states approach to semiclassics which gives Scott's correction. *Commun. Math. Phys.* **241**, no. 2-3, 383-420 (2003).

[72] T. Østergaard Sørensen, The large-Z behavior of pseudo-relativistic atoms. *J. Math. Phys.* **46** no. 5, 052307 (2005).

[73] G. Teschl, Mathematical methods in quantum mechanics, with applications to Schrödinger operators. *Graduate Studies in Mathematics*, Vol. 99, Amer. Math. Soc., Providence (2009).

[74] W. Thirring, A lower bound with the best possible constant for Coulomb Hamiltonians, *Commun. Math. Phys.* **79**, 1-7 (1981).

[75] L.H. Thomas, The calculation of atomic fields, *Proc. Cambridge Phil. Soc.* **23** (5), 542-548 (1927).

[76] X. L. Yang, S. H. Guo, F. T. Chan, K. W. Wong and W. Y. Ching, Analytic solution of a two-dimensional hydrogen atom. I. Nonrelativistic theory, *Phys. Rev. A.* **43**, 1186-1196 (1991).

[77] G. Zhislin, Discussion of the spectrum of Schrödinger operator for system of many particles, *Trudy. Mosk. Mat. Obšč.* **9**, 81 (1960).

New bounds on the maximum ionization of atoms

Phan Thanh Nam

Department of Mathematical Sciences, University of Copenhagen,
Universitetsparken 5, 2100 Copenhagen, Denmark. E-mail: ptnam@math.ku.dk

Abstract

We prove that the maximum number N_c of non-relativistic electrons that a nucleus of charge Z can bind is less than $1.22Z + 3Z^{1/3}$. This improves Lieb's upper bound $N_c < 2Z + 1$ [*Phys. Rev. A* **29**, 3018-3028 (1984)] when $Z \geq 6$. Our method also applies to non-relativistic atoms in magnetic field and to pseudo-relativistic atoms. We show that in these cases, under appropriate conditions, $\limsup_{Z\to\infty} N_c/Z \leq 1.22$.

AMS 2010 Subject Classification: 81V45

Key words: maximum ionization, Pauli operator, magnetic field, relativistic atoms

1 Introduction

Let us consider an atom with a classical nucleus of charge Z and N non-relativistic quantum electrons. The nucleus is fixed at the origin and the N-electron system is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|}$$

acting on the antisymmetric space $\bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$. The nuclear charge Z is allowed to be any positive number, although it is an integer in the physical case.

The ground state energy of N electrons is the bottom of the spectrum of $H_{N,Z}$,

$$E(N,Z) = \inf \text{spec } H_{N,Z} = \inf_{||\psi||_{L^2}=1} (\psi, H_{N,Z}\psi).$$

We say that N electrons can be *bound* if $E(N,Z) < E(N-1,Z)$, namely one cannot remove any electron without paying some positive energy. Due to the HVZ theorem (see e.g. [29], Theorem 11.2) which states that

$$\text{ess spec } H_{N,Z} = [E(N-1), \infty),$$

one always has $E(N) \le E(N-1)$. Moreover the binding inequality $E(N,Z) < E(N-1,Z)$ means that $E(N,Z)$ is an isolated eigenvalue of $H_{N,Z}$. Zhislin (1960) [30] show that binding occurs provided that $N < Z+1$.

Of our interest is the maximum number $N_c = N_c(Z)$ of electrons that can be bound. It is a long standing open problem, sometimes referred to as the *ionization conjecture* (see e.g. [11, 26, 27, 13]), that $N_c \le Z+1$, or maybe $N_c \le Z+2$. Note that $N_c \ge Z$ due to Zhislin's result. We now briefly present the status of the conjecture, and we refer to [13] (Chap. 12) for a pedagogical introduction to this problem.

It was first proved by Ruskai (1982) [20] and Sigal (1982, 1984) [23, 24] that N_c is not too large. In fact, Ruskai [20] showed that $N_c = O(Z^{6/5})$ and Sigal [24] showed that $N_c \le 18Z$ and $\liminf_{Z\to\infty} N_c/Z \le 2$. Then Lieb (1984) [11] gave a very simple and elegant proof that $N_c < 2Z+1$ for all $Z > 0$. Lieb's upper bound settles the conjecture for hydrogen but it is around twice of the conjectured bound for large Z.

For large atoms, the asymptotic neutrality $\lim_{Z\to\infty} N_c/Z = 1$ was first proved by Lieb, Sigal, Simon and Thirring (1988) [12]. Later, it was improved to $N_c \le Z + O(Z^{5/7})$ by Seco, Sigal and Solovej (1990) [21] and by Fefferman and Seco (1990) [8]. The bound $N_c \le Z + \text{const}$, for some Z-independent constant, is still unknown, although it holds true for some important approximation models such as Thomas-Fermi and related theories [9, 3] and Hartree-Fock theory [26, 27].

In spite of the asymptotic neutrality, Lieb's upper bound $N_c < 2Z+1$ [11] is still the best one for realistic atoms (corresponding to the range $1 \le Z \le 118$ in the current periodic table). The purpose in this work is to find an improved bound for all $Z > 0$. As in [11], we do not need the binding inequality; more precisely, that $E(N,Z)$ is an eigenvalue of $H_{N,Z}$ is sufficient for our analysis. One of our main result is the following.

Theorem 1 (Bound on maximum ionization of non-relativistic atoms)**.** *Let $Z > 0$ (not necessarily an integer). If $E(N,Z)$ is an eigenvalue of $H_{N,Z}$ then either $N = 1$ or*

$$N < 1.22Z + 3Z^{1/3}.$$

The factor 1.22 can be replaced by β^{-1} with β being defined by (2).

Remark 1. *The bound $1.22Z + 3Z^{1/3}$ is less than Lieb's bound $2Z+1$ when $Z \ge 6$.*

Remark 2. *While Lieb's result holds true for both of fermions and bosons, our result only holds for fermions (in fact, our method works also for bosonic case but it yields an estimate worse than Lieb's one). Note that the ionization conjecture only concerns fermions since for bosonic atoms it was shown that $\lim_{Z\to\infty} N_c/Z \approx 1.21$ by Benguria and Lieb [2] and Solovej [25] (the numerical value 1.21 is taken from [1]). In our proof below, we use Pauli's exclusion principle in Lemma 2. More precisely, we use the fact that in a fermionic atom the average distance from the* *electrons to the nucleus of charge Z is (at least) of order $Z^{-1/3}$. In contrast, the corresponding distance in the bosonic atoms is of order Z^{-1}.*

Remark 3. *Although Lieb's method [11] can be generalized to molecules, we have not yet been able to adapt our method to this case.*

Our method also applies to other models such as non-relativistic atoms in magnetic fields and relativistic atoms, and we shall discuss these extensions later. In the rest of the introduction let us outline the proof of Theorem 1. As a first step we get the following bound.

Lemma 1. *If $E(N,Z)$ is an eigenvalue of $H_{N,Z}$ then we have*

$$\alpha_N(N-1) < Z(1+0.83\ N^{-2/3}),$$

where

$$\alpha_N := \inf_{x_1,\dots,x_N\in\mathbb{R}^3} \frac{\sum\limits_{1\le i<j\le N} \frac{|x_i|^2+|x_j|^2}{|x_i-x_j|}}{(N-1)\sum\limits_{i=1}^{N}|x_i|}. \tag{1}$$

This result is shown by modifying Lieb's proof: in [11] Lieb multiplied the eigenvalue equation $(H_{N,Z}-E(N,Z))\Psi_{N,Z}=0$ by $|x_N|\overline{\Psi}_{N,Z}$. We instead multiply by $x_N^2\overline{\Psi}_{N,Z}$ and employ the Lieb-Thirring inequality to control error terms.

Roughly speaking, the number α_N^{-1} yields an upper bound on N/Z. This bound improves previous results since α_N is bigger than $1/2$ (one can see that $\alpha_2 = 1/2$ and $\alpha_N \ge \sqrt{5}/4 \approx 0.559$ when $N\ge 3$). Although we do not know the exact value of α_N, it is possible to derive some effective estimates. We may think of α_N as the lowest energy of N classical particles acting on $\mathbb{R}^3$ via the potential $V(x,y) = \frac{x^2+y^2}{|x-y|}$, under some normalizing condition. It is natural to believe that if N becomes large, then α_N converges to the statistical limit

$$\beta := \inf\left\{ \frac{\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{2|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)}{\int\limits_{\mathbb{R}^3}|x|\,\mathrm{d}\rho(x)\int\limits_{\mathbb{R}^3}\mathrm{d}\rho(x)} : \rho \text{ a positive measure in } \mathbb{R}^3 \right\}. \tag{2}$$

Results of this form in bounded domain have already appeared in [19]. Indeed, we can show that α_N actually converges to β and provide an explicit estimate on the convergence rate. Theorem 1 essentially follows by inserting the lower bound on α_N in Proposition 1 below into the inequality in Lemma 1.

Proposition 1. *The sequence $\{\alpha_N\}_{N=2}^{\infty}$ is increasing and for any $N\ge 2$ we have*

$$\beta \ge \alpha_N \ge \frac{N}{N-1}[\beta - 3(\beta/6)^{1/3}N^{-2/3}],$$

with β being defined by (2). Moreover, $\beta\in[0.8218, 0.8705)$.

Remark 4. *We do not know the exact numerical value of β, but our bound that $\beta \in [0.82188, 0.8705)$ is already rather precise. There is of course still room for improvement.*

The article is organized as follows. We shall prove Theorem 1 in Section 2. Then we discuss some possible extensions of our method in Section 3. Proposition 1 is of independent interest and we defer its proof to Section 4.

Acknowledgments. I am grateful to Mathieu Lewin and Jan Philip Solovej for very helpful discussions, and to Rupert L. Frank and Elliott H. Lieb for pointing out the lower bound (10) which improves the constants in Lemma 2 and Theorem 1. This work was done when I was a visiting student at Département de Mathématiques, Université de Cergy-Pontoise (France), and I wish to thank the Department for the warm hospitality.

2 Proof of Theorem 1: the new bound

2.1 Lieb's method

In order to make our argument transparent we start by quickly recalling the proof of Lieb [11]. Assume that $E(N,Z)$ is an eigenvalue of $H_{N,Z}$ corresponding to some normalized eigenfunction Ψ_N. Multiplying the Schrödinger equation

$$(H_{N,Z} - E(N,Z))\Psi_{N,Z} = 0 \tag{3}$$

by $|x_N|\overline{\Psi}_{N,Z}$ and then integrating, one gets

$$\begin{aligned} 0 &= \langle |x_N|\Psi_{N,Z}, (H_{N,Z} - E(N,Z))\Psi_{N,Z}\rangle \\ &= \langle |x_N|\Psi_{N,Z}, (H_{N-1,Z} - E(N,Z))\Psi_{N,Z}\rangle + \frac{1}{2}\langle |x_N|\Psi_{N,Z}, -\Delta_N \Psi_{N,Z}\rangle \\ &\quad + \left\langle \Psi_{N,Z}, \left[-Z + \sum_{i=1}^{N-1} \frac{|x_N|}{|x_i - x_N|}\right]\Psi_{N,Z}\right\rangle. \end{aligned} \tag{4}$$

The first term in the right hand side of (4) is non-negative since $H_{N-1,Z} \geq E(N-1,Z) \geq E(N,Z)$ (in the space of $N-1$ particles $x_1, ..., x_{N-1}$). The second term is also non-negative due to the inequality

$$\operatorname{Re}\langle |x|f, -\Delta f\rangle \geq 0 \quad \text{for all } f \in H^1(\mathbb{R}^3). \tag{5}$$

Thus the third term in (4) must be non-positive. Using the antisymmetry we can rewrite it as

$$\left\langle \Psi_{N,Z}, \left(-Z + \frac{1}{N}\sum_{1\leq i<j\leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|}\right)\Psi_{N,Z}\right\rangle \leq 0.$$

It follows from the triangle inequality that

$$\frac{1}{N(N-1)}\sum_{1\le i<j\le N}\frac{|x_i|+|x_j|}{|x_i-x_j|}\ge\frac{1}{2}. \tag{6}$$

Hence we obtain $-ZN+\frac{N(N-1)}{2}<0$, namely $N<2Z+1$. The inequality is strict since the triangle inequality is strict almost everywhere in $(\mathbb{R}^3)^N$. Note that the lower bound 1/2 in (6) is sharp (when $|x_i|\ll|x_j|$ if $i<j$).

2.2 Proof of Lemma 1

Instead of multiplying the equation (3) by $|x_N|\overline{\Psi}_{N,Z}$, we now multiply by $x_N^2\overline{\Psi}_{N,Z}$ and integrate. We obtain

$$\begin{aligned}0 &= \left\langle x_N^2\Psi_{N,Z},(H_{N-1,Z}-E_{N,Z})\Psi_{N,Z}\right\rangle+\frac{1}{2}\left\langle x_N^2\Psi_{N,Z},-\Delta\Psi_{N,Z}\right\rangle\\ &\quad+\left\langle\Psi_{N,Z},\left(-Z|x_N|+\sum_{1\le i<j\le N}\frac{x_i^2+x_j^2}{|x_i-x_j|}\right)\Psi_{N,Z}\right\rangle\\ &\ge \frac{1}{2}\left\langle x_N^2\Psi_{N,Z},-\Delta\Psi_{N,Z}\right\rangle+\left\langle\Psi_{N,Z},(-Z+\alpha_N(N-1))\,|x_N|\Psi_{N,Z}\right\rangle.\end{aligned}$$

Recall that α_N is defined in (1). This implies that

$$\alpha_N(N-1)\le Z-\frac{1}{2}\left\langle x_N^2\Psi_{N,Z},-\Delta\Psi_{N,Z}\right\rangle\left\langle\Psi_{N,Z},|x_N|\Psi_{N,Z}\right\rangle^{-1}. \tag{7}$$

As we will see, the main advantage of our method is that the number α_N is bigger than 1/2 when $N\ge3$. However, we do not have an inequality similar to (5) with $|x|$ replaced by x^2. In fact, for all $f\in H^1(\mathbb{R}^3)$ applying the identity

$$\operatorname{Re}\langle\varphi f,-\Delta f\rangle=\left\langle\varphi^{1/2}f,\left(-\Delta-\left|\frac{\nabla\varphi}{2\varphi}\right|^2\right)\varphi^{1/2}f\right\rangle \tag{8}$$

to $\varphi(x)=|x|^2$ we find that

$$\operatorname{Re}\left\langle x^2f,-\Delta f\right\rangle=\langle f,(|x|(-\Delta)|x|-1)f\rangle\ge-\frac{3}{4}\langle f,f\rangle \tag{9}$$

by Hardy's inequality, $-3/4$ being the sharp constant.

Our observation is that we may still control the second term in the right hand side of (7) since $\langle\Psi_{N,Z},|x_N|\Psi_{N,Z}\rangle^{-1}$ is small (in comparison with Z) . In fact, $\langle\Psi_{N,Z},|x_N|\Psi_{N,Z}\rangle$ can be understood as the average distance from N electrons to the nucleus, which is well-known to be (at least) of order $Z^{-1/3}$. We have the following explicit bound.

Lemma 2. *If $\Psi_{N,Z}$ is a ground state of $H_{N,Z}$ then*

$$\langle\Psi_{N,Z},|x_N|\Psi_{N,Z}\rangle>0.553\;Z^{-1}N^{2/3}.$$

It follows from (9) and Lemma 2 that

$$\frac{1}{2}\left\langle x_N^2\Psi_{N,Z}, -\Delta\Psi_{N,Z}\right\rangle \left\langle \Psi_{N,Z}, |x_N|\Psi_{N,Z}\right\rangle^{-1} \geq -0.68\ ZN^{-2/3}.$$

Substituting the latter estimate into (7) we obtain the inequality in Lemma 1. We now provide the

Proof of Lemma 2. The following proof essentially follows from [13] (p. 132). Note that

$$\langle \Psi_{N,Z}, |x_N|\Psi_{N,Z}\rangle = \frac{1}{N}\int_{\mathbb{R}^3} |x|\rho_{\Psi_{N,Z}}(x)\mathrm{d}x$$

where the density functional $\rho_{\Psi_{N,Z}}$ of $\Psi_{N,Z}$ is defined by

$$\rho_{\Psi_{N,Z}}(x) := N\sum_{\sigma_1=1,2}\ldots\sum_{\sigma_N=1,2}\int_{\mathbb{R}^{3(N-1)}} |\Psi_{N,Z}(x,\sigma_1;x_2,\sigma_2;\ldots;x_N,\sigma_N)|^2\mathrm{d}x_2\ldots\mathrm{d}x_N.$$

By solving for the Bohr atom as in [10] (after eq. (40) p. 560) one has the lower bound on the ground state energy

$$E(N,Z) \geq \left\langle \Psi_{N,Z}, \sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|}\right)\Psi_{N,Z}\right\rangle \geq -AZ^2N^{1/3} \tag{10}$$

where $A = (3^{1/3}/2)2^{2/3}$. Moreover, one has the Lieb-Thirring kinetic energy inequality [16]

$$\mathcal{K}_{\Psi_{N,Z}} := \frac{1}{2}\sum_{i=1}^{N}(\Psi, -\Delta_i\Psi) \geq K\int_{\mathbb{R}^3} \rho_{\Psi_{N,Z}}(x)^{5/3}dx \tag{11}$$

where $K = 2^{-2/3}(3/10)\,(2/(5L))^{2/3}$ with $L = (\pi 3^{3/2}5)^{-1} \approx 0.0123$ (this constant L is taken from [7]). Since $E(N,Z) = -\mathcal{K}_{\Psi_{N,Z}}$ by the Virial theorem, we get from (10) and (11) that

$$\int_{\mathbb{R}^3} \rho_{\Psi_{N,Z}}(x)^{5/3}\mathrm{d}x \leq K^{-1}AZ^2N^{1/3}. \tag{12}$$

On the other hand, we have the following inequality introduced by Lieb ([10], p.563)

$$\left(\int_{\mathbb{R}^3} \varphi(x)^{5/3}\mathrm{d}x\right)^{p/2}\left(\int_{\mathbb{R}^3} |x|^p\varphi(x)\mathrm{d}x\right) \geq C_p\left(\int_{\mathbb{R}^3} \varphi(x)\mathrm{d}x\right)^{1+5p/6}$$

for any nonnegative measurable function $\varphi(x)$, the sharp constant C_p being attained with $\varphi(x) = (1-|x|^p)^{3/2}$. In particular, applying this inequality to $\varphi(x) = \rho_{\Psi_{N,Z}}(x)$ and $p=1$, we get

$$\left(\int_{\mathbb{R}^3} \rho_{\Psi_{N,Z}}(x)^{5/3}\mathrm{d}x\right)^{1/2} \int_{\mathbb{R}^3} |x|\rho_{\Psi_{N,Z}}(x)\mathrm{d}x \geq C_1 N^{11/6} \tag{13}$$

where $C_1 = \pi^{-1/3}2^{-1}3^{5/3}5^{5/6}7^{1/3}11^{-3/2} \approx 0.4271$. Combining (12) and (13) we obtain the desired inequality. $\square$

2.3 Proof of Theorem 1

Let us admit Proposition 1 for the moment and derive Theorem 1. Lemma 1 and Proposition 1 together yield a lower bound of Z in terms of N,

$$\frac{N(\beta - 3(\beta/6)^{1/3}N^{-2/3})}{1+0.68\ N^{-2/3}} < Z. \tag{14}$$

It is just an elementary calculation to translate (14) into an upper bound of N in terms of Z. If $Z \leq 5$ then $\max\{2, \beta^{-1}Z + 3Z^{1/3}\} > 2Z+1$ (since $\beta < 0.8705$), and hence our bound follows from Lieb's bound. If $Z > 5$, then Lieb's bound implies that $N/Z < 2 + Z^{-1} < 2.2$. Thus the desired result follows from (14) and the following technical lemma whose proof is provided in Appendix.

Lemma 3. *For $Z > 0$, $N > 0$, $N/Z \leq 2.2$ and $\beta \geq 0.8218$ one has*

$$\beta^{-1}Z + 3Z^{1/3} \geq \min\left\{N, Z\frac{1+0.68\ N^{-2/3}}{\beta - 3(\beta/6)^{1/3}N^{-2/3}}\right\}.$$

3 Some possible extensions

3.1 Atoms in magnetic fields

In this section, we consider the ionization problem with the presence of a magnetic field. The system is now described by the Hamiltonian

$$H_{N,Z,\mathcal{A}} = \sum_{i=1}^{N}\left(T_{\mathcal{A}}^{(i)} - \frac{Z}{|x_i|}\right) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|}$$

acting on the fermionic space $\bigwedge^N (L^2(\mathbb{R}^3)\otimes\mathbb{C}^2)$. The kinetic operator is the Pauli operator

$$T_{\mathcal{A}} = |\sigma\cdot(-i\nabla + \mathcal{A}(x))|^2 = (-i\nabla + \mathcal{A}(x))^2 + \sigma\cdot\mathcal{B},$$

where $\mathcal{A}$ is the magnetic potential, $\mathcal{B} = \mathrm{curl}(A)$ is the magnetic field and $\sigma = (\sigma^1, \sigma^2, \sigma^3)$ are the Pauli matrices

$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

For simplicity we shall always assume that $\mathcal{A} \in L^4_{\rm loc}(\mathbb{R}^3, \mathbb{R}^3)$, $\nabla \cdot A \in L^2_{\rm loc}(\mathbb{R}^3)$ and $|\mathcal{B}| \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. Under these assumptions, it is well known that $(-i\nabla + \mathcal{A}(x))^2$ is essentially selfadjoint on $L^2(\mathbb{R}^3)$ with core $C_c^\infty(\mathbb{R}^3)$ [17], and $|\mathcal{B}| + Z/|x|$ is infinitesimally bounded with respect to $(-i\nabla + \mathcal{A}(x))^2$ (see e.g. [22, 18]). In particular, the ground state energy

$$E(N, Z, \mathcal{B}) = \inf \text{ spec } H_{N,Z,\mathcal{A}}$$

is finite. We shall also assume that $N \mapsto E(N, Z, \mathcal{B})$ is non-increasing (for example, this is the case if $\mathcal{B} = (0, 0, B)$ is a constant magnetic field [14]). Note that the ground state energy depends on $\mathcal{A}$ only through $\mathcal{B}$ by *gauge invariance* (see e.g. [13] p. 21).

Of our interest is the maximum number N_c such that $E(N_c, Z, \mathcal{B})$ is an eigenvalue of $H_{N,Z,\mathcal{A}}$. Seiringer [22] showed in 2001 that

$$N_c < 2Z + 1 + \frac{1}{2}\frac{E(N_c, Z, \mathcal{B}) - E(N_c, kZ, \mathcal{B})}{N_c Z(k-1)} \tag{15}$$

for all $k > 1$. In the homogeneous case, $\mathcal{B} = (0, 0, B)$, his bound yields

$$N_c < 2Z + 1 + C_1 Z^{1/3} + C_2 Z \min\left\{(B/Z^3)^{2/5}, 1 + |\ln(B/Z^3)|^2\right\}. \tag{16}$$

In particular, in the semiclassical regime $\lim_{Z\to\infty}(B/Z^3) = 0$, Seiringer's bound implies that

$$\limsup_{Z\to\infty} \frac{N_c}{Z} \le 2.$$

In contrast, it was shown by Lieb, Solovej and Yngvason (1994) [14] that if $\lim_{Z\to\infty}(B/Z^3) = \infty$, then

$$\liminf_{Z\to\infty} \frac{N_c}{Z} \ge 2.$$

We shall improve these bounds using the method in the previous section. Our result in this section is as follows.

Theorem 2 (Bounds on maximum ionization of atoms in magnetic fields)**.** *Let $Z > 0$ and let $\mathcal{B}$ satisfy the assumption stated above. Then we have, for every $k > 1$,*

$$N_c < (1.22Z + 3Z^{1/3})\left(1 + \frac{E(N_c, Z, \mathcal{B}) - E(N_c, kZ, \mathcal{B})}{N_c Z^2(k-1)}\right). \tag{17}$$

If $\mathcal{B} = (0, 0, B)$ is a constant magnetic field then

$$N_c < (1.22\ Z + 3Z^{1/3}) \quad \times \quad \Big(1 + 11.8\ Z^{-2/3} + \\ + \min\left\{0.42\left(B/Z^3\right)^{2/5}, C(1 + |\ln(B/Z^3)|^2)\right\}\Big)$$

for some universal constant C (independent of Z and B).

In particular, if $\lim_{Z\to\infty}(B/Z^3) = 0$, then

$$\liminf_{Z\to\infty} \frac{N_c}{Z} \le 1.22.$$

The number 1.22 in all bounds can be replaced by β^{-1} with β being defined by (2).

Proof. Assume that $\Psi_{N,Z,\mathcal{A}}$ is a ground state of $H_{N,Z,\mathcal{A}}$. Following the proof of Lemma 1, we have

$$\alpha_N(N-1) \le Z - \left\langle x_N^2 \Psi_{N,Z,\mathcal{A}}, T_{\mathcal{A}}\Psi_{N,Z,\mathcal{A}}\right\rangle \langle \Psi_{N,Z,\mathcal{A}}, |x_N|\Psi_{N,Z,\mathcal{A}}\rangle^{-1}, \tag{18}$$

which is the analogue of (7).

We may assume that $N \ge \beta^{-1}Z + 3Z^{-2/3}$ (otherwise we are done). In this case the left hand side of (18) can be bound by

$$\alpha_N(N-1) > \frac{N}{\beta^{-1} + 3Z^{-2/3}}. \tag{19}$$

This estimate follows from the lower bound on α_N in Proposition 1 and the following technical lemma whose proof is provided in Appendix.

Lemma 4. *For $Z > 0$, $N \in \mathbb{N}$, $N \ge \beta^{-1}Z + 3Z^{-2/3}$ and $\beta \ge 0.8218$, one has*

$$(\beta - 3(\beta/6)^{1/3}N^{-2/3})(\beta^{-1} + 3Z^{-2/3}) > 1.$$

The second term in the right hand side of (18) can be bound in the same way as in [22]. More precisely, using (8) with $-\Delta$ replaced by $T_{\mathcal{A}}$ ([18] Proposition 3.3, see also [4]) and $T_{\mathcal{A}} \ge 0$, one has

$$\left\langle x_N^2 \Psi_{N,Z,\mathcal{A}}, T_{\mathcal{A}}\Psi_{N,Z,\mathcal{A}}\right\rangle = \langle \Psi_{N,Z,\mathcal{A}}, (|x_N|T_{\mathcal{A}}|x_N| - 1)\,\Psi_{N,Z,\mathcal{A}}\rangle \ge -1. \tag{20}$$

On the other hand, for every $k > 1$,

$$\begin{aligned} \langle \Psi_{N,Z,\mathcal{A}}, |x_N|\Psi_{N,Z,\mathcal{A}}\rangle^{-1} &\le \left\langle \Psi_{N,Z,\mathcal{A}}, |x_N|^{-1}\Psi_{N,Z,\mathcal{A}}\right\rangle \\ &= \frac{\langle \Psi_{N,Z,\mathcal{A}}, H_{N,Z,\mathcal{A}}\Psi_{N,Z,\mathcal{A}}\rangle - \langle \Psi_{N,Z,\mathcal{A}}, H_{N,kZ,\mathcal{A}}\Psi_{N,Z,\mathcal{A}}\rangle}{NZ(k-1)} \\ &\le \frac{E(N,Z,\mathcal{B}) - E(N,kZ,\mathcal{B})}{NZ(k-1)} \end{aligned} \tag{21}$$

since $\Psi_{N,Z,\mathcal{A}}$ is a ground state of $H_{N,Z,\mathcal{A}}$. Then (17) follows by substituting (19), (20) and (21) into (18).

Now assume that $\mathcal{B} = (0,0,B)$ is a constant magnetic field. It follows from [15] (Theorems 2.4, 2.5) that if $N \ge Z/2$, then the ground state energy $E(N,Z,B) := E(N,Z,\mathcal{B})$ can be bounbed from below by

$$\begin{aligned} E(N,Z,B) \quad &\ge \quad -NZ^2 \Big(18.7 Z^{-2/3} + \\ &\qquad + \min \Big\{ 0.95 \left(B/Z^3 \right)^{2/5}, C \left(1 + |\ln(B/Z^3)|^2 \right) \Big\} \Big) \quad (22) \end{aligned}$$

for some universal constant C (independent of N, Z and B). (It is obtained when applying (2.27), (2.26), (2.29) in [15] to the cases: $B < Z^{4/3}$, $B \ge Z^{4/3}$, $B \gg Z^3$, respectively.)

We can choose $k = 2$ in (17). Then the desired bound follows by using the upper bound $E(N,Z,B) \le 0$ and the lower bound on $E(N,2Z,B)$ derived from (22). $\square$

Remark 5. *We may also consider the Hamiltonian $H_{N,Z,\mathcal{A}}$ on the bosonic space $\bigotimes_{sym}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$, where q is a spin number. In this case the inequality (17) still holds true. Moreover, if $\mathcal{B} = (0,0,B)$ is a constant magnetic field, then using the estimate [22] (p. 1948)*

$$E(N,Z,B) = NZ^2 E(1,1,B/Z^2) \ge -\frac{1}{4} NZ^2 \min \left\{ 1 + 4B/Z^2, C |\ln(B/Z^2)|^2 \right\}$$

we get from (17) that

$$N_c < (\beta^{-1} Z + 3 Z^{1/3}) \left(1 + \min \left\{ 1 + 4B/Z^2, C_2 |\ln(B/Z^2)|^2 \right\} \right).$$

In particular, if $\lim_{Z\to\infty} B/Z^2 = 0$, then our bound yields

$$\limsup_{Z\to\infty} N_c/Z \le 2\beta^{-1} \le 2.44.$$

It slightly improves the bosonic bound in [22] which gives $\limsup_{Z\to\infty} N_c/Z \le 2.5$.

Remark 6. *As shown in [18], one can make a slight improvement on our bounds by using the Hardy-type inequality $T_{\mathcal{A}} \ge (d_{\mathcal{B}}/4)|x|^{-2}$ instead of $T_{\mathcal{A}} \ge 0$ in (20), for some $0 < d_{\mathcal{B}} \le 1$. It allows us to include a factor $(1 - d_{\mathcal{B}})$ in front of the term involved to $E(N,Z,\mathcal{B}) - E(N,kZ,\mathcal{B})$ in (17).*

3.2 Pseudo-relativistic atoms

In this section we consider the pseudo-relativistic Hamiltonian

$$H_{N,Z}^{\text{rel}} = \sum_{i=1}^{N} \left(\alpha^{-1} (\sqrt{-\Delta_i + \alpha^{-1}} - \alpha^{-1}) - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$

acting on the fermionic space $\bigwedge^N(L^2(\mathbb{R}^3)\otimes\mathbb{C}^2)$. Here $\alpha > 0$ is the *fine-structure constant*. It is well known that the ground state energy $E^{\rm rel}(N,Z) := \inf \operatorname{spec} H^{\rm rel}_{N,Z}$ is finite if and only if $Z\alpha \le 2/\pi$ (see e.g. [13]). The physical value is $\alpha = e^2/(\hbar c) \approx 1/137$ and hence $Z < 87.22$. However, we allow α to be any positive number.

As in the previous dicussions, we are also interested in the maximum number N_c such that the ground state energy $E^{\rm rel}(N_c,Z)$ is an eigenvalue of $H^{\rm rel}_{N_c,Z}$. Note that Lieb's bound $N_c < 2Z+1$ still holds in this case. In fact, due to a technical gap the original proof of Lieb in [11] works properly only when $Z\alpha < 1/2$. However, it is posible to fill this gap to obtain the bound up to $Z\alpha < 2/\pi$ [6]. On the other hand, up to our knowledge, no result about asymptotic behavior of N_c/Z is available for the pseudo-relativistic model, although within pseudo-relativistic Hartree-Fock theory it was recently shown by Dall'Acqua and Solovej (2010) [5] that $N_c \le Z + \text{const}$.

Our result in this section is the following.

Theorem 3 (Bound on maximum ionization of pseudo-relativistic atoms)**.** *For every $Z > 0$ such that $Z\alpha \le \kappa < 2/\pi$ we have either $N_c = 1$ or*

$$N_c < 1.22Z + C_\kappa Z^{1/3}$$

for some constant C_κ depending only on κ. The number 1.22 *can be replaced by β^{-1} with β being defined by (2).*

Proof. Assume that $\Psi^{\rm rel}_{N,Z}$ is a ground state of $H^{\rm rel}_{N,Z}$. As an analogue of (7) we get

$$\begin{aligned}\alpha_N(N-1) \le Z - \left\langle x_N^2\Psi^{\rm rel}_{N,Z}, \alpha^{-1}(\sqrt{-\Delta_N+\alpha^{-1}}-\alpha^{-1})\Psi^{\rm rel}_{N,Z}\right\rangle \times \\ \times \left\langle \Psi^{\rm rel}_{N,Z}, |x_N|\Psi^{\rm rel}_{N,Z}\right\rangle^{-1}. \qquad (23)\end{aligned}$$

The left hand side of (23) can be bound by (19). Turning to the right hand side of (23), we first show that for any function $f:\mathbb{R}^3\to\mathbb{C}$ smooth enough

$$\operatorname{Re}\left\langle |x|^2, \alpha^{-1}\left(\sqrt{-\Delta+\alpha^{-1}}-\alpha^{-1}\right)f\right\rangle_{L^2(\mathbb{R}^3,{\rm dx})} \ge -\frac{3}{8}\langle f,f\rangle. \qquad (24)$$

It suffices to show (24) for $\alpha = 1$ (the general case follows by scaling). Using the Fourier transform $\widehat{f}(p) := \int_{\mathbb{R}^3} e^{-i2\pi p\cdot x}f(x){\rm d}x$ and applying (8) to

$$\varphi(p) := \sqrt{(2\pi p)^2+1}-1 = \frac{(2\pi p)^2}{\sqrt{(2\pi p)^2+1}+1}$$

we find that

$$\begin{aligned}
& \mathrm{Re}\left\langle |x|^2 f, \left[\sqrt{-\Delta_x+1}-1\right] f\right\rangle_{L^2(\mathbb{R}^3,\mathrm{d}x)} \\
= \;& (2\pi)^{-2}\,\mathrm{Re}\left\langle -\Delta_p \widehat{f}, \varphi\widehat{f}\right\rangle_{L^2(\mathbb{R}^3,\mathrm{d}p)} \\
= \;& (2\pi)^{-2}\left\langle \varphi^{1/2}\widehat{f}, \left(-\Delta_p - \left|\frac{\nabla\varphi}{2\varphi}\right|^2\right)\varphi^{1/2}\widehat{f}\right\rangle \\
= \;& (2\pi)^{-2}\left\langle \varphi^{1/2}\widehat{f}, \left(-\Delta_p - \frac{(\sqrt{(2\pi p)^2+1}+1)^2}{4p^2((2\pi p)^2+1)}\right)\varphi^{1/2}\widehat{f}\right\rangle .
\end{aligned}$$

Then it follows from Hardy's inequality $-\Delta_p \geq 1/(4p^2)$ that

$$\begin{aligned}
& \mathrm{Re}\left\langle |x|^2 f, \left[\sqrt{-\Delta_x+1}-1\right] f\right\rangle_{L^2(\mathbb{R}^3,\mathrm{d}x)} \\
\geq \;& -\left\langle \widehat{f}, \frac{2\sqrt{(2\pi p)^2+1}+1}{4((2\pi p)^2+1)(\sqrt{(2\pi p)^2+1}+1)}\widehat{f}\right\rangle_{L^2(\mathbb{R}^3,\mathrm{d}p)} \\
\geq \;& -\frac{3}{8}\left\langle \widehat{f}, \widehat{f}\right\rangle = -\frac{3}{8}\left\langle f, f\right\rangle .
\end{aligned}$$

The term $\langle \Psi, |x_N|\Psi\rangle^{-1}$ can be estimated similarly to (21), namely

$$\langle \Psi, |x_N|\Psi\rangle^{-1} \leq \left\langle \Psi, |x_N|^{-1}\Psi\right\rangle \leq \frac{E(N,Z)-E(N,kZ)}{NZ(k-1)}$$

for every $k>1$ such that $kZ\alpha < 2/\pi$. It is well known that $0 \geq E(N,Z) \geq -C_\kappa Z^{7/3}$ provided that $Z\alpha \leq \kappa$. In fact, it was shown by Sørensen [28] that, at the limit $Z\to\infty$ (and $Z\alpha=\kappa$ fixed), the leading order of the ground-state energy $E(N,Z)$ is given by the Thomas-Fermi theory which is of order $Z^{7/3}$. Thus we can conclude that

$$\langle \Psi, |x_N|\Psi\rangle^{-1} \leq C_\kappa Z^{-2/3}. \tag{25}$$

The desired result follows from (24), (25), (23) and (19). □

4 Proof of Proposition 1: Analysis of α_N

This section is devoted to the proof of Proposition 1. For the reader convenience, we split the proof into several steps. Recall that α_N and β are defined in (1) and (2), respectively.

Step 1. *The sequence α_N is increasing in N and it converges to β.*

Proof. The fact that α_N is increasing is shown as follows: for every $x_1, ..., x_N \in \mathbb{R}^3$ we have

$$\begin{aligned}
\sum_{1 \le i < j \le N} \frac{|x_i|^2 + |x_j|^2}{|x_i - x_j|} &= \sum_{k=1}^N \left(\frac{1}{(N-2)} \sum_{i<j; i \ne k, j \ne k} \frac{|x_i|^2 + |x_j|^2}{|x_i - x_j|} \right) \\
&\ge \sum_{k=1}^N \left(\alpha_{N-1} \sum_{i \ne k} |x_i| \right) = \alpha_{N-1}(N-1) \sum_{k=1}^N |x_i|,
\end{aligned}$$

where we have used the definition of α_{N-1}. This implies that $\alpha_{N-1} \le \alpha_N$.

We shall show that α_N converges to β. We start with the upper bound $\alpha_N \le \beta$. Let ρ be an arbitrary positive measure in $\mathbb{R}^3$. Multiplying ρ by some positive constant, we may assume that $\rho(\mathbb{R}^3) = 1$. Then

$$\begin{aligned}
\iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{x^2 + y^2}{2|x - y|} \mathrm{d}\rho(x) \, \mathrm{d}\rho(y) &= \int_{\mathbb{R}^{3N}} \frac{1}{N(N-1)} \sum_{1 \le i < j \le N} \frac{x_i^2 + x_j^2}{|x_i - x_j|} \mathrm{d}\rho(x_1) ... \mathrm{d}\rho(x_N) \\
&\ge \int_{\mathbb{R}^{3N}} \frac{\alpha_N}{N} \left(\sum_{i=1}^N |x_i| \right) \mathrm{d}\rho(x_1) ... \mathrm{d}\rho(x_N) = \alpha_N \int_{\mathbb{R}^3} |x| \mathrm{d}\rho(x).
\end{aligned}$$

Thus $\alpha_N \le \beta$ for all $N \ge 2$.

Let us prove a lower bound. For the reader's convenience, we give now a simple bound which is enough to get that α_N converges to β. We will provide a better lower bound in the next step.

