Letters in Mathematical Physics (2023) 113:11
https://doi.org/10.1007/s11005-023-01631-9

The Scott conjecture for large Coulomb systems: a review

Rupert L. Frank[1,2,3] · **Konstantin Merz**[4,5] · **Heinz Siedentop**[1,2]

Received: 14 June 2022 / Revised: 14 December 2022 / Accepted: 5 January 2023

Abstract
We review some older and more recent results concerning the energy and particle distribution in ground states of heavy Coulomb systems. The reviewed results are asymptotic in nature: they describe properties of many-particle systems in the limit of a large number of particles. Particular emphasis is put on models that take relativistic kinematics into account. While non-relativistic models are typically rather well understood, this is generally not the case for relativistic ones and leads to a variety of open questions.

Keywords Large Coulomb systems · Ground state energy · Ground state density · Relativistic Coulomb system · Thomas–Fermi theory · Scott conjecture

Mathematics Subject Classification 81V45 · 35Q40 · 46N50

This article belongs to the themed collection: Mathematical Physics and Numerical Simulation of Many-Particle Systems; V. Bach and L. Delle Site (eds.).

✉ Konstantin Merz
k.merz@tu-bs.de

Rupert L. Frank
r.frank@lmu.de

Heinz Siedentop
h.s@lmu.de

1 Mathematisches Institut, Ludwig-Maximilans Universität München, Theresienstr. 39, 80333 Munich, Germany

2 Munich Center for Quantum Science and Technology (MCQST), Schellingstr. 4, 80799 Munich, Germany

3 Mathematics 253-37, Caltech, Pasadena, CA 91125, USA

4 Institut für Analysis und Algebra, Technische Universität Braunschweig, Universitätsplatz 2, 38106 Braunschweig, Germany

5 Department of Mathematics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Published online: 19 January 2023

Contents

1 Introduction and historical background

1.1 Many-particle quantum mechanics

Properties of ground states of large Coulomb systems involving N electrons, such as atoms or molecules, are of fundamental interest in quantum physics and chemistry. Notable examples are the *ground state energy* and the electron distribution in the ground state. The latter may be expressed in terms of the *one-particle ground state density*, i.e., the probability density of finding one of the N electrons at a specific location in $\mathbb{R}^3$. It is well known that systems on atomic length scales are accurately described by quantum mechanics [105, 106]. This understanding relies on precise investigations of the underlying Hamilton operator.

We consider a molecule that consists of K point-like nuclei of charges $\underline{Z} = (Z_1, \dots, Z_K) \in (0, \infty)^K$, fixed at pairwise different positions $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, as well as N electrons, all interacting via Coulomb potentials in the Born–Oppenheimer approximation. The total nuclear charge is $|\underline{Z}| := \sum_{\kappa=1}^K Z_\kappa$. The number of spin degrees of freedom is denoted by $q \in \mathbb{N}$. Although in reality $q = 2$, one may, for notational convenience, choose $q = 1$ when the spin-dependence is trivial.

A non-relativistic quantum mechanical description of this system is provided by the operator:

$$H_{N,V} := \sum_{\nu=1}^{N} \left(-\frac{1}{2}\Delta_\nu - V(x_\nu) \right) + \sum_{1\le\nu<\mu\le N} \frac{1}{|x_\nu - x_\mu|} + U \quad \text{in} \quad \bigwedge_{\nu=1}^{N} L^2(\mathbb{R}^3 : \mathbb{C}^q) \tag{1.1}$$

with

$$V(x) = \sum_{\kappa=1}^{K} \frac{Z_\kappa}{|x - R_\kappa|} \tag{1.2}$$

and

$$U = \sum_{1\le\kappa<\kappa'\le K} \frac{Z_\kappa Z_{\kappa'}}{|R_\kappa - R_{\kappa'}|}. \tag{1.3}$$

We choose Hartree units, so that $\hbar = e = m = 1$, where $\hbar$, e, and m denote the rationalized Planck constant, the elementary charge, and the electron mass, respectively. In the atomic case ($K = 1, \underline{R} = 0, \underline{Z} = Z$), we have $U = 0$ and write $H_{N,Z} := H_{N,Z/|x|}$.

Since electrons are fermions, they obey the Pauli exclusion principle, i.e., the Hilbert space in which the operator (1.1) acts is given by $\bigwedge_{\nu=1}^{N} L^2(\mathbb{R}^3 : \mathbb{C}^q)$, i.e., the subspace of $L^2(\mathbb{R}^{3N} : \mathbb{C}^{q^N})$ consisting of all square-integrable, $\mathbb{C}^{q^N}$-valued functions whose sign changes under the exchange of any two particle coordinates.

We write

$$E^{\mathrm{S}}(N, \underline{Z}, \underline{R}) := \inf \operatorname{spec}(H_{N,V}) \tag{1.4}$$

for the lowest spectral point of the Hamiltonian $H_{N,V}$. This number $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ may or may not be an eigenvalue, and, if it is, it may be degenerate. While the results in this review concern (1.4), there is an important, related quantity, which has not received the mathematical attention it deserves; see (5.1) below.

In the atomic case ($K = 1, \underline{R} = 0, \underline{Z} = Z$), we write $E^{\mathrm{S}}(N, Z) := E^{\mathrm{S}}(N, Z, \underline{0})$ and, for neutral atoms, $E^{\mathrm{S}}(Z) := E^{\mathrm{S}}(Z, Z, 0)$. It is well known that $E^{\mathrm{S}}(N, Z)$ is an eigenvalue when $N < Z + 1$, see Zhislin [251] or Simon [215].

In addition to ground state energies, we will be interested in one-particle ground state densities. We recall that the one-particle density of a general (pure) state $\psi \in \bigwedge_{\nu=1}^{N} L^2(\mathbb{R}^3 : \mathbb{C}^q)$ is defined by

$$\rho(x) := N \sum_{\sigma=1}^{q} \int_{\Gamma^{N-1}} |\psi(x, \sigma; y_2, \ldots, y_N)|^2 \, \mathrm{d}y_2 \cdots \mathrm{d}y_N \tag{1.5}$$

for $x \in \mathbb{R}^3$. Here $\Gamma := \mathbb{R}^3 \times \{1, 2, \ldots, q\}$. Elements $y \in \Gamma$ are space-spin variables and the corresponding measure $\mathrm{d}y$ is the product measure consisting of Lebesgue measure on $\mathbb{R}^3$ and counting measure on $\{1, \ldots, q\}$.

If ψ in (1.5) is an eigenfunction of $H_{N,V}$ with eigenvalue $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$, we write

$$\rho_{\mathrm{S}} \tag{1.6}$$

for its density and analogously for other Hamiltonians that we discuss later. Although this might be an abuse of notation since the eigenvalue $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ could be degenerate, our statements about ρ_{S} will be true for any choice of an eigenfunction. The notion of a one-particle density and, in particular, of a one-particle ground state density can be generalized to the case of mixed states, but we do not do this here. Also, if the lowest point in the spectrum $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ is not an eigenvalue, one can still obtain meaningful statements for so-called approximate ground states, but we will not discuss these in this introduction.

The goal of this review is to summarize known results and open questions concerning the ground state energy and the one-particle ground state density in the limit of large electron numbers and nuclear charges for non-relativistic and, especially, for certain relativistic descriptions of Coulomb systems. In the rest of this introduction, we will focus on results for non-relativistic atoms. This and other settings will be treated in more detail in later sections, see the table of contents and Sect. 1.6 for relevant pointers.