Let $\{x_i\}_{i=1}^N$ be N arbitrarily distinct points in $\mathbb{R}^3$. For our purpose we may assume that $\sum_{i=1}^N |x_i| = N$. For every i, let μ_i be the uniform measure on the sphere $|x - x_i| = r_i$ with the radius $r_i := r|x_i|$ such that $\int \mu_i = 1$. Denote $\mathrm{d}\rho(x) := \sum_{i=1}^N \mathrm{d}\mu_i(x)$.

Since $\int \mathrm{d}\rho(x) = N$ and $\int |x| \mathrm{d}\rho(x) \ge N$ (due to the convexity $\int |x| \mathrm{d}\mu_i(x) \ge |x_i|$) we have

$$N^{-2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{x^2 \, \mathrm{d}\rho(x) \, \mathrm{d}\rho(y)}{|x - y|} \ge \beta.$$

On the other hand,

$$\begin{aligned}
\iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{x^2 \, \mathrm{d}\rho(x) \, \mathrm{d}\rho(y)}{|x - y|} &= \sum_{i,j} \iint \frac{x^2 \, \mathrm{d}\mu_{\mathrm{i}}(x) \, \mathrm{d}\mu_{\mathrm{j}}(y)}{|x - y|} \\
&\le (1 + r)^2 \sum_{i,j} \iint \frac{x_i^2 \, \mathrm{d}\mu_{\mathrm{i}}(x) \, \mathrm{d}\mu_{\mathrm{j}}(y)}{|x - y|} \\
&\le (1 + r)^2 \left[\sum_{i \ne j} \frac{x_i^2}{|x_i - x_j|} + \frac{N}{r} \right].
\end{aligned}$$

The first inequality follows from $|x| \leq (1+r)|x_i|$ for every x on the sphere $|x-x_i| = r_i$, and the second inequality is due to Newton's theorem (see, e.g. [13], p. 91). Thus

$$\sum_{i \neq j} \frac{x_i^2}{|x_i - x_j|} \geq (1+r)^{-2} N^2 \beta - r^{-1} N.$$

This implies that

$$\alpha_N \geq \frac{N}{N-1} \left[(1+r)^{-2}\beta - (rN)^{-1}\right] \quad \text{for all } r > 0. \tag{26}$$

We can choose, for example, $r = N^{-1/3}$ to conclude that $\alpha_N \to \beta$. This ends the proof of Step 1. $\square$

We now improve the lower bound (26).

Step 2. *We have the lower bound*

$$\alpha_N \geq \frac{N}{N-1} [\beta - 3(\beta/6)^{1/3} N^{-2/3}]$$

Proof. In fact, we shall prove that

$$\alpha_N \quad \geq \quad \frac{N}{N-1} \left[\frac{1+r^2/3}{1+r^2}\beta - \frac{1}{rN}\right] \geq \frac{N}{N-1} \left[\beta - \frac{2r^2}{3}\beta - \frac{1}{rN}\right] \tag{27}$$

for all $r \in (0,1]$. The desired result follows by choosing $r = (4\beta N/3)^{-1/3}$ which maximizes the right hand side of (27).

The bound (27) is shown by following the same method as for (26), but with more careful computations. We shall prove that (with the notation of the proof of Step 1)

$$\int_{\mathbb{R}^3} |x| \mathrm{d}\rho(x) = N \left(1 + \frac{r^2}{3}\right) \tag{28}$$

and

$$\iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{x^2 \,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)}{|x-y|} \leq (1+r^2) \left[\sum_{i \neq j} \frac{x_i^2}{|x_i - x_j|} + \frac{N}{r}\right]. \tag{29}$$

The identity (28) follows from a direct computation using the formula

$$\begin{aligned}
\int_{\mathbb{R}^3} f(x) \mathrm{d}\mu_i(x) \quad &= \quad \frac{1}{|S^2|} \int_{S^2} f(x_i + r_i \omega) d\omega \\
&= \quad \frac{1}{|S^2|} \int_0^{2\pi} \int_0^{\pi} f(x_i + r_i(\cos\theta, \sin\theta\cos\varphi, \sin\theta\sin\varphi)) \sin(\theta) \mathrm{d}\theta \,\mathrm{d}\varphi
\end{aligned}$$

for any integrable function f. Here the second identity comes from the spherical coordinates $\omega = (\cos\theta, \sin\theta\cos\varphi, \sin\theta\sin\varphi)$, where $\theta \in [0,\pi)$ and $\varphi \in [0,2\pi]$. (Note that if $r > 1$, then the right hand side of (28) becomes $Nr(1+1/(3r^2))$.)

Now we prove (29). Using Newton's theorem we have

$$\begin{aligned}
\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)}{|x-y|} &= \sum_{i,j}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2\,\mathrm{d}\mu_{\mathrm{i}}(x)\,\mathrm{d}\mu_{\mathrm{j}}(y)}{|x-y|} \\
&\le \sum_{i,j}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2\mathrm{d}\mu_i(x)}{|x-x_j|} = \sum_{i,j}\left[\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(1+r^2)x_i^2\mathrm{d}\mu_i(x)}{|x-x_j|} + V_{ij}\right] \\
&\le (1+r^2)\left[\sum_{i\neq j}\frac{x_i^2}{|x_i-x_j|} + \frac{N}{r}\right] + \sum_{i,j} V_{ij}
\end{aligned}$$

where $V_{ii} = 0$ and

$$\begin{aligned}
V_{ij} &= \int_{\mathbb{R}^3} \frac{2x_i.(x-x_i)\,\mathrm{d}\mu_{\mathrm{i}}(x)}{|x-x_j|} = \frac{1}{|S^2|}\int_{S^2} \frac{2x_i.r_i\omega}{|x_i-x_j+r_i\omega|}\,\mathrm{d}\omega \\
&= -\frac{2}{3}\frac{r_ix_i(x_i-x_j)\min\{|x_i-x_j|,r_i\}}{|x_i-x_j|(\max\{|x_i-x_j|,r_i\})^2} \quad \text{if } i\neq j.
\end{aligned}$$

Here we have used the formula

$$\frac{1}{|S^2|}\int_{S^2}\frac{\omega}{|a+s\omega|}d\omega = -\frac{1}{3}\frac{a}{|a|}\frac{\min\{|a|,s\}}{(\max\{|a|,s\})^2}, \quad a\in\mathbb{R}^3, s>0. \tag{30}$$

Thus (29) would be valid if we can show that $V_{ij}+V_{ji}\ge 0$. We distinguish three cases.

Case 1: $|x_i-x_j|\ge\max\{r_i,r_j\}$. We have

$$\begin{aligned}
V_{ij}+V_{ji} &= -\frac{2}{3}\frac{r_i^2x_i(x_i-x_j)}{|x_i-x_j|^3} - \frac{2}{3}\frac{r_j^2x_j(x_j-x_i)}{|x_i-x_j|^3} \\
&= -\frac{r^2}{3}\frac{(x_i^2-x_j^2)^2+(x_i^2+x_j^2)(x_i-x_j)^2}{|x_i-x_j|^3}\le 0.
\end{aligned}$$

Case 2: $|x_i-x_j|\le\min\{r_i,r_j\}$. In this case

$$V_{ij}+V_{ji} = -\frac{2}{3}\frac{x_i(x_i-x_j)}{r_i} - \frac{2}{3}\frac{x_j(x_j-x_i)}{r_j} = -\frac{2}{3}\frac{|x_i|+|x_j|}{r}\left(1-\frac{x_ix_j}{|x_i|.|x_j|}\right)\le 0.$$

Case 3: $r_i\le|x_i-x_j|\le r_j$ (the case $r_j\le|x_i-x_j|\le r_i$ is similar). We have

$$V_{ij}+V_{ji} = -\frac{2}{3}\frac{r_i^2x_i(x_i-x_j)}{|x_i-x_j|^3} - \frac{2}{3}\frac{x_j(x_j-x_i)}{r_j}.$$

It is obvious that $V_{ji} \leq 0$ since $|x_j| \geq |x_i|$. If $V_{ij} \leq 0$ then we are done; if $V_{ij} \geq 0$, then using $r_i \leq |x_i - x_j|$ we get

$$V_{ij} \leq -\frac{2}{3}\frac{x_i(x_i - x_j)}{r_i}.$$

It turns out that $V_{ij} + V_{ji} \geq 0$ as in Case 2. □

We now turn to direct bounds on β.

Step 3. *We have the bound* $0.8218 \leq \beta \leq 0.8705$.

Proof. The lower bound follows from the following estimate whose proof is provided in Appendix.

Lemma 5. *For any positive measure ρ in $\mathbb{R}^3$ we have*

$$\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \\
\geq\ &\max\left\{ \iint_{\mathbb{R}^3\times\mathbb{R}^3} \left(\max\{|x|,|y|\} + \frac{(\min\{|x|,|y|\})^2}{|x-y|}\right)\mathrm{d}\rho(x)\,\mathrm{d}\rho(y), \right. \\
&\qquad \left. \iint_{\mathbb{R}^3\times\mathbb{R}^3} \left(|x-y| + \frac{2}{3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\right)\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \right\}.
\end{aligned}$$

Remark 7. *If ρ is radially symmetric then in the inequality in Lemma 5 becomes an equality.*

It follows from Lemma 5 that for any positive measure ρ on $\mathbb{R}^3$ and for any $\lambda \in [0,1]$ we have

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} W_\lambda(x,y)\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)$$

where

$$\begin{aligned}
W_\lambda(x,y) \ :=\ &\lambda\left(\max\{|x|,|y|\} + \frac{(\min\{|x|,|y|\})^2}{|x-y|}\right) \\
&+ (1-\lambda)\left(|x-y| + \frac{2}{3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\right). \qquad (31)
\end{aligned}$$

It turns out that

$$\beta \geq \sup_{\lambda\in[0,1]} \inf_{x,y\in\mathbb{R}^3} \frac{W_\lambda(x,y)}{|x|+|y|}.$$

Thus the lower bound on β follows from the following lemma whose proof is provided in Appendix.

Lemma 6. *With W_λ defined in (31) one has*

$$\sup_{\lambda\in[0,1]} \inf_{x,y\in\mathbb{R}^3} \frac{W_\lambda(x,y)}{|x|+|y|} \geq 0.8218.$$

(A numerical computation shows that the sharp lower bound in Lemma 6 is approximately 0.8218066, attained with $\lambda \approx 0.843476$.)

The upper bound on β is attained by choosing some explicit trial measure ρ. By restricting ρ to radially symmetric measures we have

$$\beta \leq \beta_{\text{rad}} := \inf \left\{ \frac{\int_0^\infty \int_0^\infty \frac{r^2 dm(r) dm(s)}{\max\{r,s\}}}{\int_0^\infty r dm(r) \int_0^\infty dm(r)} : m \text{ is a positive measure on } [0,\infty) \right\}.$$

Choosing $m(r) = r^{-3/2} 1_{[1,9]}(r) dr$, dr being the Lebesgue measure, we get

$$\beta_{\text{rad}} \leq \frac{115}{81} - \frac{1}{2}\ln(3) \approx 0.87045.$$

(A numerical computation shows that $\beta_{\text{rad}} \approx 0.8702$.) □

For completeness, we show Lemma 5.

Proof of Lemma 5. We start by proving

$$\iint \frac{x^2+y^2}{|x-y|} \,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \geq \iint \left(\max\{|x|,|y|\} + \frac{(\min\{|x|,|y|\})^2}{|x-y|}\right) \mathrm{d}\rho(x)\,\mathrm{d}\rho(y). \quad (32)$$

We first show that (32) follows from the following inequality: for any $\varepsilon > 0$, if N large enough, then

$$\sum_{1\leq i<j\leq N} \frac{x_i^2+x_j^2}{|x_i-x_j|} \geq (1-\varepsilon) \sum_{1\leq i<j\leq N} \left(\max\{|x_i|,|x_j|\} + \frac{\min\{|x_i|,|x_j|\}}{|x_i-x_j|}\right) \quad (33)$$

for every $\{x_i\}_{i=1}^N \subset \mathbb{R}^3$. In fact, we may assume that $\rho(\mathbb{R}^3) = 1$. For every $\varepsilon > 0$, taking N large enough and using (33) one has

$$\begin{aligned}
&\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x^2+y^2}{|x-y|} \,\mathrm{d}\,\rho(x)\,\mathrm{d}\,\rho(y) \\
= &\int_{\mathbb{R}^{3N}} \frac{2}{N(N-1)} \left(\sum_{1\leq i<j\leq N} \frac{x_i^2+x_j^2}{|x_i-x_j|}\right) \mathrm{d}\rho(x_1)\ldots\mathrm{d}\rho(x_N) \\
\geq &\int_{\mathbb{R}^{3N}} \frac{2(1-\varepsilon)}{N(N-1)} \sum_{1\leq i<j\leq N} \left(\max\{|x_i|,|x_j|\} + \frac{\min\{|x_i|,|x_j|\}}{|x_i-x_j|}\right) \mathrm{d}\rho(x_1)\ldots\mathrm{d}\rho(x_N) \\
= &(1-\varepsilon) \iint_{\mathbb{R}^3\times\mathbb{R}^3} \left(\max\{|x|,|y|\} + \frac{\min\{|x|,|y|\}}{|x-y|}\right) \mathrm{d}\rho(x)\,\mathrm{d}\rho(y).
\end{aligned}$$

Since the latter inequality holds for every $\varepsilon > 0$, the inequality (32) follows.

Now we show (33). This inequality follows from a key result of [12]. It was shown in [12] (Theorem 3.1) that, for any $\varepsilon > 0$, if N large enough, then

$$\max_{1\le j\le N}\left\{\sum_{1\le i\le N, i\ne j}\frac{1}{|x_i-x_j|}-\frac{N(1-\varepsilon)}{|x_j|}\right\}\ge 0 \tag{34}$$

for any $\{x_i\}_{i=1}^N \subset \mathbb{R}^3$. Since

$$\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\le \min\{|x_i|,|x_j|\}+\frac{(\max\{|x_i|,|x_j|\})^2}{|x_i-x_j|},$$

we can deduce from (34) that

$$\max_{1\le j\le N}\left\{\sum_{i\ne j}\left[\frac{x_i^2+x_j^2}{|x_i-x_j|}-(1-\varepsilon)\left(\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\right)\right]\right\}\ge 0. \tag{35}$$

Now take $1 > \varepsilon > 0$. For N large enough, employing (35) repeatedly, we can assume that

$$\sum_{1\le i<j}\left[\frac{x_i^2+x_j^2}{|x_i-x_j|}-(1-\varepsilon)\left(\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\right)\right]\ge 0$$

for every $\varepsilon N \le j \le N$. It turns out that

$$\begin{aligned}
&\sum_{1\le i<j\le N}\left[\frac{x_i^2+x_j^2}{|x_i-x_j|}-(1-\varepsilon)\left(\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\right)\right]\\
&\ge \sum_{1\le i<j<\varepsilon N}\left[\frac{x_i^2+x_j^2}{|x_i-x_j|}-(1-\varepsilon)\left(\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\right)\right]\\
&\ge -\sum_{1\le i<j<\varepsilon N}\max\{|x_i|,|x_j|\}\ge -\varepsilon N\sum_{1\le i<\varepsilon N}|x_i|\ge -\frac{\varepsilon}{1-\varepsilon}\sum_{1\le i<\varepsilon N\le j\le N}|x_i|\\
&\ge -\frac{\varepsilon}{1-\varepsilon}\sum_{1\le i<j\le N}\left(\max\{|x_i|,|x_j|\}+\frac{(\min\{|x_i|,|x_j|\})^2}{|x_i-x_j|}\right).
\end{aligned}$$

Thus (33), and hence (32), follows.

Next, we show that

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{x^2+y^2}{|x-y|}\,\mathrm{d}\,\rho(x)\,\mathrm{d}\rho(y)\ge\iint_{\mathbb{R}^3\times\mathbb{R}^3}\left(|x-y|+\frac{2}{3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\right)\mathrm{d}\rho(x)\,\mathrm{d}\rho(y). \tag{36}$$

This is equivalent to

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{x\cdot y}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y)\ge\frac{1}{3}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y). \tag{37}$$

In fact, if ρ is radially symmetric, then (36) becomes an equality due to (30). In general case, let us introduce the positive, radially symmetric measure

$$\widetilde{\rho}(x) = \int\limits_{\mathrm{SO}(3)} \rho(Rx)\mathrm{d}R,$$

$\mathrm{d}R$ being the normalized Haar measure on the rotation group SO(3). Because of the positive-definiteness of the operator with the kernel $\frac{x\cdot y}{|x-y|}$, we can employ the convexity to get

$$\begin{aligned}
&\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x\cdot y}{|x-y|}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y) \geq \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{x\cdot y}{|x-y|}\,\mathrm{d}\widetilde{\rho}(x)\,\mathrm{d}\widetilde{\rho}(y)\\
=\;& \frac{1}{3}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\,\mathrm{d}\widetilde{\rho}(x)\,\mathrm{d}\widetilde{\rho}(y) = \frac{1}{3}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\min\{|x|,|y|\})^2}{\max\{|x|,|y|\}}\,\mathrm{d}\rho(x)\,\mathrm{d}\rho(y).
\end{aligned}$$

Thus (37) (and hence (36)) holds for all positive measure ρ. □

Appendix: Technical lemmas

In this appendix we provide the proofs of some technical lemmas.

Proof of Lemma 3. Let us denote $\beta_1 := 3(\beta/6)^{1/3}$ for short. If the desired inequality fails then

$$\begin{aligned}
0 \;&\leq\; 1 + 0.68\; N^{-2/3} - (\beta^{-1} + 3Z^{-2/3})(\beta - \beta_1 N^{-2/3})\\
&\quad + \beta_1 N^{-2/3}(N/Z - \beta^{-1} + 3Z^{-2/3})\\
&=\; N^{-2/3}\left[0.68 - 3\beta(N/Z)^{2/3} + \beta_1(N/Z)\right].
\end{aligned}$$

Thus the polynomial

$$h(x) := 0.68 - 3\beta x^2 + \beta_1 x^3$$

satisfies that $h(-\infty) = -\infty$, $h(0) = 0.68 > 0$, $h(\beta^{-1/3}) < 0$, $h((N/Z)^{1/3}) \geq 0$, $h((2.2)^{1/3}) < 0$ and $h(+\infty) = +\infty$ (we can verify that $h(\beta^{-1/3}) < 0$ and $h((2.2)^{1/3}) < 0$ when $\beta \geq 0.8218$). However, it is impossible since $h(x)$ has at most three distinct roots. □

Proof of Lemma 4. Denote $\beta_1 := 3(\beta/6)^{1/3}$. Assume that the desired inequality fails, namely

$$3\beta Z^{-2/3} \leq \beta_1 N^{-2/3}(\beta^{-1} + 3Z^{-2/3}). \tag{38}$$

Replacing the term $\beta^{-1} + 3Z^{-2/3}$ in the right hand side of (38) we get

$$\frac{N}{Z} \geq \left(\frac{3\beta}{\beta_1}\right)^3 > 4$$

since $\beta \geq 0.8218$. Thus $N \geq \max\{4Z, \beta^{-1} + 3Z^{-2/3}\} > 4$.

On the other hand, (38) is equivalent to

$$N^{-2/3} \geq \frac{\beta}{\beta_1} - \frac{1}{3\beta(N/Z)^{2/3}}.$$

Using $\beta \geq 0.8218$ and $N/Z > 4$ we have $N < 4.5$. It contradicts the fact that N must be an integer. $\square$

Proof of Lemma 6. For any $x, y \in \mathbb{R}^3$, denote $a = \max\{|x|, |y|\}$, $b = \min\{|x|, |y|\}$ and $c = |x - y|$. Using the inequality $u^2 + v^2 \geq 2uv$ for $u, v \geq 0$, we find that

$$\begin{aligned} W_\lambda(x,y) &= \lambda\left(a + \frac{b^2}{c}\right) + (1-\lambda)\left(c + \frac{2b^2}{3a}\right) \\ &= (\lambda - \lambda')a + \left(\lambda' a + (1-\lambda)\frac{2b^2}{3a}\right) + \left(\lambda\frac{b^2}{c} + (1-\lambda)c\right) \\ &\geq (\lambda - \lambda')a + \left(2\sqrt{\frac{2}{3}\lambda'(1-\lambda)} + 2\sqrt{\lambda(1-\lambda)}\right) b \end{aligned}$$

for every $0 \leq \lambda' \leq \lambda$. We may choose λ' such that

$$\lambda - \lambda' = 2\sqrt{\frac{2}{3}\lambda'(1-\lambda)} + 2\sqrt{\lambda(1-\lambda)}. \tag{39}$$

If $\lambda \geq 0.8$ the solution to (39) is

$$\lambda' = \left(\sqrt{\frac{\lambda+2}{3} - 2\sqrt{\lambda(1-\lambda)}} - \sqrt{\frac{2}{3}(1-\lambda)}\right)^2.$$

Thus, for every $x, y \in \mathbb{R}^3$,

$$\frac{W_\lambda(x,y)}{|x| + |y|} \geq g(\lambda) := \lambda - \lambda' = \lambda - \left(\sqrt{\frac{\lambda+2}{3} - 2\sqrt{\lambda(1-\lambda)}} - \sqrt{\frac{2}{3}(1-\lambda)}\right)^2.$$

The desired lower bound comes from $g(0.843) \approx 0.821804$. (A numerical computation shows that $g(\lambda)$ has a unique maximum at $\lambda_0 \approx 0.843476$ and $g_{\max} \approx 0.821807$). $\square$

References

[1] B. Baumgartner, On Thomas-Fermi-von Weizsäcker and Hartree energies as functions of the degree of ionization, *J. Phys. A*: Math. Gen. **17**, 1593-1602 (1984).

[2] R. Benguria and E.H. Lieb, Proof of stability of highly negative ions in the absence of the Pauli principle, *Phys. Rev. Lett.* **50**, 1771-1774 (1983).

[3] R. Benguria and E.H. Lieb, The most negative ion in the Thomas-Fermi-von Weizsäcker theory of atoms and molecules, *J. Phys. B* **18**, 1045-1059 (1985).

[4] R. Brummelhuis and M.B. Ruskai, A one-dimensional model for many-electron atoms in extremely strong magnetic fields: maximum negative ionization, *J. Phys. A: Math. Gen.* **32** 2567-82 (1999)

[5] A. Dall'Acqua and J.P. Solovej, Excess charge for pseudo-relativistic atoms in Hartree-Fock theory, *Documenta Mathematica*, to appear (2010).

[6] A. Dall'Acqua, T. Østergaard Sørensen and E. Stockmeyer, private communication.

[7] J. Dolbeault, A. Laptev, and M. Loss, Lieb-Thirring inequalities with improved constants, *J. Eur. Math. Soc.* **10**, 1121-1126 (2008).

[8] C. Fefferman and L. A. Seco, Asymptotic neutrality of large ions, *Commun. Math. Phys.* **128**, 109-130 (1990).

[9] E.H. Lieb, Thomas-Fermi and related theories of atoms and molecules, *Rev. Mod. Phys.* **53**, 603-641 (1981).

[10] E.H. Lieb, The stability of matter, *Rev. Mod. Phys.* **48**, 553-569 (1976).

[11] E.H. Lieb, Bound on the maximum negative ionization of atoms and molecules, *Phys. Rev. A* **29**, 3018-3028 (1984).

[12] E. H. Lieb, I. M. Sigal, B. Simon, and W. Thirring, Asymptotic neutrality of large-Z ions, *Commun. Math. Phys.* **116**, 635-644 (1988).

[13] E. H. Lieb and R. Seiringer, The stability of matter in quantum mechanics, *Cambridge University Press*, 2009.

[14] E.H. Lieb, J.P. Solovej and J. Yngvason, Asymptotics of heavy atoms in high magnetic fields: I. Lowest Landau band regions, *Commun. Pure Appl. Math.* **47** 513-91 (1994).

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

[16] E. H. Lieb and W. Thirring, Bound for the Kinetic Energy of Fermions which Proves the Stability of Matter, *Phys. Rev. Lett.* **35**, 687-689 (1975).

[17] H. Leinfelder and C.G. Simader, Schrödinger operators with singular magnetic vector potentials, *Math. Z.* **176**, 1-19 (1981).

[18] M. Melgaard and T. Johnson, On the maximal ionization for the atomic Pauli operator, *Proc. R. Soc. A* **461**, 3355-3364, (2005).

[19] J. Messer and H. Spohn, Statistical mechanics of the isothermal Lane-Emden equation, *J. Stat. Phys.*, Vol. 29, No. 3, 561-578 (1982).

[20] M.B. Ruskai, Absence of discrete spectrum in highly negative ions, II. Extension to Fermions, *Commun. Math. Phys.* **82**, 325 327 (1982).

[21] L. A. Seco, I. M. Sigal, and J. P. Solovej, Bound on the ionization energy of large atoms, *Commun. Math. Phys.* **131**, 307-315 (1990).

[22] R. Seiringer, On the maximal ionization of atoms in strong magnetic fields, *J. Phys. A: Math. Gen.* **34**, 1943-1948 (2001).

[23] I.M. Sigal, Geometric methods in the quantum many-body problem. Nonexistence of very negative ions, *Commun. Math. Phys.* **85**, 309-324 (1982).

[24] I.M. Sigal, How many electrons can a nucleus bind? *Ann. Phys.* **157**, 307-320 (1984).

[25] J.P. Solovej, Asymptotics for bosonic atoms, *Lett. Math. Phys.*, **20**, 165-172 (1990).

[26] J. P. Solovej, Proof of the ionization conjecture in a reduced Hartree-Fock model, *Invent. Math.* **104**, 291-311 (1991).

[27] J.P. Solovej, The ionization conjecture in Hartree-Fock theory. *Ann. of Math.* **158**, 509-576 (2003).

[28] T. Østergaard Sørensen, The large-Z behavior of pseudo-relativistic atoms. *J. Math. Phys.* **46** no. 5, 052307 (2005).

[29] G. Teschl, Mathematical methods in quantum mechanics, with applications to Schrödinger operators. *Graduate Studies in Mathematics*, Vol. 99, Amer. Math. Soc., Providence (2009).

[30] G. Zhislin, Discussion of the spectrum of Schrödinger operator for system of many particles, *Trudy. Mosk. Mat. Obšč.* **9**, 81 (1960).

Asymptotics for Two-dimensional Atoms

Phan Thanh Nam, Fabian Portmann and Jan Philip Solovej

Abstract

We prove that the ground state energy of an atom confined to two dimensions with an infinitely heavy nucleus of charge $Z > 0$ and N quantum electrons of charge -1 is $E(N,Z) = -\frac{1}{2}Z^2 \ln Z + (E^{\mathrm{TF}}(\lambda) + \frac{1}{2}c^{\mathrm{H}})Z^2 + o(Z^2)$ when $Z \to \infty$ and $N/Z \to \lambda$, where $E^{\mathrm{TF}}(\lambda)$ is given by a Thomas-Fermi type variational problem and $c^{\mathrm{H}} \approx -2.2339$ is an explicit constant. We also show that the radius of a two-dimensional neutral atom is unbounded when $Z \to \infty$, which is contrary to the expected behavior of three-dimensional atoms.

AMS 2010 Subject Classification: 81Q20, 81V45.

Keywords: Large atoms, Thomas-Fermi theory, semiclassical approximation.

Contents

1 Introduction **60**

2 Preliminaries **62**
- 2.1 Spectral Properties 62
- 2.2 Useful Inequalities 63
- 2.3 Coulomb Potential 65

3 Thomas-Fermi Theory **66**
- 3.1 Thomas-Fermi Equation 68

4 Semiclassics for the TF Potential **71**
- 4.1 Localization 71
- 4.2 Hydrogen Comparison in Interior Region 73
- 4.3 Semiclassics in Exterior Region 74
- 4.4 Trial Density Matrix 77

5 Proofs of the Main Theorems **78**
- 5.1 Ground State Energy 78
- 5.2 Extensivity of Neutral Atoms 80
- 5.3 Semiclassics for Coulomb Singular Potentials 80

A Appendix **82**

1 Introduction

We consider an atom confined to two dimensions. It has a fixed nucleus of charge $Z > 0$ and N non-relativistic quantum electrons of charge -1. For simplicity we shall assume that electrons are spinless because the spin only complicates the notation and our coefficients in an obvious way. The system is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$

acting on the antisymmetric space $\bigwedge_{i=1}^N L^2(\mathbb{R}^2)$. Note that we are using the three-dimensional Coulomb potential to describe the confined atom. The ground state energy of the system is the bottom of the spectrum of $H_{N,Z}$, denoted by

$$E(N,Z) = \inf \operatorname{spec} H_{N,Z} = \inf_{\|\psi\|_{L^2}=1} (\psi, H_{N,Z}\psi).$$

One possible approach to obtain the above Hamiltonian is to consider a three-dimensional atom confined to a thin layer $\mathbb{R}^2 \times (-a, a)$ in the limit $a \to 0^+$ (see [3], Section 3, for a detailed discussion on the hydrogen case).

To the best of our knowledge, there is no existing result on the ground state energy and the ground states of the system, except for the case of hydrogen [29, 19]. The purpose of this article is to give a rigorous analysis for large Z-atom asymptotics and our main results are the following theorems.

Theorem 1 (Ground state energy)**.** *Fix $\lambda > 0$. When $Z \to \infty$ and $N/Z \to \lambda$ one has*

$$E(N,Z) = -\frac{1}{2} Z^2 \ln Z + \left(E^{\mathrm{TF}}(\lambda) + \frac{1}{2} c^{\mathrm{H}} \right) Z^2 + o(Z^2)$$

where $E^{\mathrm{TF}}(\lambda)$ is the Thomas-Fermi energy (defined in Section 3) and $c^{\mathrm{H}} = -3\ln(2) - 2\gamma_E + 1 \approx -2.2339$ with $\gamma_E \approx 0.5772$ being Euler's constant [4]. In particular, $\lambda \mapsto E^{\mathrm{TF}}(\lambda)$ is strictly convex and decreasing on $(0,1]$ and $E^{\mathrm{TF}}(\lambda) = E^{\mathrm{TF}}(1)$ if $\lambda \ge 1$.

Remark. By considering the hydrogen semiclassics we conjecture that the next term of $E(\lambda Z, Z)$ is of order $Z^{3/2}$. In contrast, the ground state energy in three dimensions behaves as

$$E(Z,Z) = c^{\mathrm{TF}} Z^{7/3} + c^{\mathrm{S}} Z^2 + c^{\mathrm{DS}} Z^{5/3} + o(Z^{5/3}),$$

where the leading (Thomas-Fermi [28, 6]) term was established in [15], the second (Scott [21]) term was proved in [7, 23], and the third (Dirac-Schwinger [2, 20]) term was shown in [5].

For three-dimensional atoms the leading term in the energy asymptotics of order $Z^{7/3}$ may be understood entirely from semiclassics. The contribution to this term comes from the bulk of the electrons located mainly at a distance of order $Z^{-1/3}$ from the nucleus. The term of order Z^2, the Scott term, is a pure quantum correction coming from the essentially finitely many inner most electrons at a distance of order Z^{-1} from the nucleus.

In the two-dimensional case the situation is more complicated. The leading term of order $Z^2\ln(Z)$ is semiclassical and comes from the fact that the semiclassical integral is logarithmically divergent, but has a natural cut-off at a distance of order Z^{-1} from the nucleus. The term of order Z^2 has two contributions. One part is semiclassical and comes essentially from electrons at distances of order 1 from the nucleus and another part, which corresponds to the three-dimensional Scott correction, coming from the essentially finitely many inner most electrons at a distance of order Z^{-1} from the nucleus.

Thus the two-dimensional atom has two regions. The innermost region of size Z^{-1} contains a finite number of electrons and contributes with Z^2 to the total energy. The outer region from Z^{-1} to order 1 has a high density of electrons and can be understood semiclassically. It contributes to the energy with both $Z^2\ln(Z)$ from the short distance divergence and with Z^2 from the bulk at distance 1.

Theorem 2 (Extensivity of neutral atoms)**.** *Assume that $N/Z \to 1$ and $\Psi_{N,Z}$ is a ground state of $H_{N,Z}$. Then, for any $R > 0$ there exists $C_R > 0$ such that*

$$\int_{|x|\geq R} \rho_{\Psi_{N,Z}}(x)dx \geq C_R Z + o(Z).$$

Remark. If we define the radius R_Z of a neutral atom ($N = Z$) by

$$\int_{|x|\geq R_Z} \rho_{\Psi_{Z,Z}}(x)dx = 1$$

then Theorem 2 implies that $\lim_{Z\to\infty} R_Z = \infty$. In three dimensions, however, the radius is expected to be bounded independently of Z (see [22, 24]).

Our main tool to understand the ground state energy and the ground states is the Thomas-Fermi (TF) theory introduced in Section 3. In this theory, the Z-ground state scales as $Z\rho^{\mathrm{TF}}_{N/Z}(x)$ and the absolute ground state ρ^{TF}_1 (when $N = Z$) has unbounded support. Roughly speaking, the extensivity of the TF ground state implies the extensivity of neutral atoms (in contrast, the three-dimensional TF Z-ground state scales as $Z^2\rho^{\mathrm{TF}}(Z^{1/3}x)$, i.e. its core *shrinks* as $Z^{-1/3}$).

The challenging point of the two-dimensional TF theory is that the TF potential $V^{\mathrm{TF}}(x)$ is *not* in $L^2_{loc}(\mathbb{R}^2)$ (it behaves like $|x|^{-1}$ near the origin). Consequently, one *cannot* write the semiclassics of $\mathrm{Tr}\left[-h^2\Delta - V^{\mathrm{TF}}\right]_-$ in the usual way because

$$(2\pi)^{-2}\iint [h^2p^2 - V^{\mathrm{TF}}(x)]_- dpdx = -(8\pi h^2)^{-1}\int [V^{\mathrm{TF}}(x)]^2_+ dx = -\infty.$$

This property complicates matters in the semiclassical approximation. In contrast, the three-dimensional semiclassical approximation leads to the behavior $-(15\pi^2 h^3)^{-1}\int_{\mathbb{R}^3}[V^{\mathrm{TF}}(x)]_+^{5/2}dx$ which is finite for the Coulomb singularity $V^{\mathrm{TF}}(x)\sim |x|^{-1}\in L^{5/2}_{\mathrm{loc}}(\mathbb{R}^3)$.

We shall follow the strategy of proving the Scott's correction given by Solovej and Spitzer [26] (see also [25]), that is to compare the semiclassics of TF-type potentials with hydrogen. More precisely, in the region close to the origin we shall compare directly with hydrogen, whereas in the exterior region we can employ the coherent state approach. We do not use the new coherent state approach introduced in [26], since the usual one [9, 27] is sufficient for our calculations. In fact, we prove the following semiclassical estimate for potentials with Coulomb singularities.

Theorem 3 (Semiclassics for Coulomb singular potentials)**.** *Let $V\in L^2_{\mathrm{loc}}(\mathbb{R}^2\backslash\{0\})$ be a real-valued potential such that $1_{\{|x|\ge 1\}}V_+\in L^2(\mathbb{R}^2)$ and*

$$|V(x)-\kappa|x|^{-1}|\le C|x|^{-\theta}\quad \textit{for all } |x|\le\delta,$$

where $\kappa>0$, $\delta>0$, $1>\theta>0$ and $C>0$ are universal constants. Then, as $h\to 0^+$,

$$\begin{aligned}\mathrm{Tr}\left[-h^2\Delta-V\right]_- &= -(8\pi h^2)^{-1}\int_{\mathbb{R}^2}\left([V(x)]_+^2-\kappa^2[|x|^{-1}-1]_+^2\right)dx\\ &\quad +\kappa^2(4h^2)^{-1}\left[\ln(2\kappa^{-1}h^2)+c^{\mathrm{H}}\right]+o(h^{-2}),\end{aligned}$$

where $c^{\mathrm{H}}=-3\ln(2)-2\gamma_E+1\approx-2.2339$ with $\gamma_E\approx 0.5772$ being Euler's constant [4].

The article is organized as follows. In Section 2 we give a brief summary of the existing results concerning atoms confined to two dimensions. Section 3 contains basic information on the TF theory. The most technical part of the article is in Section 4, where we show the semiclassics for the TF potential. The main theorems are proved in Section 5. Some technical proofs are deferred to the Appendix.

2 Preliminaries

2.1 Spectral Properties

For completeness, we start by collecting some basic properties of the spectrum of $H_{N,Z}$, whose proofs can essentially be adapted from the usual three-dimensional case (see the Appendix).

Theorem 4 (Spectrum of $H_{N,Z}$)**.** *Let $H_{N,Z}$ be the operator defined above.*

(*i*) *(HVZ Theorem) The essential spectrum of* $H_{N,Z}$ *is*

$$\operatorname{ess\,spec} H_{N,Z} = [E(N-1,Z), \infty).$$

Consequently, for non-vanishing binding energy $E(N-1) - E(N) =: \varepsilon > 0$, *the operator* $H_{N,Z}$ *has (at least) one ground state. Moreover, in this case any ground state* $\Psi_{N,Z}$ *of* $H_{N,Z}$ *has exponential decay as*

$$\rho_{\Psi_{N,Z}}(x) \leq C|x|^{\frac{4Z}{\sqrt{2\varepsilon}}-2} e^{-2\sqrt{2\varepsilon}|x|} \quad \textit{for } |x| \textit{ large}$$

where the density $\rho_{\Psi_{N,Z}}$ *is defined as in Section 2.2.*

(*ii*) *(Zhislin's Theorem) If* $N < Z+1$ *then the binding condition* $E(N) < E(N-1)$ *is satisfied, and hence* $H_{N,Z}$ *has a ground state.*

(*iii*) *(Asymptotic neutrality) The largest number* $N = N_c(Z)$ *of electrons such that* $H_{N,Z}$ *has a ground state is finite and satisfies* $\lim_{Z\to\infty} N_c(Z)/Z = 1$.

In particular, the spectrum of hydrogen ($N = 1$) is explicitly known [29] (see also [19] for a review).

Theorem 5 (Hydrogen spectrum)**.** *All negative eigenvalues of the operator* $-\frac{1}{2}\Delta - |x|^{-1}$ *in* $L^2(\mathbb{R}^2)$ *are*

$$E_n = -\frac{1}{2(n+1/2)^2},$$

with multiplicity $2n+1$, *where* $n = 0, 1, 2, ...$

The following consequence will be useful in our estimates. The proof can be found in the Appendix.