Remark 1.1 Some remarks on our goals are in order.

(1) It is well known that the spectral analysis of N-particle systems *for fixed* N is prohibitively difficult already when $N \geq 2$, since the $\mathcal{O}(N^2)$ many interparticle interactions prohibit a reduction to a three-dimensional (possibly) soluble one-particle problem. (For instance, if the electron–electron repulsion was absent and $K = 1$ in $H_{N,V}$, then one could separate variables to end up with the direct sum of Schrödinger operators describing hydrogen.) Instead, one often considers the properties of a system for a large number of particles. This leads to the study of *asymptotic properties*. In this review, we entirely focus on results in the limit $Z_1, \dots, Z_K, N \to \infty$. The precise way of carrying out this limit when $K > 1$ is explained later.

(2) Studying asymptotics clearly leads to less quantitative mathematical statements and is also questionable from a physical point of view since experimentally observed values of Z are bounded, e.g., by 92 for stable atoms. However, the mathematical analysis is drastically simpler and, interestingly, leads to theorems that coincide astonishingly well with experimentally measured data. (This observation has been made repeatedly in different contexts in mathematical physics. Stell [228, p. 48] calls it the *principle of unreasonable utility of asymptotic expansions* and makes some interesting philosophical remarks.)

(3) There are some notable exceptions, however.

   (a) For instance, recently much progress has been made in the investigation of smoothness properties of single eigenfunctions and sums of squares of eigenfunctions of many-particle Coulomb Hamiltonians, such as $H_{N,Z}$, for fixed N. In this regard see, e.g., the works [75–78, 81] for non-relativistic and [80] for (pseudorelativistic) Chandrasekhar atoms. Such a priori estimates for many-particle eigenfunctions are important, e.g., for the derivation of eigenvalue asymptotics for the associated one-particle density matrix [220] and the one-particle kinetic energy density matrix [221].

   (b) Another example concerns the maximal ionization of atoms (and molecules). Experiments indicate that doubly or higher charged anions do not exist (Massey

[164, 165]), i.e., one expects at most $Z+1$ many electrons to be bound to the nucleus, while any further electrons are located infinitely far away with vanishingly small kinetic energy. Proving this claim is a notoriously difficult problem in mathematical physics, see, e.g., Nam [179, 180] for recent reviews. A slightly weaker formulation, the so-called *ionization conjecture*, states that there is a number $Q < \infty$ such that, if $E^{\mathrm{S}}(N, Z)$ is an eigenvalue, then $N \leq Z + Q$. Two well-known results in this direction are due to Lieb [145] and Fefferman and Seco [66, 67], who proved that $N < 2Z+1$ and $N \leq Z + CZ^{\frac{47}{56}}$, respectively, are necessary conditions for $E^{\mathrm{S}}(N, Z)$ to be an eigenvalue. Recently, Nam [178] improved Lieb's result and showed $N < 1.22Z + 3Z^{\frac{1}{3}}$, which leads to a sharper result when $Z \geq 6$. Lieb's result implies the fact that doubly negatively charged hydrogen atoms do not exist.

1.2 Glimpse at Thomas–Fermi density functional theories

The N particle quantum Coulomb problem of computing $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ and the associated eigenspace is—like its classical analogue, the Kepler problem—prohibitively difficult to solve (even numerically) already for $N \geq 2$ because of the $\mathcal{O}(N^2)$ many interactions between the N electrons. This necessitates the derivation of so-called effective theories, i.e., energy functionals or equations, which depend only on a fixed, but small number of variables, like three or six, and describe at least the macroscopically observed properties of the given system "sufficiently accurately". Although these theories are usually more accessible to numerical analysis, they also pose some interesting mathematical challenges in view of the presence of nonlinearities, which simulate the interparticle interactions. Here we focus on so-called *density functional theories*, i.e., energy functionals, that only depend on the one-particle density.

Remark 1.2 We chose to bypass density *matrix* functionals (e.g., due to Hartree [102, 103], Fock [73], Slater [218], Müller [175], and Sharma et al. [201]), as it would go far beyond the scope of this review. In addition to referring to [206], we highlight pioneering works by Lieb and Simon [150, 151], Bach [3, 4], Graf and Solovej [97], as well as the works [84], [203, 204], and Kehle [131].

For simplicity, assume from now on the neutral, atomic case ($K = 1$, $\underline{R} = 0$, $\underline{Z} = Z = N$). The breakthrough in the description of ground state properties of $H_{N,V}$ came with the help of a particularly simple density functional theory, the so-called Thomas–Fermi theory [71, 72, 235], which will be reviewed in Sect. 2.1. In their seminal work [152], Lieb and Simon connected Thomas–Fermi theory to the quantum problem of finding $E^{\mathrm{S}}(Z)$ and showed that the Thomas–Fermi energy $E^{\mathrm{TF}}(Z)$, i.e., the infimum of the Thomas–Fermi functional $\mathcal{E}^{\mathrm{TF}}_Z$ (Lenz [138]), is the leading term of the asymptotic expansion of $E^{\mathrm{S}}(Z)$ when $Z \to \infty$. The Thomas–Fermi energy scales like $E^{\mathrm{TF}}(Z) = E^{\mathrm{TF}}(1) \cdot Z^{7/3}$, which is a consequence of

$$\mathcal{E}^{\mathrm{TF}}_Z[Z^2\rho(Z^{1/3}\cdot)] = Z^{7/3}\mathcal{E}^{\mathrm{TF}}_Z[\rho].$$

Thus, the result of Lieb and Simon for the ground state energy reads

$$E^{\mathrm{S}}(Z) = E^{\mathrm{TF}}(1) \cdot Z^{7/3} + o(Z^{7/3}) \quad \text{as } Z \to \infty, \tag{1.7}$$

see also Theorem 3.1. A numerical computation shows that $E^{\mathrm{TF}}(1) \approx -0.484\,29 \cdot q^{2/3}$, cf. Gombás [94, p. 60].

Figuratively speaking, the leading order in (1.7) is generated by the bulk of the electrons, which are located on distances $\mathcal{O}(Z^{-1/3})$ from the nucleus and are described semiclassically. It should not come as a surprise that this energetic result is accompanied by a result connecting the quantum ground state density ρ_{S} with the minimizer of $\mathcal{E}^{\mathrm{TF}}_Z$, the Thomas–Fermi density ρ^{TF}_Z. Indeed, Lieb and Simon [152], and Baumgartner [12] showed that the suitably rescaled ground state density ρ_{S} converges to the minimizer of the Thomas–Fermi theory for hydrogen. More precisely, one has, due to the scaling properties of Thomas–Fermi theory, the convergence

$$\lim_{Z\to\infty} Z^{-2}\rho_{\mathrm{S}}(Z^{-1/3}\,\cdot\,) = \rho^{\mathrm{TF}}_{Z=1} \tag{1.8}$$

when both sides are integrated against characteristic functions of bounded, measurable subsets of $\mathbb{R}^3$. In the context of the ionization conjecture, Fefferman and Seco [66] obtained (as a corollary) the convergence in a stronger topology, namely in the so-called Coulomb norm; see (2.6). The precise result is contained in Theorem 3.1.