Lemma 6 (Hydrogen semiclassics)**.** *When* $\mu \to 0^+$ *we have*

$$\operatorname{Tr}\left[-\frac{1}{2}\Delta - |x|^{-1} + \mu\right]_- = \frac{1}{2}\left[\ln(\mu) - 3\ln(2) - 2\gamma_E + 1\right] + o(1). \tag{1}$$

By scaling, for $\mu > 0$ *fixed and* $h \to 0^+$,

$$\operatorname{Tr}\left[-h^2\Delta - |x|^{-1} + \mu\right]_- = (4h^2)^{-1}\left[\ln(2h^2) + \ln(\mu) + c^{\mathrm{H}}\right] + o(h^{-2}), \tag{2}$$

where $c^{\mathrm{H}} = -3\ln(2) - 2\gamma_E + 1 \approx -2.2339$ *with* $\gamma_E \approx 0.5772$ *being Euler's constant [4].*

2.2 Useful Inequalities

For the readers' convenience, we recall some usual notations. We shall denote by $L^2(\mathbb{R}^2)$ the Hilbert space with the inner product $(f,g) = \int_{\mathbb{R}^2} \overline{f(x)} g(x) dx$. An operator γ on $L^2(\mathbb{R}^2)$ is called a (one-body) *density matrix* if $0 \leq \gamma \leq 1$ and $\operatorname{Tr}(\gamma) < \infty$. Its *density* is $\rho_\gamma(x) := \gamma(x,x)$, where $\gamma(x,y)$ is the kernel of γ. More precisely, if γ is written in the spectral decomposition $\gamma = \sum_i t_i |u_i\rangle\langle u_i|$ then $\gamma(x,y) := \sum_i t_i u_i(x)\overline{u_i(y)}$ and $\rho_\gamma(x) := \sum_i t_i |u_i(x)|^2$. For example, the density matrix γ_Ψ of a (normalized) wave function $\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^2)$ is

$$\gamma_\Psi(x,y) := N \int_{\mathbb{R}^{2(N-1)}} \Psi(x, x_2, ..., x_N)\overline{\Psi(y, x_2, ..., x_N)} dx_2 ... dx_N,$$

which satisfies $0 \leq \gamma_\Psi \leq 1$ and $\mathrm{Tr}(\gamma_\Psi) = N$. Moreover, its density is

$$\rho_\Psi(x) := \rho_{\gamma_\Psi}(x) = N \int_{\mathbb{R}^{2(N-1)}} |\Psi(x, x_2, ..., x_N)|^2 dx_2 ... dx_N.$$

The following theorem regarding the spectrum of Schrödinger operators is important for our analysis (see e.g. [12] for a proof). The analogue in three dimensions was first proved by Lieb and Thirring [17].

Theorem 7 (Lieb-Thirring inequalities). *There exists a finite constant $L_{1,2} > 0$ such that for any real-valued potential V with $V_+ \in L^2(\mathbb{R}^2)$ one has*

$$\mathrm{Tr}[-\Delta - V]_- \geq -L_{1,2} \int_{\mathbb{R}^2} V_+^2(x) dx, \tag{3}$$

where $a_+ := \max\{a, 0\}$ and $a_- := \min\{a, 0\}$. Hence $\mathrm{Tr}[-\Delta - V]_-$ is the sum of all negative eigenvalues of $-\Delta - V$ in $L^2(\mathbb{R}^2)$.

Equivalently, there exists a finite constant $K_2 > 0$ such that for any density matrix γ one has

$$\mathrm{Tr}[-\Delta\gamma] \geq K_2 \int_{\mathbb{R}^2} \rho_\gamma^2(x) dx. \tag{4}$$

Note that in general there is no upper bound on $\mathrm{Tr}\, 1_{(-\infty,0]}(-\Delta - V)$, the number of negative eigenvalues of $-\Delta - V$, in term of $\int V_+^\alpha$ for any $\alpha > 0$. However, we shall only need some localized versions of this bound. The proof of the following lemma can be found in the Appendix. The estimate in (ii) is useful to treat the Coulomb singularity in the region close to the origin (recall that $|x|^{-1} \notin L^2_{\mathrm{loc}}(\mathbb{R}^2)$).

Lemma 8. *Let $V : \mathbb{R}^2 \to \mathbb{R}$ and let $0 \leq \phi(x) \leq 1$ supported in a subset $\Omega \subset \mathbb{R}^2$ with finite measure $|\Omega|$. Let $0 \leq \gamma \leq 1$ be an operator on $L^2(\mathbb{R}^2)$ such that*

$$\mathrm{Tr}[(-h^2\Delta - V)\phi\gamma\phi] \leq 0 \textit{ for some } 1/2 > h > 0.$$

(i) If $V_+ \in L^2_{\mathrm{loc}}(\mathbb{R}^2)$ then $\phi\gamma\phi$ is trace class and there exists a universal constant $C > 0$ (independent of V, γ and h) such that for any $\alpha \in [0,1]$,

$$\int_{\mathbb{R}^2} \rho_{\phi\gamma\phi}^{2\alpha}(x) dx \leq C h^{-4\alpha} ||V_+||_{L^2(\Omega)}^{2\alpha} |\Omega|^{1-\alpha}.$$

(*ii*) *If* $V(x) \leq C_0(|x|^{-1}+1)$ *then* $\phi\gamma\phi$ *is trace class and there exists a constant* $C > 0$ *dependent only on* C_0 *(but independent of* V, ϕ, Ω, γ *and* h*) such that for any* $\alpha \in [0,1]$,

$$\int_{\mathbb{R}^2} \rho_{\phi\gamma\phi}^{2\alpha}(x)dx \leq Ch^{-4\alpha}\left(|\ln h| + |\Omega|\right)^{\alpha} |\Omega|^{1-\alpha}.$$

We shall approximate the ground state energy $E(N,Z)$ by one-body densities. For the lower bound, we need the following inequality to control the electron-electron repulsion energy. The three-dimensional analogue of this bound was first proved by Lieb [10] and was then improved by Lieb and Oxford [13]. The two-dimensional version below was taken from [16].

Theorem 9 (Lieb-Oxford inequality)**.** *For any (normalized) wave function* $\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^2)$ *it holds that*

$$\left(\Psi, \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|}\Psi\right) \geq D(\rho_\Psi) - C_{\mathrm{LO}} \int \rho_\Psi^{3/2},$$

with $C_{\mathrm{LO}} = 192(2\pi)^{1/2}$*, where the direct term* $D(\rho_\Psi)$ *is defined as in Section 2.3.*

For the upper bound, we shall need the next result [11].

Theorem 10 (Lieb's variational principle)**.** *For* $Z > 0$, $N \in \mathbb{N}$ *and any density matrix* γ *with* $\mathrm{Tr}(\gamma) \leq N$*, one has*

$$E(N,Z) \leq \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma\right] + D(\rho_\gamma) - \frac{1}{2}\iint \frac{|\gamma(x,y)|^2}{|x-y|}dxdy,$$

where the direct term $D(\rho_\gamma)$ *is defined as in Section 2.3.*

2.3 Coulomb Potential

Here we study the Coulomb potential $f * |\,.\,|^{-1}$ of some function f. Associated to this potential is the Coulomb energy of two functions,

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

That $D(f,g)$ is well-defined at least in $L^{4/3}(\mathbb{R}^2)$ is due to the Hardy-Littlewood-Sobolev inequality (see [12], Theorem 4.3)

$$D(|f|,|g|) \leq C_{\mathrm{HLS}} \|f\|_{L^{4/3}} \|g\|_{L^{4/3}} \quad \text{for all } f,g \in L^{4/3}(\mathbb{R}^2).$$

Moreover, $|x-y|^{-1}$ is a strictly positive kernel since the 2D Fourier transform of $|\,.\,|^{-1}$ is itself up to a constant (see [12] Theorem 5.9). Therefore, $D(f) := D(f,f)$ is always nonnegative and $(f,g) \mapsto D(f,g)$ is a positive inner product in $L^{4/3}(\mathbb{R}^2)$. These observations allow us to formulate the following theorem.

Theorem 11 (Coulomb norm)**.** *There exists* C_{HLS} *such that*

$$0 < D(f) \le C_{\text{HLS}} \, \|f\|_{L^{4/3}}^2 \quad \textit{for all } f \in L^{4/3}(\mathbb{R}^2)\backslash\{0\}.$$

Consequently, $f \mapsto \sqrt{D(f)}$ *is a norm in* $L^{4/3}(\mathbb{R}^2)$*.*

In three dimensions, the Coulomb potential $\rho * |\,.\,|^{-1}$ of a radially symmetric function ρ is represented beautifully by Newton's Theorem (see [12], Theorem 9.7). In two dimensions, however, we do not have such a representation since $|\,.\,|^{-1}$ is not the fundamental solution to the two-dimensional Laplace operator. Therefore, the following bounds will be useful in our context and their proofs can be found in the Appendix. The lower bound is similar to Newton's Theorem in three dimensions, but the upper bounds are more involved. We do not claim that they are optimal but they are sufficient for our purposes.

Lemma 12 (Coulomb potential bound)**.** *Assume that* ρ *is radially symmetric,* $0 \le \rho(x) \le (2\pi|x|)^{-1}$ *and* $\int \rho = \lambda$*. We have the following bounds on the potential* $\rho * |\,.\,|^{-1}$*.*

(*i*) *(Lower bound) For all* $x \in \mathbb{R}^2\backslash\{0\}$*,*

$$(\rho * |\,.\,|^{-1})(x) \ge \int_{\mathbb{R}^2} \frac{\rho(y)}{\max\{|x|, |y|\}} dy.$$

(*ii*) *(Upper bound) For all* $x \in \mathbb{R}^2\backslash\{0\}$*,*

$$(\rho * |\,.\,|^{-1})(x) \le 2\sqrt{2\lambda}|x|^{-1/2} + 3.$$

Moreover, for any $\delta > 0$ *there exists* $R = R(\rho, \delta) > 0$ *and a universal constant* $C_1 > 0$ *such that for any* $|x| \ge R$*,*

$$(\rho * |\,.\,|^{-1})(x) \le \frac{\lambda + \delta}{|x|} + C_1 \frac{\ln(|x|)}{|x|} \int_{3|x|/2 \ge |y| \ge |x|/2} \rho(y) dy.$$

3 Thomas-Fermi Theory

In this section, we introduce the two-dimensional Thomas-Fermi (TF) theory which will turn out to be the main tool to understand the ground state energy and ground states. The three-dimensional TF theory was studied in great mathematical detail by Lieb-Simon [15, 9]. In fact, the simplest version of TF theory (see [12], Chap. 11) is sufficient for our discussion here.

Definition 13 (Thomas-Fermi functional)**.** For any nonnegative function $\rho \in L^1(\mathbb{R}^2)$ we define the *TF functional* as

$$\mathcal{E}^{\text{TF}}(\rho) \;\; := \;\; \int_{\mathbb{R}^2} \left(\pi\rho^2(x) - \frac{\rho(x)}{|x|} + (4\pi)^{-1}[|x|^{-1} - 1]_+^2 \right) dx + D(\rho).$$

For any $\lambda > 0$ we define the *TF energy* as

$$E^{\rm TF}(\lambda) := \inf \left\{ \mathcal{E}^{\rm TF}(\rho) | \rho \geq 0, \|\rho\|_{L^1(\mathbb{R}^2)} \leq \lambda \right\}. \tag{5}$$

Remark. (i) The term $\pi\rho^2$ comes from the semiclassics of the kinetic energy while $-\int \rho(x)|x|^{-1}$ and the direct term $D(\rho) = \frac{1}{2}\iint \rho(x)\rho(y)|x-y|^{-1}dxdy$ stand for the Coulomb interactions.

(ii) The appearance of $(4\pi)^{-1}[|x|^{-1} - 1]_+^2$ ensures that the TF functional is bounded from below. In fact,

$$\begin{aligned} \mathcal{E}^{\rm TF}(\rho) &= \int\limits_{|x|\leq 1} \pi \left(\rho(x) - \frac{1}{2\pi|x|}\right)^2 dx + \int\limits_{|x|>1} \left(\pi\rho^2(x) - \frac{\rho(x)}{|x|}\right) dx \\ &\quad + D(\rho) - \frac{3}{4} \\ &\geq -\int \rho - \frac{3}{4}. \end{aligned}$$

(iii) If $\rho_\lambda^{\rm TF}$ is the ground state of the above TF theory then $Z\rho_\lambda^{\rm TF}$ is expected to approximate the density $\rho_{\Psi_{N,Z}}$ of a ground state $\Psi_{N,Z}$ of $H_{N,Z}$ with $N \approx \lambda Z$ (in some appropriate sense). In other words, the Z-dependent TF theory can be defined from the above TF theory by the scaling $\rho \mapsto Z\rho$.

Basic information about the TF theory is collected in the following theorem.

Theorem 14 (Thomas-Fermi theory)**.** *Let* $\lambda > 0$.

(i) (Existence) The variational problem (5) *has a unique minimizer* $\rho_\lambda^{\rm TF}$*. Moreover, the functional* $\lambda \mapsto E^{\rm TF}(\lambda)$ *is strictly convex, decreasing on* $(0,1]$ *and* $E^{\rm TF}(\lambda) = E^{\rm TF}(1)$ *if* $\lambda \geq 1$.

*(ii) (*TF *equation)* $\rho_\lambda^{\rm TF}$ *satisfies the TF equation*

$$2\pi\rho_\lambda^{\rm TF}(x) = \left[|x|^{-1} - (\rho_\lambda^{\rm TF} * |\,.\,|^{-1})(x) - \mu_\lambda^{\rm TF}\right]_+$$

with some constant $\mu_\lambda^{\rm TF} > 0$ *if* $\lambda < 1$ *and* $\mu_\lambda^{\rm TF} = 0$ *if* $\lambda \geq 1$.

*(iii) (*TF *minimizer)* $\rho_\lambda^{\rm TF}$ *is radially symmetric;* $\int \rho_\lambda^{\rm TF} = \min\{\lambda, 1\}$ *and*

$$0 \leq |x|^{-1} - 2\pi\rho_\lambda^{\rm TF} \leq C|x|^{-1/2} \quad \textit{for all } x \neq 0.$$

Moreover, $\operatorname{supp} \rho_\lambda^{\rm TF}$ *is compact if and only if* $\lambda < 1$.

Remark. Henceforth we shall always denote by C some finite positive constant depending only on $\lambda > 0$ (the total mass in the TF theory). Two C's in the same line may refer to two different constants.

Proof. (i-ii) Formula (6) implies that $\rho \mapsto \mathcal{E}^{\rm TF}(\rho)$ is strictly convex. Therefore, the existence and uniqueness of the TF minimizer, and the TF equation follow from standard variational methods similarly to the three-dimensional TF theory (see [12], Theorems 11.12 and 11.13). The property of $\mu_\lambda^{\rm TF}$ is a consequence of the TF equation and is shown in Lemma 15 below.

That $E^{\rm TF}(\lambda)$ is decreasing follows from the definition. When $\lambda \ge 1$, $E^{\rm TF}(\lambda) = E^{\rm TF}(1)$ since $\rho_\lambda^{\rm TF} = \rho_1^{\rm TF}$ (by (iii)). When $\lambda \in (0,1]$, the TF energy is also strict convex because the unique minimizer satisfies $\int \rho_\lambda^{\rm TF} = \lambda$ (by (iii)) and the TF functional is strict convex.

(iii) Since the TF functional is rotation invariant and the minimizer is unique, it must be radially symmetric. The inequality $0 \le |x|^{-1} - 2\pi\rho_\lambda^{\rm TF} \le C|x|^{-1/2}$ follows from the TF equation and the following estimate in Lemma 12,

$$(\rho^{\rm TF} * |\,.\,|^{-1})(x) \le 2\sqrt{2\lambda}|x|^{-1/2} + 3.$$

We defer the proof that $\int \rho_\lambda^{\rm TF} = \min\{\lambda, 1\}$ and property of $\operatorname{supp} \rho_\lambda^{\rm TF}$ to Lemma 15. $\square$

3.1 Thomas-Fermi Equation

Lemma 15 (TF equation)**.** *Assume that ρ is a nonnegative, radially symmetric, integrable solution to the TF equation*

$$2\pi\rho(x) = \left[|x|^{-1} - (\rho * |\,.\,|^{-1})(x) - \mu\right]_+ \tag{6}$$

for some constant $\mu \ge 0$.

(*i*) *If $\mu > 0$ then $\int \rho < 1$ and* $\operatorname{supp} \rho$ *is compact.*

(*ii*) *If $\mu = 0$ then $\int \rho = 1$ and*

$$\int_{|x|\ge r} \rho(x)dx \ge e^{-2\sqrt{r}} \quad \textit{for all } r \ge 0.$$

Proof. Denote $\int \rho =: \lambda > 0$. For $r > 0$ we shall write $\rho(r)$ instead of $\rho(x)|_{|x|=r}$.

1. We start by proving $\lambda \le 1$. Since ρ is nonnegative and radially symmetric, we have by Lemma 12

$$(\rho * |\,.\,|^{-1})(x) \ge \int_{\mathbb{R}^2} \frac{\rho(y)}{\max\{|x|, |y|\}} dy.$$

Hence, the TF equation (6) yields

$$2\pi\rho(x)|x| \le \left[1 - \int_{\mathbb{R}^2} \frac{|x|\rho(y)}{\max\{|x|,|y|\}} dy - \mu|x|\right]_+ \quad \text{for all } x \ne 0. \tag{7}$$

For any $\varepsilon \in (0, \lambda)$, we can find $R_\varepsilon > 0$ such that $\int_{|x|\geq R_\varepsilon} \rho = \varepsilon$. When $|x| \geq R_\varepsilon$, using

$$\int_{\mathbb{R}^2} \frac{|x|\rho(y)}{\max\{|x|, |y|\}} dy \geq \int_{|y|\leq R_\varepsilon} \rho(y) = \lambda - \varepsilon$$

we can deduce from (7) that

$$2\pi\rho(x)|x| \leq [1 - \lambda + \varepsilon - \mu|x|]_+ \leq [1 - \lambda + \varepsilon - \mu R_\varepsilon]_+ \ \text{ for all } |x| \geq R_\varepsilon.$$

Since $\int_{|x|\geq R_\varepsilon} \rho = \varepsilon > 0$, there exists $|x| \geq R_\varepsilon$ such that $\rho(x) > 0$. Therefore, it follows from the latter estimate that

$$1 - \lambda + \varepsilon - \mu R_\varepsilon \geq 0 \ \text{ for all } \varepsilon \in (0, \lambda). \tag{8}$$

For any $\mu \geq 0$, (8) implies that $\lambda \leq 1$.

2. If $\mu > 0$ then (8) yields

$$\limsup_{\varepsilon\to 0} R_\varepsilon \leq R_0 := \mu^{-1}(1 - \lambda).$$

Since $\int_{|x|\geq R_\varepsilon} \rho = \varepsilon$ and $\limsup_{\varepsilon\to 0} R_\varepsilon \leq R_0$, we get $\int_{|x|\geq R_0} \rho = 0$. Thus $\operatorname{supp} \rho \subset \{|x| \leq R_0\}$ and $\lambda < 1$ (because $R_0 > 0$).

3. From now on we assume that $\mu = 0$. We shall prove that $\lambda = 1$. Suppose that $\lambda < 1 - 3\varepsilon$ for some $\varepsilon > 0$. Because ρ is nonnegative, radially symmetric and $\rho(x) \leq (2\pi|x|)^{-1}$ (due to the TF equation (6)), by Lemma 12 we can find $R > 0$ and $C_1 > 0$ such that

$$(\rho * |\,.\,|^{-1})(x) \leq \frac{1 - 2\varepsilon}{|x|} + C_1 \frac{\ln(|x|)}{|x|} \int_{3|x|/2\geq|y|\geq|x|/2} \rho(y)dy \ \text{ for all } |x| \geq R. \tag{9}$$

Define $\varepsilon_1 := \varepsilon/C_1$ and

$$A := \left\{ r \geq R : \int_{3r/2\geq|y|\geq r/2} \rho(y)dy \leq \frac{\varepsilon_1}{\ln(r^{-1})} \right\}.$$

If $|x| \in A$, then (9) gives $(\rho * |\,.\,|^{-1})(x) \leq (1 - \varepsilon)|x|^{-1}$, and the TF equation (6) with $\mu = 0$ gives

$$2\pi\rho(x) = \left[\frac{1}{|x|} - (\rho * |x|^{-1})(x)\right]_+ \geq \frac{\varepsilon}{|x|}.$$

Taking the integral of the previous inequality over $\{x \in \mathbb{R}^2 : |x| \in A\}$ one has

$$\infty > 2\pi \int\limits_{\mathbb{R}^2} \rho \geq 2\pi \int\limits_{|x|\in A} \rho(x)dx \geq \int\limits_{|x|\in A} \frac{\varepsilon}{|x|} dx = 2\pi\varepsilon\mathcal{L}^1(A)$$

where $\mathcal{L}^1$ is the one-dimensional Lebesgue measure. Thus A has finite measure, and consequently we can choose a sequence $\{R_n\}_{n=1}^{\infty} \subset \mathbb{R}\backslash A$ such that $3R <$

$3R_n < R_{n+1} < 4R_n$ for all $n \geq 1$. Because $R_n > R$ and $R_n \notin A$ we have, by the definition of A,

$$\int\limits_{3R_n/2 \geq |y| \geq R_n/2} \rho(y)dy > \frac{\varepsilon_1}{\ln(R_n)} \quad \text{for all } n \geq 1.$$

Taking the sum over all $n \in \mathbb{N}$ and using $R_{n+1} > 3R_n$, we find that

$$\infty > \int\limits_{\mathbb{R}^2} \rho \geq \sum_{n=1}^{\infty} \int\limits_{3R_n/2 \geq |y| \geq R_n/2} \rho(y)dy \geq \sum_{n=1}^{\infty} \frac{\varepsilon_1}{\ln(R_n)}.$$

On the other hand, since $R_{n+1} < 4R_n$ we get $R_n \leq 4^n R_1 \leq [4(1+R_1)]^n$ for all $n \geq 1$. Therefore,

$$\sum_{n=1}^{\infty} \frac{\varepsilon_1}{\ln(R_n)} \geq \sum_{n=1}^{\infty} \frac{\varepsilon_1}{n \ln(4(1+R_1))} = +\infty$$

The last two inequalities yield a contradiction.

4. Finally, we show the lower bound on $\int_{|x| \geq r} \rho$. With $\mu = 0$ and $\lambda = 1$, inequality (7) becomes

$$2\pi\rho(x)|x| \leq \int\limits_{|y| \geq |x|} \left(1 - \frac{|x|}{|y|}\right) \rho(y)dy \quad \text{for all } x \neq 0. \tag{10}$$

Denote

$$g(r) := \int\limits_{|y| \geq r} \left(1 - \frac{r}{|y|}\right) \rho(y)dy = 2\pi \int\limits_{r}^{\infty} (s-r)\,\rho(s)ds.$$

Then $g(0) = 1$, $g(+\infty) = 0$ and

$$g'(r) = -2\pi \int\limits_{r}^{\infty} \rho(s)ds < 0, \quad g''(r) = 2\pi\rho(r) \quad \text{for all } r > 0.$$

Thus (10) can be rewritten as

$$rg''(r) \leq g(r) \quad \text{for all } r > 0.$$

Note that $g_0(r) := e^{-2\sqrt{r}}$ satisfies $g_0(0) = 1$, $g_0(+\infty) = 0$ and

$$rg_0''(r) - g_0(r) = \frac{1}{2\sqrt{r}} e^{-2\sqrt{r}} > 0.$$

Therefore, $h(x) := g(x) - g_0(x)$ satisfies that $h(0) = h(+\infty) = 0$ and $rh''(r) \leq h(r)$. If the set $U := \{r > 0 : h(r) < 0\}$ is not empty, then h is a strict concave function on this open set. By the maximum principle and $h(0) = h(+\infty) = 0$, we can argue to get a contradiction. Thus $h(r) \geq 0$ for all $r \geq 0$. This yields $\int_{|x| \geq r} \rho(x)dx \geq g(r) \geq g_0(r) = e^{-2\sqrt{r}}$. $\square$

4 Semiclassics for the TF Potential

In this section, we consider the semiclassics for the TF potential

$$V_\lambda^{\rm TF}(x) := |x|^{-1} - (\rho_\lambda^{\rm TF} * |\,.\,|^{-1})(x) - \mu_\lambda^{\rm TF}.$$

From the TF equation and the properties of the TF minimizer (see Theorem 14) we have $[V_\lambda^{\rm TF}]_+ \in L^1(\mathbb{R}^2)$ and

$$|V_\lambda^{\rm TF}(x) - |x|^{-1}| \le C(|x|^{-1/2} + 1) \ \text{ for all } x \neq 0.$$

The following theorem will turn out to be the main ingredient to prove Theorems 1 and 2. The parameter h will eventually be replaced by $(2Z)^{-1/2}$ in our application.

Theorem 16 (Semiclassics for TF potential)**.** *When $h \to 0^+$ one has*

$$\begin{aligned} \operatorname{Tr}\left[-h^2\Delta - V_\lambda^{\rm TF}\right]_- &= -(8\pi h^2)^{-1}\int_{\mathbb{R}^2}\left([V_\lambda^{\rm TF}(x)]_+^2 - [|x|^{-1}-1]_+^2\right)dx \\ &\quad + (4h^2)^{-1}\left[\ln(2h^2) + c^{\rm H}\right] + o(h^{-2}). \qquad (11)\end{aligned}$$

where $c^{\rm H} = -3\ln(2) - 2\gamma_E + 1 \approx -2.2339$.

Moreover, there is a density matrix γ_h such that

$$\operatorname{Tr}\left[(-h^2\Delta - V_\lambda^{\rm TF})\gamma_h\right] = \operatorname{Tr}\left[-h^2\Delta - V_\lambda^{\rm TF}\right]_- + o(h^{-2}) \qquad (12)$$

and

$$2h^2\operatorname{Tr}(\gamma_h) \le \int \rho_\lambda^{\rm TF}, \quad D((2h^2)\rho_{\gamma_h} - \rho_\lambda^{\rm TF}) = o(1). \qquad (13)$$

Note that (11) is a special case of Theorem 3. In this section, we shall prove (11) in detail. The proof of Theorem 3 is provided in the next section.

As in [26] we shall prove the semiclassical approximation (11) by comparing with the hydrogen. In fact, because of the hydrogen semiclassics (2), the approximation (11) is equivalent to

$$\begin{aligned} &\operatorname{Tr}\left[-h^2\Delta - V_\lambda^{\rm TF}\right]_- - \operatorname{Tr}\left[-h^2\Delta - |x|^{-1}+1\right]_- \\ &= -(8\pi h^2)^{-1}\int_{\mathbb{R}^2}\left([V_\lambda^{\rm TF}]_+^2 - [|x|^{-1}-1]_+^2\right)dx + o(h^{-2}). \qquad (14)\end{aligned}$$

4.1 Localization

To treat the singularity of the TF potential we shall distinguish between three regions. In the interior region (close to the origin), we shall compare directly with hydrogen; while in the exterior region (not too close and not too far from the origin) we can employ the usual semiclassical techniques; and finally, the region very far from the origin has negligible contribution.

Definition 17 (Partition of unity)**.** Let φ be a nonnegative, smooth function (with bounded derivatives) such that $\varphi(x) = 1$ if $|x| \le 1$ and $\varphi(x) = 0$ if $|x| \ge 2$. Choose $r := h^{1/2}$, $\Lambda := |\ln h|$ and denote

$$\begin{aligned}\Phi_1(x) &= \varphi(x/r),\\ \Phi_2(x) &= (1-\varphi^2(x/r))^{1/2}\varphi(x/\Lambda),\\ \Phi_3(x) &= (1-\varphi^2(x/\Lambda))^{1/2}.\end{aligned}$$

Then $\sum_{i=1}^3 \Phi_i^2 = 1$, $\operatorname{supp}\Phi_1 \subset \{|x| \le 2r\}$, $\operatorname{supp}\Phi_2 \subset \{r \le |x| \le 2\Lambda\}$, $\operatorname{supp}\Phi_3 \subset \{|x| \ge \Lambda\}$.

The localization cost is controlled by the following lemma.

Lemma 18 (Localization)**.** *Let V be either $V_\lambda^{\rm TF}$ or $(|x|^{-1}-1)$. When $\Lambda = |\ln h|$ and $r = h^{1/2} \to 0^+$ one has*

$$\operatorname{Tr}[-h^2\Delta - V]_- \;=\; \sum_{i=1,2} \operatorname{Tr}[\Phi_i(-h^2\Delta - V)\Phi_i]_- + o(h^{-2})$$

Note that in the sum on the right-hand side the contribution of region $\operatorname{supp}\Phi_3$ does not appear.

Proof. 1. To prove the lower bound, using the IMS formula

$$-\Delta = \sum_{i=1}^3 \Phi_i(-\Delta - u)\Phi_i \quad \text{with } u := \sum_{i=1}^3 |\nabla\Phi_i|^2 \le Cr^{-2}1_{\{|x|\le 2\Lambda\}}$$

one has

$$\operatorname{Tr}[-h^2\Delta - V]_- \ge \sum_{i=1}^3 \operatorname{Tr}[\Phi_i(-h^2\Delta - V - Ch^2r^{-2}1_{\{|x|\le 2\Lambda\}})\Phi_i]_-.$$

The term involving Φ_3 has negligible contribution. Indeed, since $\operatorname{supp}\Phi_3 \subset \{|x| \ge \Lambda\}$, it follows from the Lieb-Thirring inequality (3) that

$$\begin{aligned}&\operatorname{Tr}[\Phi_3(-h^2\Delta - V - Ch^2r^{-2}1_{\{|x|\le 2\Lambda\}})\Phi_3]_-\\ \ge\;& \operatorname{Tr}[-h^2\Delta - 1_{\{|x|\ge\Lambda\}}(V_+ + Ch^2r^{-2}1_{\{|x|\le 2\Lambda\}})]_-\\ \ge\;& -L_{1,2}h^{-2}\int_{|x|\ge\Lambda}[V_+(x) + Ch^2r^{-2}1_{\{|x|\le 2\Lambda\}}]^2dx = o(h^{-2}).\end{aligned}$$

Here note that $\lim_{\Lambda\to\infty}\int_{|x|\ge\Lambda} V_+^2 = 0$ since $1_{\{|x|\ge 1\}}V_+ \in L^2(\mathbb{R}^2)$ and $h^4r^{-4}\int_{|x|\le 2\Lambda} \to 0$ because $\Lambda = |\ln h|$.

Moreover, for $i = 1, 2$, if we denote

$$\gamma_i := 1_{(-\infty,0]}\left(\Phi_i(-h^2\Delta - V - Ch^2r^{-2})\Phi_i\right)$$

then $\mathrm{Tr}(\Phi_i\gamma_i\Phi_i) \le Ch^{-2}(|\ln h| + \Lambda^2)$ by Lemma 8 (ii). Therefore,

$$\begin{aligned} & \mathrm{Tr}[\Phi_i(-h^2\Delta - V - Ch^2r^{-2})\Phi_i]_- \\ = \; & \mathrm{Tr}[\Phi_i(-h^2\Delta - V - Ch^2r^{-2})\Phi_i\gamma_i] \\ = \; & \mathrm{Tr}[\Phi_i(-h^2\Delta - V)\Phi_i\gamma_i] - Ch^2r^{-2}\,\mathrm{Tr}(\Phi_i\gamma_i\Phi_i) \\ \ge \; & \mathrm{Tr}[\Phi_i(-h^2\Delta - V)\Phi_i]_- + o(h^{-2}). \end{aligned}$$

2. To show the upper bound, we choose

$$\gamma^{(i)} := 1_{(-\infty,0]}\left(\Phi_i(-h^2\Delta - V)\Phi_i\right), \; \gamma^{(0)} := \sum_{i=1,2}\Phi_i\gamma_i\Phi_i.$$

Since $0 \le \gamma^{(i)} \le 1$ $(i = 1, 2)$ and $\sum_{i=1,2}\Phi_i^2 \le 1$ we have $0 \le \gamma^{(0)} \le 1$. Thus,

$$\mathrm{Tr}[-h^2\Delta - V]_- \le \mathrm{Tr}[(-h^2\Delta - V)\gamma^{(0)}] = \sum_{i=1,2}\mathrm{Tr}[\Phi_i(-h^2\Delta - V)\Phi_i]_-.$$

□

4.2 Hydrogen Comparison in Interior Region

In the interior region, we shall compare the semiclassics of the TF potential directly with hydrogen. Note that

$$\left|(8\pi h^2)^{-1}\int [V_\lambda^{\mathrm{TF}}]_+^2(x) - [|x|^{-1} - 1]_+^2\Phi_1^2(x)^2dx\right| \le Crh^{-2} = o(h^{-2})$$

because $|V_\lambda^{\mathrm{TF}} - |x|^{-1}| \le C(|x|^{-1/2} + 1)$ and $\mathrm{supp}\,\Phi_1 \subset \{|x| \le 2r\}$. This inequality is the semiclassial version of the following bound.

Lemma 19 (Hydrogen comparison in interior region)**.** *When $r = h^{1/2} \to 0$ we have*

$$\mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - V_\lambda^{\mathrm{TF}}\right)\Phi_1\right]_- - \mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - |x|^{-1} + 1\right)\Phi_1\right]_- = o(h^{-2}).$$

Proof. The lower and upper bounds can be proved in the same way. We prove for example the upper bound. If we denote

$$\gamma^{(1)} := 1_{(-\infty,0]}\left[\Phi_1\left(-h^2\Delta - |x|^{-1} + 1\right)\Phi_1\right]$$

then by Lemma 8 (ii),

$$\mathrm{Tr}[\Phi_1\gamma^{(1)}\Phi_1] \le Crh^{-2}|\ln h|^{1/2}. \tag{15}$$

By using $|V_\lambda^{\mathrm{TF}}(x) - |x|^{-1} + 1| \le C(|x|^{-1/2} + 1) \le Cr^{-1/2}$ for $x \in \mathrm{supp}\,\Phi_1$ we get

$$\begin{aligned} & \mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - |x|^{-1} + 1\right)\Phi_1\right]_- \\ = \; & \mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - |x|^{-1} + 1\right)\Phi_1\gamma^{(1)}\right] \\ \ge \; & \mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - V_\lambda^{\mathrm{TF}}\right)\Phi_1\gamma_1\right] - Cr^{-1/2}\,\mathrm{Tr}[\Phi_1\gamma^{(1)}\Phi_1] \\ \ge \; & \mathrm{Tr}\left[\Phi_1\left(-h^2\Delta - V_\lambda^{\mathrm{TF}}\right)\Phi_1\right]_- + o(h^{-2}). \end{aligned}$$

□

4.3 Semiclassics in Exterior Region

In the exterior region, the standard semiclassiccal technique of using coherent states [9, 27] (see also [12, 24]) is available.

Definition 20 (Coherent states)**.** Let g be a radially symmetric, smooth function such that $0 \le g(x) \le 1$, $g(x) = 0$ if $|x| \ge 1$ and $\int_{\mathbb{R}^2} g^2(x)dx = 1$. For $s > 0$ (small), denote $g_s(x) = s^{-1}g(x/s)$ and

$$\Pi_{s,u,p} = |f_{s,u,p}\rangle \langle f_{s,u,p}| \quad \text{where } f_{s,u,p}(x) = e^{ip\cdot x} g_s(x-u) \text{ for all } u, p \ \in \mathbb{R}^2.$$

From the coherent identity,

$$(2\pi)^{-2} \iint\limits_{\mathbb{R}^2\times\mathbb{R}^2} \Pi_{s,u,p}\, dpdu = I \quad \text{on } L^2(\mathbb{R}^2), \tag{16}$$

it is straightforward to see that for any density matrix γ and for any potential V satisfying $V_+ \in L^1(\mathbb{R}^2)$,

$$\begin{aligned} \operatorname{Tr}\left[-h^2\Delta\gamma\right] &= (2\pi)^{-2} \iint \operatorname{Tr}\left[-h^2\Delta\Pi_{s,u,p}\gamma\right] dpdu \\ &= (2\pi)^{-2} \iint h^2p^2 \operatorname{Tr}\left[\Pi_{s,u,p}\gamma\right] dpdu - ||\nabla g||_{L^2}^2 h^2 s^{-2} \operatorname{Tr}(\gamma), \end{aligned} \tag{17}$$

$$\begin{aligned} \operatorname{Tr}[(-V * g_s^2)\gamma] &= (2\pi)^{-2} \iint \operatorname{Tr}[(-V*g^2)\Pi_{s,u,p}\gamma] dpdu \\ &= (2\pi)^{-2} \iint -V(u) \operatorname{Tr}[\Pi_{s,u,p}\gamma] dpdu. \end{aligned} \tag{18}$$

Motivated by (18), it is useful to have some estimate for $(V - V * g_s^2)$. The proof of the following lemma can be found in the Appendix.

Lemma 21. *If V is either V_λ^{TF} or $(|x|^{-1} - 1)$ and $\Lambda = |\ln h|$, $r = h^{1/2}$, $s = h^{2/3}$ then*

$$\int_{r\le|x|\le2\Lambda} |V - V * g_s^2|^2(x)dx \le Ch^{1/4}.$$

Lemma 22 (Semiclassics in exterior region)**.** *Let V be either V_λ^{TF} or $(|x|^{-1} - 1)$. When $\Lambda = |\ln h|$ and $r = h^{1/2} \to 0$ one has*

$$\operatorname{Tr}\left[\Phi_2\left(-h^2\Delta - V\right)\Phi_2\right]_- = -(8\pi h^2)^{-1} \int V_+^2(x)\Phi_2^2(x)dx + o(h^{-2}).$$

Proof. 1. To prove the lower bound, we choose the density matrix

$$\gamma_2 := 1_{(-\infty,0]}\left[\Phi_2\left(-h^2\Delta - V\right)\Phi_2\right].$$

Taking $s = h^{2/3}$ and using identities (17) and (18) we can write

$$\begin{aligned}
\operatorname{Tr}\left[\Phi_2\left(-h^2\Delta - V\right)\Phi_2\right]_- &= \operatorname{Tr}\left[\left(-h^2\Delta - V\right)\Phi_2\gamma_2\Phi_2\right] \\
&= (2\pi)^{-2}\iint\left[h^2p^2 - V(u)\right]\operatorname{Tr}\left[\Pi_{s,u,p}\Phi_2\gamma_2\Phi_2\right]dpdu \\
&\quad + \operatorname{Tr}\left[\left(V * g_s^2 - V - Ch^2s^{-2}\right)\Phi_2\gamma_2\Phi_2\right]. \qquad (19)
\end{aligned}$$

2. To bound the second term of the right-hand side of (19), we can apply Hölder's inequality, Lemma 8 (i) with $\Omega := \operatorname{supp}\Phi_2 \subset \{r \le |x| \le 2\Lambda\}$ and Lemma 21 to get

$$\begin{aligned}
&\operatorname{Tr}\left[\left(V * g_s^2 - V - Ch^2s^{-2}\right)\Phi_2\gamma_2\Phi_2\right] \\
\ge\ & -\left\|V * g_s^2 - V\right\|_{L^2(\Omega)}\|\rho_{\Phi_2\gamma_2\Phi_2}\|_{L^2(\mathbb{R}^2)} - Ch^2s^{-2}\operatorname{Tr}[\Phi_2\gamma_2\Phi_2] \\
\ge\ & -Ch^{-2}\left\|V * g_s^2 - V\right\|_{L^2(\Omega)}\|V_+\|_{L^2(\Omega)} - Cs^{-2}\|V_+\|_{L^2(\Omega)}|\Omega|^{1/2} \\
\ge\ & -Ch^{-2}h^{1/8}|\ln h|^{1/2} - Cs^{-2}|\ln h|^{1/2}\Lambda = o(h^{-2}). \qquad (20)
\end{aligned}$$

For the first term of the right-hand side of (19), because

$$0 \le \operatorname{Tr}\left[\Pi_{s,u,p}\Phi_2\gamma_2\Phi_2\right] \le \operatorname{Tr}\left[\Pi_{s,u,p}\Phi_2^2\right] = (\Phi_2^2 * g_s^2)(u)$$

we obtain

$$\begin{aligned}
&(2\pi)^{-2}\iint\left[h^2p^2 - V(u)\right]\operatorname{Tr}\left[\Pi_{s,u,p}\Phi_2\gamma_2\Phi_2\right]dpdu \\
\ge\ & -(2\pi)^{-2}\iint\left[h^2p^2 - V(u)\right]_-(\Phi_2^2 * g_s^2)(u)dpdu \\
=\ & -(8\pi h^2)^{-1}\int V_+^2(u)(\Phi_2^2 * g_s^2)(u)du \\
=\ & -(8\pi h^2)^{-1}\int V_+^2(u)\Phi_2^2(u)du + o(h^{-2}). \qquad (21)
\end{aligned}$$

Here the last estimate follows from

$$\begin{aligned}
&\int V_+^2(u)|\Phi_2^2 - \Phi_2^2 * g_s^2|(u)du \\
\le\ & Csr^{-1}\int_{|x|\ge r/2} V_+(u)^2du \le Csr^{-1}|\ln r| = o(h^{-2}), \qquad (22)
\end{aligned}$$

where we have used $|\Phi_2^2 - \Phi_2^2 * g_s^2|(x) \le Csr^{-1}1_{\{|u|\ge r/2\}}$ when $|x| \ge r \gg s$. Replacing (20) and (21) into (19) we get the lower bound in the lemma.

3. To show the upper bound, we choose

$$\gamma^{(2)} := (2\pi)^{-2}\iint_M \Pi_{s,u,p}\,dpdu, \quad M := \left\{(u,p) : h^2p^2 - V(u) \le 0\right\}.$$

Using the coherent identity (16) and the IMS formula, it is straightforward to compute that

$$
\begin{aligned}
& \operatorname{Tr}\left[\Phi_2\left(-h^2\Delta - V\right)\Phi_2\right]_- \le \operatorname{Tr}\left[\Phi_2\left(-h^2\Delta - V\right)\Phi_2\gamma^{(2)}\right] \\
= \;& (2\pi)^{-2}\iint\limits_{M} \left\langle f_{s,u,p}(x)\right|\Phi_2(x)\left(-h^2\Delta_x - V(x)\right)\Phi_2(x)\left|f_{s,u,p}(x)\right\rangle_{L^2(\mathbb{R}^2,dx)} dpdu \\
= \;& (2\pi)^{-2}\iint\limits_{M} \left\langle e^{ip\cdot x}\right| - (g_s\Phi_2)^2\frac{h^2}{2}\Delta - \frac{h^2}{2}\Delta(g_s\Phi_2)^2 + \\
& \qquad\qquad + h^2|\nabla(g_s\Phi_2)|^2 - (g_s\Phi_2)^2V\left|e^{ip\cdot x}\right\rangle dpdu \\
= \;& (2\pi)^{-2}\iint\limits_{M} [h^2p^2(\Phi_2^2 * g_s^2)(u) + h^2\int\limits_{\mathbb{R}^2}|\nabla(g_s\Phi_2)(x)|^2dx - ((\Phi_2^2V) * g_s^2)(u)]dpdu \\
= \;& -(8\pi h^2)^{-1}\int V_+^2(u)\Phi_2^2(u)du + (8\pi h^2)^{-1}\int\left[V_+^2(\Phi_2^2 * g_s^2) - V_+^2\Phi_2^2\right]du + \\
& +(4\pi)^{-1}\iint V_+(u)|\nabla(g_s\Phi_2)(x)|^2dxdu \\
& +(4\pi h^2)^{-1}\int\Phi_2^2V\left[V_+ - (V_+ * g_s^2)\right]du.
\end{aligned} \tag{23}
$$

4. Finally we verify that the last three terms of the right-hand side of (23) are of $o(h^{-2})$. The second term was already treated by (22). Using

$$\int_{\mathbb{R}^2}|\nabla(g_s\Phi_2)(x)|^2dx \le C(r^{-2}+s^{-2})1_{\{r/2\le|u|\le 3\Lambda\}}.$$

we can bound the third term as

$$\iint V_+(u)|\nabla(g_s\Phi_2)(x)|^2dxdu \le C(r^{-2}+s^{-2})\int_{r/2\le|x|\le 3\Lambda}V_+(u)du = o(h^{-2}).$$

To estimate the last term, we introduce a universal constant $\Lambda_0 > 0$ such that $V(x)\ge 0$ when $|x|\le 2\Lambda_0$ (such Λ_0 exists since $|V(x)-|x|^{-1}|\le C(|x|^{-1/2}+1)$). Using $V_+(u) = V(u)$ and $(V_+ * g_s^2)(u) = (V * g_s^2)(u)$ when $|u|\le\Lambda_0$, and Lemma 21 we get

$$
\begin{aligned}
\int_{|u|\le\Lambda_0}|\Phi_2^2V|.|V_+ - V_+ * g_s^2|du &\le \|V\|_{L^2(\Omega)}\left\|V * g_s^2 - V\right\|_{L^2(\Omega)} \\
&\le C|\ln h|^{1/2}h^{1/8} = o(1)
\end{aligned}
$$

where $\Omega = \operatorname{supp}\Phi_2 \subset \{r\le|u|\le\Lambda\}$. On the other hand, because $|V(u)|\le C$ when $|u|\ge\Lambda_0$ and $V_+\in L^1(\mathbb{R}^2)$,

$$\int_{|u|\ge\Lambda_0}|\Phi_2^2V|.|V_+ - V_+ * g_s^2|du \le C\left\|V_+ * g_s^2 - V_+\right\|_{L^1(\mathbb{R}^2)} = o(1).$$

Thus the last term of the right-hand side of (23) is also of $o(h^{-2})$. This completes the proof. □

Lemmas 18, 19 and 22 together yield (14), which is equivalent to (11).

4.4 Trial Density Matrix

The last step in proving Theorem 16 is to construct a trial density matrix.

Lemma 23. *There exists a density matrix* γ_h *satisfying* (12) *and* (13).

Proof. Recall that we always choose $\Lambda = |\ln h|$, $r = h^{1/2}$ and $s = h^{2/3}$.

1. From the proof of Lemmas 18, 19 and 22, if we choose the density matrices

$$\begin{aligned} \gamma^{(1)} &:= 1_{(-\infty,0]}\left[\Phi_1\left(-h^2\Delta - |x|^{-1} + 1\right)\Phi_1\right], \\ \gamma^{(2)} &:= (2\pi)^{-2} \iint\limits_{h^2p^2 - V_\lambda^{\mathrm{TF}}(u) \le 0} \Pi_{s,u,p}\, dpdu, \\ \gamma^{(0)} &:= \Phi_1\gamma^{(1)}\Phi_1 + \Phi_2\gamma^{(2)}\Phi_2 \end{aligned}$$

then

$$\mathrm{Tr}[-h^2\Delta - V_\lambda^{\mathrm{TF}}]_- = \mathrm{Tr}[(-h^2\Delta - V_\lambda^{\mathrm{TF}})\gamma^{(0)}] + o(h^{-2}). \tag{24}$$

2. Using the coherent identity (16) and the TF equation $\rho_\lambda^{\mathrm{TF}} = (2\pi)^{-1}[V_\lambda^{\mathrm{TF}}]_+$ we can compute explicitly that

$$\begin{aligned} \rho_{\gamma^{(2)}}(x) &:= \gamma^{(2)}(x,x) = (2\pi)^{-2} \iint\limits_{h^2p^2 - V_\lambda^{\mathrm{TF}}(u) \le 0} \Pi_{s,u,p}(x,x)\, dpdu \\ &= (4\pi h^2)^{-1}([V_\lambda^{\mathrm{TF}}]_+ * g_s^2)(x) = (2h^2)^{-1}(\rho_\lambda^{\mathrm{TF}} * g_s^2)(x). \end{aligned}$$

Therefore,

$$2h^2\rho_{\gamma^{(0)}} = 2h^2\rho_{\Phi_1\gamma^{(1)}\Phi_1} + \Phi_2^2\rho_\lambda^{\mathrm{TF}} * g_s^2. \tag{25}$$

Since $\int \rho_\lambda^{\mathrm{TF}} * g_s^2 = \int \rho_\lambda^{\mathrm{TF}}$ and $\mathrm{Tr}[\Phi_1\gamma^{(1)}\Phi_1] \le Crh^{-2}|\ln h|^{1/2}$ (see (15)), we have

$$2h^2 \int_{\mathbb{R}^2} \rho_{\Phi_1\gamma^{(1)}\Phi_1}(x)dx \le \int_{\mathbb{R}^2} \rho_\lambda^{\mathrm{TF}}(x)dx + Cr|\ln h|^{1/2}. \tag{26}$$

On the other hand, we can write from (25) that

$$2h^2\rho_{\gamma^{(0)}} - \rho_\lambda^{\mathrm{TF}} = 2h^2\rho_{\Phi_1\gamma^{(1)}\Phi_1} + \Phi_2^2(\rho_\lambda^{\mathrm{TF}} * g_s^2 - \rho_\lambda^{\mathrm{TF}}) + (1-\Phi_2^2)\rho_\lambda^{\mathrm{TF}}.$$

Since $\rho_\lambda^{\mathrm{TF}} \in L^{4/3}(\mathbb{R}^2)$, we have $\rho_\lambda^{\mathrm{TF}} * g_s^2 - \rho_\lambda^{\mathrm{TF}}$ and $(\Phi_2^2 - 1)\rho_\lambda^{\mathrm{TF}}$ converge to 0 in $L^{4/3}(\mathbb{R}^2)$. Moreover, using Lemma 8 we have $2h^2\rho_{\Phi_1\gamma^{(1)}\Phi_1} \to 0$ in $L^{4/3}(\mathbb{R}^2)$. Thus $2h^2\rho_{\gamma^{(0)}} - \rho_\lambda^{\mathrm{TF}} \to 0$ in $L^{4/3}(\mathbb{R}^2)$. Since the Coulomb norm is dominated by the $L^{4/3}$-norm (see Theorem 11), we then also have

$$D(2h^2\rho_{\gamma^{(0)}} - \rho_\lambda^{\mathrm{TF}}) \to 0. \tag{27}$$

3. Finally, we choose ℓ such that $|\ln h|^{-1} \gg \ell \gg r|\ln h|^{1/2}$ (e.g. $\ell = r^{1/2} = h^{1/4}$) and define

$$\gamma_h := (1-\ell)\gamma^{(0)}.$$

Then using (26) and $\ell \gg r|\ln h|^{1/2}$ we have

$$2h^2 \operatorname{Tr}(\gamma_h) \le (1-\ell)(1 + Cr|\ln h|^{1/2}) \int \rho_\lambda^{\mathrm{TF}} \le \int \rho_\lambda^{\mathrm{TF}}$$

for h small enough. Moreover, since $|\ln h|^{-1} \gg \ell$, the inequalities (24) and (27) still hold true with $\gamma^{(0)}$ replaced by γ_h. □

5 Proofs of the Main Theorems

5.1 Ground State Energy

Having the semiclassics in Theorem 16, the proof of Theorem 1 is standard (see [9]).

Proof of Theorem 1. 1. We first prove the lower bound. Taking any (normalized) wave function $\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^2)$, we need to show that

$$(\Psi, H_{N,Z}\Psi) \ge -\frac{1}{2}Z^2 \ln Z + E^{\mathrm{TF}}(\lambda)Z^2 + o(Z^2).$$

Starting with the Lieb-Oxford inequality (Theorem 9)

$$\left(\Psi, \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\Psi\right) \ge D(\rho_\Psi) - C_{\mathrm{LO}} \int \rho_\Psi^{3/2},$$

we want to bound $\int \rho_\Psi^{3/2}$. It of course suffices to assume that $(\Psi, H_{N,Z}\Psi) \le 0$. Using the Lieb-Thirring inequality (4), the hydrogen spectrum in Theorem 5 and $\operatorname{Tr}(\gamma_\Psi) = N \le CZ$ we arrive at

$$\begin{aligned} 0 \ge 4\,(\Psi, H_{N,Z}\Psi) &\ge \operatorname{Tr}[-\Delta\gamma_\Psi] + \operatorname{Tr}\left[\left(-\Delta - 4Z|x|^{-1}\right)\gamma_\Psi\right] \\ &\ge K_2 \int_{\mathbb{R}^2} \rho_\Psi^2(x)dx - CZ^2|\ln Z| \end{aligned}$$

By Hölder's inequality and $\int \rho_\Psi = N \le CZ$ again we conclude

$$\int_{\mathbb{R}^2} \rho_\Psi^{3/2}(x)dx \le \left(\int_{\mathbb{R}^2} \rho_\Psi^2(x)dx\right)^{1/2} \left(\int_{\mathbb{R}^2} \rho_\Psi(x)dx\right)^{1/2} \le CZ^{3/2}|\ln Z|^{1/2}.$$

Thus the Lieb-Oxford inequality gives

$$\begin{aligned} (\Psi, H_{N,Z}\Psi) &\ge \operatorname{Tr}\left[\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma_\Psi\right] + D(\rho_{\gamma_\Psi}) - CZ^{3/2}|\ln Z|^{1/2} \\ &= Z\operatorname{Tr}\left[\left(-(2Z)^{-1}\Delta - V_\lambda^{\mathrm{TF}}\right)\gamma_\Psi\right] - Z^2\left[\mu_\lambda^{\mathrm{TF}}(N/Z) + D(\rho_\lambda^{\mathrm{TF}})\right] \\ &\quad + Z^2 D(Z^{-1}\rho_{\gamma_\Psi} - \rho_\lambda^{\mathrm{TF}}) - CZ^{3/2}|\ln Z|^{1/2}. \end{aligned} \tag{28}$$

For the lower bound, we can ignore the nonnegative term $D(Z^{-1}\rho_{\gamma_\Psi} - \rho_\lambda^{\rm TF}) \geq 0$. With the semiclassics of the TF potential in Theorem 16 and $h^2 = (2Z)^{-1}$, one has

$$\begin{aligned} & \operatorname{Tr}\left[\left(-(2Z)^{-1}\Delta - V_\lambda^{\rm TF}\right)\gamma_\Psi\right] \geq \operatorname{Tr}\left[-(2Z)^{-1}\Delta - V_\lambda^{\rm TF}\right]_- \\ \geq & -\frac{1}{2}Z\ln Z + Z\left[-(4\pi)^{-1}\int\left([V_\lambda^{\rm TF}(x)]_+^2 - [|x|^{-1}-1]_+^2\right)dx + \frac{1}{2}c^{\rm H}\right] + o(Z). \end{aligned}$$

Together with $N/Z \to \lambda$, we obtain from (28) that

$$(\Psi, H_{N,Z}\Psi) \geq -\frac{1}{2}Z^2\ln Z + e(\lambda)Z^2 + o(Z^2)$$

where

$$e(\lambda) := -(4\pi)^{-1}\int\left([V_\lambda^{\rm TF}(x)]_+^2 - [|x|^{-1}-1]_+^2\right)dx - \mu_\lambda^{\rm TF}\lambda - D(\rho_\lambda^{\rm TF}) + \frac{1}{2}c^{\rm H}.$$

By the TF equation $2\pi\rho_\lambda^{\rm TF} = [V_\lambda^{\rm TF}]_+$ we have

$$-[V_\lambda^{\rm TF}]_+^2 = [V_\lambda^{\rm TF}]_+^2 - 2[V_\lambda^{\rm TF}]_+V_\lambda^{\rm TF} = 4\pi^2[\rho_\lambda^{\rm TF}]^2 - 4\pi\rho_\lambda^{\rm TF}[|x|^{-1} - \rho_\lambda^{\rm TF} * |\,.\,|^{-1} - \mu_\lambda^{\rm TF}].$$

Replacing this identity and $\mu_\lambda^{\rm TF}\lambda = \mu_\lambda^{\rm TF}\int\rho_\lambda^{\rm TF}$ into the definition of $e(\lambda)$, we see that $e(\lambda) = E^{\rm TF}(\lambda) + c^{\rm H}/2$. Thus we get the lower bound on the ground state energy.

2. To show the upper bound, because $\lambda \mapsto E^{\rm TF}(\lambda)$ is continuous, it suffices to show that for any $0 < \lambda' < \lambda$ fixed, one has

$$E(N,Z) \leq -\frac{1}{2}Z^2\ln Z + E^{\rm TF}(\lambda')Z^2 + o(Z^2).$$

Using Lieb's variational principle (see Theorem 10) we want to find a density matrix γ such that $\operatorname{Tr}(\gamma) \leq N$ and

$$\operatorname{Tr}\left[\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma\right] + D(\rho_\gamma) \leq -\frac{1}{2}Z^2\ln Z + E^{\rm TF}(\lambda')Z^2 + o(Z^2).$$

This condition can be rewritten, using the same calculation of proving the lower bound (see (28)), as

$$\begin{aligned} & \operatorname{Tr}\left[\left(-(2Z)^{-1}\Delta - V_{\lambda'}^{\rm TF}\right)\gamma\right] + ZD(Z^{-1}\rho_\gamma - \rho_{\lambda'}^{\rm TF}) \\ \leq & \operatorname{Tr}\left[-(2Z)^{-1}\Delta - V_{\lambda'}^{\rm TF}\right]_- + o(Z). \end{aligned} \tag{29}$$

According to Theorem 16 with $h^2 = (2Z)^{-1}$, we can find a trial density matrix γ satisfying (29) such that $\operatorname{Tr}(\gamma) \leq Z\int\rho_{\lambda'}^{\rm TF} \leq \lambda' Z$. Since $N/Z \to \lambda > \lambda'$, one has $\operatorname{Tr}(\gamma) \leq \lambda' Z \leq N$ for Z large enough and it ends the proof. □

5.2 Extensivity of Neutral Atoms

Proof of Theorem 2. Let θ_R be a smooth function such that $\theta_R(x) = 0$ if $|x| \le R$ and $\theta_R(x) = 1$ if $|x| \ge 2R$. From the proof of Theorem 16 and Theorem 1, we have, with $\gamma := \gamma_{\Psi_{N,Z}}$ and $h^2 = (2Z)^{-1}$,

$$\mathrm{Tr}[(-h^2\Delta - V_1^{\mathrm{TF}})\gamma] = \mathrm{Tr}[-h^2\Delta - V_1^{\mathrm{TF}}]_- + o(h^{-2}).$$

Using the localization as in Lemma 18 and the semiclassics of Lemma 22 we get

$$\begin{aligned}\mathrm{Tr}[\theta_R(-h^2\Delta - V_1^{\mathrm{TF}})\theta_R\gamma] &\le \mathrm{Tr}[\theta_R(-h^2\Delta - V_1^{\mathrm{TF}})\theta_R]_- + o(h^{-2})\\ &= -(8\pi h^2)^{-1}\int [V_1^{\mathrm{TF}}]_+^2(x)\theta_R^2(x)dx + o(h^{-2}). \qquad (30)\end{aligned}$$

On the other hand, since $V_1^{\mathrm{TF}} \le |x|^{-1} \le R^{-1}$ in $\mathrm{supp}\,\theta_R$,

$$\mathrm{Tr}[\theta_R(-h^2\Delta - V_1^{\mathrm{TF}})\theta_R\gamma] \ge -R^{-1}\,\mathrm{Tr}[\theta_R\gamma\theta_R] = -R^{-1}\int \theta_R^2(x)\rho_\gamma(x)dx. \qquad (31)$$

Putting (30) and (31) together we arrive at

$$\int \theta_R^2(x)\rho_\gamma(x)dx \ge R(8\pi h^2)^{-1}\int [V_1^{\mathrm{TF}}]_+^2(x)\theta_R^2(x)dx + o(h^{-2}).$$

Replacing $h^2 = (2Z)^{-1}$, we can conclude that

$$\int_{|x|\ge R}\rho_\gamma(x)dx \ge \int \theta_R^2(x)\rho_\gamma(x)dx \ge C_R Z + o(Z)$$

where

$$C_R := R(4\pi)^{-1}\int [V_1^{\mathrm{TF}}]_+^2(x)\theta_R^2(x)dx \ge \pi R\int_{|x|\ge 2R}(\rho_1^{\mathrm{TF}}(x))^2dx.$$

Note that $C_R > 0$ because $\mathrm{supp}\,\rho_1^{\mathrm{TF}}$ is unbounded (see Theorem 14). □

5.3 Semiclassics for Coulomb Singular Potentials

Proof of Theorem 3. We shall show how to adapt the proof of (11) in the previous section to the general case. We however leave some details to the readers. By scaling we can assume $\kappa = 1$.

1. The main difficulty of the general case is that we do not have the estimate in Lemma 21 in the exterior region. Therefore, we need a more complicated localization. Let $r = h^{1/2}, s = h^{2/3}$ and let g_s be as in Definition 20. For any $\varepsilon > 0$ small, denote

$$W(\varepsilon,h) := \int_{\varepsilon\le|x|\le\varepsilon^{-1}}|V|^2dx\int_{\varepsilon\le|x|\le\varepsilon^{-1}}|V_+ - V_+ * g_s^2|^2dx$$

Because $V \in L^2_{\rm loc}(\mathbb{R}^2\backslash\{0\})$, for any $\varepsilon > 0$ fixed we have $W(\varepsilon, h) \to 0$ as $h \to 0^+$. Therefore, we can choose $\varepsilon = \varepsilon(h)$ such that $\varepsilon(h) \geq |\ln h|^{-1}$, $\varepsilon(h) \to 0$ and $W(\varepsilon(h), h) \to 0$ as $h \to 0^+$. Let φ as in Definition 17 and define

$$\begin{aligned}
\widetilde{\Phi}_1(x) &= \varphi(x/r), \\
\widetilde{\Phi}_2(x) &= (1-\varphi^2(x/r))^{1/2}\varphi(x/\varepsilon), \\
\widetilde{\Phi}_3(x) &= (1-\varphi^2(x/\varepsilon)^{1/2}\varphi(x\varepsilon/2), \\
\widetilde{\Phi}_4(x) &= (1-\varphi^2(x\varepsilon/2))^{1/2}.
\end{aligned}$$

Then $\sum_{i=1}^4 \widetilde{\Phi}_i^2 = 1$, $\operatorname{supp}\widetilde{\Phi}_1 \subset \{|x| \leq 2r\}$, $\operatorname{supp}\widetilde{\Phi}_2 \subset \{r \leq |x| \leq 2\varepsilon\}$, $\operatorname{supp}\widetilde{\Phi}_3 \subset \{\varepsilon \leq |x| \leq \varepsilon^{-1}\}$, and $\operatorname{supp}\widetilde{\Phi}_4 \subset \{|x| \geq (2\varepsilon)^{-1}\}$.

2. Following the proof of Lemma 18 we can show that

$$\operatorname{Tr}[-h^2\Delta - V]_- = \sum_{i=1}^{3} \operatorname{Tr}[\widetilde{\Phi}_i(-h^2\Delta - V)\widetilde{\Phi}_i]_- + o(h^{-2}). \tag{32}$$

Note that the assumptions $1_{\{|x|\geq 1\}}V_+ \in L^2(\mathbb{R}^2)$ and $|\ln h| \geq \varepsilon^{-1} \to \infty$ is sufficient to bound the contribution of the region $\operatorname{supp}\widetilde{\Phi}_4$ by the Lieb-Thirring inequality (3). To control the localization cost in the region $\operatorname{supp}\widetilde{\Phi}_3$, we may use Lemma 8 (i) instead of Lemma 8 (ii).

3. Because $|V(x) - |x|^{-1} + 1| \leq C(|x|^{-\theta} + 1) \leq Cr^{-\theta}$ for $x \in \operatorname{supp}\widetilde{\Phi}_1$, we can follow the proof of Lemma 19 to get

$$\operatorname{Tr}\left[\widetilde{\Phi}_1\left(-h^2\Delta - V\right)\widetilde{\Phi}_1\right]_- = \operatorname{Tr}\left[\widetilde{\Phi}_1\left(-h^2\Delta - |x|^{-1} + 1\right)\widetilde{\Phi}_1\right]_- + o(h^{-2}). \tag{33}$$

4. Adapting the coherent state approach in the proof of Lemma 22, we can show that

$$\operatorname{Tr}\left[\widetilde{\Phi}_3\left(-h^2\Delta - V\right)\widetilde{\Phi}_3\right]_- = -(8\pi h^2)^{-1}\int V_+^2(x)\widetilde{\Phi}_3^2(x)dx + o(h^{-2}). \tag{34}$$

To obtain the lower bound it suffices to consider $\operatorname{Tr}[\widetilde{\Phi}_3\left(-h^2\Delta - V_+\right)\widetilde{\Phi}_3]_-$ and then use the assumption $W(\varepsilon(h), h) \to 0$ instead of Lemma 21 in (20). When proving the upper bound, the assumption $W(\varepsilon(h), h) \to 0$ is again enough to estimate the last term of (23).

5. In the intermediate region $\operatorname{supp}\widetilde{\Phi}_2 \subset \{r \leq |x| \leq 2\varepsilon\}$, we have

$$V_1(x) := |x|^{-1} + C|x|^{-\theta} \geq V(x) \geq |x|^{-1} - C|x|^{-\theta} =: V_2(x) \geq 0.$$

We start with the lower bound

$$\operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V\right)\widetilde{\Phi}_2\right]_- \geq \operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V_1\right)\widetilde{\Phi}_2\right]_-.$$

Using the coherent state approach as in the proof of Lemma 22, we can show that

$$\operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V_1\right)\widetilde{\Phi}_2\right]_- = \int {V_1}^2(x)\widetilde{\Phi}_2(x)^2dx + o(h^{-2}).$$

To do that, we just need to replace Lemma 21 by the following estimate

$$\int_{r\le|x|\le 2\varepsilon} |V_1 - V_1 * g_s^2|^2 dx \le Cs^2 |\ln r|.$$

Moreover, since $\operatorname{supp}\widetilde{\Phi}_2 \subset \{r \le |x| \le 2\varepsilon\}$ with $\varepsilon = \varepsilon(h) \to 0$ and $|V - V_1| \le C|x|^{-\theta}$, we have

$$\int V_1^2(x)\widetilde{\Phi}_2(x)^2 dx = \int V^2(x)\widetilde{\Phi}_2(x)^2 dx + o(h^{-2}).$$

Therefore, we arrive at

$$\operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V\right)\widetilde{\Phi}_2\right]_- \ge \int V_+^2(x)\widetilde{\Phi}_2(x)^2 dx + o(h^{-2}).$$

Similarly, again using the coherent state approach we get the reverse inequality

$$\begin{aligned} &\operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V\right)\widetilde{\Phi}_2\right]_- \le \operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V_2\right)\widetilde{\Phi}_2\right]_- \\ = &\int {V_2}^2(x)\widetilde{\Phi}_2(x)^2 dx + o(h^{-2}) = \int V^2(x)\widetilde{\Phi}_2(x)^2 dx + o(h^{-2}). \end{aligned}$$

Thus we obtain the semiclassics

$$\operatorname{Tr}\left[\widetilde{\Phi}_2\left(-h^2\Delta - V\right)\widetilde{\Phi}_2\right]_- = \int V_+^2(x)\widetilde{\Phi}_2(x)^2 dx + o(h^{-2}). \tag{35}$$

6. The desired semiclassics follows from (32), (33), (34) and (35). □

A Appendix

In this appendix we provide several technical proofs.

Proof of Theorem 4. (i) The HVZ Theorem indeed holds for all dimension $d \ge 2$ (see e.g. [8] Theorem 2.1 for a short proof). The decay property is essentially taken from [18] where the only change is of solving equation (3.8) in [18]. In fact, the two-dimensional solution $w_2(r)$ (with $r = |x|$) is obtained by scaling the three-dimensional solution $w_3(r)$ in [18] as $w_2 = w_3|_{\varepsilon\mapsto 4\varepsilon, Z\mapsto 4Z, r\mapsto r/2}$.

(ii) The proof of Zhislin's Theorem is standard and there is no difference between two and three dimensions. The idea is that by induction we can use the ground state $H_{N,Z}$ to construct a $(N+1)$-particle wave function with strictly lower energy whereas $N < Z$. It should be mentioned that some certain decay of the ground state is necessary to control the localization error when we consider the cut-off wave function in a compact set.

(iii) The asymptotic neutrality follows from the original proof in three dimensions of Lieb, Sigal, Simon and Thirring [14]. The key point of their proof is the construction of a partition of unity. But a partition of unity in three dimensions obviously yields a partition of unity in two dimensions, hence this part of the proof can be adopted. Note that the Pauli exclusion principle enters when solving the hydrogen atom. □

Proof of Lemma 6. For any $m \in \mathbb{N}$, one has

$$\begin{aligned}
&\operatorname{Tr}\left[-\frac{1}{2}\Delta - |x|^{-1} + \frac{1}{2(m+1/2)^2}\right]_- \\
= &\sum_{n=0}^{m}(2n+1)\left[-\frac{1}{2(n+1/2)^2} + \frac{1}{2(m+1/2)^2}\right] \\
= &-\sum_{n=0}^{m}\frac{1}{n+1/2} + \frac{(m+1)^2}{2(m+1/2)^2}.
\end{aligned}$$

Using Euler's approximation

$$\sum_{n=0}^{m}\frac{1}{n+1/2} = \ln(m) + 2\ln(2) + \gamma_E + o(1)_{m\to\infty}$$

we get

$$\operatorname{Tr}\left[-\frac{1}{2}\Delta - |x|^{-1} + \frac{1}{2(m+1/2)^2}\right]_- = -\ln(m) - 2\ln(2) - \gamma_E + \frac{1}{2} + o(1)_{m\to\infty}$$

which implies (1). Moreover, (2) follows from (1) by scaling $x \mapsto (2h^2)^{-1}x$, namely

$$\operatorname{Tr}\left[-h^2\Delta - |x|^{-1} + \mu\right]_- \;=\; (2h^2)^{-1}\operatorname{Tr}\left[-\frac{1}{2}\Delta - |x|^{-1} + 2h^2\mu\right]_- .$$

□

Proof of Lemma 8. (i) For any constant $a \geq 0$, using the Lieb-Thirring inequality (3) we have

$$\begin{aligned}
0 \;&\geq\; \operatorname{Tr}[(-h^2\Delta - V)\phi\gamma\phi] \\
&\geq\; \operatorname{Tr}[(-(h^2/2)\Delta + a)\phi\gamma\phi] + \operatorname{Tr}[(-(h^2/2)\Delta - (a+V_+).1_\Omega)\phi\gamma\phi] \\
&\geq\; \operatorname{Tr}[(-(h^2/2)\Delta + a)\phi\gamma\phi] - 4L_{1,2}h^{-4}||a+V_+||^2_{L^2(\Omega)}.
\end{aligned}$$

Choosing $a=1$ and using $\operatorname{Tr}[-\Delta\phi\gamma\phi] \geq 0$ and $(1+V_+) \in L^2(\Omega)$ we get $\operatorname{Tr}[\phi\gamma\phi] < \infty$, namely $\phi\gamma\phi$ is trace class. On the other hand, choosing $a=0$ and using the Lieb-Thirring inequality (4) to estimate $\operatorname{Tr}[-\Delta\phi\gamma\phi]$, we arrive at

$$\int_{\mathbb{R}^2}\rho^2_{\phi\gamma\phi}(x)dx \leq Ch^{-4}||V_+||^2_{L^2(\Omega)}.$$

Because $\operatorname{supp}\rho_{\phi\gamma\phi} \subset \Omega$, the above estimate and Hölder's inequality yield the desired bound on $\int \rho^{2\alpha}_{\phi\gamma\phi}$ for any $\alpha \in [0,1]$.

(ii) We can use the same idea of the above proof. The only adaption we need in this case is to use both of the Lieb-Thirring inequality (3) and the hydrogen semiclassics (2) to bound $\mathrm{Tr}[(-(h^2/2)\Delta-(a+V_+).1_\Omega)\phi\gamma\phi]$. More precisely, since $V\le C_0(|x|^{-1}+1)$, we have

$$\begin{aligned}\mathrm{Tr}[(-(h^2/2)\Delta-(a+V_+).1_\Omega)\phi\gamma\phi] &\ge \mathrm{Tr}[(-(h^2/4)\Delta-C_0|x|^{-1}+1)\phi\gamma\phi]\\ &\quad+\mathrm{Tr}[(-(h^2/4)\Delta-(C_0+a+1).1_\Omega)\phi\gamma\phi]\\ &\ge -Ch^{-2}|\ln h|-C(a+1)^2h^{-2}|\Omega|.\end{aligned}$$

□

Proof of Lemma 12. 1. The lower bound follows from the radial symmetry of ρ and the fact that $\Delta(|x|^{-1})=|x|^{-3}>0$ pointwise for all $x\neq 0$.

In fact, since ρ is radially symmetric we can write

$$(\rho*|\,.\,|^{-1})(x)=\int\limits_{|y|<|x|}\left(\int\limits_{S_y}\frac{1}{|x-z_2|}dz_2\right)\rho(y)dy+\int\limits_{|y|>|x|}\left(\int\limits_{S_x}\frac{1}{|z_1-y|}dz_1\right)\rho(y)dy$$

where dz_1 and dz_2 are normalized Lebesgue measure on the circles $S_x:=\{z\in\mathbb{R}^2:|z|=|x|\}$ and $S_y:=\{z\in\mathbb{R}^2:|z|=|y|\}$.

If $|x|>|y|$ then using the subharmonic property of the mapping $z\mapsto|x-z|^{-1}$ in the open set $\{z\in\mathbb{R}^2:|z|<|x|\}$ we get

$$\int\limits_{S_y}\frac{1}{|x-z_2|}dz_2\ge\frac{1}{|x|}.$$

Together with the similar inequality for $|y|>|x|$, we obtain the desired lower bound on $\rho*|\,.\,|^{-1}$.

2. Because $\rho(x)\le(2\pi|x|)^{-1}$ and $\int\rho=\lambda$, for any $\kappa>1$,

$$\begin{aligned}(\rho*|\,.\,|^{-1})(x) &= \int\limits_{\mathbb{R}^2}\frac{\rho(y)}{|x-y|}dy\le\int\limits_{|x-y|\le|x|/2}+\int\limits_{|x-y|\ge|x|/2,|y|\le\kappa|x|}+\int\limits_{|y|\ge\kappa|x|}\\ &\le \int\limits_{|x-y|\le|x|/2}\frac{(2\pi)^{-1}}{(|x|/2)|x-y|}dy+\int\limits_{|y|\le\kappa|x|}\frac{(2\pi)^{-1}dy}{|y|(|x|/2)}+\int\limits_{\mathbb{R}^2}\frac{\rho(y)dy}{(\kappa-1)|x|}\\ &\le 1+2\kappa+\frac{\lambda}{(\kappa-1)|x|}.\end{aligned}$$

Optimizing the latter estimate over $\kappa>1$ yields the first upper bound on $\rho*|\,.\,|^{-1}$.

3. We now prove the second upper bound on $(\rho*|\,.\,|^{-1})(x)$ for $|x|$ large. We start by decomposing $\mathbb{R}^2$ into three subsets

$$\begin{aligned}\Omega_1 &:= \left\{y\in\mathbb{R}^2:|x-y|\ge|x|/2\right\},\\ \Omega_2 &:= \left\{y\in\mathbb{R}^2:||x|-|y||\le|x|^{-2}\right\},\\ \Omega_3 &:= \left\{y\in\mathbb{R}^2:|x-y|<|x|/2,||x|-|y||>|x|^{-2}\right\}.\end{aligned}$$

Fix $\varepsilon > 0$ small. For $|x|$ large enough,

$$\begin{aligned}
\int_{\Omega_1} \frac{\rho(y)}{|x-y|} dy &= \int_{|y|<|x|^{1/2}} \frac{\rho(y)}{|x-y|} dy + \int_{|x-y|\geq|x|/2, |y|\geq|x|^{1/2}} \frac{\rho(y)}{|x-y|} dy \\
&\leq \frac{\int \rho}{|x|-|x|^{1/2}} + \int_{|y|\geq|x|^{1/2}} \frac{\rho(y)}{(|x|/2)} dy \leq \frac{\lambda+2\varepsilon}{|x|}. \qquad (36)
\end{aligned}$$

Moreover, since $\rho(y) \leq (2\pi|y|)^{-1}$,

$$\begin{aligned}
\int_{\Omega_2} \frac{\rho(y)}{|x-y|} dy &\leq \int_{|x-y|\leq\varepsilon} \frac{1}{2\pi|y||x-y|} dy + \int_{|x-y|\geq\varepsilon, ||x|-|y||\leq|x|^{-2}} \frac{1}{2\pi|y||x-y|} dy \\
&\leq \int_{|x-y|\leq\varepsilon} \frac{1}{2\pi(|x|-\varepsilon).|x-y|} dy + \int_{||x|-|y||\leq|x|^{-2}} \frac{1}{(2\pi|y|)\varepsilon} dy \\
&= \frac{\varepsilon}{|x|-\varepsilon} + \frac{2}{\varepsilon|x|^2} \leq \frac{2\varepsilon}{|x|}. \qquad (37)
\end{aligned}$$

Next, using the polar integral in

$$\Omega_3 \subset \{y \in \mathbb{R}^2 : 3|x|/2 \geq |y| \geq |x|/2, ||x|-|y|| > |x|^{-2}\}$$

we have, with notation $s := \min\{|x|, r\}/\max\{|x|, r\}$,

$$\int_{\Omega_3} \frac{\rho(y)}{|x-y|} dy \leq \int_{\frac{3}{2}|x|\geq r\geq\frac{1}{2}|x|, |r-|x||\geq|x|^{-2}} \int_0^{2\pi} \frac{\rho(r)r}{\max\{|x|, r\}\sqrt{1+s^2-2s\cos(\theta)}} d\theta dr. \qquad (38)$$

The singularity of the integral w.r.t. θ (at $s \to 1^-$) is controlled by the following technical lemma (we shall prove later).

Lemma 24 (Upper bound on elliptic integral)**.** *There exists a finite constant $C > 0$ such that*

$$\int_0^{2\pi} \frac{d\theta}{\sqrt{1+s^2-2s\cos(\theta)}} \leq C(1+|\ln(1-s)|) \quad \textit{for all } 0 < s < 1.$$

Note that if $|r-|x|| \geq |x|^{-2}$ and $|x| \geq 1$ then

$$1-s \geq 1 - \frac{|x|-|x|^{-2}}{|x|+|x|^{-2}} = \frac{2|x|^{-3}}{1+|x|^{-3}} \geq |x|^{-3}.$$

Using (38) and Lemma 24 we get, for $|x|$ large enough,

$$\int_{\Omega_3} \frac{\rho(y)}{|x-y|} dy \leq C_1 \frac{\ln(|x|)}{|x|} \int_{3|x|/2\geq|y|\geq|x|/2} \rho(y) dy \qquad (39)$$

for some universal constant C_1.

Putting (36), (37) and (39) together, we conclude that for any $\varepsilon > 0$ there exists $R = R(\varepsilon, \rho)$ such that for any $|x| \geq R$,

$$(\rho * |x|^{-1})(x) \leq \frac{\lambda + 4\varepsilon}{|x|} + C_1 \frac{\ln(|x|)}{|x|} \int\limits_{3|x|/2 \geq |y| \geq |x|/2} \rho(y) dy.$$

□

For completeness we provide the proof of the upper bound on the elliptic integral.