1.3 Quantum effects close to the nucleus

Although Thomas–Fermi theory correctly predicts the leading order of $E^{\mathrm{S}}(Z)$, it turned out that, as Scott [200, p. 859] wrote in 1952, the Thomas–Fermi energy gives values for the binding energy $(-1) \cdot E^{\mathrm{S}}(Z)$ "*which are too high by roughly* 20%. *The actual binding energies increase quite smoothly with increasing* Z, *which suggests the existence of a more appropriate formula.*" Naturally, this defect of simple Thomas–Fermi theory triggered some discussions. One year before Scott's publication, Foldy [74] had proposed the formula $E^{\mathrm{S}}(Z) = c_1 \cdot Z^{12/5} + c_2(Z)$. Here $c_2(Z)$ depends on $E^{\mathrm{S}}(2)$ and the sum of the ionization potentials of all atoms with atomic number greater than or equal to three and less than or equal to Z. (Foldy does not give a bound on $c_2(Z)$ but seems to assume that $c_2(Z) = o(Z^{12/5})$.) More importantly for us, c_1 is a constant that only depends on the chosen units and obeys $c_1 > E^{\mathrm{TF}}(1)$. The exponent $12/5$ was derived from numerical values of the electrostatic potential close to the nucleus as a function of Z (Dickinson [35]). Since these values were only available for $Z \leq 80$, Foldy's formula was not expected to hold asymptotically as $Z \to \infty$. In the discussion of his formula, Foldy [74, p. 398] points out that Thomas–Fermi theory does not correctly take into account the following two effects close to the nucleus. On the one hand, such electrons are bound stronger to the nucleus, but, on the other hand, they screen the bulk of the electrons at larger distances to the nucleus. Foldy suspected the screening to dominate, which explains the inequality $c_1 > E^{\mathrm{TF}}(1)$ despite the fact that $Z^{12/5} \gg Z^{7/3}$ for $Z \gg 1$.

Scott [200, p. 867] made Foldy's observations more precise and suggested a different formula for $E^{\mathrm{S}}(Z)$. He believed that Thomas–Fermi theory does correctly describe the leading order of the ground state energy expansion, but that the failure of Thomas–Fermi theory "*is due partly to the shortcomings of the statistical model in the region nearest the nucleus, and partly to the effect of exchange*". Like Foldy, Scott suggested that the few, but high-energy electrons that are located close to the nucleus should generate this correction. Due to their proximity to the nucleus, these electrons should be described quantum mechanically. Since the correction would be generated only by "finitely many" electrons, the electron–electron repulsion should be irrelevant and the order of the correction should be $\mathcal{O}(Z^2)$, i.e., in agreement with the magnitude of the eigenvalues of the hydrogenic Hamiltonian

$$S_Z^H := -\frac{1}{2}\Delta - \frac{Z}{|x|} \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}) \tag{1.9}$$

with nuclear charge Z. By a simple calculation (see Sect. 3.1.4 for March's derivation), Scott was led to

$$E^{\mathrm{S}}(Z) = E^{\mathrm{TF}}(1) \cdot Z^{7/3} + \frac{q}{4} \cdot Z^2 + o(Z^2) \quad \text{as } Z \to \infty. \tag{1.10}$$

If one drops the electron–electron repulsion in the Hamiltonian (1.1), the corresponding ground state energy will also behave to leading order like a constant times $Z^{7/3}$ as $Z \to \infty$, but with a constant different from $E^{\mathrm{TF}}(1)$. There will also be a subleading correction, given by a constant times Z^2, and, remarkably, the constant here is the same $q/4$ as in (1.10). This is not a coincidence and will become clear in the discussion below.

1.3.1 Scott correction

About thirty years later, Lieb [143, Problem 6] and [144, pp. 623–624] and Simon [214, Problem 10b] revisited the problem of finding the second term in the asymptotic expansion of $E^{\mathrm{S}}(Z)$. Because of Scott's compelling arguments, Formula (1.10) was coined *Scott correction/conjecture*.

In the same decade, Hughes [113, 114] (lower bound) and the authors of [208–210] (upper and lower bound) proved this conjecture. That is, they rigorously derived the expansion (1.10); see Theorem 3.4. The proof in [208–210] relied in part on the mathematical and physical intuition gained in the precursor [213], where the Scott correction is proved in the absence of electron–electron repulsion. We will present this motivating result and its short proof in Sect. 2.3.

Remark 1.3 As has been observed, e.g., by Conlon [28], Huxtable [115], or Sobolev [219], the Z^2-correction is a consequence of the singularity of the Coulomb potential and cannot be explained semiclassically. For instance, Huxtable's result [115, Theorem 7] states

$$\inf_{\substack{\psi\in\bigwedge_{\nu=1}^{Z} L^2(\mathbb{R}^3:\mathbb{C}^q)\\ \|\psi\|_2=1}} \left\langle \psi, \left[\sum_{\nu=1}^{Z}\left(-\frac{1}{2}\Delta_\nu - Z^{\frac{4}{3}} W(Z^{\frac{1}{3}} x_\nu)\right)\right]\psi\right\rangle = c_{\mathrm{TF}} Z^{\frac{7}{3}} + \mathcal{O}(Z^{\frac{5}{3}}) \tag{1.11}$$

as $Z \to \infty$ for any potential $W \in C^\infty(\mathbb{R}^3)$ satisfying $c|x|^2 \leq -W(x) \leq C|x|^2$ and $|\nabla W(x)| \leq c'|x|$ for some $c, C, c' > 0$. Here c_{TF} is related to the non-relativistic Thomas–Fermi theory with potential W.

1.3.2 Strong Scott conjecture

The Scott conjecture has a close relative that concerns the ground state density, the so-called strong form of the Scott correction (in short "strong Scott conjecture" from now on). It was formulated by Lieb [144, pp. 623–624]; see also Heilmann and Lieb [104, p. 3629]. The strong Scott conjecture states that the suitably rescaled ground state density ρ_{S} on distances of order Z^{-1} from the nucleus converges to q times the three-dimensional *hydrogenic density*, i.e.,

$$\rho_{\mathrm{S}}^H(x) := q \cdot \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n=0}^{\infty} |\psi^{\mathrm{S}}_{n,\ell,m}(x)|^2, \quad x \in \mathbb{R}^3. \tag{1.12}$$

The latter is the sum of squares of the $L^2(\mathbb{R}^3 : \mathbb{C})$-normalized eigenfunctions $\psi^{\mathrm{S}}_{n,\ell,m}$ of the hydrogen Hamiltonian

$$S^H = -\frac{1}{2}\Delta - \frac{1}{|x|} \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}). \tag{1.13}$$

The hydrogenic density ρ_{S}^H is rather well understood; see Theorem 3.11. In particular, the right side of (1.12) converges and is spherically symmetric. (The labeling of the eigenfunctions $\psi^{\mathrm{S}}_{n,\ell,m}$ uses the decomposition into angular momentum channels and will be further explained in Sect. 3.1.2.)

Note that S^H is unitarily equivalent to $Z^{-2}S_Z^H$ by scaling $x \mapsto x/Z$, where S_Z^H is defined in (1.9). Any eigenfunction φ_Z of S_Z^H scales like $\varphi_Z(x) = Z^{3/2}\varphi_1(Zx)$, where φ_1 denotes the corresponding eigenfunction of $S_1^H = S^H$.