Proof of Lemma 24. We just need to consider the singularity when $s \to 1^-$. Write

$$1 + s^2 - 2s\cos(2\theta) = (1+s)^2 - 2s(1+\cos(\theta)) = (1+s)^2 - 4s\cos^2(\theta/2).$$

Denoting $k^2 = 4s/(1+s)^2$ and making a change of variable ($\theta \mapsto \pi - 2\theta$), we need to show that

$$K(k) := \int\limits_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2(\theta)}} = \int\limits_0^1 \frac{dt}{\sqrt{(1-t^2)(1-k^2t^2)}} \leq C|\ln(1-k)|$$

when $k \to 1^-$. This upper bound follows from the identity

$$\int\limits_0^1 \frac{dt}{\sqrt{(1-t)(1-kt)}} = \frac{1}{\sqrt{k}} \ln\left(\frac{1+\sqrt{k}}{1-\sqrt{k}}\right).$$

□

Remark. The function $K(k)$ is the complete elliptic integral of the first kind. Its asymptotic behavior at $k \to 1^-$ is well known. It is (see [1], eq. (17.3.26), p. 591)

$$K(k) = \frac{1}{2}|\ln(1-k)| + \frac{3}{2}\ln(2) + o(1)_{k \to 1^-}.$$

Proof of Lemma 21. Recall that we are working on the region $2\Lambda \geq |x| \geq r \gg s$. We start with the triangle inequality

$$|V - V * g_s^2| \leq \left||\,.\,|^{-1} - |\,.\,|^{-1} * g_s^2\right| + \left|\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} - \rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} * g_s^2\right|. \tag{40}$$

(If $V(x) = |x|^{-1} - 1$ then the term invloved $\rho_\lambda^{\mathrm{TF}}$ disappears.)

When $|x| \geq r \gg s \geq |y|$ using

$$\left||x|^{-1} - |x-y|^{-1}\right| \leq Cs|x|^{-2}$$

one has

$$\left||\,.\,|^{-1} - |\,.\,|^{-1} * g_s^2\right|(x) \leq \int \left||x|^{-1} - |x-y|^{-1}\right| g_s^2(y) dy \leq Cs|x|^{-2}. \tag{41}$$

Moreover,

$$\begin{aligned}
&\left|\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} - \rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} * g_s^2\right|(x) \\
\leq\ & \iint \rho_\lambda^{\mathrm{TF}}(x-y)\left||y|^{-1} - |y-z|^{-1}\right| g_s^2(z)dydz. \qquad (42)
\end{aligned}$$

We divide the integral into two domains. If $|y| \geq r/2$ then using

$$\left||y|^{-1} - |y-z|^{-1}\right| \leq Cs|y|^{-2} \leq Csr^{-1}|y|^{-1}$$

and $(\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1})(x) \leq C(|x|^{-1/2}+1)$ (see Lemma 12) we obtain

$$\begin{aligned}
&\iint_{|y|\geq r/2} \rho_\lambda^{\mathrm{TF}}(x-y)\left||y|^{-1} - |y-z|^{-1}\right| g_s^2(z)dydz \\
\leq\ & Csr^{-1}(\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1})(x) \leq Csr^{-1}|x|^{-1/2}. \qquad (43)
\end{aligned}$$

If $|y| \leq r/2$ then using

$$\rho_\lambda^{\mathrm{TF}}(x-y) \leq C(|x-y|^{-1}+1) \leq C(|x|^{-1}+1)$$

and $\int_{|y|\leq 2r} |y|^{-1}dy \leq Cr$ we obtain

$$\begin{aligned}
&\iint_{|y|\leq \delta/2} \rho_\lambda^{\mathrm{TF}}(x-y)\left||y|^{-1} - |y-z|^{-1}\right| g_s^2(z)dydz \\
\leq\ & C(|x|^{-1}+1) \iint_{|y|\leq r/2, |y-z|\leq 2r} \left(|y|^{-1} + |y-z|^{-1}\right) g_s^2(z)dydz \\
\leq\ & Cr(|x|^{-1}+1) \qquad (44)
\end{aligned}$$

Replacing (43) and (44) into (42) we arrive at

$$\left|\rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} - \rho_\lambda^{\mathrm{TF}} * |\,.\,|^{-1} * g_s^2\right|(x) \leq C(sr^{-1}|x|^{-1/2} + r|x|^{-1} + r) \ \text{ when } |x| \geq r.$$

From the latter inequality and (41) we can deduce from (40) that

$$|V * g_s^2 - V|(x) \leq C(s|x|^{-2} + sr^{-1}|x|^{-1/2} + r|x|^{-1} + r) \ \text{ when } |x| \geq r.$$

Taking the square integral of the previous inequality over $\{r \leq |x| \leq 2\Lambda\}$ we get (with $\Lambda = |\ln h|$, $r = h^{1/2}$, $s = h^{2/3}$)

$$\int_{r\leq|x|\leq 2\Lambda} |V - V * g_s^2|^2(x)dx \leq C(s^2r^{-2}\Lambda + r|\ln(\Lambda/r)| + r^2\Lambda^2) \leq Ch^{1/4}.$$

$\square$

Acknowledgments: P.T.N. and F.P. would like to thank KTH Stockholm and the University of Copenhagen, respectively, for hospitality. F.P. is grateful to A. Laptev for discussion. We thank the referee for constructive suggestions. This work was partially supported by the Danish council for independent research.

References

[1] M. Abramowitz and Irene A. Stegun (eds.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, New York: Dover Publications, 9th-Printing (1970).

[2] P.A.M. Dirac, Note on exchange phenomena in the Thomas-Fermi atom, *Proc. Cambridge Phil. Soc.*, **26**, 376-385 (1930)

[3] P. Duclos, P. Štoviček and M. Tušek, On the two-dimensional Coulomb-like potential with a central point interaction, *J. Phys. A: Math. Theor.* **43**, 474020 (2010).

[4] L. Euler, *Inventio summae cuiusque seriei ex dato termino generali*, St. Petersbourg, (1736)

[5] C. Fefferman and L. Seco, On the energy of a large atom, *Bulletin of the A.M.S.*, **23**, 525-530 (1990).

[6] E. Fermi, Un Metodo Statistico per la Determinazione di alcune Prioprietà dell'Atomo. *Rend. Accad. Naz. Lincei* **6**, 602-607 (1927).

[7] W. Hughes, An atomic energy bound that gives Scott's correction, *Adv. Math.*, **79**, 213-270 (1990)

[8] M. Lewin, Geometric methods for nonlinear many-body quantum systems, *J. Funct. Anal.*, **260**, 3535-3595 (2011)

[9] E.H. Lieb, Thomas-Fermi and related theories of atoms and molecules, *Rev. Mod. Phys.* **53**, 603-641 (1981).

[10] E. H. Lieb, A lower bound for Coulomb energies, *Phys. Lett. A* **70**, 444-446 (1979).

[11] E.H. Lieb, Variational principle for many-fermion systems, *Phys. Rev. Lett.* **46**, 457-459 (1981).

[12] E.H. Lieb and M. Loss, *Analysis*, 2nd Ed., AMS., Providence, Rhode Island (2001).

[13] E.H. Lieb and S. Oxford, An improved lower bound on the indirect Coulomb energy, *Internat. J. Quantum Chem.* **19**, 427-439 (1981).

[14] E.H. Lieb, I. M. Sigal, B. Simon and W. Thirring, Asymptotic neutrality of large-Z ions, *Commun. Math. Phys.* **116**, 635-644 (1988).

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

[16] E.H. Lieb, J.P. Solovej, J. Yngvason, Ground States of Large Quantum Dots in Magnetic Fields, *Phys. Rev. B.* **51**, no. 16, 10646-10666 (1995).

[17] E.H. Lieb and W. Thirring, Bound for the Kinetic Energy of Fermions which Proves the Stability of Matter, *Phys. Rev. Lett.* **35**, 687-689 (1975).

[18] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, "Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules, *Phys. Rev. A* **16**, 1782-1785 (1977).

[19] D.G.W. Parfitt and M.E. Portnoia, The two-dimensional hydrogen atom revisited, *J. Math. Phys.* **43**, no. 10 (2002).

[20] J. Schwinger, Thomas-Fermi model: The second correction, *Phys. Rev. A*, **24**, vol. 5, 2353-2361 (1981).

[21] J.M.C. Scott, The binding energy of the Thomas-Fermi atom, *Phys. Rev.* **43**, no. 343, 859-867 (1952).

[22] L.A. Seco, I.M. Sigal, and J.P. Solovej, Bound on the ionization energy of large atoms, *Commun. Math. Phys.* **131**, 307-315 (1990).

[23] 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)

[24] J.P. Solovej, The ionization conjecture in Hartree-Fock theory. *Annals of Math.* **158**, 509-576 (2003).

[25] J.P. Solovej, T. Ø. Sørensen, W. Spitzer, The relativistic Scott correction for atoms and molecules, *Comm. Pure Appl. Math.* Vol. **LXIII**, 39-118 (2010).

[26] J.P. Solovej and W. Spitzer, A new coherent states approach to semiclassics which gives Scott's correction. *Commun. Math. Phys.* **241**, no. 2-3, 383-420 (2003).

[27] W. Thirring, A lower bound with the best possible constant for Coulomb Hamiltonians, *Commun. Math. Phys.* **79**, 1-7 (1981).

[28] L.H. Thomas, The calculation of atomic fields, *Proc. Cambridge Phil. Soc.* **23** (5), 542-548 (1927).

[29] X.L. Yang, S.H. Guo, F.T. Chan, K.W. Wong and W.Y. Ching, Analytic solution of a two-dimensional hydrogen atom. I. Nonrelativistic theory, *Phys. Rev. A.* **43**, 1186-1196 (1991).

(P.T. Nam) Department of Mathematical Sciences, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.
E-mail: ptnam@math.ku.dk

(F. Portmann) Department of Mathematics, Royal Institute of Technology, Lindstedtsvägen 25, SE-10044 Stockholm, Sweden.
E-mail: fabianpo@kth.se

(J.P. Solovej) Department of Mathematical Sciences, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.
E-mail: solovej@math.ku.dk

Bogoliubov theory and bosonic atoms

Phan Thanh Nam

Department of Mathematical Sciences, University of Copenhagen,
Universitetsparken 5, 2100 Copenhagen, Denmark. E-mail: ptnam@math.ku.dk

Abstract

We formulate the Bogoliubov variational principle in a mathematical framework similar to the generalized Hartree-Fock theory. Then we analyze the Bogoliubov theory for bosonic atoms in details. We discuss heuristically why the Bogoliubov energy should give the first correction to the leading energy of large bosonic atoms.

Contents

Contents **91**

1 Bogoliubov theory **91**
1.1 One-body density matrices 92
1.2 Bogoliubov transformations 93
1.3 Quasi-free states and quadratic Hamiltonians 98
1.4 Bogoliubov variational theory 105

2 Bosonic atoms **109**
2.1 Introduction 109
2.2 Existence of Bogoliubov minimizers 112
2.3 Analysis of quadratic forms 116
2.4 Bogoliubov ground state energy 121
2.5 Comparison to quantum energy: a heuristic discussion 123

Appendix **125**

Acknowledgments **130**

1 Bogoliubov theory

In this section we formulate the Bogoliubov variational principle in the same spirit of the generalized Hartree-Fock theory [4]. Our formulation bases on the earlier discussions in [18, 19].

1.1 One-body density matrices

We start by introducing some conventional notations. Let $\mathfrak{h}$ be a complex separable Hilbert space with the inner product $(.,.)$ which is linear in the second variable and anti-linear in the first. Let $\mathfrak{h}_N := \bigotimes_{\text{sym}}^N \mathfrak{h}$ be the symmetric tensor product space of N particles and let $\mathcal{F} = \mathcal{F}(\mathfrak{h}) := \bigoplus_{N=0}^{\infty} \mathfrak{h}_N$ be the bosonic *Fock space.*

Let $\mathcal{B}(\mathcal{F})$ be the space of linear bounded operators on $\mathcal{F}$. Any *quantum mechanical state* (*state* for short) $\rho : \mathcal{B}(\mathcal{F}) \to \mathbb{C}$ is identified with a positive semi-definite trace class operator P on $\mathcal{F}$ with $\text{Tr}(P) = 1$ in such a way that

$$\rho(B) = \text{Tr}(BP) \text{ for all } B \in \mathcal{B}(\mathcal{F}).$$

For example, a *pure state* is a state corresponding to the one-dimensional projection $|\Psi\rangle\langle\Psi|$ of a unit vector $\Psi \in \mathcal{F}$, and a *Gibbs state* is a state corresponding to $\text{Tr}(\exp(-H))^{-1}\exp(-H)$ for some Hamiltonian $H : \mathcal{F} \to \mathcal{F}$ such that $\exp(-H)$ is trace class.

The *dual space* $\mathfrak{h}^*$ can be identified to $\mathfrak{h}$ by the *anti-unitary* $J : \mathfrak{h} \to \mathfrak{h}^*$,

$$J(x)(y) = (x, y)_{\mathfrak{h}}, \text{ for all } x, y \in \mathfrak{h}.$$

It is convenient to introduce the *generalized annihilation* and *creation* operators on $\mathfrak{h} \oplus \mathfrak{h}^*$ by

$$\begin{aligned} A(f \oplus Jg) &= a(f) + a^*(g), \\ A^*(f \oplus Jg) &= a^*(f) + a(g), \text{ for all } f, g \in \mathfrak{h} \end{aligned}$$

where $a(f)$ and $a^*(f)$ are the usual annihilation and creation operators. Note that if we denote

$$\mathcal{S} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathcal{J} = \begin{pmatrix} 0 & J^* \\ J & 0 \end{pmatrix},$$

then we have the *conjugate relation* and the *canonical commutation relation* (CCR)

$$A^*(F_1) = A(\mathcal{J}F_1), [A(F_1), A^*(F_2)] = (F_1, \mathcal{S}F_2) \text{ for all } F_1, F_2 \in \mathfrak{h} \oplus \mathfrak{h}^*$$

where $[X, Y] = XY - YX$.

Now we can define the *one-particle density matrix* (*1-pdm* for short) $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ of a state ρ by

$$(F_1, \Gamma F_2) = \rho(A^*(F_2)A(F_1)) \text{ for all } F_1, F_2 \in \mathfrak{h} \oplus \mathfrak{h}^*.$$

Such a 1-pdm may be also written as

$$\Gamma = \begin{pmatrix} \gamma & \alpha \\ J\alpha J & 1 + J\gamma J^* \end{pmatrix} \tag{1}$$

where $\gamma : \mathfrak{h} \to \mathfrak{h}$ and $\alpha : \mathfrak{h}^* \to \mathfrak{h}$ are linear bounded operators defined by

$$(f, \gamma g) = \rho(a^*(g)a(f)), \ (f, \alpha Jg) = \rho(a(g)a(f)) \text{ for all } f, g \in \mathfrak{h}.$$

It is obvious that any 1-pdm is *positive semi-definite*. The following lemma expresses the condition $\Gamma \geq 0$ in terms of γ and α. Its proof is provided in the Appendix.

Lemma 1.1. *Let Γ be of the form (1). Then $\Gamma \geq 0$ if and only if $\gamma \geq 0$, $\alpha^* = J\alpha J$ and*

$$\gamma \geq \alpha J(1+\gamma)^{-1}J^*\alpha^*. \tag{2}$$

Remark. The fermionic analogue of the inequality (2) is $\alpha\alpha^* \leq \gamma(1-\gamma)$ [4]. We do not know if (2) can be reduced to $\alpha\alpha^* \leq \gamma(1+\gamma)$ or not.

Of primary physical interest are the states with *finite particle number expectation.* Recall the *particle number operator*

$$\mathcal{N} := \sum_{N=0}^{\infty} N 1_{\mathfrak{h}_N} = \sum_n a^*(u_n)a(u_n)$$

for any orthonormal basis $\{u_n\}_{n=1}^{\infty}$ for $\mathfrak{h}$. It is straightforward to see that if a state ρ has the 1-pdm of the form (1) then

$$\rho(\mathcal{N}) = \mathrm{Tr}(\gamma).$$

Hence ρ has finite particle number expectation if and only if γ is trace class.

1.2 Bogoliubov transformations

Definition (Bogoliubov transformations)**.** A bosonic *Bogoliubov transformation* is a linear bounded isomorphism $\mathcal{V}: \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ satisfying

$$\mathcal{J}\mathcal{V}\mathcal{J} = \mathcal{V} \text{ and } \mathcal{V}^*\mathcal{S}\mathcal{V} = \mathcal{S}.$$

These conditions ensure that the Bogoliubov transformations preserve the conjugate relation and the canonical commutation relation, namely

$$A^*(\mathcal{V}F_1) = A(\mathcal{V}\mathcal{J}F_1) \text{ and } [A(\mathcal{V}F_1), A^*(\mathcal{V}F_2)] = (F_1, \mathcal{S}F_2),\ \forall F_1, F_2 \in \mathfrak{h} \oplus \mathfrak{h}^*.$$

The Bogoliubov transformations form a subgroup of the isomorphisms in $\mathfrak{h} \oplus \mathfrak{h}^*$; in particular, if $\mathcal{V}$ is a Bogoliubov transformation then $\mathcal{V}^{-1}$ and $\mathcal{V}^*$ are also Bogoliubov transformations. Note that any mapping $\mathcal{V}$ satisfying $\mathcal{J}\mathcal{V}\mathcal{J} = \mathcal{V}$ must have the form

$$\mathcal{V} = \begin{pmatrix} U & V \\ JVJ & JUJ^* \end{pmatrix} \tag{3}$$

for some linear operators $U: \mathfrak{h} \to \mathfrak{h}$, $V: \mathfrak{h}^* \to \mathfrak{h}$.

We say that a Bogoliubov transformation $\mathcal{V}$ is *unitarily implementable* if it is implemented by a unitary mapping $\mathbb{U}_{\mathcal{V}}: \mathcal{F} \to \mathcal{F}$, namely

$$A(\mathcal{V}F) = \mathbb{U}_{\mathcal{V}} A(F) \mathbb{U}_{\mathcal{V}}^* \text{ for all } F \in \mathfrak{h} \oplus \mathfrak{h}^*. \tag{4}$$

The following result determines whenever a Bogoliubov transformation is unitarily implementable. This result is well-known and we provide its proof in the Appendix for the reader's convenience. For the fermionic analogue, see [4] (Theorem 2.2) .

Theorem 1.2 (Unitarily implementable Bogoliubov transformations)**.** *A Bogoliubov transformation $\mathcal{V} : \mathfrak{h}\oplus\mathfrak{h}^* \to \mathfrak{h}\oplus\mathfrak{h}^*$ of the form (3) is unitarily implementable if and only if the Shale-Stinespring condition* $\mathrm{Tr}_{\mathfrak{h}}(VV^*) < \infty$ *holds.*

Unlike to the fermionic case [4], the bosonic Bogoliubov transformations are *not* unitary mappings on $\mathfrak{h}\oplus\mathfrak{h}^*$. However, we can still use the Bogoliubov transformations to diagonalize some certain operators on $\mathfrak{h}\oplus\mathfrak{h}^*$. Of our particular interest is the diagonalization of the 1-pdm's.

Theorem 1.3 (Diagonalization 1-dpm's by Bogoliubov transformations)**.** *If Γ has the form (1) with $\Gamma \geq 0$ and $Tr(\gamma) < \infty$ then for an arbitrary orthonormal basis $\{u_n\}$ for $\mathfrak{h}$, there is a unitarily implementable Bogolubov transformation $\mathcal{V} : \mathfrak{h}\oplus\mathfrak{h}^* \to \mathfrak{h}\oplus\mathfrak{h}^*$ diagonalizing Γ in in the basis $u_1\oplus 0$, $u_2\oplus 0$, ..., $0\oplus Ju_1$, $0\oplus Ju_2$, ..., namely*

$$\mathcal{V}^*\Gamma\mathcal{V} = \begin{pmatrix} \lambda_1 & & & & & \\ & \lambda_2 & & & 0 & \\ & & \ddots & & & \\ & & & 1+\lambda_1 & & \\ & 0 & & & 1+\lambda_2 & \\ & & & & & \ddots \end{pmatrix}, \tag{5}$$

Remark. The finite-dimensional case is Theorem 9.8 in [19]. See [4] (the proof of Theorem 2.3) for the fermionic analogue.

To prove Theorem 1.3, we start with a simple diagonalization lemma. This is a generalization to infinity dimensions of Lemma 9.6 in [19].

Lemma 1.4. *Let $\mathcal{A}$ be a positive definite operator on $\mathfrak{h}\oplus\mathfrak{h}^*$ such that $\mathcal{J}\mathcal{A}\mathcal{J} = \mathcal{A}$ and $\mathcal{S}\mathcal{A}$ admits an eigenbasis on $\mathfrak{h}\oplus\mathfrak{h}^*$. Then for any orthonormal basis $u_1, u_2, ...$ for $\mathfrak{h}$, there exists a Bogoliubov transformation $\mathcal{V}$ such that the operator $\mathcal{V}^*\mathcal{A}\mathcal{V}$ has eigenvectors of the form $\{u_n\oplus 0\}\cup\{0\oplus Ju_n\}$.*

Remark. In this result the Bogoliubov transformation $\mathcal{V}$ needs *not* be unitarily implementable.

Proof. 1. Let $\{u_i\}$ be an orthonormal basis for $\mathfrak{h}$. We shall define the Bogoliubov transformation $\mathcal{V}$ by

$$\mathcal{V}(u_i\oplus 0) = v_i,\ \mathcal{V}(0\oplus Ju_i) = \widetilde{v}_i,$$

where $\{v_i\}\cup\{\widetilde{v}_i\}$ is an eigenbasis of $\mathcal{S}\mathcal{A}$ such that

(i) $(v_i, \mathcal{S}v_j) = \delta_{ij}, (\widetilde{v}_i, \mathcal{S}\widetilde{v}_j) = -\delta_{ij}$ and $(v_i, \mathcal{S}\widetilde{v}_j) = 0$ for all $i, j = 1, 2, \ldots$

(ii) $\mathcal{J} v_j = \widetilde{v}_j$ for all $j = 1, 2, \dots$

2. Let v_1 be a normalized eigenvector of $\mathcal{SA}$ with eigenvalue λ_1. Using $\mathcal{A}v_1 = \lambda_1 \mathcal{S} v_1$ we find that

$$(v_1, \mathcal{A}v_1) = \lambda_1 (v_1, \mathcal{S}v_1).$$

Since $\mathcal{A}$ is positive definite and $\mathcal{S}$ is Hermitian, both of λ_1 and (v_1, Sv_1) must be real and non-zero. Therefore, we can normalized v_1 in such a way that $(v_1, \mathcal{S}v_1) \in \{\pm 1\}$.

Defining $\widetilde{v}_1 = \mathcal{J} v_1$ and using $\mathcal{JAJ} = \mathcal{A}$ we have that

$$\mathcal{SA}\widetilde{v}_1 = \mathcal{SJA}v_1 = -\mathcal{JSA}v_1 = -\mathcal{J}\lambda_1 v_1 = -\lambda_1 v_{M+1},$$

where we have used that λ_1 is real and that $\mathcal{JS} = -\mathcal{SJ}$. Thus $\widetilde{v}_1$ is an eigenvector of $\mathcal{SA}$ with the eigenvalue $\widetilde{\lambda}_1 = -\lambda_1$.

Since $\lambda_1 \neq 0$, $\widetilde{\lambda}_1$ and λ_1 must be different. On the other hand,

$$\widetilde{\lambda}_1 (v_1, \mathcal{S}\widetilde{v}_1) = (v_1, \mathcal{A}\widetilde{\lambda}_1) = (\mathcal{A}v_1, \widetilde{v}_1) = \lambda_1 (v_1, \mathcal{S}\widetilde{v}_1).$$

Thus $(v_1, \mathcal{S}\widetilde{v}_1) = 0$. Moreover, since

$$(\widetilde{v}_1, \mathcal{S}\widetilde{v}_1) = (\mathcal{J}v_1, \mathcal{SJ}v_1) = (\mathcal{J}v_1, -\mathcal{JS}v_1) = -(\mathcal{S}v_1, v_1) = -(v_1, \mathcal{S}v_1),$$

by interchanging v_1 and $\widetilde{v}_1$ if necessary we can assume that $(v_1, \mathcal{S}v_1) = 1$ and $(\widetilde{v}_1, \mathcal{S}\widetilde{v}_1) = -1$.

3. Let $V = \operatorname{Span}\{v_1, \widetilde{v}_1\}$ and $W = (\mathcal{S}V)^{\perp} = \mathcal{S}(V^{\perp})$. We shall show that

$$\mathfrak{h} \oplus \mathfrak{h}^* = V \oplus W.$$

Indeed, if $a \in V \cap W$ then $a \in V = \operatorname{Span}\{v_1, \widetilde{v}_1\}$ and $(a, Sv) = 0$ for all $v \in V$. Because $(v_1, \mathcal{S}v_1) = 1$, $(\widetilde{v}_1, \mathcal{S}\widetilde{v}_1) = -1$ and $(v_1, \mathcal{S}\widetilde{v}_1) = 0$, we must have $a = 0$. Thus $V \cap W = \{0\}$.

On the other hand, if $a \in (V \oplus W)^{\perp} \subset V^{\perp} \cap W^{\perp}$ then $\mathcal{S}a \in S(V^{\perp}) \cap \mathcal{S}(W^{\perp}) = W \cap V = \{0\}$, and hence $a = 0$. Therefore, $(V \oplus W)^{\perp} = \{0\}$.

Moreover, since V is finite dimensional and W is closed, the direct sum space $V \oplus W$ is a closed subspace of $\mathfrak{h} \oplus \mathfrak{h}^*$. Thus $\mathfrak{h} \oplus \mathfrak{h}^* = V \oplus W$.

4. We prove that $\mathcal{SA}$ maps W into itself. Indeed, using $V = \mathcal{SA}V$ we have $W \perp \mathcal{S}V = \mathcal{S}(\mathcal{SA}V) = \mathcal{A}V$. Since A is symmetric, we get $\mathcal{A}W \perp V$, and hence $\mathcal{SA}W \perp \mathcal{S}V$. Thus $\mathcal{SA}W \subset (\mathcal{S}V)^{\perp} = W$.

Because $\mathcal{SA}$ admits an eigenbasis on $\mathfrak{h} \oplus \mathfrak{h}^* = V \oplus W$ and $\mathcal{SA}$ leaves V and W invariant, $\mathcal{SA}$ also admits an eigenbasis on W. We then can restrict $\mathcal{SA}$ on W and conclude the desired result by an induction argument. □

Next, we show that $\Gamma + \frac{1}{2}\mathcal{S}$ satisfies all assumptions on $\mathcal{A}$ in Lemma 1.4.

Lemma 1.5. *Let* Γ *be of the form (1) with* $\Gamma \geq 0$ *and* $Tr(\gamma) < \infty$ *and let* $\Gamma_1 := \Gamma + \frac{1}{2}\mathcal{S}$*. Then* Γ_1 *is positive definite on* $\mathfrak{h} \oplus \mathfrak{h}^*$*; moreover,* $\mathcal{J}\Gamma_1\mathcal{J} = \Gamma_1$ *and* $\mathcal{S}\Gamma_1$ *admits an eigenbasis on* $\mathfrak{h} \oplus \mathfrak{h}^*$*.*

Proof. 1. It is straightforward to check that $\mathcal{J}\Gamma_1\mathcal{J} = \Gamma_1$. We now prove that Γ_1 is positive definite.

First at all, it follows from $\Gamma \geq 0$ that

$$\langle f \oplus Jg, (\Gamma + \mathcal{S}) f \oplus Jg \rangle = \langle g \oplus Jf, \Gamma(g \oplus Jf) \rangle \geq 0,$$

namely $\Gamma + \mathcal{S} \geq 0$. Thus

$$\Gamma_1 = \Gamma + \frac{1}{2}\mathcal{S} = \frac{1}{2}[\Gamma + (\Gamma + \mathcal{S})] \geq 0.$$

Next, we check that Γ_1 is injective. Assume that there exists $\varphi \in \mathrm{Ker}(\Gamma_1)\backslash\{0\}$. Then since $\mathcal{J}$ and Γ_1 commute, we have $\mathcal{J}\varphi \in \mathrm{Ker}(\Gamma_1)\backslash\{0\}$. Because $\mathcal{J}$ leaves the subspace $\mathrm{Span}\{\varphi, \mathcal{J}\varphi\} \subset \mathrm{Ker}(\Gamma_1)$ invariant, $\mathcal{J}$ must have a non-trivial fixed point in this subspace. Thus there exists $f \in \mathfrak{h}\backslash\{0\}$ such that $\Gamma_1(f \oplus Jf) = 0$. Using this equation we find that

$$\begin{aligned} \langle f \oplus J(tf), \Gamma(f \oplus J(tf)) \rangle &= (f, \gamma f) + t^2(f, (1+\gamma)f) - t\,(f, (2\gamma+1)f) \\ &= (t-1)^2(f, \gamma f) + (t^2 - t)\,\|f\|^2 < 0 \end{aligned}$$

for some $t < 1$ and near 1 sufficiently. However, it is contrary to $\Gamma \geq 0$. Thus Γ_1 must be injective.

To see that Γ_1 is positive definite we can introduce $\Gamma_1^{1/2}$, the unique positive semi-definite square root $\Gamma_1^{1/2}$ on $\mathfrak{h}\oplus\mathfrak{h}^*$. Since Γ_1 is injective, $\Gamma_1^{1/2}$ is also injective, and hence

$$(\varphi, \Gamma_1\varphi) = ||\Gamma_1^{1/2}v||^2 > 0 \text{ for all } \varphi \neq 0.$$

2. We show that $\mathcal{S}\Gamma_1$ has an eigenbasis on $\mathfrak{h} \oplus \mathfrak{h}^*$. Although $\mathcal{S}\Gamma_1$ is not a Hermitian, we may associate it with the Hermitian $C = \Gamma_1^{1/2}\mathcal{S}\Gamma_1^{1/2}$.

We can see that C has an orthonormal eigenbasis for $\mathfrak{h} \oplus \mathfrak{h}^*$. Indeed, it is straightforward to see that

$$\begin{aligned} C^2 &= \Gamma_1^{1/2}(S\Gamma S)\Gamma_1^{1/2} = \Gamma_1^{1/2}\left[\begin{pmatrix} \gamma & -\alpha \\ -\alpha^* & J\gamma J^* \end{pmatrix} + \frac{1}{2}\mathrm{I}\right]\Gamma_1^{1/2} \\ &= \Gamma_1^{1/2}\begin{pmatrix} \gamma & -\alpha \\ -\alpha^* & J\gamma J^* \end{pmatrix}\Gamma_1^{1/2} + \frac{1}{2}\Gamma_1 \\ &= \Gamma_1^{1/2}\begin{pmatrix} \gamma & -\alpha \\ -\alpha^* & J\gamma J^* \end{pmatrix}\Gamma_1^{1/2} + \frac{1}{2}\begin{pmatrix} \gamma & \alpha \\ \alpha^* & J\gamma J^* \end{pmatrix} + \frac{1}{4}\mathrm{I}\,. \end{aligned}$$

Because γ is trace class, $\alpha\alpha^*$ is also trace class due to inequality (2). Thus $(C^2 - \frac{1}{4}\mathrm{I})$ is a self-adjoint Hilbert-Schmidt operator, and hence it has an orthonormal eigenbasis on $\mathfrak{h}\oplus\mathfrak{h}^*$. Therefore, C^2 has an orthonormal eigenbasis. Note that if φ is an eigenvector of C^2 then $C\varphi$ is also an eigenvector of C^2 with the same eigenvalue. Because C maps the subspace $\mathrm{Span}\{\varphi, C\varphi\}$ into itself, we can diagonalize to obtain an orthonormal eigenbasis of C on this subspace. By induction, we get an orthonormal eigenbasis of C on $\mathfrak{h} \oplus \mathfrak{h}^*$.

Now note that if φ is an eigenvector of C then $\mathcal{S}\Gamma_1^{1/2}\varphi$ is an eigenvector of $\mathcal{S}\Gamma_1$ with the same eigenvalue since

$$S\Gamma_1(S\Gamma_1^{1/2}\varphi) = S\Gamma_1^{1/2}(\Gamma_1^{1/2}S\Gamma_1^{1/2})\varphi = S\Gamma_1^{1/2}(C\varphi).$$

Moreover, because both of S and $\Gamma_1^{1/2}$ are injective, $\mathcal{S}\Gamma_1^{1/2}$ maps a basis on $\mathfrak{h}\oplus\mathfrak{h}^*$ to another basis. In particular, $\mathcal{S}\Gamma_1^{1/2}$ maps an eigenbasis of C to an eigenbasis of $\mathcal{S}\Gamma_1$. $\square$

Now we can prove Theorem 1.3 similarly to Theorem 2.3 in [4]).

Proof of Theorem 1.3. 1. Apply Lemma 1.4 with $\mathcal{A} = \Gamma_1 := \Gamma + \frac{1}{2}\mathcal{S}$, we can find a Bogoliubov transformation $\mathcal{V}$ on $\mathfrak{h}\oplus\mathfrak{h}^*$ such that, with respect to the orthonormal basis $\{u_n \oplus 0\} \cup \{0 \oplus Ju_n\}$,

$$\mathcal{V}^*\Gamma_1\mathcal{V} = \begin{pmatrix} \lambda_1+\frac{1}{2} & & & & & \\ & \lambda_2+\frac{1}{2} & & & 0 & \\ & & \ddots & & & \\ & & & \lambda_1+\frac{1}{2} & & \\ & 0 & & & \lambda_2+\frac{1}{2} & \\ & & & & & \ddots \end{pmatrix},$$

which is equivalent to (5).

We claim that in (5) we must have $\lambda_n \geq 0$ and $\sum_n \lambda_n < \infty$. It follows from (5) and $\mathcal{V}^*\Gamma\mathcal{V} \geq 0$ that $\lambda_n \geq 0$. In order to prove the boundedness $\sum_n \lambda_n < \infty$ we note that

$$\Gamma S(\Gamma+S) = \begin{pmatrix} \gamma(\gamma+1)-\alpha\alpha^* & \gamma\alpha-\alpha J\gamma J^* \\ \alpha^*\gamma - J\gamma J^*\alpha^* & \alpha^*\alpha - J\gamma(\gamma+1)J^* \end{pmatrix}$$

is a self-adjoint trace class operator. Using the diagonal form

$$\begin{aligned} &\mathcal{V}^*\Gamma\mathcal{S}(\Gamma+\mathcal{S})\mathcal{V} = [\mathcal{V}^*\Gamma\mathcal{V}]\,\mathcal{S}\,[\mathcal{V}^*(\Gamma+\mathcal{S})\mathcal{V}] \\ &= \begin{pmatrix} \lambda_1(\lambda_1+1) & & & & & \\ & \lambda_2(\lambda_1+1) & & & 0 & \\ & & \ddots & & & \\ & & & -\lambda_1(\lambda_1+1) & & \\ & 0 & & & -\lambda_2(\lambda_1+1) & \\ & & & & & \ddots \end{pmatrix} \end{aligned}$$

we conclude that $\sum_n \lambda_n(\lambda_n+1) < \infty$, which is equivalent to $\sum_n \lambda_n < \infty$.

2. Finally we show that the Bogoliubov transformation $\mathcal{V}$ constructed above is unitarily implementable. Assume $\mathcal{V}$ has the form (3). Then by Theorem 1.2, it suffices to prove that VV^* is a trace class operator on $\mathfrak{h}$.

It follows from the representation (5) that the upper left block of $\mathcal{V}^*\Gamma\mathcal{V}$ is a positive semi-definite trace class operator on $\mathfrak{h}$. By direct computation, we can see that the upper left block of

$$\mathcal{V}^*\Gamma\mathcal{V} = \begin{pmatrix} U^* & J^*V^*J^* \\ V^* & JU^*J^* \end{pmatrix} \begin{pmatrix} \gamma & \alpha \\ \alpha^* & 1+J\gamma J^* \end{pmatrix} \begin{pmatrix} U & V \\ JVJ & JUJ^* \end{pmatrix},$$

is

$$U^*\gamma U + J^*V^*J^*U + U^*\alpha JVJ + J^*V^*VJ + J^*V^*\gamma VJ.$$

Because γ is trace class, we have $U^*\gamma U$ and $J^*V^*\gamma VJ$ are trace class. Thus $J^*V^*J^*U + U^*\alpha JVJ + J^*V^*VJ$ is trace class.

Moreover, using the Cauchy-Schwarz inequality

$$|\operatorname{Tr}(XY + Y^*X^*)| \leq 2(\operatorname{Tr}(XX^*))^{1/2}(\operatorname{Tr}(YY^*))^{1/2}$$

we find that

$$\begin{aligned} \infty &> \operatorname{Tr}\left[U^*\alpha JVJ + J^*V^*J^*\alpha^*U + J^*V^*VJ\right] \\ &= \operatorname{Tr}\left[(U^*\alpha J)(VJ) + (VJ)^*(U^*\alpha J)^*\right] + \operatorname{Tr}(VV^*) \\ &\geq -2(\operatorname{Tr}(U^*\alpha\alpha^*U^*))^{1/2}(\operatorname{Tr}(VV^*))^{1/2} + \operatorname{Tr}(VV^*). \end{aligned}$$

Note that $\operatorname{Tr}(U^*\alpha\alpha^*U^*) < \infty$ because $\alpha\alpha^*$ is trace class. Thus $\operatorname{Tr}(VV^*) < \infty$. $\square$

1.3 Quasi-free states and quadratic Hamiltonians

Definition (Quasi-free states)**.** A *quasi-free state* ρ is a state satisfying Wick's Theorem, namely

$$\rho[A(F_1)...A(F_{2m-1})] = 0 \text{ for all } m \geq 1 \tag{6}$$

and

$$\rho[A(F_1)...A(F_{2m})] = \sum_{\sigma\in P_{2m}} \rho[A(F_{\sigma(1)})A(F_{\sigma(2)})]...\rho[A(F_{\sigma(2m-1)})A(F_{\sigma(2m)})] \tag{7}$$

where P_{2m} is the set of pairings

$$\begin{aligned} P_{2m} = \{\sigma \in S_{2m} \mid \sigma(2j-1) < \sigma(2j+1), j = 1, \ldots, m-1, \\ \sigma(2j-1) < \sigma(2j),\ j = 1, \ldots, m\}. \end{aligned}$$

A crucial point is that we have *one-to-one correspondence* between the set of quasi-free states with finite particle numbers and the set of 1-pdm's. If a quasi-free state is a pure state, namely a one-dimensional projection on the Fock space, we call it a *quasi-free pure state.*

Theorem 1.6 (Quasi-free states and quasi-free pure states)**.**

(i) Any operator $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ *of the form (1) satisfying* $\Gamma \geq 0$ *and* $\mathrm{Tr}(\gamma) < \infty$ *is the 1-pdm of a quasi-free state with finite particle number expectation.*

(ii) A pure state $|\Psi\rangle\langle\Psi|$ *with finite particle number expectation is a quasi-free state if and only if* $\Psi = \mathbb{U}_{\mathcal{V}}|0\rangle$ *for some Bogoliubov unitary mapping* $\mathbb{U}_{\mathcal{V}}$ *as in (4).*

Moreover, any operator $\Gamma : \mathfrak{h} \oplus \mathfrak{h}^* \to \mathfrak{h} \oplus \mathfrak{h}^*$ *of the form (1) satisfying* $\Gamma \geq 0$ *and* $\mathrm{Tr}(\gamma) < \infty$ *is the 1-pdm of a quasi-free pure state if and only if* $\Gamma\mathcal{S}\Gamma = -\Gamma$.

Remark. The characterization of quasi-free pure states were already proved in [19] (with a different proof). For the fermionic analogues see [4] (Theorem 2.3 and Theorem 2.6).

Proof. **(i)** Note that the set of quasi-free states is *invariant* under Bogoliubov unitary mappings. Indeed, if the Bogoliubov transformation $\mathcal{V}$ is implemented by the unitary mapping $\mathbb{U}_{\mathcal{V}} : \mathcal{F} \to \mathcal{F}$ as in (4) and Γ is the 1-pdm of a quasi-free state ρ then $\mathcal{V}^*\Gamma\mathcal{V}$ is the 1-pdm of the quasi-free state $\rho_{\mathcal{V}^*\Gamma\mathcal{V}}$ defined by

$$\rho_{\mathcal{V}^*\Gamma\mathcal{V}}(B) := \rho(\mathbb{U}_{\mathcal{V}} B \mathbb{U}_{\mathcal{V}}^*) \text{ for all } B \in \mathcal{B}(\mathcal{F}).$$

Therefore, due to the diagonalization result in Theorem 1.3, it remains to show that any operator of the form

$$\Gamma = \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix},$$

where ξ is a positive semi-definite trace class operator on $\mathfrak{h}$, is indeed the 1-pdm of some quasi-free state.

Because ξ is trace class, it admits an orthogonal eigenbasis $\{u_i\}_{i=1}^{\infty}$ for $\mathfrak{h}$ corresponding to eigenvalues $\{\lambda_i\}_{i=1}^{\infty}$. Let $I = \{i \in \mathbb{N} | \lambda_i > 0\}$. Then we may choose $e_i \in (0, \infty)$ such that

$$(1 - \exp(-e_i))^{-1} = 1 + \lambda_i, \ i \in I. \tag{8}$$

Denote $a_i = a(u_i)$ for short. Let

$$G = \Pi_0 \exp\left[-\sum_{i \in I} e_i a_i^* a_i\right] \tag{9}$$

where Π_0 is the orthogonal projection onto the subspace $\mathrm{Ker}[\sum_{i \notin I} a_i^* a_i]$. Similarly to the fermionic case (see Theorem 2.3 in [4]), it is straightforward to check that Γ is the 1-pdm of the state $\rho = \mathrm{Tr}[G]^{-1}G$ and that ρ is a quasi-free state. For the reader's convenience we provide this part of the proof in the Appendix.

(ii) If $\Psi = \mathbb{U}_\mathcal{V} |0\rangle$ for some Bogoliubov unitary mapping $\mathbb{U}_\mathcal{V}$ then using $\mathbb{U}_\mathcal{V}^* = \mathbb{U}_{\mathcal{V}^{-1}}$ and (4) we have $A(\mathcal{V}^{-1}F) = \mathbb{U}_\mathcal{V}^* A(F) \mathbb{U}_\mathcal{V}$. Therefore,

$$\begin{aligned} \langle\Psi| A(F_1)A(F_2)...A(F_n) |\Psi\rangle &= \langle 0| \mathbb{U}_\mathcal{V}^* A(F_1)\mathbb{U}_\mathcal{V}\mathbb{U}_\mathcal{V} A(F_2)\mathbb{U}_\mathcal{V}...\mathbb{U}_\mathcal{V}^* A(F_n)\mathbb{U}_\mathcal{V} |0\rangle \\ &= \langle 0| A(\mathcal{V}^{-1}F_1)A(\mathcal{V}^{-1}F_2)...A(\mathcal{V}^{-1}F_n) |0\rangle . \end{aligned}$$

It is then obvious that the state $|\Psi\rangle\langle\Psi|$ satisfies equations (6)-(7) in Wick's Theorem, and hence it is a quasi-free state.

Reversely, suppose that the pure state $|\Psi\rangle\langle\Psi|$ is a quasi-free state with finite particle number expectation. Then by the first statement in Theorem 1.6,

$$|\Psi\rangle\langle\Psi| = \mathrm{Tr}[G]^{-1}\mathbb{U}_\mathcal{V} G \mathbb{U}_\mathcal{V}^*$$

for some Bogoliubov unitary mapping $\mathbb{U}_\mathcal{V}$ and for some G given by (9). On the other hand, the only rank-one operator G of the form (9) is the vacuum projection $|0\rangle\langle 0|$ (namely $\xi = 0$). Thus, up to a complex phase, Ψ is equal to $\mathbb{U}_\mathcal{V}|0\rangle$.

Now we consider the 1-dpm's of quasi-free pure states. Suppose that Ψ is a quasi-free pure state with finite particle number expectation and its 1-dpm is Γ. Due to Theorem 1.6, there is a unitarily implementable Bogoliubov transformation $\mathcal{V}$ such that

$$\mathcal{V}^*\Gamma\mathcal{V} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

The identity $\Gamma\mathcal{S}\Gamma = -\Gamma$ follows from

$$\begin{aligned} \mathcal{V}^*\Gamma\mathcal{S}\Gamma\mathcal{V} &= (\mathcal{V}^*\Gamma\mathcal{V})(\mathcal{V}^*\mathcal{S}\mathcal{V})^{-1}(\mathcal{V}^*\Gamma\mathcal{V}) \\ &= \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \mathcal{S}^{-1} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\ &= -\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = -\mathcal{V}^*\Gamma\mathcal{V}. \end{aligned}$$

Reversely, let $\Gamma : \mathfrak{h}\oplus\mathfrak{h}^* \to \mathfrak{h}\oplus\mathfrak{h}^*$ be of the form (1) such that $\Gamma \geq 0$, $\mathrm{Tr}(\gamma) < \infty$ and $\Gamma\mathcal{S}\Gamma = -\Gamma$. Then by Theorem 1.6, Γ is the 1-dpm of a quasi-free state and there is a unitarily implementable Bogoliubov transformation $\mathcal{V}$ such that

$$\mathcal{V}^*\Gamma\mathcal{V} = \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}$$

for some positive semi-definite trace class operator ξ on $\mathfrak{h}$. The identity $\Gamma\mathcal{S}\Gamma = -\Gamma$ implies that

$$\begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix} \mathcal{S} \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix} = -\begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}.$$

The only solution to this equation is $\xi = 0$. Therefore, Γ is the 1-dpm of a quasi-free pure state with finite particle number expectation. □

One of the main motivation of considering the quasi-free pure states is that they minimize the quadratic Hamiltonians.

Definition (Quadratic Hamiltonian). Let $\mathcal{A}$ be a positive semi-definite operator on $\mathfrak{h} \oplus \mathfrak{h}^*$ and $\mathcal{J}\mathcal{A}\mathcal{J} = \mathcal{A}$. The operator

$$H_{\mathcal{A}} = \sum_{i,j=1} (F_i, \mathcal{A}F_j) A^*(F_i) A(F_j),$$

acting on $\mathcal{F}$ is called a *quadratic Hamiltonian* corresponding to $\mathcal{A}$. Here $\{F_i\}_{i\geq 1}$ is an orthonormal basis for $\mathfrak{h} \oplus \mathfrak{h}^*$ (the sum is independent of the choice of $\{F_i\}_{i\geq 1}$).

Remark. (i) Alternatively, we can describe $H_{\mathcal{A}}$ by

$$(\Psi, H_{\mathcal{A}}\Psi) = \operatorname{Tr}[\mathcal{A}\Gamma_\Psi] \text{ for all normalized vector } \Psi \in \mathcal{F},$$

where Γ_Ψ is the 1-pdm of the pure state $|\Psi\rangle\langle\Psi|$.

(ii) The condition $\mathcal{J}\mathcal{A}\mathcal{J} = \mathcal{A}$ is just a conventional assumption since if this condition does not holds then we can consider $A' = \frac{1}{2}(\mathcal{A} + \mathcal{J}\mathcal{A}\mathcal{J})$ which satisfies that $\mathcal{J}\mathcal{A}'\mathcal{J} = \mathcal{A}'$ and, formally,

$$H_{\mathcal{A}'} = H_{\mathcal{A}} + \frac{1}{2}\operatorname{Tr}[\mathcal{A}\mathcal{S}].$$

This formal formula makes sense when, for example, $\mathcal{A}$ is trace class.

(ii) As we shall see below, that $A \geq 0$ is the necessary and sufficient condition such that $H_{\mathcal{A}}$ is bounded from below. Moreover, in this case $H_{\mathcal{A}} \geq 0$.

We are interested in the ground state energy of $H_{\mathcal{A}}$,

$$E(H_{\mathcal{A}}) \quad := \quad \inf\{\rho(H_{\mathcal{A}}) | \rho \text{ is a state with } \rho(\mathcal{N}) < \infty\} \tag{10}$$

Theorem 1.7 (Minimizing quadratic Hamiltonians). *Let $\mathcal{A}$, $H_{\mathcal{A}}$ and $E(H_{\mathcal{A}})$ as above.*

(i) We have $E(H_{\mathcal{A}}) = \inf\{\rho(H_{\mathcal{A}}) | \rho \text{ is a quasi-free pure state}\}$.

(ii) If there is a unitarily implementable Bogoliubov transformation $\mathcal{V}_{\mathcal{A}}$ such that $\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}}$ is diagonal then there is a quasi-free pure state ρ_0 such that $\rho_0(H_{\mathcal{A}}) = E(H_{\mathcal{A}})$. Moreover, if $\mathcal{A}$ is positive definite then ρ_0 is unique.

(iii) If the variational problem (10) has a minimizer then $\mathcal{A}$ is diagonalized by a unitarily implementable Bogoliubov transformation $\mathcal{V}_{\mathcal{A}}$. Moreover, if Γ is the 1-pdm of the minimizer then we have

$$\mathcal{A}\Gamma = -\mathcal{A}\mathcal{S}1_{(-\infty,0)}[\mathcal{A}\mathcal{S}].$$

In particular, $\mathcal{A}\Gamma\mathcal{S} = \mathcal{S}\Gamma\mathcal{A} \leq 0$.

Remark. (i) The above statements (i) and (ii) already appeared in [19] in the finite-dimensional case (in this case $\mathcal{A}$ is always diagonalizable by Lemma 1.4).

(ii) If the operator W is not self-adjoint but $U^{-1}WU$ is self-adjoint for some invertible operator U then we can still define the projection $1_{(-\infty,0)}[W]$ by

$$1_{(-\infty,0)}[W] := U 1_{(-\infty,0)}[U^{-1}WU]U^{-1}.$$

It is easy to check that the definition is independent of the choice of U. In particular, we can define

$$1_{(-\infty,0)}[\mathcal{AS}] := (\mathcal{V}_{\mathcal{A}}^*)^{-1} 1_{(-\infty,0)}[\mathcal{V}_{\mathcal{A}}^* \mathcal{AS} (\mathcal{V}_{\mathcal{A}}^*)^{-1}]\mathcal{V}_{\mathcal{A}}^*$$

where $\mathcal{V}_{\mathcal{A}}^* \mathcal{AS} (\mathcal{V}_{\mathcal{A}}^*)^{-1}$ is self-adjoint.

Proof. **(i)** We show that for any state ρ with finite number particle expectation, there is a quasi-free pure state $\widetilde{\rho}$ such that $\widetilde{\rho}(H_{\mathcal{A}}) \le \rho(H_{\mathcal{A}})$.

By Theorem 1.3, there is a unitarily implementable Bogoliubov transformation $\mathcal{V}$ such that

$$\Gamma = \mathcal{V} \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix} \mathcal{V}^*$$

where $\xi : \mathfrak{h} \to \mathfrak{h}$ is a positive semi-definite trace class operator. Thus

$$\rho(H_{\mathcal{A}}) = \mathrm{Tr}[\mathcal{A}\Gamma] = \mathrm{Tr}\left[\mathcal{V}^* \mathcal{A} \mathcal{V} \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}\right].$$

Because $\mathcal{V}^*\mathcal{A}\mathcal{V}$ commutes with $\mathcal{J}$, it has the block form

$$\mathcal{V}^*\mathcal{A}\mathcal{V} = \begin{pmatrix} a & b \\ JbJ & JaJ^* \end{pmatrix}$$

where $0 \le a : \mathfrak{h} \to \mathfrak{h}$ and $b : \mathfrak{h}^* \to \mathfrak{h}$. Thus

$$\rho(H_{\mathcal{A}}) = \mathrm{Tr}\left[\begin{pmatrix} a & b \\ JbJ & JaJ^* \end{pmatrix}\begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}\right] = 2\,\mathrm{Tr}[a\xi] + \mathrm{Tr}[a] \ge \mathrm{Tr}[a].$$

By Theorem 1.6, there is a quasi-free pure state $\widetilde{\rho}$ whose 1-pdm is

$$\mathcal{V}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}\mathcal{V}^*.$$

It follows from the above discussion that $\widetilde{\rho}(H_{\mathcal{A}}) \le \rho(H_{\mathcal{A}})$.

(ii) Assume that $\mathcal{A}$ is diagonalized by the unitarily implementable Bogoliubov transformation $\mathcal{V}_{\mathcal{A}}$, namely

$$\mathcal{A} = \mathcal{V}_{\mathcal{A}}^* \begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix} \mathcal{V}_{\mathcal{A}}$$

where $d : \mathfrak{h} \to \mathfrak{h}$ is positive semi-definite. For any state ρ we have

$$\rho(H_{\mathcal{A}}) = \mathrm{Tr}[\mathcal{A}\Gamma] = \mathrm{Tr}\left[\begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix} \mathcal{V}_{\mathcal{A}}\Gamma\mathcal{V}_{\mathcal{A}}^*\right]$$

where Γ is the 1-pdm of ρ. We may write $\mathcal{V}_{\mathcal{A}}\Gamma_\Psi\mathcal{V}_{\mathcal{A}}^*$ in the block form

$$\mathcal{V}_{\mathcal{A}}\Gamma\mathcal{V}_{\mathcal{A}}^* = \begin{pmatrix} \gamma & \alpha \\ \alpha^* & 1 + J\gamma J^* \end{pmatrix}$$

where $0 \leq \gamma : \mathfrak{h} \to \mathfrak{h}$ and $\alpha : \mathfrak{h}^* \to \mathfrak{h}$. Thus

$$\rho(H_{\mathcal{A}}) = \mathrm{Tr}\left[\begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix}\begin{pmatrix} \gamma & \alpha \\ \alpha^* & 1 + J\gamma J^* \end{pmatrix}\right] = 2\,\mathrm{Tr}[d\gamma] + \mathrm{Tr}[d] \geq \mathrm{Tr}[d]$$

Denote by ρ_0 the quasi-free pure state having the 1-dpm

$$\mathcal{V}_A^{-1}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}V_{\mathcal{A}}^{*-1} = \mathcal{S}\mathcal{V}_A^*\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}V_{\mathcal{A}}\mathcal{S}.$$

Then $\rho_0(H_{\mathcal{A}}) = \mathrm{Tr}[d]$ and hence ρ_0 is a ground state of $H_{\mathcal{A}}$.

Moreover, if $\mathcal{A}$ is positive definite then $\mathrm{Tr}[d\gamma] > 0$ unless $\gamma = 0$. Therefore, ρ_0 is the unique ground state of $H_{\mathcal{A}}$ among the quasi-free states.

(iii) Assume that problem (10) has a minimizer and Γ is the 1-dpm of the minimizer.

1. We first prove that $\mathcal{AS}$ and $\mathcal{S}\Gamma$ commute. Let a be an arbitrary trace class operator on $\mathfrak{h} \oplus \mathfrak{h}^*$ such that $a = a^* = \mathcal{J}a\mathcal{J}$. It is straightforward to check that $\exp(i\varepsilon H\mathcal{S})$ is a Bogoliubov unitarily implementable transformation for any $\varepsilon \in \mathbb{R}$. Similarly to the variational argument for Hartree-Fock-Bogoliubov theory in [12] (p. 284), we consider the trial states

$$\Gamma_\varepsilon := \exp(-i\varepsilon\mathcal{S}a)\Gamma\exp(i\varepsilon a\mathcal{S}) = \Gamma + \varepsilon[i\Gamma a\mathcal{S} - i\mathcal{S}a\Gamma] + O(\varepsilon^2),\ \varepsilon \in \mathbb{R}.$$

Since $\varepsilon = 0$ minimizes the functional $\varepsilon \mapsto \mathrm{Tr}[\mathcal{A}(\Gamma_\varepsilon - \Gamma)]$ we find that

$$0 = \frac{d}{d\varepsilon}\mathrm{Tr}[\mathcal{A}(\Gamma_\varepsilon - \Gamma)] = \mathrm{Tr}[aB] \text{ with } B := i\mathcal{SA}\Gamma - i\Gamma\mathcal{AS}.$$

Note that $B = B^* = \mathcal{J}B\mathcal{J}$.

Now let b be any trace class operator on $\mathfrak{h}\oplus\mathfrak{h}^*$. Since $a := b + b^* + \mathcal{J}b\mathcal{J} + \mathcal{J}b^*\mathcal{J}$ satisfies that $a = a^* = \mathcal{J}a\mathcal{J}$, we have

$$0 = \mathrm{Tr}[aB] = 4\Re\,\mathrm{Tr}[bB].$$

By changing b a complex phase, we conclude that $\mathrm{Tr}[bB] = 0$ for any trace class operator b. This implies that $B = 0$. Thus $\mathcal{AS}\Gamma = \Gamma\mathcal{AS}$, namely $[\mathcal{AS}, \mathcal{S}\Gamma] = 0$.

2. Now let $\mathcal{V}_\Gamma$ be the unitarily implementable Bogoliubov transformation such that

$$\mathcal{V}_\Gamma^* \Gamma \mathcal{V}_\Gamma = \begin{pmatrix} \xi & 0 \\ 0 & 1 + J\xi J^* \end{pmatrix}$$

for some trace class operator $\xi \geq 0$ on $\mathfrak{h}$. Thus the operator $\mathcal{V}_\Gamma^{-1} \mathcal{S}\Gamma\mathcal{V}_\Gamma = \mathcal{S}\mathcal{V}_\Gamma^*\Gamma\mathcal{V}_\Gamma$ leaves the spaces $\mathfrak{h} \oplus 0$ and $0 \oplus \mathfrak{h}^*$ invariant . Since $\mathcal{V}_\Gamma^{-1}\mathcal{A}\mathcal{S}\mathcal{V}_\Gamma$ commutes with $\mathcal{V}_\Gamma^{-1}\mathcal{S}\Gamma\mathcal{V}_\Gamma$, it also leaves the spaces $\mathfrak{h} \oplus 0$ and $0 \oplus \mathfrak{h}^*$ invariant. Moreover, since $\mathcal{V}_\Gamma^{-1}\mathcal{A}\mathcal{S}\mathcal{V}_\Gamma$ commutes with $\mathcal{J}$, it must have the form

$$\mathcal{V}_\Gamma^{-1}\mathcal{A}\mathcal{S}\mathcal{V}_\Gamma = \begin{pmatrix} d & 0 \\ 0 & -JdJ^* \end{pmatrix}.$$

Using $\mathcal{V}_\Gamma^{-1} = \mathcal{S}\mathcal{V}_\Gamma^*\mathcal{S}$ we then conclude that

$$\mathcal{S}\mathcal{V}_\Gamma^*\mathcal{S}\mathcal{A}\mathcal{S}\mathcal{V}_\Gamma\mathcal{S} = \begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix}$$

where $d \geq 0$ since $\mathcal{A} \geq 0$. Thus the unitarily implementable Bogoliubov transformation $\mathcal{V}_\mathcal{A} := \mathcal{S}\mathcal{V}_\Gamma\mathcal{S}$ diagonalizes $\mathcal{A}$.

3. Finally we prove that $\mathcal{A}\Gamma = -\mathcal{A}\mathcal{S}1_{(-\infty,0)}[\mathcal{A}\mathcal{S}]$. Denote

$$\mathcal{V}_\mathcal{A}^{-1}\Gamma(\mathcal{V}_\mathcal{A}^{-1})^* = \begin{pmatrix} \widetilde{\gamma} & \widetilde{\alpha} \\ (\widetilde{\alpha})^* & J\widetilde{\gamma}J^* \end{pmatrix} \text{ and } \mathcal{V}_\mathcal{A}^{-1}\Gamma'(\mathcal{V}_\mathcal{A}^{-1})^* = \begin{pmatrix} \widetilde{\gamma}' & \widetilde{\alpha}' \\ (\widetilde{\alpha}')^* & J\widetilde{\gamma}'J^* \end{pmatrix}$$

for any 1-dpm Γ'. We find that

$$\begin{aligned} 0 &\leq \operatorname{Tr}\left[\mathcal{A}(\Gamma' - \Gamma)\right] = \operatorname{Tr}\left[(\mathcal{V}_\mathcal{A}^*\mathcal{A}\mathcal{V}_\mathcal{A})\mathcal{V}_\mathcal{A}^{-1}(\Gamma' - \Gamma)(\mathcal{V}_\mathcal{A}^*)^{-1}\right] \\ &= \operatorname{Tr}\left[\begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix}\begin{pmatrix} \widetilde{\gamma}' - \widetilde{\gamma} & \widetilde{\alpha}' - \widetilde{\alpha} \\ (\widetilde{\alpha}' - \widetilde{\alpha})^* & J(\widetilde{\gamma}' - \widetilde{\gamma})J^* \end{pmatrix}\right] \\ &= 2\operatorname{Tr}[d\widetilde{\gamma}'] - 2\operatorname{Tr}[d\widetilde{\gamma}]. \end{aligned}$$

Because this inequality holds true for any positive semi-definite trace class operator $\widetilde{\gamma}'$ on $\mathfrak{h}$, we conclude that $\operatorname{Tr}(d\widetilde{\gamma}) = 0$. By writing

$$\operatorname{Tr}[d\widetilde{\gamma}] = \operatorname{Tr}[(d^{1/2}\widetilde{\gamma}^{1/2})^* d^{1/2}\widetilde{\gamma}^{1/2}]$$

we obtain $d^{1/2}\widetilde{\gamma}^{1/2} = 0$, and hence $d\widetilde{\gamma} = 0$. This also implies that $d\widetilde{\alpha} = 0$ since

$$(\widetilde{\alpha}d)^*(\widetilde{\alpha}d) = d(\widetilde{\alpha})^*\widetilde{\alpha}d \leq d(1 + ||\widetilde{\gamma}||_{\mathcal{L}(\mathfrak{h})})\widetilde{\gamma}d = 0.$$

Thus

$$\begin{aligned} \begin{pmatrix} 0 & 0 \\ 0 & JdJ^* \end{pmatrix} &= \begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix}\begin{pmatrix} \widetilde{\gamma} & \widetilde{\alpha} \\ (\widetilde{\alpha})^* & 1 + J\widetilde{\gamma}J \end{pmatrix} \\ &= (\mathcal{V}_\mathcal{A}^*\mathcal{A}\mathcal{V}_\mathcal{A})(\mathcal{V}_\mathcal{A}^{-1}\Gamma(\mathcal{V}_\mathcal{A}^*)^{-1}) = \mathcal{V}_\mathcal{A}^*\mathcal{A}\Gamma(\mathcal{V}_\mathcal{A}^*)^{-1}. \end{aligned}$$

It can be rewritten as

$$\mathcal{A}\Gamma = (\mathcal{V}_{\mathcal{A}}^*)^{-1}\begin{pmatrix} 0 & 0 \\ 0 & JdJ^* \end{pmatrix}\mathcal{V}_{\mathcal{A}}^*. \tag{11}$$

Moreover, since $d \geq 0$ we find that

$$\begin{aligned}
\begin{pmatrix} 0 & 0 \\ 0 & JdJ^* \end{pmatrix} &= -\begin{pmatrix} d & 0 \\ 0 & JdJ^* \end{pmatrix} 1_{(-\infty,0)}\left[\begin{pmatrix} d & 0 \\ 0 & -JdJ^* \end{pmatrix}\right] S \\
&= -(\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}})1_{(-\infty,0)}\left[\mathcal{S}\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}}\right]\mathcal{S} \\
&= -\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}}1_{(-\infty,0)}\left[(\mathcal{S}\mathcal{V}_{\mathcal{A}})^{-1}(\mathcal{A}\mathcal{S})\mathcal{S}\mathcal{V}_{\mathcal{A}}\right]\mathcal{S} \\
&= -\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{V}_{\mathcal{A}}(\mathcal{S}\mathcal{V}_{\mathcal{A}})^{-1}1_{(-\infty,0)}(\mathcal{A}\mathcal{S})\mathcal{S}\mathcal{V}_{\mathcal{A}}\mathcal{S} \\
&= -\mathcal{V}_{\mathcal{A}}^*\mathcal{A}\mathcal{S}1_{(-\infty,0)}(\mathcal{A}\mathcal{S})(\mathcal{V}_{\mathcal{A}}^*)^{-1}.
\end{aligned}$$

Thus (11) can be rewritten as

$$\mathcal{A}\Gamma = -\mathcal{S}\mathcal{A}1_{(-\infty,0)}[\mathcal{A}\mathcal{S}].$$

Moreover, it follows from (11) that

$$\mathcal{A}\Gamma\mathcal{S} = (\mathcal{V}_{\mathcal{A}}^*)^{-1}\begin{pmatrix} 0 & 0 \\ 0 & JdJ^* \end{pmatrix}\mathcal{V}_{\mathcal{A}}^*\mathcal{S} = \mathcal{S}\mathcal{V}_{\mathcal{A}}\begin{pmatrix} 0 & 0 \\ 0 & -JdJ^* \end{pmatrix}\mathcal{V}_{\mathcal{A}}^*\mathcal{S} \leq 0.$$

□

1.4 Bogoliubov variational theory

The Bogoliubov variational states should include not only the quasi-free states (like the Hartree-Fock theory) but also the coherent states, which correspond to the condensation. To describe the formulation precisely we need the following result (see [19], Theorem 13.1).

Theorem 1.8. *For every $\phi \in \mathfrak{h}$ there exists (uniquely up to a complex phase) a* coherent unitary $\mathbb{U}_\phi : \mathcal{F} \to \mathcal{F}$ *such that*

$$\mathbb{U}_\phi^* a(f)\mathbb{U}_\phi = a(f) + (f,\phi) \text{ for all } f \in \mathfrak{h}.$$

Proof. We can proceed similarly the proof of Theorem 1.2 (see the Appendix) by translating the orthonormal basis

$$|n_{i_1},...,n_{i_M}\rangle = (n_{i_1}!...n_{i_M}!)^{-1/2}\, a^*(u_{i_M})^{n_{i_M}}...a^*(u_{i_1})^{n_{i_1}}\,|0\rangle$$

to

$$\begin{aligned}
&\mathbb{U}_\phi\,|n_{i_1},...,n_{i_M}\rangle \\
=\;& (n_{i_1}!...n_{i_M}!)^{-1/2}\,[a^*(u_{i_M}) + (\phi,u_{i_M})]^{n_{i_M}}...[a^*(u_{i_1}) + (\phi,u_{i_1})]^{n_{i_1}}\,\mathbb{U}_\phi\,|0\rangle
\end{aligned}$$

with the new vacuum

$$\mathbb{U}_\phi\,|0\rangle = \exp\left[-\frac{1}{2}\,\|\phi\|^2\right]\exp\left[-a^*(\phi)\right]|0\rangle\,.$$

□

Remark. (i) The condensate vector $\phi \in \mathfrak{h}$ needs not be normalized. Any pure state $|\Psi\rangle\langle\Psi|$ with $\Psi = \mathbb{U}_\phi |0\rangle \in \mathcal{F}$ for some $\phi \in \mathfrak{h}$ is called a *coherent state*.

(ii) For generalized annihilation operators we get

$$\mathbb{U}_\phi^* A(F)\mathbb{U}_\phi = A(F) + (F, \phi \oplus J\phi)_{\mathfrak{h}\oplus\mathfrak{h}^*} \text{ for all } F \in \mathfrak{h} \oplus \mathfrak{h}^*.$$

Now we can describe the Bogoliubov variational states. Denote

$$\mathcal{G}^{\mathrm{B}} := \left\{(\gamma, \alpha) | \Gamma_{\gamma,\alpha} = \begin{pmatrix} \gamma & \alpha \\ J\alpha J & 1 + J\gamma J^* \end{pmatrix} \geq 0, \mathrm{Tr}(\gamma) < \infty\right\}.$$

The *Bogoliubov variational state* $\rho_{\gamma,\alpha,\phi}$ associated with $(\gamma, \alpha, \phi) \in \mathcal{G}^{Bo} \times \mathfrak{h}$ is defined by

$$\rho_{\gamma,\alpha,\phi}(B) := \rho_{\gamma,\alpha}(\mathbb{U}_\phi^* B \mathbb{U}_\phi) \text{ for all } B \in \mathcal{B}(\mathcal{F}),$$

where $\rho_{\gamma,\alpha}$ is the quasi-free state with the 1-pdm $\Gamma_{\gamma,\alpha}$. In particular, the particle number expectation of the Bogoliubov variational state $\rho_{\gamma,\alpha,\phi}$ is

$$\rho_{\gamma,\alpha,\phi}(\mathcal{N}) = \mathrm{Tr}(\gamma) + ||\phi||^2.$$

For a given Hamiltonian $\mathbb{H} : \mathcal{F} \to \mathcal{F}$ and $\lambda \geq 0$ we can define the *Bogoliubov ground state energy*

$$E^{\mathrm{B}}(\lambda) = \inf\left\{\rho_{\gamma,\alpha,\rho}(\mathbb{H}) | (\gamma, \alpha, \phi) \in \mathcal{G}^{\mathrm{B}} \times \mathfrak{h}, \mathrm{Tr}(\gamma) + ||\phi||^2 = \lambda\right\}$$

where $\rho_{\gamma,\alpha,\rho}(\mathbb{H})$ is the *Bogoliubov energy functional* and λ stands for the total particle number of the system.

Remark. (i) Due to the variational principle, the Bogoliubov ground state energy $E^{\mathrm{B}}_{\mathbb{H}}(\lambda)$ is always an upper bound to the quantum grand canonical energy

$$E^{\mathrm{g}}(\lambda) = \inf\{(\Psi, \mathbb{H}\Psi) : \Psi \in \mathcal{F}, ||\Psi|| = 1, (\Psi, \mathcal{N}\Psi) = \lambda\}.$$

(ii) If $N \in \mathbb{N}$ then the grand canonical energy $E^{\mathrm{g}}(N)$ is always a lower bound to the canonical energy

$$E(N) = \inf\{(\Psi, \mathbb{H}\Psi) : \Psi \in \bigotimes_{\mathrm{sym}}^{N}, ||\Psi|| = 1\}.$$

Moreover, if $E(N)$ is convex w.r.t. N then $E^{\mathrm{g}}(N) = E(N)$ for all N.

Example 1.9 (A toy model)**.** Let $\mathfrak{h} = \mathbb{R}$ and the Hamiltonian

$$\mathbb{H} = a^*(1)a^*(1)a(1)a(1).$$

A straightforward computation shows that for $N \in \mathbb{N}$ then the quantum energy is

$$E^{\mathrm{g}}(N) = E(N) = N^2 - N$$

and the Bogoliubov energy is

$$\begin{aligned} E^B(N) &= \inf_{\lambda\ge 0, x\ge 0, \lambda+x=N} \left[x^2 + x(4\lambda - 2\sqrt{\lambda(1+\lambda)}) + 2\lambda^2 + \lambda(1+\lambda)\right] \\ &= \inf_{0\le\lambda\le N} \left[N^2 + 2N(\lambda - \sqrt{\lambda(1+\lambda)}) + \lambda + 2\lambda\sqrt{\lambda(1+\lambda)}\right] \\ &= N^2 - N + O(N^{2/3}) \text{ as } N\to\infty. \end{aligned}$$

Of our particular interest is the Bogoliubov variational theory for interacting Bose gases which we shall describe briefly below.

Let $\mathfrak{h} = L^2(\Omega)$ for some measure space Ω with the inner product

$$(u,v) = \int_\Omega \overline{u(x)} v(x) dx.$$

In this case the mapping $J : \mathfrak{h} \to \mathfrak{h}^*$ is simply the complex conjugate, i.e. $Ju(x) = \overline{u(x)}$. Therefore, for simplicity we shall use notation $\overline{\gamma} = J\gamma J^*$ and $\overline{\alpha} = J\alpha J$.

The Hamiltonian consists of a *one-body kinetic operator* T, which is a self-adjoint operator on $\mathfrak{h}$, and a *two-body potential operator* W which is the multiplication operator corresponding to the funtion $W(x,y) : \Omega\times\Omega \to \mathbb{R}$ satisfying $W(x,y) = W(y,x)$. The grand canonical Hamiltonian $\mathbb{H} : \mathcal{F} \to \mathcal{F}$ can be represented in the second quantization as

$$\begin{aligned} \mathbb{H} &= \bigoplus_{N=0}^{\infty} \left(\sum_{i=1}^{N} T_i + \sum_{1\le i<j\le N} W_{ij} \right) \\ &= \sum_{m,n} (u_m, T u_n)_{\mathfrak{h}} a_m^* a_n + \frac{1}{2} \sum_{m,n,p,q} (u_m \otimes u_n, W u_p \otimes u_q)_{\mathfrak{h}\times\mathfrak{h}} a_m^* a_n^* a_p a_q \end{aligned}$$

where $a_n := a(u_n)$ and $\{u_n\}_{n=1}^{\infty}$ is an orthonormal basis for $\mathfrak{h}$ (the sum is independent of the choice of $\{u_n\}$).

To represent the Bogoliubov energy functional explicitly in terms of (γ, α, ϕ), it is convenient to introduce the *integral kernel* $\alpha(x,y)$ of the Hilbert-Schmidt operator which satisfies

$$(\alpha f)(x) = \int_\Omega \alpha(x,y) f(y) dy \text{ for all } f \in L^2(\Omega).$$

Similarly, we have the kernel $\gamma(x,y)$ of γ and the density functional is *formally* defined by $\rho_\gamma(x) := \gamma(x,x)$. More precisely, because γ is a positive semi-definite trace class operator, we have the spectral decomposition $\gamma = \sum_i t_i |u_i\rangle\langle u_i|$ and then we can define $\gamma(x,y) := \sum_i t_i u_i(x)\overline{u_i(y)}$ and $\rho_\gamma(x) := \sum_i t_i |u_i(x)|^2$. Note that $\int \rho(x)dx = \mathrm{Tr}(\gamma)$.

Using the coherent transformations

$$\mathbb{U}_\phi^* a_n U_\phi = a_n + (u_n, \phi)$$

and Wick's Theorem we find that

$$\begin{aligned}\rho_{\gamma,\alpha,\phi}(\mathbb{H}) &= \operatorname{Tr}(T\widetilde{\gamma}) + D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}) + X(\gamma,\gamma) + X(\alpha,\alpha) \\ &\quad + \operatorname{Re}\iint_{\Omega\times\Omega}\left[\gamma(x,y)\overline{\phi(x)}\phi(y) + \alpha(x,y)\overline{\phi(x)\phi(y)}\right]W(x,y)dxdy\end{aligned}$$

where $\widetilde{\gamma} := \gamma + |\phi\rangle\langle\phi|$, $\rho_{\widetilde{\gamma}}(x) = \widetilde{\gamma}(x,x)$ and

$$\begin{aligned}D(f,g) &= \frac{1}{2}\iint_{\Omega\times\Omega}\overline{f(x)}g(y)W(x,y)dxdy, \\ X(\gamma,\gamma') &= \frac{1}{2}\iint_{\Omega\times\Omega}\overline{\gamma(x,y)}\gamma'(x,y)W(x,y)dxdy.\end{aligned}$$

Here are some specific examples with respect to three cases: $W > 0$, W changes sign, and $W < 0$.

Example 1.10 (Bosonic atoms)**.** In this case we have

$$\mathfrak{h} = L^2(\mathbb{R}^3),\ T = -\Delta - \frac{Z}{|x|},\ W(x,y) = \frac{1}{|x-y|}.$$

We shall investigate the Bogoliubov theory for bosonic atoms in details in the next sections. In particular, we can show that the Bogoliubov ground state energy and the full quantum mechanics energy agree up to the leading order, and we conjecture that they even agree up to the second order.

Example 1.11 (Two-component Bose gases)**.** This is the case when

$$\mathfrak{h} = L^2(\mathbb{R}^3\times\{\pm1\}),\ T = -\Delta_x,\ W(x,e,y,e') = \frac{ee'}{|x-y|}.$$

It is already known that the Bogoliubov theory is also correct to the full quantum theory up to the leading order. More precisely, for large N, the correct leading term $-AN^{7/5}$ was predicted by Dyson [7] using the Bogoliubov principle and then it was mathematically established by Lieb-Solovej [14] (lower bound) and Solovej [18] (upper bound).

Example 1.12 (Bosonic stars)**.** The system now corresponds to

$$\mathfrak{h} = L^2(\mathbb{R}^3),\ T = \sqrt{-\Delta + m^2} - m,\ W(x,y) = -\frac{\kappa}{|x-y|}$$

where $m > 0$ is the neutron mass and $\kappa = Gm^2 > 0$. Up to the leading order, the ground state energy is approximated by the Hartree model [15]. Because the Hartree ground state energy is strictly concave, replacing the canonical setting by the grand canonical setting would make the energy much lower. Therefore, it is easy to see that the Bogoliubov ground state energy is much lower than the one of the full quantum model, although by adapting the ideas in [10] we can show that the Bogoliubov variational model still has minimizers.

2 Bosonic atoms

2.1 Introduction

For a bosonic atom we mean a system including a nucleus fixed at the origin in $\mathbb{R}^3$ with nucleus charge $Z > 0$ and N "bosonic electrons" with charge -1. The system is described by the Hamiltonian

$$H_{N,Z} = \sum_{i=1}^{N}\left(-\Delta_i - \frac{Z}{|x|}\right) + \sum_{1\le i<j\le N}\frac{1}{|x_i - x_j|}$$

acting on the symmetric space $\mathcal{H}_N = \bigotimes_{\text{sym}}^N L^2(\mathbb{R}^3)$. The ground state energy of the system is given by

$$E(N,Z) = \inf\{(\Psi, H_{N,Z}\Psi) | \Psi \in \mathcal{H}_N, ||\Psi||_{L^2} = 1\}.$$

In fact, the ground state energy $E(N,Z)$ does not change if we replace the symmetric subspace $\mathcal{H}_N$ by the full N-particle space $\bigotimes^N L^2(\mathbb{R}^3) = L^2(\mathbb{R}^{3N})$ (see, e.g., [13] p. 59-60). For usual atoms (with fermionic electrons), the Hamiltonian $H_{N,Z}$ acts on the anti-symmetric subspace $\bigwedge_{i=1}^{N}(L^2(\mathbb{R}^3)\otimes\mathbb{C}^2)$ instead. For simplicity, we only consider the spinless electrons because the spin number play no role in the mathematical analysis here.

We recall some well-known fact about the full quantum problem. Due to the HVZ Theorem (see e.g. [13] Lemma 12.1), $E(N,Z) \le E(N-1,Z)$ and if $E(N,Z) < E(N-1,Z)$ then $E(N,Z)$ is an isolated eigenvalue of $H_{N,Z}$. Unlike the asymptotic neutrality of fermionic atoms, in the bosonic case, the binding $E(N,Z) < E(N-1,Z)$ holds for all $0 \le N \le N_c(Z)$ with $\lim_{Z\to\infty} N_c(Z)/Z = t_c \approx 1.21$ (see [6, 17, 5, 1]).