Iantchenko et al. [117] showed, among other things, that

$$\lim_{Z\to\infty} \frac{1}{4\pi}\int_{\mathbb{S}^2} Z^{-3}\rho_{\mathrm{S}}(Z^{-1}r\omega)\,\mathrm{d}\omega = \rho_{\mathrm{S}}^H(r) \quad \text{for each } r > 0, \tag{1.14}$$

see also Theorem 3.5. It follows from the convergence results there that the one-particle ground state density ρ_{S} is approximately spherically symmetric in the limit $Z \to \infty$ on distances Z^{-1} from the nucleus.

1.4 Dirac–Schwinger correction

As mentioned in the previous subsection, Scott anticipated that the subleading terms in the expansion of the ground state energy $E^{\mathrm{S}}(Z)$ should take into account the extreme quantum effects close to the nucleus, but also the *exchange energy of the electrons*, as proposed by Dirac [39].

On a formal level, Schwinger [199], as well as Englert and Schwinger [45–47] (see also Englert [44] for a textbook treatment) derived the third term in the asymptotic expansion of the ground state energy, which grows like $Z^{5/3}$. In fact, this term is not only generated by the exchange energy of the electrons, but is also due to the semiclassical asymptotics of the eigenvalue sum of the operator $-\frac{1}{2}\Delta - \Phi^{\mathrm{TF}}$ with the semiclassical parameter $Z^{-1/3}$ and the Z-dependent Thomas–Fermi potential Φ^{TF} (see (2.15)). In view of the results in Sect. 1.2, the occurrence of $-\frac{1}{2}\Delta - \Phi^{\mathrm{TF}}$ in the analysis of $E^{\mathrm{S}}(Z)$ is not unexpected.

A decade later, Schwinger's and Englert's derivation was made mathematically rigorous in the monumental work of Fefferman and Seco [61–65, 68, 70]; see also Bach [3, 4] and Graf and Solovej [97] for simplifications and improvements of parts of Fefferman's and Seco's arguments and see [60] for a review of Fefferman's and Seco's proof. They proved the existence of a constant $C_{\mathrm{DS}} > 0$, which can be computed in terms of the Thomas–Fermi density $\rho^{\mathrm{TF}}_{Z=1}$, see [68, p. 528], such that

$$E^{\mathrm{S}}(Z) = E^{\mathrm{TF}}(1)Z^{7/3} + \frac{q}{4}Z^2 - C_{\mathrm{DS}}Z^{5/3} + o(Z^{5/3}). \tag{1.15}$$

In [60, pp. 6, 9–10] and [64, pp. 13–14], Fefferman and Seco make a conjecture concerning a fourth, possibly oscillating term in the expansion of $E^{\mathrm{S}}(Z)$. Córdoba et al. [29–31] analyzed this term in detail and showed, in particular, that it is bounded from below and above by constants times $Z^{3/2}$.

1.5 The necessity of a relativistic description

From a physical point of view, it is questionable whether one can describe atoms with large nuclear charges non-relativistically since already the bulk of the electrons is localized in orbitals whose distance to the nucleus is roughly $Z^{-1/3}$ or less. As Z increases, the electrons become localized closer to the nucleus and, by Heisenberg's uncertainty principle, one expects that at least the velocities of the innermost electrons are a substantial fraction of the speed of light c. In fact, the non-relativistic energy for electrons on the length scale Z^{-1} in the field of a nucleus of charge Z is already $-Z^2/2$. Thus, the virial theorem implies that its kinetic energy is $Z^2/2$. In classical mechanics, this would show that the velocity of the electron is Z. Since the velocity of light is 137 in our units, a single electron in the field of a uranium nucleus ($Z = 92$) would therefore move with a speed of $\approx \frac{92}{137} \cdot c$, which indeed is a substantial fraction of the speed of light. For this reason, a relativistic description is mandatory, in particular on the short length scale Z^{-1}. Meanwhile, at distances $Z^{-1/3}$, electrons are expected to move with velocities $\lesssim 10\%$ of the speed of light and, indeed, as we will see momentarily, relativistic effects are negligible to the leading, i.e., Thomas–Fermi order of $E^{\mathrm{S}}(Z)$.

Before turning to details, we point out that already Scott [200, p. 866] anticipated possible shortcomings of his non-relativistic formula for large Z:

> "*Relativity effects of all kinds have been disregarded so far. Though this simplification has no serious consequences for $Z < 30$, these effects are quite important for heavy elements. It would be a difficult task to calculate them accurately. A straightforward extension of Thomas' statistical method (Vallarta and Rosen* [241]) *is inapplicable to our present problem, because most of the correction originates in the region close to the nucleus where the statistical method is vitiated by the boundary effect, and, in fact, such methods would give an infinite binding energy. Moreover, the interaction between the electrons is not wholly electrostatic.*"

Concerning an extension of "*Thomas' statistical method*", we refer to Sect. 2.4 for recent developments in this direction.

From a fundamental physical point of view, heavy atoms and molecules should be treated by relativistic quantum electrodynamics (QED) and the corresponding field theory. Unfortunately, many fundamental mathematical elements, e.g., the state space and the Hamiltonian, lack mathematical understanding. As a consequence, one is thrown back to approximate models. Here we will review three such approximate Hamiltonian models that have been derived by physical arguments from QED, and proven useful in applications. Moreover, we consider a mathematical simplification thereof and a density functional obtained in this vein.

The first model can be traced back at least to Chandrasekhar [24] in the context of stability of neutron stars. In it the single-particle kinetic energy, $-\Delta/2$ is replaced by $\sqrt{-c^2\Delta + c^4} - c^2$ with c being the velocity of light. Despite its mathematical simplicity, the resulting operator features many physical defects, such as the violation of the principle of locality. More crucially for us, it leads to ground state energies that are much too low compared to experimental data and can only be applied to atoms with nuclear charge $Z < 88$.

Physically and chemically more accurate models are based on projected Coulomb–Dirac [37, 38] operators, such as the Brown–Ravenhall [22] or the Furry [93] operator, which are applicable to atoms with nuclear charge $Z < 125$ and $Z < 138$, respectively. The latter is used in quantum chemistry to compute the ground state energy of large atoms or molecules to chemical accuracy, see, e.g., Reiher and Wolf [192].

A common property of relativistic operators is the fact that, at least for large momenta, the kinetic energy scales like the Coulomb potential. On a heuristic level, it is clear that the sole limit $Z \to \infty$ is meaningless since the potential energy cannot be controlled by the kinetic energy anymore. Consequently, the total energy will not be bounded from below, and the atom becomes "unstable" for fractions Z/c beyond a critical model-dependent coupling constant. To make mathematically meaningful statements about asymptotics, one considers the limit when both Z and c tend to infinity simultaneously with a fixed ratio $Z/c =: \gamma$. (Of course, like the limit $Z \to \infty$, the limit $c \to \infty$ is questionable since c has a fixed value). The idea to introduce γ as a separate parameter goes back at least to Schwinger [198].

For $\gamma \leq 2/\pi$, Sørensen [184] proved that in the above-described limit, the leading order of the ground state energy in the Chandrasekhar model is given by the Thomas–

Fermi energy. Moreover, the ground state density on the Thomas–Fermi length scale converges weakly and in the so-called Coulomb norm (see (2.6)) to the hydrogenic Thomas–Fermi density [168, 169]. This indicates that the bulk of the electrons on the length scale $Z^{-1/3}$ does not behave relativistically.

On the other hand, electrons on the hydrogenic length scale Z^{-1} are located much closer to the nucleus and, as described before, are expected to lead to relativistic corrections of the Scott correction. In fact, Schwinger [198] derived a relativistic Z^2-correction, which is lower than Scott's. This lowering was proved, by two different approaches, in Solovej et al. [224] and in [90]. Later, a relativistic correction of the Scott correction was also proved for the Brown–Ravenhall [91] and the Furry operator [100].

The relativistic generalization of the strong Scott conjecture was proved recently in [87] (see also [85]), i.e., the convergence of the suitably rescaled one-particle ground state density of Chandrasekhar atoms on the hydrogenic length scale $1/Z$ to the sum of the squares of the eigenfunctions of the one-particle Chandrasekhar operator. Shortly thereafter, the corresponding statement for the physically and chemically accurate Furry operator was proved [170]. These results underscore the fact that electrons close to the nucleus behave relativistically and that self-interactions of the innermost electrons are negligible.

1.6 Organization

We briefly summarize the contents of the present review.

In Sect. 2, we review three examples of density functional theories. For the first two, we refer to March's and Lieb's reviews [144, 161]; see also [206] for a recent review. First, and most important for us, we discuss Thomas–Fermi theory. Secondly, we review Weizsäcker's extension of Thomas–Fermi theory, which is physically and mathematically richer than Thomas–Fermi theory. Qualitatively, this extension correctly accounts for quantum effects of electrons close to the nucleus. Thirdly, we investigate the Hellmann–Weizsäcker functional, which served as the basis for Siedentop's and Weikard's proof of the Scott correction. Finally, we consider a density functional that reduces to the Thomas–Fermi–Weizsäcker functional in the non-relativistic limit. It was derived by Engel and Dreizler and was recently investigated from a mathematical point of view.

In Sect. 3, we consider non-relativistic atoms, ions, and molecules, both in the presence and absence of a self-generated magnetic field, and summarize theorems concerning the energy asymptotics and the convergence of the quantum density on both the Thomas–Fermi and the Scott length scales. Emphasis will be put on Scott's original derivation of the energy correction, as well as the initial motivating results in [213].

Section 4 is concerned with relativistic descriptions. We summarize results concerning the energetic asymptotics as well as the convergence of the density for all the three different relativistic models discussed in the introduction—the Chandrasekhar, the Brown–Ravenhall, and the Furry model.

In Sect. 5, we discuss some open questions.

Notation

We write $A \lesssim B$ for two non-negative quantities $A, B \geq 0$ to indicate that there is a constant $C > 0$ such that $A \leq CB$. If $C = C_\tau$ depends on a parameter τ, we sometimes write $A \lesssim_\tau B$. The notation $A \sim B$ means $A \lesssim B \lesssim A$. The indicator function of a set Ω is denoted by $\mathbf{1}_\Omega$. The negative part of a real number or a self-adjoint operator A is defined by $A_- := \max\{0, -A\} \geq 0$.

2 Density functional theories

In this section, we briefly review three examples of effective theories that are known to describe correctly at least the leading order of the ground state energy of large atoms and molecules. They are known as *density functionals*, i.e., energy functionals that only depend on the one-particle density of a given many-particle system. We refer to Lieb's detailed review [144] on Thomas–Fermi-type theories and to [206] for a recent survey of density (matrix) functional theories. In particular, [144] also treats extensions of Thomas–Fermi theory like Weizsäcker's inhomogeneity [240] and Dirac's exchange [39] correction. The first one will be of some interest for us since it generates a Scott correction, whereas the second one will be discussed in passing only.

2.1 Thomas–Fermi theory

We begin with the simplest non-relativistic "statistical model of the atom" (Fermi [71, 72], Gombás [94]), which was formulated in the late 1920s independently by Thomas [235] and Fermi [71, 72]. In the molecular case with K nuclei of charges $\underline{Z} = (Z_1, \dots, Z_K) \in (0, \infty)^K$ situated at positions $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, the so-called Thomas–Fermi (TF from now on) functional (Lenz [138]) is given by:

$$\mathcal{E}^{\mathrm{TF}}_V(\rho) := \int_{\mathbb{R}^3} \left(\frac{3}{5} \gamma_{\mathrm{TF}} \rho^{5/3}(x) - V(x)\rho(x) \right) \mathrm{d}x + D(\rho, \rho) + U \tag{2.1}$$

with V and U as in (1.2) and (1.3), respectively. In the atomic case $K = 1$, we write $\mathcal{E}^{\mathrm{TF}}_Z := \mathcal{E}^{\mathrm{TF}}_{Z/|x|}$.

The first term of $\mathcal{E}^{\mathrm{TF}}_V(\rho)$ represents the kinetic energy and is derived via the following argument based on a semiclassical phase space integration. The TF model views the N non-relativistic quantum particles in a potential W as a classical gas in phase space. Since Planck's constant is $h = 2\pi\hbar = 2\pi$ in our units, the density of the semiclassical gas is:

$$\rho(x) = q \int \mathbf{1}_{\{p^2/2 \leq W(x)\}} \frac{\mathrm{d}p}{(2\pi)^3} = \frac{q \cdot 4\pi}{3 \cdot (2\pi)^3} (2W(x))^{3/2}. \tag{2.2}$$

Thus, the semiclassical kinetic energy is:

$$q\int \frac{p^2}{2}\mathbf{1}_{\{p^2/2\le W(x)\}}\frac{\mathrm{d}p}{(2\pi)^3}=\frac{q}{(2\pi)^3}\cdot\frac{1}{2}\cdot\frac{4\pi}{5}\cdot(2W(x))^{5/2}=\frac{3}{5}\gamma_{\mathrm{TF}}\cdot\rho(x)^{5/3} \tag{2.3}$$

with the *Thomas–Fermi constant*

$$\gamma_{\mathrm{TF}}:=(6\pi^2)^{2/3}\hbar^2(2mq^{2/3})^{-1}=(6\pi^2/q)^{2/3}/2. \tag{2.4}$$

The second term in (2.1) represents the interaction energy between the electrons and the nuclei.

The third term in (2.1) is the electrostatic self-energy of the charge density ρ. It is defined, more generally, for ρ and σ by

$$D(\rho,\sigma)=\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{\rho(x)}\sigma(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y. \tag{2.5}$$

Note that (by Plancherel and the convolution theorem), $D(\rho,\sigma)$ is sesquilinear and positive, and (by Cauchy–Schwarz), $D(\rho,\sigma)\le\sqrt{D(\rho,\rho)}\cdot\sqrt{D(\sigma,\sigma)}$. In fact, $D(\cdot,\cdot)$ defines a scalar product on the set $\mathcal{I}$ defined in (2.7) below. Thus, the right side of

$$\|\rho\|_{\mathrm{C}}:=D(\rho,\rho)^{1/2} \tag{2.6}$$

defines a norm on that space. This norm is sometimes called the *Coulomb norm*.