The leading term of the ground state energy $E(N,Z)$ is given by the Hartree theory [6]. In the Hartree theory, the ground state energy is

$$E^{\mathrm{H}}(N,Z) = \inf\{\mathcal{E}^{\mathrm{H}}(u,Z) : ||u||_{L^2}^2 = N\}$$

where

$$\mathcal{E}^{\mathrm{H}}(u,Z) = \int_{\mathbb{R}^3} |\nabla u(x)|^2\,dx - \int_{\mathbb{R}^3}\frac{Z|u(x)|^2}{|x|} + \iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{|u(x)|^2|u(y)|^2}{|x-y|}dxdy.$$

By the scaling $u(x) = Z^2 u_1(Zx)$ we have

$$\mathcal{E}^{\mathrm{H}}(u,Z) = Z^3\mathcal{E}^{\mathrm{H}}(u_1,1).$$

Therefore,

$$E^{\mathrm{H}}(N,Z) = Z^3 e(N/Z,1) \text{ where } e(t) = E^{\mathrm{H}}(t,1).$$

It is well-known (see e.g. [5, 11]) that $e(t)$ is convex, $e(t)' < 0$ when $t < t_c \approx 1.21$ and $e'(t) = 0$ when $t \geq t_c$. Moreover, for any $0 < t < t_c \approx 1.21$, $e(t)$ has a unique minimizer ϕ_t, which is positive, radially-symmetric and it is the unique solution to the nonlinear equation $h_t\phi_t = 0$ where

$$h_t = -\Delta - \frac{1}{|x|} + |\phi_t|^2 * \frac{1}{|x|} - e'(t).$$

As a consequence, $h_t \geq 0$. Moreover, since $\sigma_{\text{ess}}(h_t) = [-e'(t), 0]$, there is a gap $\Delta_t > 0$ if $t < t_c$ such that $(h_t - \Delta_t)P_t^{\perp} \geq 0$ where $P_{\phi_t}^{\perp} = 1 - P_t$ with P_t being the one-dimensional projection onto $\text{Span}\{\phi_t\}$.

By scaling back, we conclude that $E^{\text{H}}(tZ, Z)$ has the unique minimizer and the operator

$$h_{t,Z} = -\Delta - \frac{Z}{|x|} + |\phi_{t,Z}|^2 * \frac{1}{|x|} - Z^2 e'(t)$$

satisfies $h_{t,Z}\phi_{t,Z} = 0$ and $(h_{t,Z} - Z^2\Delta_t)P_{\phi_{t,Z}}^{\perp} \geq 0$ when $t < t_c$.

Our aim is to investigate the first correction to the ground state energy $E(tZ, Z)$. We shall analyze the Bogoliubov variational model for bosonic atoms and compare to the full quantum theory. From the general discussion on the Bogoliubov theory, we have the Bogoliubov variational problem

$$E^{\text{B}}(N, Z) = \inf \left\{ \mathcal{E}^{\text{B}}(\gamma, \alpha, \phi, Z) | (\gamma, \alpha, \phi) \in \mathcal{G}^{\text{B}} \times L^2(\mathbb{R}^3), \text{Tr}(\gamma) + ||\phi||^2 = N \right\} \tag{12}$$

where

$$\begin{aligned}
\mathcal{E}^{\text{B}}(\gamma, \alpha, \phi, Z) \quad &= \quad \text{Tr}(-[\Delta - Z|x|^{-1}]\widetilde{\gamma}) + D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + X(\gamma, \gamma) + X(\alpha, \alpha) \\
&\quad + \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\gamma(x, y)\overline{\phi(x)}\phi(y)}{|x - y|} dxdy + \text{Re} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\alpha(x, y)\overline{\phi(x)\phi(y)}}{|x - y|} dxdy.
\end{aligned}$$

Here we are using the notations $\widetilde{\gamma} := \gamma + |\phi\rangle\langle\phi|$ and

$$D(f, g) = \frac{1}{2} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\overline{f(x)}g(y)}{|x - y|} dxdy, \;\; X(\gamma, \gamma') = \frac{1}{2} \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\overline{\gamma(x, y)}\gamma'(x, y)}{|x - y|} dxdy.$$

The properties of the Bogoliubov theory for bosonic atoms are the following, which will be proved in the next subsections.

Theorem 2.1 (Existence of minimizers)**.** *Let the nucleus charge Z and the electron number N be any positive numbers (not necessarily integers).*

(i) If the binding inequality

$$E^{\text{B}}(N, Z) < E^{\text{B}}(N', Z) \text{ for all } 0 < N' < N$$

holds then $E^B(N, Z)$ has a minimizer.

(ii) The energy $E^{\mathrm{B}}(N,Z)$ *is strictly decreasing on* $N \in [0, N_c(Z)]$ *with* $N_c(Z) \geq Z$ *for all* Z *and*

$$\liminf_{Z\to\infty} \frac{N_c(Z)}{Z} \geq t_c \approx 1.21.$$

Theorem 2.2 (Bogoliubov ground state energy)**.** *If* $Z \to \infty$ *and* $N/Z = t \in (0, t_c)$ *then*

$$E^{\mathrm{B}}(N,Z) = Z^3 e(t) + Z^2 \mu(t) + o(Z^2)$$

where

$$\mu(t) := \inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} \left[\mathrm{Tr}[h_t\gamma] + \mathrm{Re} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma(x,y)+\alpha(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} dxdy \right].$$

The coefficient $\mu(t)$ *is finite and satisfies the lower bound*

$$\mu(t) \leq t^{-1}e(t) - e'(t) + \widetilde{\mu}(t) < t^{-1}e(t) - e'(t) < 0$$

where

$$\widetilde{\mu}(t) := \min_{(\gamma',\alpha')\in G^B, \gamma'\phi_t=0} \left\{ \mathrm{Tr}[h_t\gamma'] + \mathrm{Re} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma'(x,y)+\alpha'(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} \right\}.$$

Remark. (i) If we restrict the Hamiltonian $H_{N,Z}$ into the class of N-particle product functions $\Psi_u = u \otimes u \otimes ... \otimes u$ then by scaling $u(x) = (N-1)^{-1/2} Z^2 u_0(Zx)$ we have

$$\begin{aligned}\inf_{||u||=1} \langle \Psi_u, H_{N,Z}\Psi_u\rangle &= \frac{NZ^3}{N-1} \inf_{||u||_0=(N-1)/Z} \mathcal{E}^{\mathrm{H}}(u_0,1) = \frac{NZ^3}{N-1} e\left(\frac{N-1}{Z}\right) \\ &= Z^3 e(t) + Z^2[t^{-1}e(t) - e'(t)] + o(Z^2).\end{aligned}$$

Because $\mu(t) < t^{-1}e(t) - e'(t)$, the Bogoliubov ground state energy is strictly lower than the lowest energy of the product wave functions at the second oder.

(ii) We believe, but do not have a rigorous proof, that the identity $\mu(t) = t^{-1}e(t) - e'(t) + \widetilde{\mu}(t)$ holds and a minimizing sequence of $\mu(t)$ is given by

$$\gamma = \lambda \left|\frac{\phi_t}{||\phi_t||}\right\rangle \left\langle \frac{\phi_t}{||\phi_t||}\right| + \gamma', \ \alpha = -\sqrt{\lambda(1+\lambda)} \left|\frac{\phi_t}{||\phi_t||}\right\rangle \left\langle \frac{\phi_t}{||\phi_t||}\right| + \alpha'$$

with $\lambda \to \infty$, where (γ', α') is a minimizer for $\widetilde{\mu}(t)$. In fact, the upper bound $\mu(t) \geq t^{-1}e(t) - e'(t) + \widetilde{\mu}(t)$ follows from the heuristic discussion on comparison between Bogoliubov energy and quantum energy below.

We *conjecture* that the Bogoliubov theory determines the first correction to the quantum energy $E(N,Z)$.

Conjecture 2.3 (First correction to the leading energy). *If $Z \to \infty$ and $N/Z = t \in (0, t_c)$ then*

$$E(N,Z) = E^{\mathrm{B}}(N,Z) + o(Z^2) = Z^3 e(t) + Z^2 \mu(t) + o(Z^2).$$

A heuristic discussion supporting the conjecture is made in the last subsection of the article. While the picture is rather clear, some technical work is still needed to make the argument rigorous.

2.2 Existence of Bogoliubov minimizers

To prove the first claim of Theorem 2.1, we shall follow the extending variational argument (see e.g. [12], Theorem 11.12). Before studying the variational problem $E^{\mathrm{B}}(N,Z)$ in (12), we start by considering the extended problem with the constraint $\mathrm{Tr}(\gamma) \le N$, namely

$$E^{\mathrm{B}}(_{\le}N, Z) = \inf\left\{\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) | (\gamma,\alpha,\phi) \in \mathcal{G}^{\mathrm{B}}, \mathrm{Tr}(\gamma) + ||\phi||^2 \le N\right\}. \qquad (13)$$

Lemma 2.4 (Extended problem). *The ground state energy $E^{\mathrm{B}}(N,Z)$ is finite and decreasing on N. Moreover, the extended variational problem $E^{\mathrm{B}}(_{\le}N,Z)$ in (13) always has a minimizer.*

Proof. 1. By simply ignoring the non-negative two-body interaction and using the hydrogen bound, we have

$$\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) \ge \mathrm{Tr}\left[\left(-\Delta - \frac{Z}{|x|}\right)\widetilde{\gamma}\right] \ge \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) - \frac{Z^2 N}{2} > -\infty. \qquad (14)$$

2. Next, we prove that $E^{\mathrm{B}}(N',Z) \ge E^{\mathrm{B}}(N,Z)$ for $N' < N$. For any trial state (γ,α,ϕ) with $(\gamma,\alpha) \in \mathcal{G}^{\mathrm{B}}$ and $\mathrm{Tr}\,\gamma + ||\phi||^2 = N'$, choose $g \in C_c^\infty(\mathbb{R}^3)$ such that $\mathrm{Tr}(\gamma) + ||\phi||^2 + ||g||^2 = N$ and consider

$$\gamma_\varepsilon = \gamma + |g_\varepsilon\rangle\langle g_\varepsilon|$$

where $g_\varepsilon(x) = \varepsilon^{3/2} g(\varepsilon x)$. Then $(\gamma_\varepsilon,\alpha) \in \mathcal{G}^{\mathrm{B}}$ and $\mathrm{Tr}(\gamma_\varepsilon) + ||\phi||^2 = N$. Moreover, since $|\nabla g_\varepsilon| \to 0$ in $L^2(\mathbb{R}^3)$ and $|g_\varepsilon|^2 \to 0$ in $L^p(\mathbb{R}^3)$ for any $p > 1$, a simple calculation shows that

$$\mathcal{E}^{\mathrm{B}}(\gamma_\varepsilon,\alpha,\phi,Z) \to \mathcal{E}_Z^{\mathrm{B}}(\gamma,\alpha,\phi,Z) \text{ as } \varepsilon \to 0.$$

This ensures that $E^{\mathrm{B}}(N',Z) \ge E^{\mathrm{B}}(N',Z)$.

3. To show that $E^{\mathrm{B}}(_{\le}N,Z)$ has a minimizer, let us take a minimizing sequence $(\gamma_n,\alpha_n,\phi_n)$ for $E^{\mathrm{B}}(_{\le}N,Z)$. The lower bound (14) ensures that $\mathrm{Tr}(-\Delta\gamma_n)$ is bounded. Consequently, all of $\|\gamma_n(x,y)\|_{H^1(\mathbb{R}^3\times\mathbb{R}^3)}$, $\|\alpha_n(x,y)\|_{H^{1/2}(\mathbb{R}^3\times\mathbb{R}^3)}$ and

$\|\phi_n\|_{H^1(\mathbb{R}^3)}$ are bounded. By passing to a subsequence if necessary, we may assume that $\gamma_n \rightharpoonup \gamma, \alpha_n \rightharpoonup \gamma, \phi_n \rightharpoonup \phi$ weakly in the corresponding Hilbert spaces, and their kernels converge pointwisely. It is straightforward to check that $(\gamma, \alpha) \in \mathcal{G}^{\mathrm{B}}$ and by Fatou's lemma, $\mathrm{Tr}(\gamma) + ||\phi||^2 \leq N$.

Fatou'lemma also implies that

$$\liminf_{n\to\infty} \mathrm{Tr}(-\Delta\gamma) \geq \mathrm{Tr}(-\Delta\gamma).$$

The two-body interaction part of $\mathcal{E}^{\mathrm{B}}(\gamma_n, \alpha_n, \phi_n, Z)$ can be rewritten as

$$\iint \frac{W(\gamma_n, \alpha_n, \phi_n)}{|x-y|}$$

where

$$\begin{aligned} W(\gamma_n, \alpha_n, \phi_n) &= \rho_{\gamma_n}(x)\rho_{\gamma_n}(y) + |\gamma_n(x,y)|^2 + |\alpha_n(x,y) + \phi_n(x)\phi_n(y)|^2 \\ &+ \left[\rho_{\gamma_n}(x)|\phi(y)|^2 + \rho_{\gamma_n}(y)|\phi(x)|^2 + 2\,\mathrm{Re}(\gamma_n(x,y)\overline{\phi_n(x)}\phi_n(y))\right] \geq 0. \end{aligned}$$

Therefore, we may use Fatou'lemma again to obtain

$$\lim\inf_{n\to\infty} \iint \frac{W(\gamma_n, \alpha_n, \phi_n)}{|x-y|} \geq \iint \frac{W(\gamma, \alpha, \phi)}{|x-y|}.$$

Finally, because $\sqrt{\rho_{\gamma_n}} \rightharpoonup \sqrt{\rho_\gamma}$ in $H^1(\mathbb{R}^3)$ we have the convergence

$$\int_{\mathbb{R}^3} \frac{\rho_{\gamma_n}(x)}{|x|} dx \to \int_{\mathbb{R}^3} \frac{\rho_\gamma(x)}{|x|} dx \text{ as } n \to \infty.$$

Therefore, we have

$$\liminf_{n\to\infty} \mathcal{E}^{\mathrm{B}}(\gamma_n, \alpha_n, \phi_n, Z) \geq \mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi, Z)$$

and hence (γ, α, ϕ) is a minimizer for $E^{\mathrm{B}}(\leq N, Z)$. □

We now prove the existence of minimizers for the original problem $E^{\mathrm{B}}(N, Z)$.

Proof of Theorem 2.1. 1. If $E^{\mathrm{B}}(N, Z) < E^{\mathrm{B}}(N', Z)$ for all $0 < N' < N$ then any minimizer (γ, α, ϕ) for the extended problem $E^{\mathrm{B}}(\leq N, Z)$ must satisfy $\mathrm{Tr}(\gamma) + ||\phi||^2 = N$, and hence it is a minimizer for $E^{\mathrm{B}}(N, Z)$.

2. That $E(N, Z)$ is strictly decreasing on $N \in [0, Z]$ follows by the same argument as in [8]. Assume that $E^{\mathrm{B}}(N, Z) = E^{\mathrm{B}}(N', Z)$ for some $0 \leq N' < N \leq Z$. Let (γ, α, ϕ) be a minimizer for $E^{\mathrm{B}}(\leq N', Z)$. For any $\varphi \in H^1(\mathbb{R}^3)$, let us consider the trial state $(\gamma_\varepsilon, \alpha, \phi)$ with

$$\gamma_\varepsilon = \gamma + \varepsilon \,|\varphi\rangle\,\langle\varphi|\,,\ \varepsilon > 0.$$

For $\varepsilon > 0$ small we have $\operatorname{Tr}\gamma_\varepsilon + ||\phi|| \le N$ and hence

$$\mathcal{E}^{\mathrm{B}}(\gamma_\varepsilon, \alpha, \phi, Z) \ge E^{\mathrm{B}}(N, Z) = E^{\mathrm{B}}(N', Z) = \mathcal{E}^{\mathrm{B}}(\gamma, \alpha, \phi, Z).$$

Therefore,

$$\begin{aligned} 0 \le \frac{d}{d\varepsilon}\bigg|_{\varepsilon=0} \mathcal{E}^{\mathrm{B}}(\gamma_\varepsilon, \alpha, \phi, Z) \quad &= \quad (\varphi, -\Delta\varphi)_{L^2} - \int\limits_{\mathbb{R}^3} \frac{Z|\varphi(x)|^2}{|x|} dx + 2D(\rho_{\widetilde{\gamma}}, |\varphi|^2) \\ &\quad + 2 \operatorname{Re} X(\widetilde{\gamma}, |\varphi\rangle\langle\varphi|). \end{aligned} \tag{15}$$

On the other hand, let us replace φ by $\varphi_L(x) := L^{-3/2}\varphi_1(x/L)$ where $\varphi_1 \in H^1(\mathbb{R}^3)$ such that φ_1 is radially-symmetric and $\varphi_1(x) = 0$ if $|x| < 1$ and $\varphi_1(x) > 0$ if $|x| > 1$. Then for large L one has

$$\begin{aligned} \langle \varphi_L, -\Delta\varphi_L \rangle \quad &= \quad L^{-2}\langle \varphi_1, -\Delta\varphi_1\rangle = O(L^{-2}), \\ -Z\int\limits_{\mathbb{R}^3} \frac{|\varphi_L(x)|^2}{|x|} dx \quad &= \quad -ZL^{-1}\int\limits_{\mathbb{R}^3} \frac{|\varphi_1(x)|^2}{|x|} dx. \end{aligned}$$

Moreover, by Newton's theorem,

$$2D(\rho_{\widetilde{\gamma}}, |\varphi_L|^2) = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\gamma(x)|\varphi_L(y)|^2}{\max\{|x|,|y|\}} dy \le N'L^{-1} \int\limits_{\mathbb{R}^3} \frac{|\varphi_1(y)|^2}{|y|} dy,$$

and by Hölder's inequality,

$$2 \operatorname{Re} X(\widetilde{\gamma}, |\varphi_L\rangle\langle\varphi_L|) = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\overline{\widetilde{\gamma}(x,y)\varphi_L(x)}\varphi_L(y)}{|x-y|} dxdy$$

$$\le \left(\iint\limits_{|x|\ge L, |y|\ge L} |\widetilde{\gamma}(x,y)| dxdy \right)^{1/2} \left(\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\varphi_L(x)|^2|\varphi_L(y)|^2}{|x-y|^2} dxdy \right)^{1/2} = o(L^{-1}).$$

Thus if we replace φ in (15) by φ_L then we obtain

$$0 \le O(L^{-2}) - (Z - N')L^{-1} \int\limits_{\mathbb{R}^3} \frac{|\varphi_1(x)|^2}{|x|} dx + o(L^{-1})$$

which is a contradiction to the assumption $N' < Z$. Thus $N \mapsto E^{\mathrm{B}}(N, Z)$ is strictly decreasing when $0 < N \le Z$.

3. Now we show that $E^{\mathrm{B}}(Z, N)$ is strictly decreasing on $N \in [Z, N_c(Z)]$ with

$$\liminf_{Z\to\infty} N_c(Z)/Z \ge t_c \approx 1.21$$

We shall need some properties of the Bogoliubov ground state in Lemma 2.7, which is derived in the next section.

Take a large number Z and assume that $N \mapsto E^{\rm B}(N,Z)$ is not strictly decreasing on $Z \le t'Z$ for a fixed value $t' < t_c$. Then there exists $N = tZ \in [Z, t'Z]$ and $\delta > 0$ such that $E^{\rm B}(N,Z) = E^{\rm B}(N+\delta, Z)$ and $E^{\rm B}(N,Z)$ has a ground state (γ, α, ϕ). Because

$$\mathcal{E}^{\rm B}(\gamma,\alpha,\phi,Z) = E^{\rm B}(N,Z) = E^{\rm B}(N+\delta,Z) \le \mathcal{E}^{\rm B}(\gamma,\alpha,\sqrt{1+\varepsilon}\phi,Z)$$

for $\varepsilon > 0$ small, we have

$$\begin{aligned} 0 &\le \left.\frac{d}{d\varepsilon}\right|_{\varepsilon=0} \mathcal{E}^{\rm B}(\gamma,\alpha,\sqrt{1+\varepsilon}\phi,Z) \\ &= \left\langle \phi, \left(-\Delta - \frac{Z}{|x|} + \rho_{\widetilde{\gamma}} * |.|^{-1}\right)\phi \right\rangle + \\ &\quad + \iint \frac{\gamma(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} + \mathrm{Re} \iint \frac{\alpha(x,y)\overline{\phi(x)\phi(y)}}{|x-y|}. \end{aligned}$$

Because

$$\mathcal{E}^{\rm B}(\gamma,\alpha,\phi) = E^{\rm B}(N,Z) \le E^{\rm H}(N,Z) \le \mathrm{Tr}\left[\left(-\Delta - \frac{Z}{|x|}\right)\widetilde{\gamma}\right] + D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}})$$

we get

$$\iint \frac{\gamma(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} + \mathrm{Re} \iint \frac{\alpha(x,y)\overline{\phi(x)\phi(y)}}{|x-y|} \le 0.$$

Thus

$$\begin{aligned} 0 &\le \left\langle \phi, \left(-\Delta - \frac{Z}{|x|} + \rho_{\widetilde{\gamma}} * |.|^{-1}\right)\phi \right\rangle \\ &= \langle \phi, h_{t,Z}\phi\rangle + 2D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, |\phi|^2) + e'(t)Z^2||\phi||^2. \end{aligned}$$

On the other hand, using the estimates in Lemma 2.7 we have

$$\begin{aligned} \langle \phi, h_{t,Z}\phi\rangle &= o(Z^2), \\ e'(t)Z^2||\phi||^2 &\le e'(t)Z^2(tZ + o(Z)) = te'(t)Z^3 + o(Z^3), \\ D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, |\phi|^2) &\le \sqrt{D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, \rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2)}.\sqrt{D(|\phi_{t,Z}|^2, |\phi_{t,Z}|^2)} \\ &= o(Z^{5/2}). \end{aligned}$$

Therefore,

$$0 \le \langle \phi, h_{t,Z}\phi\rangle + 2D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, |\phi|^2) + e'(t)Z^2||\phi||^2 \le te'(t)Z^3 + o(Z^3).$$

However, it is a contradiction because $te'(t) < 0$ when $1 \le t \le t' < t_c$. $\square$

2.3 Analysis of quadratic forms

We consider the minimization problem $\mu(t)$ of the quadratic form in Theorem 2.2. Recall that

$$\mu(t) := \inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} q_t(\gamma,\alpha) \text{ and } \widetilde{\mu}(t) := \inf_{(\gamma',\alpha')\in\mathcal{G}^{\mathrm{B}},\gamma'\phi_t=0} q_t(\gamma',\alpha')$$

where

$$q_t(\gamma,\alpha) := \left[\mathrm{Tr}[h_t\gamma] + \mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma(x,y)+\alpha(x,y)]\phi_t(x)\phi_t(y)}{|x-y|}dxdy\right].$$

Lemma 2.5 (Analysis of the quadratic form $q_t(\gamma,\alpha)$)**.** *For any $0<t<t_c$ we have*

$$-\infty < \mu(t) \leq t^{-1}e(t) - e'(t) + \widetilde{\mu}(t).$$

Moreover, the minimization problem $\widetilde{\mu}(t)$ has a minimizer (γ',α') and $\widetilde{\mu}(t)<0$.

Proof. 1. Because $q_t(\gamma,\alpha)$ is a quadratic form of (γ,α), for considering the ground state energy we may restrict (γ,α) into the class of quasi-free pure state, i.e. $\alpha\alpha^* = \gamma(1+\gamma)$. Since $\gamma\geq 0$ is trace class and $\alpha^T=\alpha$, we can write

$$\gamma(x,y) = \sum_n \lambda_n u_n(x)\overline{u_n(y)},\ \ \alpha(x,y) = -\sum_n \sqrt{\lambda_n(1+\lambda_n)}u_n(x)u_n(y),$$

where $\lambda_n\geq 0$ and $\{u_n\}_n$ is an orthonormal family on $L^2(\mathbb{R}^3)$. Then

$$q_t(\gamma,\alpha) = \sum_n [\lambda_n(u_n,h_tu_n) + A_n]$$

with

$$A_n = \lambda_n \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_n(x)\overline{u_n(y)}\phi_t(x)\phi_t(y)}{|x-y|} - \sqrt{\lambda_n(1+\lambda_n)}\,\mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_n(x)u_n(y)\phi_t(x)\phi_t(y)}{|x-y|}.$$

2. We may assume that $\lambda_n(u_n,h_{t,Z}u_n)+A_n \leq 0$ for all n; otherwise, if $\lambda_n(u_n,h_{t,Z}u_n)+A_n<0$ then

$$q_t(\gamma,\alpha) > q_t(\gamma',\alpha')$$

where

$$\gamma' = \gamma - \lambda_n\left|u_n\right\rangle\left\langle u_n\right|, \alpha' = \alpha + \sqrt{\lambda_n(1+\lambda_n)}\left|u_n\right\rangle\left\langle\overline{u_n}\right|.$$

We have the gap $(u_n,h_tu_n)\geq \Delta_t||P^\perp u_n||^2$ for all n. Moreover, $|\mathrm{Re}(D(\overline{u},u))|\leq D(u,u)$ for all functions u we have

$$\begin{aligned} A_n &\geq 2D(u_n\phi_t,u_n\phi_t)(\lambda_n - \sqrt{\lambda_n(1+\lambda_n)}) \\ &\geq 2D(u_n\phi_t,u_n\phi_t)\max\left\{-\frac{1}{2},-\sqrt{\lambda_n}\right\}. \end{aligned} \tag{16}$$

Thus it follows from the assumption $\lambda_n(u_n, h_{t,Z}u_n) + A_n \leq 0$ that

$$\Delta_t^2 \lambda_n ||P^\perp u_n||^4 \leq 4|D(u_n\phi_t, u_n\phi_t)|^2 \text{ for all } n. \tag{17}$$

On the other hand, observe that

$$||P^\perp u_n||^2 + ||P^\perp u_m||^2 = 2 - ||Pu_n||^2 - ||Pu_m||^2 \geq 1 \text{ for all } m \neq n.$$

Therefore, there exists (at most) an element i_0 such that $||P^\perp u_n||^2 \geq 1/2$ for all $n \neq i_0$. As a consequence, (17) implies that

$$\sum_{n\neq i_0} \lambda_n \leq 16\Delta_t^{-2} \sum_{n\neq i_0} |D(u_n\phi_t, u_n\phi_t)|^2 \leq 4\Delta_t^{-2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\phi_t(x)|^2|\phi_t(y)|^2}{|x-y|^2} dxdy \leq C.$$

3. Using $h_t \geq 0$ and (16) we have

$$\begin{aligned}
q_t(\gamma,\alpha) &\geq A_{i_0} + \sum_{n\neq i_0} A_n \geq -D(u_{i_0}\phi_t, u_{i_0}\phi_t) - \sum_{n\neq i_0} 2\sqrt{\lambda_n} D(u_n\phi_t, u_n\phi_t) \\
&\geq -D(u_{i_0}\phi_t, u_{i_0}\phi_t) - 2\left(\sum_{n\neq i_0} \lambda_n\right)^{1/2} \left(\sum_{n\neq i_0} |D(u_n\phi_t, u_n\phi_t)|^2\right)^{1/2} \\
&\geq -\frac{1}{2}\left(\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\phi_t(x)|^2|\phi_t(y)|^2}{|x-y|^2}\right)^{1/2} - 2\Delta_t^{-1}\left(\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\phi_t(x)|^2|\phi_t(y)|^2}{|x-y|^2}\right) \\
&\geq -C.
\end{aligned}$$

4. To see the upper bound on $\mu(t)$ let us consider the trial state

$$\gamma = \lambda \left|\frac{\phi_t}{||\phi_t||}\right\rangle \left\langle \frac{\phi_t}{||\phi_t||}\right| + \gamma',\ \alpha = -\sqrt{\lambda(1+\lambda)} \left|\frac{\phi_t}{||\phi_t||}\right\rangle \left\langle \frac{\phi_t}{||\phi_t||}\right| + \alpha'$$

where $(\gamma', \alpha') \in \mathcal{G}^{\mathrm{B}}$ such that $\gamma'\phi_t = 0$. One has

$$\mu(t) \quad \leq \quad q_t(\gamma,\alpha) = 2\left(\lambda - \sqrt{\lambda(1+\lambda)}\right) D(u_1\phi_t, u_1\phi_t) + q_t(\gamma', \alpha').$$

Taking the infimum over all (γ', α') and letting $\lambda \to \infty$ we obtain

$$\mu(t) \leq -t^{-1} D(|\phi_t|^2, |\phi_t|^2) + \widetilde{\mu}(t) = t^{-1}e(t) - e'(t) + \widetilde{\mu}(t).$$

5. Now we consider $\widetilde{\mu}(t)$. The above argument shows that if $\{(\gamma'_n, \alpha'_n)\}_{n=1}^\infty$ is a minimizing sequence for $\widetilde{\mu}(t)$ then $\mathrm{Tr}(\gamma'_n)$ is bounded. Therefore, it follows from the standard compactness argument that $\widetilde{\mu}(t)$ has a minimizer. To see that $\widetilde{\mu}(t) < 0$, let us consider

$$\gamma' = \lambda' |u\rangle \langle u|,\ \alpha' = -\sqrt{\lambda'(1+\lambda')}\, |u\rangle \langle u|$$

where u is a normalized real-valued function in $L^2(\mathbb{R}^3)$ such that $(u,\phi_t) = 0$. Because $D(u\phi_t, u\phi_t) > 0$ we have

$$\widetilde{\mu}(t) \le q_t(\gamma',\alpha') = \lambda'(u,h_t u) + 2\left(\lambda' - \sqrt{\lambda'(1+\lambda')}\right) t^{-1} D(u\phi_t,u\phi_t) < 0$$

for some $\lambda' > 0$ small enough. $\square$

Remark. The analysis here works out for a more general setting. For example, if h is a positive semi-definite operator on $L^2(\Omega)$ with $\inf \sigma_{\mathrm{ess}}(h) > 0$ and W is a positive semi-definite Hilbert-Schmidt operator on $L^2(\Omega)$ with a real-valued kernel $W(x,y)$ then

$$\inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} \left(\mathrm{Tr}[h\gamma] + \mathrm{Re} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} (\gamma(x,y)+\alpha(x,y)) W(x,y) dxdy \right) > -\infty.$$

By scaling $\phi_{t,Z}(x) = Z^2\phi_t(Zx)$, $\gamma(x) = Z^3\gamma'(Zx,Zy)$, $\alpha(x) = Z^3\alpha'(Zx,Zy)$ we have

$$\inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} q_{t,Z}(\gamma,\alpha) = \inf_{(\gamma',\alpha')\in\mathcal{G}^{\mathrm{B}}} Z^2 q_t(\gamma',\alpha') = Z^2\mu(t)$$

where

$$q_{t,Z}(\gamma',\alpha') = \mathrm{Tr}[h_{t,Z}\gamma'] + \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\gamma'(x,y)+\alpha'(x,y))\phi_{t,Z}(x)\phi_{t,Z}(y)}{|x-y|} dxdy.$$

To prove Theorem 2.2, we need to consider some perturbation form of $q_{t,Z}$.

Lemma 2.6 (Analysis of pertubative quadratic forms)**.** *Let $\phi \in L^2(\mathbb{R}^3)$ such that $||\phi|| \le ||\phi_{t,Z}||$, $||\nabla\phi|| \le CZ^{3/2}$ and $||P^\perp\phi|| \le C$ where $P^\perp = 1-P$ with P being the one-dimensional projection onto $\phi_{t,Z}$. Then for Z large we have*

$$\inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} q_{t,Z}(\gamma,\alpha,\phi) \ge \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - CZ^{2-1/10}$$

where

$$q_{t,Z}(\gamma,\alpha,\phi) = \mathrm{Tr}[h_{t,Z}\gamma] + \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} + \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\alpha(x,y)\overline{\phi(x)\phi(y)}}{|x-y|}.$$

Proof. 1. We first consider the case when $\mathrm{Tr}\,\gamma$ is small. Assume that $\mathrm{Tr}\,\gamma \le Z^{1/2-\varepsilon}$, where $\varepsilon = 1/10$. In the integral involved with γ, we use the decomposition

$$\overline{\phi(x)}\phi(y) = \overline{P\phi(x)}P\phi(y) + \overline{P\phi(x)}P^\perp\phi(y) + \overline{P^\perp\phi(x)}\phi(y).$$

Observe that all terms involved with $P^\perp\phi$ have negligible contribution. For example,

$$\left| \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma(x,y)\overline{P^\perp\phi(x)}\phi(y)}{|x-y|} \right| \le 2\,\mathrm{Tr}(\gamma^2)^{1/2}||P^\perp\phi||.||\nabla\phi|| \le CZ^{2-\varepsilon}.$$

Thus

$$\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma_\varepsilon(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} \ge \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma_\varepsilon(x,y)\overline{P\phi(x)}P\phi(y)}{|x-y|} - CZ^{2-\varepsilon}.$$

Together with the similar bound on the integral involved with α, we arrive at

$$\begin{aligned} q_{t,Z}(\gamma,\alpha,\phi) &\ge \left(1-\frac{||P\phi||^2}{||\phi||^2}\right)\mathrm{Tr}[h_{t,Z}\gamma] + \frac{||P\phi||^2}{||\phi_{t,Z}||^2} q_{t,Z}(\gamma,\alpha) - CZ^{2-\varepsilon} \\ &\ge \frac{||P\phi||^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - CZ^{2-\varepsilon}. \end{aligned}$$

2. Now we consider the case when $\mathrm{Tr}\,\gamma$ is large. Assume $\mathrm{Tr}\,\gamma \ge Z^{1/2-\varepsilon}$. Following the proof of Lemma 2.5, we may assume that

$$\gamma = \lambda_1 |u_1\rangle\langle u_1| + \gamma', \alpha = -\sqrt{\lambda_1(1+\lambda_1)}\,|u_1\rangle\langle\overline{u_1}| + \alpha'$$

where $||u_1|| = 1$ and (γ',α') is the 1-pdm of a pure quasi-free state such that

$$\mathrm{Tr}\,\gamma' \le C,\ \lambda_1||P^\perp u_1||^2 \le C \text{ and } \gamma' u_1 = 0 = \alpha' u_1.$$

Because $\lambda_1 = \mathrm{Tr}\,\gamma - \mathrm{Tr}\,\gamma' \ge Z^{1/2-\varepsilon} - C$ and $\lambda_1||P^\perp u_1||^2 \le C$, we have

$$||P^\perp u_1||^2 \le CZ^{-1/2+\varepsilon}.$$

As a consequence,

$$\mathrm{Tr}(P\gamma') = \sum_{n\neq 1}\lambda_n||Pu_n||^2 \le \mathrm{Tr}\,\gamma'\sum_{n\neq1}||Pu_n||^2 \le \mathrm{Tr}\,\gamma'||P^\perp u_1||^2 \le Z^{-1/2+\varepsilon}.$$

3. We shall compare $q_{t,Z}(\gamma,\alpha,\phi)$ with $q_{t,Z}(\gamma'',\alpha'')$ where

$$\begin{aligned} \gamma'' &= \lambda_1 P|u_1\rangle\langle u_1|P + P^\perp\gamma' P^\perp, \\ \alpha'' &= -\sqrt{\lambda_1(1+\lambda_1)}P|u_1\rangle\langle\overline{u_1}|P + P^\perp\alpha' P^\perp. \end{aligned}$$

It is easy to see that $(\gamma'',\alpha'') \in \mathcal{G}^{\mathrm{B}}$.

We first consider the terms involved with u_1. We have

$$\lambda_1 \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)\overline{u_1(y)\phi(x)}\phi(y)}{|x-y|} - \sqrt{\lambda_1(1+\lambda_1)}\,\mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)u_1(y)\overline{\phi(x)\phi(y)}}{|x-y|}$$

$$\ge (\lambda_1 - \sqrt{\lambda_1(1+\lambda_1)})\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)\overline{u_1(y)\phi(x)}\phi(y)}{|x-y|}.$$

Then we use the decomposition

$$\begin{aligned} u_1(x)\overline{u_1(y)} &= Pu_1(x)\overline{Pu_1(y)} + Pu_1(x)\overline{P^\perp u_1(y)} + P^\perp u_1(x)\overline{u_1(y)}, \\ \overline{\phi(x)}\phi(y) &= \overline{P\phi(x)}P\phi(y) + \overline{P\phi(x)}P^\perp\phi(y) + \overline{P^\perp\phi(x)}\phi(y). \end{aligned}$$

Note that all terms involved with either $P^\perp u_1$ or $P^\perp \phi$ have negligible contribution. For example, we have

$$\left| \iint \frac{Pu_1(x)\overline{Pu_1(y)P^\perp\phi(x)}\phi(y)}{|x-y|} \right| \le 2||Pu_1||^2||P^\perp\phi||.||\nabla P\phi|| \le CZ^{3/2},$$

$$\left| \iint \frac{P^\perp u_1(x)\overline{u_1(y)P\phi(x)}P\phi(y)}{|x-y|} \right| \le 2||P^\perp u_1||.||u_1||.||P\phi||.||\nabla P\phi|| \le CZ^{2-1/4+\varepsilon/2}.$$

Thus

$$\begin{aligned} &\lambda_1 \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)\overline{u_1(y)\phi(x)}\phi(y)}{|x-y|} - \sqrt{\lambda_1(1+\lambda_1)}\,\mathrm{Re} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)u_1(y)\overline{\phi(x)\phi(y)}}{|x-y|} \\ \ge\ & (\lambda_1 - \sqrt{\lambda_1(1+\lambda_1)}) \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{u_1(x)\overline{u_1(y)\phi(x)}\phi(y)}{|x-y|} \\ \ge\ & (\lambda_1 - \sqrt{\lambda_1(1+\lambda_1)}) \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{Pu_1(x)\overline{Pu_1(y)P\phi(x)}P\phi(y)}{|x-y|} - CZ^{2-1/4+\varepsilon/2}. \quad (18) \end{aligned}$$

Next, consider the terms involved with (γ', α'). In the integral,

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma'(x,y)\overline{\phi(x)}\phi(y)}{|x-y|}$$

we use the decomposition

$$\begin{aligned} \gamma' &= P^\perp\gamma' P^\perp + P^\perp \gamma' P + P\gamma', \\ \overline{\phi(x)}\phi(y) &= \overline{P\phi(x)}P\phi(y) + \overline{P^\perp\phi(x)}P\phi(y) + \overline{P^\perp\phi(x)}\phi(y). \end{aligned}$$

Observe that all terms involved with either $P\gamma'$ or $P^\perp\phi$ have negligible contribution. For example, we have

$$\begin{aligned} \left| \iint \frac{(P\gamma')(x,y)\overline{P\phi(x)}P\phi(y)}{|x-y|} \right| &\le 2[\mathrm{Tr}(P(\gamma')^2P)]^{1/2}||P\phi||.||\nabla P\phi|| \\ &\le 2[\mathrm{Tr}(\gamma')]^{1/2}[\mathrm{Tr}(P\gamma')]^{1/2}||P\phi||.||\nabla P\phi|| \\ &\le CZ^{2-1/8+\varepsilon/4} \end{aligned}$$

and

$$\left| \iint \frac{(P^\perp \gamma' P^\perp)(x,y)\overline{P^\perp \phi(x)}\phi(y)}{|x-y|} \right| \leq 2[\mathrm{Tr}(P^\perp (\gamma')^2 P^\perp)]^{1/2} ||P^\perp \phi||.||\nabla P\phi|| \leq CZ^{3/2}.$$

Thus

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma'(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} \geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(P^\perp \gamma' P^\perp)(x,y)\overline{P\phi(x)}P\phi(y)}{|x-y|} - CZ^{2-1/8+\varepsilon/4}. \quad (19)$$

Similarly we have

$$\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\alpha'(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} \geq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(P^\perp \alpha' P^\perp)(x,y)\overline{P\phi(x)}P\phi(y)}{|x-y|} - CZ^{2-1/8+\varepsilon/4}. \quad (20)$$

Putting (18), (19), (20) together and using the fact $h_{t,Z} \geq 0$ and $h_{t,Z}P = 0$, we obtain

$$q_{t,Z}(\gamma,\alpha,\phi) \geq \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} q_{t,Z}(\gamma'',\alpha'') - CZ^{2-1/8+\varepsilon/2} \geq \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - CZ^{2-1/8+\varepsilon/4}.$$

4. In summary, from Case 1 and Case 2 we have in any case

$$q_{t,Z}(\gamma,\alpha,\phi) \geq \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - C\max\{Z^{2-\varepsilon}, Z^{2-1/8+\varepsilon/4}\}.$$

Choosing $\varepsilon = 1/10$ we obtain

$$\inf_{(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}} q_{t,Z}(\gamma,\alpha,\phi) \geq \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - CZ^{2-1/10}.$$

□

2.4 Bogoliubov ground state energy

We are now ready to give the proof of Theorem 2.2.