The TF functional (2.1) is defined on its natural domain (Simon [216])

$$\mathcal{I}=\left\{\rho\in L^{5/3}(\mathbb{R}^3):\ D(\rho,\rho)<\infty,\ \rho\ge 0\right\}, \tag{2.7}$$

i.e., for nonnegative densities with finite kinetic energy and finite electron–electron repulsion. These conditions automatically guarantee the finiteness of the electron–nucleus interaction. (The local singularities at the nuclei are controlled by the kinetic energy, whereas the long-range part is controlled by the electron–electron repulsion.)

To describe a system of N electrons, we restrict the TF functional to the set

$$\begin{aligned}\mathcal{I}_N&=\left\{\rho\in\mathcal{I}:\ \int\rho=N\right\}\\&=\left\{\rho\in L^{5/3}(\mathbb{R}^3):\ D(\rho,\rho)<\infty,\ \rho\ge 0,\ \int\rho=N\right\}.\end{aligned} \tag{2.8}$$

Here, mathematically speaking, N need not be an integer.

In their seminal work [152], Lieb and Simon were the first to analyze this functional with mathematical rigor. (See also [144, Section II] and [206, Subsection 4.1] for more detailed reviews.) The following theorem asserts the existence and uniqueness of minimizers of the TF functionals on $\mathcal{I}$ and $\mathcal{I}_N$.

Theorem 2.1 *Let $\underline{Z} = (Z_1, \dots, Z_K) \in (0,\infty)^K$ and $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$. Then, the following statements hold.*

(1) (Unconstrained problem): *There exists a unique $0 \leq \rho^{\mathrm{TF}}(\underline{Z}, \underline{R}, x)$ such that $\int_{\mathbb{R}^3} \rho^{\mathrm{TF}}(\underline{Z}, \underline{R}, x)\,\mathrm{d}x = |\underline{Z}| = \sum_{\kappa=1}^K Z_\kappa$ and*

$$\mathcal{E}_V^{\mathrm{TF}}[\rho^{\mathrm{TF}}] = \inf\{\mathcal{E}_V^{\mathrm{TF}}[\rho] : \rho \in \mathcal{I}\} =: E^{\mathrm{TF}}(\underline{Z}, \underline{R}). \tag{2.9}$$

(2) (Constrained problem): *If $N \leq |\underline{Z}|$, then there exists a unique, non-negative $\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x)$ such that $\int_{\mathbb{R}^3} \rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x)\,\mathrm{d}x = N$ and*

$$\mathcal{E}_V^{\mathrm{TF}}[\rho^{\mathrm{TF}}] = \inf\{\mathcal{E}_V^{\mathrm{TF}}[\rho] : \rho \in \mathcal{I}_N\} =: E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}). \tag{2.10}$$

In particular, $N \mapsto E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ is strictly decreasing. If $N > \sum_{\kappa=1}^K Z_\kappa$, then $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ is not a minimum, i.e., there are no negatively charged ions in TF theory.

(3) (Unconstrained Thomas–Fermi equation) *In the unconstrained problem, the minimizer $\rho^{\mathrm{TF}} \in \mathcal{I}$ obeys $\int \rho^{\mathrm{TF}} = |\underline{Z}|$ and*

$$\gamma_{\mathrm{TF}}(\rho^{\mathrm{TF}})^{\frac{2}{3}} = V - \left(\rho^{\mathrm{TF}}(\underline{Z}, \underline{R}, \cdot) * \frac{1}{|\cdot|}\right). \tag{2.11}$$

Moreover, if $\rho \in \mathcal{I}$ satisfies (2.11), then it minimizes $\mathcal{E}_V^{\mathrm{TF}}$ on $\mathcal{I}$. If $K = 1$, then ρ^{TF} is spherically symmetric and decreasing.

(4) (Thomas–Fermi equation in constrained problem) *In the constrained problem with $0 < N \leq |\underline{Z}|$, the minimizer $\rho^{\mathrm{TF}} \in \mathcal{I}_N$ satisfies*

$$\gamma_{\mathrm{TF}}\rho^{\mathrm{TF}}(x)^{\frac{2}{3}} = \left(V(x) - \left(\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, \cdot) * \frac{1}{|\cdot|}\right)(x) - \mu\right)_+ \tag{2.12}$$

for some (unique) $\mu = \mu(N) \geq 0$. Moreover, there is no solution $\rho \in \mathcal{I}_N$ to (2.12) for any μ other than ρ^{TF}. When $N = Z$, then $\mu = 0$, and otherwise $\mu > 0$. As N varies from 0 to $|\underline{Z}|$, μ varies continuously from ∞ to 0. Moreover, μ is a convex, decreasing function of N.

(5) (Scaling) *For any $a > 0$, the scaling relations*

$$\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x) = a^{-2}\rho^{\mathrm{TF}}(aN, a\underline{Z}, a^{-1/3}\underline{R}, a^{-1/3}x), \tag{2.13a}$$

$$E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}) = a^{-7/3}E^{\mathrm{TF}}(aN, a\underline{Z}, a^{-1/3}\underline{R}) \tag{2.13b}$$

hold.

Remark 2.2 (1) The number $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ is called the *Thomas–Fermi energy* and the minimizer ρ^{TF} is called the *Thomas–Fermi density*.

(2) Although $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ is not a minimum on $\mathcal{I}_N$ and (2.12) has no solution with $\int \rho = N$ if $N > \sum_{\kappa=1}^K Z_\kappa$, the number $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ still exists and we have $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}) = E^{\mathrm{TF}}(|\underline{Z}|, \underline{Z}, \underline{R})$ in that case.

(3) If $K = 1$ in the unconstrained problem, then we write $\rho^{\mathrm{TF}}(Z, 0, x) =: \rho_Z^{\mathrm{TF}}(x)$ and $E^{\mathrm{TF}}(Z, 0) =: E^{\mathrm{TF}}(Z)$. Similarly, in the constrained problem we shall write $\rho^{\mathrm{TF}}(N, Z, 0, x) =: \rho_Z^{\mathrm{TF}}(N, x)$ and $E^{\mathrm{TF}}(N, Z, 0) =: E^{\mathrm{TF}}(N, Z)$.
(4) The scaling relations for $K = 1$ show, in particular, that TF theory has "natural" length and energy scales, the *Thomas–Fermi length scale* $Z^{-1/3}$ and the *Thomas–Fermi energy scale* $Z^{7/3}$, respectively. For $Z = 1$, the minimizer ρ^{TF} (either in the unconstrained or constrained problem) is called the *hydrogenic Thomas–Fermi density*. The numerical value of the associated infimum is: $E^{\mathrm{TF}}(1) \approx -3.678\,74 \cdot \gamma_{\mathrm{TF}}^{-1}$, cf. Gombás [94, p. 60].

The following theorem due to Lieb and Simon [152, Theorem IV.5] (see also [144, Theorem 2.8]) summarizes some important properties of the TF density.