Proof. **Upper bound.** Fix $\varepsilon > 0$ small. Choose $(\gamma_{t,\varepsilon}, \alpha_{t,\varepsilon}) \in \mathcal{G}^{\mathrm{B}}$ such that

$$q_t(\gamma_{t,\varepsilon}, \alpha_{t,\varepsilon}) \leq \mu(t) + \varepsilon.$$

Choosing

$$\begin{aligned} \gamma(x,y) &= Z^3 \gamma_{t,\varepsilon}(Zx, Zy), \\ \alpha(x,y) &= Z^3 \alpha_{t,\varepsilon}(Zx, Zy), \\ \phi(x) &= Z^2 \phi_{t-\mathrm{Tr}(\gamma_{t,\varepsilon})/Z}(Zx) \end{aligned}$$

we have $\mathrm{Tr}(\gamma) + ||\phi||^2 = tZ$ and

$$\begin{aligned}
\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) &= Z^3 E^H_{Z=1}(\phi_{t-\mathrm{Tr}(\gamma_{t,\varepsilon})/Z}) + Z^2\left[q_t(\gamma_{t,\varepsilon},\alpha_{t,\varepsilon}) + e'(t)\,\mathrm{Tr}(\gamma_{t,\varepsilon})\right] \\
&\quad + Z\left[D(\rho_{\gamma_{t,\varepsilon}},\rho_{\gamma_{t,\varepsilon}}) + X(\gamma_{t,\varepsilon},\gamma_t) + X(\alpha_{t,\varepsilon},\alpha_{t,\varepsilon})\right] \\
&\leq Z^3 e(t - \mathrm{Tr}(\gamma_{t,\varepsilon})/Z) + Z^2[\mu(t) + e'(t)\,\mathrm{Tr}(\gamma_{t,\varepsilon})] + ZC_\varepsilon \\
&= Z^3\left[e(t) - (\mathrm{Tr}(\gamma_{t,\varepsilon})/Z)e'(t) + o(Z^{-1})\,\mathrm{Tr}\,\gamma_\varepsilon\right] \\
&\quad + Z^2\left[\mu(t) + \varepsilon + \mathrm{Tr}(\gamma_{t,\varepsilon})e'(t)\right] + ZC_\varepsilon \\
&= Z^3 e(t) + Z^2(\mu(t) + \varepsilon + o(1)C_\varepsilon).
\end{aligned}$$

Thus

$$E^{\mathrm{B}}(N,Z) \leq Z^3 e(t) + Z^2(\mu(t) + \varepsilon + o(1)C_\varepsilon).$$

Because $\varepsilon > 0$ can be chosen as small as we want, we can conclude that

$$E^{\mathrm{B}}(N,Z) \leq Z^3 e(t) + Z^2\mu(t) + o(Z^2).$$

Lower bound. It suffices to consider (γ,α,ϕ) such that $\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) \leq Z^3 e(t)$, and hence $\mathrm{Tr}[-\Delta\widetilde{\gamma}] \leq CZ^3$. We shall denote by P the one-dimensional projection onto the Hartree ground state $\phi_{t,Z}$ and $P^\perp = 1 - P$.

In the expression of $\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z)$, if we ignore the non-negative terms $X(\gamma,\gamma)$, $X(\alpha,\alpha)$ and estimate the direct term by

$$\begin{aligned}
D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}) &= 2D(\rho_{\widetilde{\gamma}},|\phi_{t,Z}|^2) - D(|\phi_{t,Z}|^2,|\phi_{t,Z}|^2) + D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, \rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2) \\
&\geq 2D(\rho_{\widetilde{\gamma}},|\phi_{t,Z}|^2) - D(|\phi_{t,Z}|^2,|\phi_{t,Z}|^2) \\
&= 2D(\rho_{\widetilde{\gamma}},|\phi_{t,Z}|^2) + Z^3 e(t) - Z^2 e'(t)\,\mathrm{Tr}(\widetilde{\gamma})
\end{aligned}$$

then we arrive at

$$\begin{aligned}
\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) &\geq Z^3 e(t) + \mathrm{Tr}(h_{t,Z}\widetilde{\gamma}) + \\
&\quad + \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} + \mathrm{Re}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\alpha(x,y)\overline{\phi(x)\phi(y)}}{|x-y|}. \quad (21)
\end{aligned}$$

By the same argument of the proof of Lemma 2.5 we have

$$\frac{1}{2}\,\mathrm{Tr}[h_{t,Z}\gamma] + \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma(x,y)\overline{\phi(x)}\phi(y)}{|x-y|} + \mathrm{Re}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\alpha(x,y)\overline{\phi(x)\phi(y)}}{|x-y|} \geq -CZ^2.$$

Putting this bound together with the gap $\mathrm{Tr}[h_{t,Z}\widetilde{\gamma}] \geq \Delta_t Z^2\,\mathrm{Tr}(P^\perp\widetilde{\gamma})$ into (21), and comparing with the upper bound $\mathcal{E}^{\mathrm{B}}(\gamma,\alpha,\phi,Z) \leq Z^3 e(t)$ we obtain $||P^\perp\phi|| \leq C$.

We are now able to apply Lemma 2.6 to conclude from (21) that

$$E^{\mathrm{B}}(\gamma,\alpha,\phi,Z) \geq Z^3 e(t) + (\phi, h_{t,Z}\phi) + \frac{\|P\phi\|^2}{||\phi_{t,Z}||^2} Z^2\mu(t) - CZ^{2-1/10}.$$

Because $\|P\phi\|^2 \leq \|\phi_{t,Z}\|^2 = tZ$, we obtain the desired lower bound. $\square$

From the above proof of the lower bound, we also obtain the following estimates on the ground state, which will be useful in the proof of the binding up to the critical number $t_c Z$.

Lemma 2.7 (Properties of Bogoliubov minimizers). *If (γ, α, ϕ) is a minimizer for $E^{\rm B}(N,Z)$ (or more generally, if $E^{\rm B}(\gamma,\alpha,\phi,Z) = Z^3 e(t) + Z^2\mu(t) + o(Z^2)$) then $\mathrm{Tr}(P^\perp \widetilde{\gamma}) \le C$, $\langle \phi, h_{t,Z}\phi\rangle = o(Z^2)$ and*

$$D(\rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2, \rho_{\widetilde{\gamma}} - |\phi_{t,Z}|^2) = o(Z^2).$$

In particular, it follows from $\langle \phi, h_{t,Z}\phi\rangle = o(Z^2)$ that $\|P\phi\|^2 = tZ + o(Z)$. Here P is the one-dimensional projection onto the Hartree ground state $\phi_{t,Z}$.

2.5 Comparison to quantum energy: a heuristic discussion

Let us discuss on the comparison between the Bogoliubov ground state energy $E^{\rm B}(N,Z)$ and the quantum energy $E(N,Z)$ in Conjecture 2.3.

First at all, due to the variational principle, the Bogoliubov energy $E^{\rm B}(N,Z)$ is a rigorous upper bound to the quantum grand canonical energy

$$E^{\rm g}(N,Z) = \inf\{(\Psi, \bigoplus_{N=0}^{\infty} H_{N,Z}\Psi), \Psi \in \mathcal{F}, ||\Psi|| = 1\}.$$

It is believed that the ground state energy $E(N,Z)$ is a convex function on N (see [13], p. 229), which is equivalent to $E^{\rm g}(N,Z) = E(N,Z)$. If this conjecture is correct then the Bogoliubov energy $E^{\rm B}(N,Z)$ is also an upper bound to the canonical energy $E(N,Z)$.

In the following, we shall argue heuristically why the Bogoliubov energy $E^{\rm B}(N,Z)$ is a lower bound to $E(N,Z)$ (up to an error $o(Z^2)$). Some further work is required to make the argument rigorous.

Choosing an orthonormal basis $\{u_n\}_{n=0}^{\infty}$ for $\mathfrak{h}$ with $u_0 = \phi_{t,Z}/||\phi_{t,Z}||$, we can represent the Hamiltonian $\mathbb{H}_Z = \bigoplus_{N=0}^{\infty} H_{N,Z}$ in the second quantization

$$\mathbb{H}_Z = \sum_{m,n\ge 0} h_{m,n} a_m^* a_n + \frac{1}{2}\sum_{m,n,p,q\ge 0} W_{m,n,p,q} a_m^* a_n^* a_p a_q$$

where $a_n = a(u_n)$ and

$$h_{m,n} = (u_m, (-\Delta - Z|x|^{-1})u_n), W_{m,n,p,q} = \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\overline{u_m(x)u_n(y)}u_p(x)u_q(y)}{|x-y|}.$$

Assume that Ψ is a ground state for $E(N,Z)$. We shall denote by $\langle \mathbb{H}_Z\rangle_\Psi$ the expectation $\langle \Psi, \mathbb{H}_Z\Psi\rangle$.

Step 1. As in [3] we have the condensation $\mathrm{Tr}(P^\perp\gamma_\Psi) \le C$ where P is the one-dimensional projection onto u_0. Let us denote $\gamma = P^\perp \gamma_\Psi P^\perp$, $\alpha = P^\perp\alpha_\Psi P^\perp$, $\mathcal{N}_0 = a_0^* a_0$ and $N_0 = \langle \mathcal{N}_0\rangle_\Psi$. Then $(\gamma,\alpha) \in \mathcal{G}^{\rm B}$ and $N - N_0 = \mathrm{Tr}(\gamma) \le C$.

Step 2. The leading term $Z^3 e(t)$ of the ground state energy $E(N,Z)$ comes from the terms of full condensation, namely $h_{00}a_0^* a_0$ and $W_{0000}a_0^* a_0^* a_0 a_0$. Similarly to the computation to the energy of product functions, we have

$$\begin{aligned}
& h_{00}\left\langle a_0^* a_0\right\rangle_\Psi + W_{0000}\left\langle a_0^* a_0^* a_0 a_0\right\rangle_\Psi \\
= \; & \left\langle u_0, \left(-\Delta - Z|x|^{-1}\right) u_0\right\rangle N_0 + \left(\left\langle \mathcal{N}_0^2\right\rangle_\Psi - N_0\right) D(|u_0|^2, |u_0|^2) \\
\geq \; & \left\langle u_0, \left(-\Delta - Z|x|^{-1}\right) u_0\right\rangle N_0 + (N_0^2 - N_0) D(|u_0|^2, |u_0|^2) \\
\geq \; & \frac{N_0 Z^3}{N_0 - 1} e\left(\frac{N_0 - 1}{Z}\right) \\
= \; & Z^3 e(t) - Z^2 e'(t)\operatorname{Tr}(\gamma) + Z^2[t^{-1}e(t) - e'(t)] + o(Z^2).
\end{aligned} \tag{22}$$

As a consequence, the expectation of the rest of the Hamiltonian $\mathbb{H}_Z$ should be of order $O(Z^2)$.

Step 3. Because almost of particles live in the condensation u_0, we may hope to eliminate all terms $W_{m,n,p,q}a_m^* a_n^* a_p a_q$ in the two-body interaction which have only 0 or 1 operator $a_0^\#$ (where $a_0^\#$ is either a_0 or a_0^*).

Step 4. Now we apply the Bogoliubov principle in which we replace any $a_0^\#$ by $\sqrt{N_0} \approx \sqrt{N}$. We can see that the terms with 1 and 3 operators $a_0^\#$ should be canceled together. In fact,

$$\begin{aligned}
& \sum_{m\geq 1} \left(h_{0m}\langle a_0^* a_m\rangle_\Psi + W_{000m}\langle a_0^* a_0^* a_0 a_m\rangle_\Psi\right) \\
\approx \; & \sum_{m\geq 1} \left(h_{0m}\langle a_0^* a_m\rangle_\Psi + W_{000m}\langle a_0^* a_m\rangle_\Psi\right) \\
= \; & \sum_{m\geq 1} \left\langle u_m, \left(-\Delta - Z|x|^{-1} + N|u_0| * |.|^{-1}\right) u_0\right\rangle \langle a_0^* a_m\rangle_\Psi = 0 \\
= \; & \sum_{m\geq 1} \left\langle u_m, Z^2 e'(t) u_0\right\rangle \langle a_0^* a_m\rangle_\Psi = 0.
\end{aligned}$$

Here we use the fact that u_0 is the ground state for the Hartree mean-field operator

$$h_{t,Z} = -\Delta - Z|x|^{-1} + |\phi_{t,Z}|^2 * |.|^{-1} - Z^2 e'(t)$$

It remains the terms with precisely 0 or 2 operators $a_0^\#$,

$$\begin{aligned}
& \sum_{m,n\geq 1} \left(h_{mn}\langle a_m^* a_n\rangle_\Psi + W_{m00n}\langle a_m^* a_0^* a_0 a_n\rangle_\Psi\right) \\
\approx \; & \sum_{m,n\geq 1} \left(h_{mn}\langle a_m^* a_n\rangle_\Psi + N W_{m00n}\langle a_m^* a_n\rangle_\Psi\right) \\
= \; & \operatorname{Tr}\left[\left(-\Delta - Z|x|^{-1} + N|u_0|^2 * |.|^{-1}\right)\gamma\right]
\end{aligned} \tag{23}$$

and

$$\begin{aligned}
&\sum_{m,n\geq 1} (W_{m0n0}\langle a_m^* a_0^* a_0 a_n\rangle_\Psi + \mathrm{Re}[W_{mn00}\langle a_m^* a_n^* a_0 a_0\rangle_\Psi]) \\
\approx &\sum_{m,n\geq 1} (NW_{m0n0}\langle a_m^* a_n\rangle_\Psi + N\,\mathrm{Re}[W_{mn00}\langle a_m^* a_n^*\rangle_\Psi]) \\
= &\ \mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\gamma(x,y)+\alpha(x,y))\phi_{t,Z}(x)\phi_{t,Z}(y)}{|x-y|}dxdy. \qquad (24)
\end{aligned}$$

Step 5. Putting the approximations (22), (23) and (24) together we obtain the desired lower bound

$$\begin{aligned}
\langle \mathbb{H}_Z\rangle_\Psi \geq\ & Z^3 e'(t) + Z^2[t^{-1}e(t) - e'(t)] \\
&+ \mathrm{Tr}[h_{t,Z}\gamma] + \mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{[\gamma(x,y)+\alpha(x,y)]\phi_t(x)\phi_t(y)}{|x-y|} + o(Z^2).
\end{aligned}$$

Because $(\gamma,\alpha)\in\mathcal{G}^{\mathrm{B}}$ and $\gamma\phi_{t,Z}=0$ one has

$$Z^2[t^{-1}e(t)-e'(t)]+\mathrm{Tr}[h_{t,Z}\gamma]+\mathrm{Re}\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3}\frac{[\gamma(x,y)+\alpha(x,y)]\phi_{t,Z}(x)\phi_{t,Z}(y)}{|x-y|}\geq Z^2\mu(t).$$

Thus we arrive at the desired lower bound

$$\langle \mathbb{H}_Z\rangle_\Psi \geq Z^3 e'(t) + Z^2\mu(t) + o(Z^2).$$

Appendix

Proof of Lemma 1.1. It is obvious that $\Gamma\geq 0$ if and only if $\gamma\geq 0$, $\alpha^* = J\alpha J$ and

$$\langle f\oplus Jg, \Gamma f\oplus Jg\rangle = (f,\gamma f) + (g,(1+\gamma)g) + 2\,\mathrm{Re}(\alpha Jf, g)\geq 0,\ \forall f,g\in\mathfrak{h}.$$

Using a simple scaling $g = tg$, $t\in\mathbb{C}$, we can see that the latter inequality is equivalent to

$$(f,\gamma f)(g,(1+\gamma)g)\geq |(\alpha Jf,g)|^2,\ \forall f,g\in\mathfrak{h}.$$

Replacing g by $(1+\gamma)^{-1}g$, we can rewrite the latter inequality as

$$(f,\gamma f)(g,(1+\gamma)^{-1}g)\geq |(\alpha Jf,(1+\gamma)^{-1}g)|^2,\ \forall f,g\in\mathfrak{h}. \qquad (25)$$

Note that (2) follows from (25) by choosing $g=\alpha Jf$. Reversely, we can see that (2) implies (25) by using the Cauchy-Schwarz inequality for the positive definite quadratic form $Q(u,v) = (u,(1+\gamma)^{-1}v)$, i.e.

$$(f,\gamma f)(g,(1+\gamma)^{-1}g)\geq (\alpha Jf,(1+\lambda)^{-1}\alpha Jf)(g,(1+\gamma)^{-1}g)\geq \left|(\alpha Jf,(1+\gamma)^{-1}g)\right|^2.$$

$\square$

Proof of Theorem 1.2. The proof below follows [19] Theorem 9.5 (sufficiency) and [16] Theorem 6.1 (necessity).

Sufficiency. Assume that VV^* is trace class on $\mathfrak{h}$. We shall construct the unitary $\mathbb{U}_{\mathcal{V}}$.

1. Let $\{u_i\}_{i\geq 1}$ be an orthonormal basis for $\mathfrak{h}$. Recall that an orthonormal basis for $\mathcal{F}^{B,F}(\mathfrak{h})$ is given by

$$|n_{i_1},...,n_{i_M}\rangle = (n_{i_1}!...n_{i_M}!)^{-1/2}\, a^*(u_{i_M})^{n_{i_M}}...a^*(u_{i_1})^{n_{i_1}}\, |0\rangle\,,$$

where n_j run over $0,1,2,...$ such that there are only finite $n_j > 0$.

We start by constructing the new vacuum $|0\rangle_{\mathcal{V}} = \mathbb{U}_{\mathcal{V}}\,|0\rangle$ which is characterized by

$$A(\mathcal{V}(u_i \oplus 0))\,|0\rangle_{\mathcal{V}} = 0.$$

for all $i = 1,2,...$, namely

$$A(\mathcal{V}(u_i \oplus 0)) = A(Uu_i \oplus JVJu_i) = a(Uu_i) + a^*(VJu_i)$$

are the new annihilation operators.

2. The first step is to choose an convenient basis $\{u_i\}$. From $\mathcal{V}^*\mathcal{S}\mathcal{V} = \mathcal{S} = \mathcal{V}\mathcal{S}\mathcal{V}^*$ we have

$$UU^* = 1 + VV^*,\ U^*U = 1 + J^*V^*VJ$$

and $C = C^*$ where $C = U^*VJ$. Since $U^*U - 1$ is trace class, U^*U has an orthonormal eigenbasis on $\mathfrak{h}$. On the other hand, because U^*U commutes with the conjugate linear map $C = U^*J^*V$ and C^*C is trace class on $\mathfrak{h}$, we can find an orthonormal basis $\{u_i\}_{i\geq 1}$ for $\mathfrak{h}$ consisting of eigenvectors of U^*U such that they are also eigenvectors of C.

Denote $\mu_i := ||Uu_i|| \geq 1$ and $f_i := \mu_i^{-1}Uu_i$. Then $\{f_i\}_{i\geq 1}$ is an orthonormal basis for $\mathfrak{h}$. Since

$$(f_j, VJu_i) = \mu_j^{-1}(Uu_j, VJu_i) = \mu_j^{-1}(u_j, Cu_i) = 0$$

for all $j \neq i$, we must have $VJu_i \in \mathrm{Span}\{f_i\}$. Note that if we change u_i's by complex phases then it still holds that $(u_j, Cu_i) = 0$ for all $i \neq j$ (although u_i's maybe no longer eigenvectors of C). Therefore, we can change u_i's by complex phases to obtain $VJu_i = \nu_i f_i$ for some $\nu_i \geq 0$. Thus there is an orthonormal basis $\{f_i\}_{i\geq 1}$ for $\mathfrak{h}$ such that the new annihilation operators are

$$A(\mathcal{V}(u_i \oplus 0)) = \mu_i a(f_i) + \nu_i a^*(f_i),\ i = 1,2,...$$

where $\mu_i \geq 1$, $\nu_i \geq 0$, $\mu_i^2 - \nu_i^2 = 1$ and $\sum_{i=1}\nu_i^2 = \mathrm{Tr}(VV^*) < \infty$.

3. This representation allows us to construct the new vacuum $|0\rangle_{\mathcal{V}}$ explicitly

$$\begin{aligned} |0\rangle_{\mathcal{V}} &= \lim_{M\to\infty}\prod_{j=1}^{M}(1-(\nu_j/\mu_j)^2)^{1/4}\left[\sum_{n=0}^{\infty}\left(-\frac{\nu_j}{2\mu_j}\right)^n \frac{a^*(f_j)^{2n}}{n!}\right]|0\rangle \\ &= \prod_{j=1}(1-(\nu_j/\mu_j)^2)^{1/4}\exp\left[-\sum_{i=1}\frac{\nu_i}{2\mu_i}a^*(f_i)^2\right]|0\rangle\,. \end{aligned}$$

It is straightforward to check that $|0\rangle_{\mathcal{V}}$ is well defined and is annihilated by the new annihilation operators $A(\mathcal{V}(u_i \oplus 0))$. Having the new vacuum $|0\rangle_{\mathcal{V}}$, we can define $|n_{i_1}, ..., n_{i_M}\rangle_{\mathcal{V}} = \mathbb{U}\,|n_{i_1}, ..., n_{i_M}\rangle$ by

$$|n_{i_1}, ..., n_{i_M}\rangle_{\mathcal{V}} = (n_{i_1}!...n_{i_M}!)^{-1/2} A^*(\mathcal{V}(u_{i_M} \oplus 0))^{n_{i_M}} ... A^*(\mathcal{V}(u_{i_1} \oplus 0))^{n_{i_1}}\,|0\rangle_{\mathcal{V}}\,.$$

4. Finally we need to prove that the new vectors $|n_{i_1}, ..., n_{i_M}\rangle_{\mathcal{V}}$ indeed form a basis for $\mathcal{F}$. The trick is to use the formula

$$|0\rangle = \prod_{j=1} (1 - (\nu_j/\mu_j)^2)^{-1/4} \exp\left[\sum_{i=1} \frac{\nu_j}{2\mu_j} a_+^*(f_i)^2\right] |0\rangle_{\mathcal{V}}\,,$$

and express the old basis vectors $|n_{i_1}, ..., n_{i_M}\rangle$ in terms of the new ones. Since the new vectors $|n_{i_1}, ..., n_{i_M}\rangle_{\mathcal{V}}$ span all of the old basis vectors $|n_{i_1}, ..., n_{i_M}\rangle$, the new ones also span the whole Fock space $\mathcal{F}$.

Necessity. Assume that there exists a normalized vector $|0\rangle_{\mathcal{V}} \in \mathcal{F}$ such that $A(V(u \oplus 0))\,|0\rangle_{\mathcal{V}} = 0$ for all $u \in \mathfrak{h}$. We shall prove that VV^* must be trace class on $\mathfrak{h}$.

5. Let $|0\rangle_{\mathcal{V}} = \bigoplus_{N=0}^{\infty} \Psi_N$ where $\Psi_N \in \bigotimes_{\text{sym}}^N \mathfrak{h}$. Then the condition $A(V(u \oplus 0))\,|0\rangle_{\mathcal{V}} = 0$ is equivalent to

$$a(Uu)\Psi_1 = 0 \text{ and } \ a(Uu)\Psi_{N+2} + a^*(VJu)\Psi_N = 0 \text{ for all } u \in \mathfrak{h}, N = 0, 1, 2, ... \tag{26}$$

Since $UU^* = 1 + VV^* \geq 1$ we have $\mathrm{Ker}(U^*) = \{0\}$, and hence $\overline{\mathrm{Ran}(U)} = \mathfrak{h}$. Therefore, it follows from $a(Uu)\Psi_1 = 0$ for all $u \in \mathfrak{h}$ that $\Psi_1 = 0$. Then, by induction using (26) we obtain $\Psi_1 = \Psi_3 = \Psi_5 = ... = 0$.

If $\Psi_0 = 0$ then the same argument deduces $\Psi_0 = \Psi_2 = \Psi_4 = ... = 0$ which contradicts with $|0\rangle_{\mathcal{V}} \neq 0$. Thus $\Psi_0 \in \mathbb{C}\backslash\{0\}$ and from (26) with $N = 0$ we have

$$a(Uu)\Psi_2 + \Psi_0 VJu = 0 \text{ for all } u \in \mathfrak{h}. \tag{27}$$

6. Introducing the conjugate linear map $H : \mathfrak{h} \to \mathfrak{h}$ defined by

$$(H\varphi_1, \varphi_2) = (\Psi_2, \varphi_1 \otimes \varphi_2) \text{ for all } \varphi_1, \varphi_2 \in \mathfrak{h}.$$

A straightforward computation shows that $\mathrm{Tr}(H^*H) = \|\Psi_2\|^2$. Moreover using (27) and the symmetry of Ψ_2 we have

$$\begin{aligned}(-\Psi_0 VJ\varphi_1, \varphi_2) &= (a(U\varphi_1)\Psi_2, \varphi_2) = (\Psi_2, a^*(U\varphi_1)\varphi_2,) \\ &= \sqrt{2}(\Psi_2, U\varphi_1 \otimes \varphi_2) = \sqrt{2}(HU\varphi_1, \varphi_2)\end{aligned}$$

for all $\varphi_1, \varphi_2 \in \mathfrak{h}$. This means $-\Psi_0 VJ = HU$. Because U is bounded and H^*H is trace class on $\mathfrak{h}$, we conclude that

$$VV^* = 2\Psi_0^{-2} HUU^*H^*$$

is trace class on $\mathfrak{h}$. $\square$

The rest part of proof of Theorem 1.6. We now prove that Γ is the 1-pdm of the state $\rho = \mathrm{Tr}[G]^{-1}G$. Recall that $\mathcal{F}$ has the orthonormal basis

$$|n_1, n_2, ...\rangle = (n_1!n_2!...)^{-1/2}(a_1^*)^{n_1}(a_2^*)^{n_2}... |0\rangle$$

where $|0\rangle$ is the vacuum and $n_1, n_2...$ run over $0, 1, 2, ...$ such that there are only finite $n_j > 0$. A straightforward computation shows that

$$\begin{aligned}
\mathrm{Tr}(G) &= \sum_{n_j=0,1,2,...} \langle n_1, n_2, ...| G |n_1, n_2, ...\rangle \\
&= \sum_{n_j=0,1,...;j\in I} (n_1!n_2!...)^{-1} \langle 0| \prod_{i\in I} (a_i^{n_i} \exp[-\lambda_i a_i^* a_i](a_i^*)^{n_i}) |0\rangle \\
&= \sum_{n_j=0,1,...;j\in I} (n_1!n_2!...)^{-1} \langle 0| \prod_{i\in I} \left(a_i^{n_i} \sum_{k=0}^{\infty} \frac{(-\lambda_i)^k (a_i^* a_i)^k}{k!} (a_i^*)^{n_i} \right) |0\rangle \\
&= \sum_{n_j=0,1,...;j\in I} (n_1!n_2!...)^{-1} \langle 0| \prod_{i\in I} \left(\sum_{k=0}^{\infty} \frac{(-e_i)^k (n_i)^k (n_i!)}{k!} \right) |0\rangle \\
&= \sum_{n_j=0,1,...;j\in I} \prod_{i} e^{-\lambda_i n_i} = \prod_{i\in I} \frac{1}{1-e^{-\lambda_i}} < \infty
\end{aligned}$$

since $\sum_{i\in I} e^{-\lambda_i} < \infty$. Thus ρ is well-defined.

We check that Γ is indeed the 1-pdm of ρ. Note that $|n_1, n_2, ...\rangle$ and $G|n_1, n_2, ...\rangle$ have the same number of particle u_i for any $i = 1, 2, ...$ By the same way of determining $\mathrm{Tr}(G)$ we find that $\mathrm{Tr}(a_i a_j G) = 0$ and

$$\begin{aligned}
& \mathrm{Tr}(a_i^* a_j G) = \delta_{ij}\, \mathrm{Tr}(a_i^* a_i G) \\
= \; & \delta_{ij} \left(\prod_{k\in \mathrm{I}, k\neq i} (1+\lambda_k) \right) \left(\sum_{n_i=0}^{\infty} (n_i!)^{-1} \langle 0| a_i^{n_i} a_i^* a_i \exp(-c_i a_i^* a_i)(a_i^*)^{n_i} |0\rangle \right) \\
= \; & \delta_{ij} \left(\prod_{k\in \mathrm{I}, k\neq i} (1+\lambda_k) \right) \left(\sum_{n_i=0}^{\infty} (n_i!)^{-1} \langle 0| a_i^{n_i} a_i^* a_i \sum_{r=0}^{\infty} \frac{(-c_i)^r (a_i^* a_i)^r}{r!} (a_i^*)^{n_i} |0\rangle \right) \\
= \; & \delta_{ij} \left(\prod_{k\in \mathrm{I}, k\neq i} (1+\lambda_k) \right) \left(\sum_{n_i=0}^{\infty} (n_i!)^{-1} \langle 0| \sum_{r=0}^{\infty} \frac{(-c_i)^r (n_i)^{r+1} (n_i!)}{r!} |0\rangle \right) \\
= \; & \delta_{ij} \left(\prod_{k\in \mathrm{I}, k\neq i} (1+\lambda_k) \right) \left(\sum_{n_i=0}^{\infty} \exp(-c_i n_i) n_i \right) = \delta_{ij}\lambda_i \prod_{k\in \mathrm{I}} (1+\lambda_k)
\end{aligned}$$

in which we have used

$$\begin{aligned}
\sum_{n_i=0}^{\infty} \exp(-c_i n_i) n_i &= -\frac{d}{dc_i} \sum_{n_i=0}^{\infty} \exp(-c_i n_i) = -\frac{d}{dc_i} \frac{1}{1-\exp(-c_i)} \\
&= \frac{\exp(-c_i)}{(1-\exp(-c_i))^2} = \lambda_i(1+\lambda_i).
\end{aligned}$$

From the above computations we find that

$$\rho(a_i a_j) = (\mathrm{Tr}(G))^{-1}\,\mathrm{Tr}(a_i a_j G) = 0 = (u_i, \alpha J u_j)$$

and

$$\rho(a_i^* a_j) = (\mathrm{Tr}(G))^{-1}\,\mathrm{Tr}(a_i^* a_j G) = \delta_{ij}\lambda_i = (u_i, \gamma u_j)$$

for any i, j. Thus Γ is indeed the 1-pdm of ρ.

3. Finally, we check that ρ is a quasi-free state. One way to do it is to consider ρ as a limit of appropriate Gibbs states, see [4] (eq. (2b.34)). In the following, we shall give a more direct approach by mimicking the proof of Wick's Theorem in [9].

It suffices to prove (6)-(7) when $A(F_i)$ is either a creation or annihilation operator, which we denote by c_i. Our aim is to show that

$$\begin{aligned}\mathrm{Tr}[c_1c_2c_3c_4...c_kG] &= \frac{\mathrm{Tr}[c_1c_2G]}{\mathrm{Tr}[G]}\mathrm{Tr}[c_3c_4...c_kG] \\ &+\frac{\mathrm{Tr}[c_1c_3G]}{\mathrm{Tr}[G]}\mathrm{Tr}[c_2c_4...c_kG] + ... + \frac{\mathrm{Tr}[c_1c_kG]}{\mathrm{Tr}[G]}\mathrm{Tr}[c_2c_3...c_{k-1}G]\end{aligned} \tag{28}$$

and the result follows immediately by a simple induction. By the same way of computating $\mathrm{Tr}[G]$ we may check that

$$\frac{\mathrm{Tr}[c_1c_2G]}{\mathrm{Tr}[G]} = f(c_1)[c_1, c_2] \tag{29}$$

where $[c_1, c_2] = c_1c_2 - c_2c_1 \in \{0, -1, 1\}$ and

$$f(c_1) = \begin{cases} (1-e^{-\lambda_j})^{-1} \text{ if } c_1 = a_j,\ j \in I, \\ (1-e^{\lambda_j})^{-1} \text{ if } c_1 = a_j^*,\ j \in I, \\ 1 \text{ if } c_1 = a_j,\ j \notin I, \\ 0 \text{ if } c_1 = a_j^*,\ j \notin I. \end{cases} \tag{30}$$

Thus (28) is equivalent to

$$\begin{aligned}\mathrm{Tr}[c_1c_2c_3c_4...c_kG] &= f(c_1)[c_1,c_2]\mathrm{Tr}[c_3c_4...c_kG] \\ &+ f(c_1)[c_1,c_3]\mathrm{Tr}[c_2c_4...c_kG] + ... + f(c_1)[c_1,c_k]\mathrm{Tr}[c_2c_3...c_{k-1}G].\end{aligned} \tag{31}$$

We can prove (31) as follows. From the identity

$$c_1c_2c_3c_4...c_k = [c_1,c_2]c_3c_4...c_k + ... + c_2c_4...c_{k-1}[c_1,c_k] + c_2c_3c_4...c_kc_1$$

we deduce that

$$\begin{aligned}\mathrm{Tr}\,[c_1c_2c_3c_4...c_kG] &= \mathrm{Tr}\,[[c_1,c_2]c_3c_4...c_kG] \\ &+ ... + \mathrm{Tr}\,[c_2c_4...c_{k-1}[c_1,c_k]G] + \mathrm{Tr}\,[c_2c_3c_4...c_kc_1G]\,.\end{aligned} \tag{32}$$

We first consider when c_1 is either a_j or a_j^* with $j \in I$. In this case it is straightforward to see that $c_1 G = e^{\pm\lambda_j} c_1 G$ where (+) if $c_1 = a_j^*$ and (-) if $c_1 = a_j$. This implies that

$$\mathrm{Tr}\,[c_2 c_3 c_4 ... c_k c_1 G] = e^{\pm\lambda_j}\,\mathrm{Tr}\,[c_2 c_3 c_4 ... c_k G c_1] = e^{\pm\lambda_j}\,\mathrm{Tr}\,[c_1 c_2 c_3 c_4 ... c_k G]\,. \qquad (33)$$

Substituting (33) into (33) we conclude that

$$\begin{aligned}\mathrm{Tr}\,[c_1 c_2 c_3 c_4 ... c_k G] &= \frac{[c_1, c_2]}{1 - e^{\pm\lambda_j}}\mathrm{Tr}\,[c_3 c_4 ... c_k G] \\ &+ \frac{[c_1, c_3]}{1 - e^{\pm\lambda_j}}\mathrm{Tr}\,[c_2 c_4 ... c_k G] + ... + \frac{[c_1, c_k]}{1 - e^{\pm\lambda_j}}\mathrm{Tr}\,[c_2 c_4 ... c_{k-1} G]\end{aligned}$$

which is precisely the desired identity (31).

If $c_1 = a_j$ for some $j \notin I$ then

$$\mathrm{Tr}[c_2 c_3 c_4 ... c_k c_1 G] = 0$$

since $a_j G = 0$ and (31) follows from (33).

Finally if $c_1 = a_j^*$ for some $j \notin I$ then

$$\mathrm{Tr}[c_1 c_2 c_3 c_4 ... c_k G] = \mathrm{Tr}[c_2 c_3 c_4 ... c_k G c_1] = 0$$

since $G a_j^* = 0$ and we obtain (31). □

Acknowledgments: I thank my advisor Jan Philip Solovej for giving me the problem and various helpful discussions.

References

[1] V. Bach, Ionization energies of bosonic coulomb systems, *Lett. Math. Phys.*, **21**, 139-149 (1991).

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

[3] V. Bach, R. Lewis, E.H. Lieb and H. Siedentop, On the number of bound states of a bosonic N-particle Coulomb system, *Math. Z.* **214**, 441-460 (1993)

[4] V. Bach, E.H. Lieb and J.P. Solovej, Generalized Hartree-Fock theory and the Hubbard model, *J. Stat. Phys.* Vol. 76, No. 1-2, 3-89 (1994)

[5] B. Baumgartner, On the Thomas-Fermi-von Weizäcker and Hartree energies as functions of the degree of ionization, *J. Phys. A* **17**, 1593-1602 (1984).

[6] R. Benguria and E.H. Lieb, Proof of stability of highly negative ions in the absence of the Pauli principle, *Phys. Rev. Lett.* **50**, 1771-1774 (1983).

[7] F.J. Dyson, Ground State Energy of a Finite System of Charged Particles. *J. Math. Phys.* **8**, 1538–1545 (1967).

[8] R. L. Frank, E. H. Lieb, R. Seiringer, and H. Siedentop, Müller exchange-correlation energy in density-matrix-functional theory, *Phys. Rev. A* **76**, 052517 (2007).

[9] M. Gaudin, Une démonstartion simpliflée du théorème de Wick en méchanique statistique. *Nucl. Phys.* **15** (1960)

[10] E. Lenzmann and M. Lewin, Minimizers for the Hartree-Fock-Bogoliubov theory of neutron stars and white dwarfs, *Duke Math. Journal*, **152**, no. 2, 257–315 (2010).

[11] E.H. Lieb, Thomas-Fermi and related theories of atoms and molecules, *Rev. Mod. Phys.* **53**, 603-641 (1981).

[12] E.H. Lieb and M. Loss, *Analysis*, 2nd Ed., AMS., Providence, Rhode Island (2001).

[13] E. H. Lieb and R. Seiringer, The stability of matter in quantum mechanics, Cambridge University Press, 2009.

[14] E.H. Lieb and J.P. Solovej, Ground State Energy of the Two-Component Charged Bose Gas. *Commun. Math. Phys.* **252**, 485–534 (2004)

[15] E.H. Lieb and H.-T. Yau, The Chandrasekhar theory of stellar collapse as the limit of quantum mechanics, *Commun. Math. Phys.* 112 (1987), 147-174.

[16] S.N.M. Ruijsenaars, On Bogoliubov transformations for systems of relativistic charged particles, *J. Math. Phys.*, vol. 18, No. 3 (1977).

[17] J.P. Solovej, Asymptotics for bosonic atoms, *Lett. Math. Phys.* **20**, 165-172 (1990)

[18] J.P. Solovej, Upper Bounds to the Ground State Energies of the One- and Two-Component Charged Bose Gases, *Commun. Math. Phys.* **266**, 797–818 (2006)

[19] J.P. Solovej, Many body quantum mechanics, Lectures notes at LMU Münich, 2007. Online available at `http://www.mathematik.uni-muenchen.de/~lerdos/WS08/QM/solovejnotes.pdf`