Theorem 2.3 (Properties of ρ^{TF}) *Let $\underline{Z} = (Z_1, \ldots, Z_K) \in (0, \infty)^K$ and $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$ and let ρ^{TF} denote the solution to the constrained Thomas–Fermi equation (2.12) with $\int \rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x) = N$. Then, the following statements hold:*

(1) Let $\kappa \in \{1, \ldots, K\}$ be arbitrary. Then, as $x \to R_\kappa$, one has

$$\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x) = \left(\frac{Z_\kappa}{\gamma_{\mathrm{TF}}}\right)^{\frac{3}{2}} |x - R_\kappa|^{-3/2} + o(|x - R_\kappa|^{-1/2}). \tag{2.14}$$

(2) $\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x) \to 0$ as $|x| \to \infty$.
(3) ρ^{TF} is real analytic on $\{x \in \mathbb{R}^3 : x \neq R_\kappa \ \forall \kappa, \rho^{\mathrm{TF}}(x) > 0\}$.
(4) In the neutral case ($N = |\underline{Z}|$, $\mu = 0$), one has $\rho^{\mathrm{TF}}(x) > 0$ for all $x \in \mathbb{R}^3$.
(5) In the ionic case ($N < |\underline{Z}|$, $\mu > 0$), ρ^{TF} is compactly supported and C^1 away from the R_κ.
(6) (Thomas–Fermi equation) *Let the* Thomas–Fermi potential Φ^{TF} *be defined by*

$$\Phi^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x) := V(x) - (\rho^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, \cdot) * |\cdot|^{-1})(x). \tag{2.15}$$

Then, Φ^{TF} obeys the Thomas–Fermi differential equation

$$-\frac{1}{4\pi}(\Delta\Phi^{\mathrm{TF}})(N, \underline{Z}, \underline{R}, x) = \sum_{\kappa=1}^{K} Z_\kappa \delta(x - R_\kappa) - \gamma_{\mathrm{TF}}^{-3/2}(\Phi^{\mathrm{TF}} - \mu)_+^{3/2}. \tag{2.16}$$

(7) (Sommerfeld) In the neutral case ($\mu = 0$), the Sommerfeld solution

$$\psi(x) = \psi(|x|) = \gamma_{\mathrm{TF}}^3 \cdot (3/\pi)^2 \cdot |x|^{-4} \tag{2.17}$$

solves the TF differential equation (2.16) for $|x| > 0$ and $x \neq R_\kappa$ and it is the only power law that does so. Moreover,

$$\lim_{s\to\infty} \frac{\max_{|x|=s} \Phi^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x)}{\psi(s)} = \lim_{s\to\infty} \frac{\min_{|x|=s} \Phi^{\mathrm{TF}}(N, \underline{Z}, \underline{R}, x)}{\psi(s)} = 1. \tag{2.18}$$

In the atomic case ($K = 1$), the TF density ρ^{TF} obeys

$$\rho^{\mathrm{TF}}(N, Z, x) = \left(\frac{3\gamma_{\mathrm{TF}}}{\pi}\right)^3 |x|^{-6} + o(|x|^{-6}) \tag{2.19}$$

as $|x| \to \infty$.

Remark 2.4 Observe that Sommerfeld's solution (2.17) (see [227]) is *independent of* Z and even solves the molecular TF equation; due to the scaling of the TF density, the Sommerfeld asymptotics $|x|^{-6}$ of the TF density still has magnitude $\mathcal{O}(Z^2)$ for $|x| \lesssim Z^{-1/3}$. Sommerfeld-type estimates are contained in Solovej's proof of the ionization conjecture in Hartree–Fock theory [223, Theorems 4.6, 5.2, 5.4]; see also [144, Theorem 2.10] and [119, Section 1] for further estimates for the TF density and potential.

In the absence of electron repulsion, the Thomas–Fermi energy can be computed easily. This is important for the heuristic derivation of the Scott correction (Sect. 3.1.4) and is done in the following remark.

Remark 2.5 (Thomas–Fermi energy for the Bohr atom) Let $K = 1$ and $Z > 0$, and consider TF theory for an atom in the absence of electron repulsion, i.e.,

$$\mathcal{E}^{\mathrm{TF}}_{Z,\mathrm{Bohr}}(\rho) = \int_{\mathbb{R}^3} \left(\frac{3}{5}\gamma_{\mathrm{TF}}\rho(x)^{5/3} - \frac{Z}{|x|}\rho(x)\right) \mathrm{d}x. \tag{2.20}$$

For $N > 0$, let

$$E^{\mathrm{TF}}_{\mathrm{Bohr}}(N, Z) = \inf\left\{\mathcal{E}^{\mathrm{TF}}_{Z,\mathrm{Bohr}}(\rho) : 0 \le \rho \in L^{5/3}(\mathbb{R}^3), \int \rho = N\right\}.$$

It is elementary to see that there is a unique minimizer $\rho^{\mathrm{TF}}_{\mathrm{Bohr}}(N, Z)$ and that this minimizer satisfies the Euler–Lagrange equation

$$\gamma_{\mathrm{TF}} \cdot \rho^{\mathrm{TF}}_{\mathrm{Bohr}}(N, Z, x)^{2/3} = \left(\frac{Z}{|x|} - \mu\right)_+ \tag{2.21}$$

with some $\mu > 0$. Integrating the $3/2$-th power of this identity leads to the relation

$$\mu = \left(\frac{\pi^2}{4}\right)^{\frac{2}{3}} \frac{1}{\gamma_{\mathrm{TF}}} \frac{Z^2}{N^{\frac{2}{3}}},$$

and then to the formula for the energy

$$E^{\mathrm{TF}}_{\mathrm{Bohr}}(N, Z) = \mathcal{E}^{\mathrm{TF}}_{Z,\mathrm{Bohr}}(\rho^{\mathrm{TF}}_{\mathrm{Bohr}}(N, Z)) = -\frac{3}{\gamma_{\mathrm{TF}}}\left(\frac{\pi^2}{4}\right)^{\frac{2}{3}} Z^2 N^{\frac{1}{3}}. \tag{2.22}$$

2.2 Thomas–Fermi–Weizsäcker theory

The semiclassical derivation of TF theory assumes that the density is locally constant. In this regard, we recall Scott's observations [200, p. 859, p. 867]:

> "*The Thomas–Fermi statistical model of the atom leads to the formula* $20 \cdot 92\, Z^{7/3}$ ev *for the total binding energy of an atom with atomic number* Z, *but this formula gives values which are too high by roughly* 20%. *The actual binding energies increase quite smoothly with increasing* Z, *which suggests the existence of a more appropriate formula. [...] The failure of the currently quoted formula is due partly to the shortcomings of the statistical model in the region nearest the nucleus, and partly to the effect of exchange.*"

In 1935, Weizsäcker [240] proposed a correction of Thomas–Fermi theory that penalizes rapid changes of the density, which are expected to occur close to the nucleus.

Remark 2.6 Some words on the history: Weizsäcker introduced this correction to explain the rise of the mass defect per nucleon in a nucleus from very heavy (say uranium) to semi-heavy nuclei (like iron). To that end he consulted Gamow's liquid drop model for nuclei and argued that, as a consequence of the uncertainty principle, the "surface of the nucleus" must be smeared out. For otherwise, an instantaneous drop of the density with infinite slope would lead to an infinite kinetic energy, which is unreasonable. This smearing of the surface could be accounted for by replacing the eigenfunctions that are used in the derivation of the Thomas–Fermi functional, namely plane waves, by waves with linearly varying amplitude. This gives rise to Weizsäcker's term $\rho^{-1}(\nabla\rho)^2$.

We consider the Thomas–Fermi–Weizsäcker (TFW from now on) functional

$$\mathcal{E}_V^{\mathrm{TFW}}(\rho) := \frac{A}{2}\int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 + \mathcal{E}_V^{\mathrm{TF}}(\rho) \tag{2.23}$$

with nuclei of charges $\underline{Z} = (Z_1, \ldots, Z_K) \in (0,\infty)^K$ situated at positions $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$. It is naturally defined on the set

$$\mathcal{A} := \{\rho \in L^1_{\mathrm{loc}}(\mathbb{R}^3) :\ \rho \geq 0,\ \nabla\sqrt{\rho} \in L^2(\mathbb{R}^3),\ \|\rho\|_{\mathrm{C}} < \infty\}, \tag{2.24}$$

where the gradient is understood in the sense of distributions. For fixed particle number $N \in (0,\infty)$, the functional is defined on

$$\mathcal{A}_N := \left\{\rho \in \mathcal{A} :\ \int \rho = N\right\}. \tag{2.25}$$

Weizsäcker introduced (2.23) with $A = 1$. However, it is convenient to have $A > 0$ as an adjustable parameter, as we shall see soon.

The mathematical analysis of $\mathcal{E}_V^{\mathrm{TFW}}$ started with the works of Benguria [13] and Benguria et al. [14]. Besides its mathematical richness, it turned out that TFW theory describes—at least qualitatively—the physics of real atoms more accurately than

Thomas–Fermi theory. For instance, the TFW minimizer is finite at the nuclei and decays exponentially at infinity. Moreover, binding is possible and anions can be stable in TFW theory. For a concise summary of TFW theory, we encourage the reader to consult [13, 14], as well as [144, Sect. VII]. Here we restrict ourselves to a summary of the energy expansion and the minimizing density as $|\underline{Z}| \to \infty$. Our presentation closely follows Lieb [144] and Lieb and Liberman [146]. We start with the following result on existence and uniqueness of minimizers of the TFW functional.

Theorem 2.7 *Let $A > 0$, $\underline{Z} = (Z_1, \dots, Z_K) \in (0, \infty)^K$, and $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$. Then, the following statements hold.*

(1) (Unconstrained problem) There is $N_c \in (|\underline{Z}|, 2|\underline{Z}|)$ such that the TFW functional $\mathcal{E}_V^{\mathrm{TFW}}$ has a unique minimizer $\rho^{\mathrm{TFW}}(\underline{Z}, \underline{R}, x)$ on $\mathcal{A}$ with particle number $\int \rho^{\mathrm{TFW}}(\underline{Z}, \underline{R}, x)\,\mathrm{d}x = N_c$. This minimizer satisfies the TFW equation

$$\left(-\frac{A}{2}\Delta + W\right)\sqrt{\rho^{\mathrm{TFW}}} = 0 \tag{2.26}$$

with

$$W(x) = \gamma_{\mathrm{TF}}\rho^{\mathrm{TFW}}(\underline{Z}, \underline{R}, x)^{2/3} - V(x) + \int_{\mathbb{R}^3} \frac{\rho^{\mathrm{TFW}}(\underline{Z}, \underline{R}, y)}{|x - y|}\,\mathrm{d}y. \tag{2.27}$$

The infimum is denoted by:

$$E^{\mathrm{TFW}}(\underline{Z}, \underline{R}) := \inf\{\mathcal{E}_V^{\mathrm{TFW}}[\rho] : \rho \in \mathcal{A}\}. \tag{2.28}$$

(2) (Constrained problem) If $N \le N_c$, then the TFW functional has a unique minimizer $\rho^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}, x)$ on $\mathcal{A}_N$. This minimizer satisfies the TFW equation

$$\left(-\frac{A}{2}\Delta + W\right)\sqrt{\rho^{\mathrm{TFW}}} = -\mu\sqrt{\rho^{\mathrm{TFW}}} \tag{2.29}$$

with $W(x)$ as in (2.27), $\mu \ge 0$, and $\mu = 0$ for $N = N_c$. The infimum is denoted by

$$E^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}) := \inf\{\mathcal{E}_V^{\mathrm{TFW}}[\rho] : \rho \in \mathcal{A}_N\}. \tag{2.30}$$

If $N > N_c$, there is no minimizer on $\mathcal{A}_N$.

Remark 2.8 Benguria and Lieb [15] proved the previously mentioned ionization conjecture for TFW molecules and showed $0 < N_c - |\underline{Z}| \le 270.74 \cdot (\frac{A}{2\gamma_{\mathrm{TF}}})^{3/2} \cdot K$. As we shall see below, the value $A = 0.1859$ is in some sense natural. Together with the value of $\gamma_{\mathrm{TF}} = (6\pi^2/2)^{2/3}/2$, this leads to the bound $N_c - |\underline{Z}| < 0.7335 \cdot K$.

Theorem 2.7 shows, in particular, that anions can be stable in TFW theory. The next theorem says that ρ^{TFW} on the TF length scale is described by ρ^{TF}; see also Solovej [222] for results when only some of the nuclear charges tend to infinity.

Theorem 2.9 ([144, Theorem 7.30], [146, (2.25)]) *Let $A > 0$, $\underline{Z} = (Z_1, \dots, Z_K) \in (0,\infty)^K$, $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, and $N > 0$ so that $\lambda := N/|\underline{Z}|$ is fixed. Define $\underline{z}$ and $\underline{r}$ by $\underline{Z} = |\underline{Z}|\underline{z}$ and $\underline{R} = |\underline{Z}|^{-1/3}\underline{r}$, respectively. Then*

$$\lim_{|\underline{Z}|\to\infty} |\underline{Z}|^{-2}\rho^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}, |\underline{Z}|^{-1/3}x) = \rho^{\mathrm{TF}}(\lambda, \underline{z}, \underline{r}, x) \tag{2.31}$$

weakly in L^1 if $\lambda \le |\underline{Z}|$ and weakly in L^1_{loc} if $\lambda > |\underline{Z}|$.

Naturally, the question arises of how close the two infima $E^{\mathrm{TFW}}(N, \underline{Z}, \underline{R})$ and $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ are, i.e., one seeks an upper bound on the right side of

$$0 \le E^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}) - E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}). \tag{2.32}$$

Already in the neutral, atomic case ($K = 1$, $\underline{R} = 0$, $\underline{Z} = Z = N$) one might be tempted to say that the difference is $\mathcal{O}(Z^{5/3})$ by plugging in the TF density ρ_Z^{TF} and using the scaling relation $\rho_Z^{\mathrm{TF}}(x) = Z^2\rho_1^{\mathrm{TF}}(Z^{1/3}x)$. However, this is not correct, as can be seen heuristically as follows. By Theorem 2.3, one has $\rho_1^{\mathrm{TF}}(x) \sim \mathrm{const}\,|x|^{-3/2}$ as $|x| \to 0$, which makes it plausible that $|\nabla\sqrt{\rho_1^{\mathrm{TF}}}| \sim \mathrm{const}\,|x|^{-7/4}$, but this is not square-integrable and leads to an infinite Weizsäcker term. Instead, as the following theorem shows, the difference $E^{\mathrm{TFW}}(Z, Z, 0) - E^{\mathrm{TF}}(Z, Z, 0)$ is given, to leading order as $Z \to \infty$, by a constant times Z^2. This is the Scott correction in TFW theory. As in the quantum problem, the Z^2-term originates from effects on the hydrogenic length scale Z^{-1} rather than the TF length scale $Z^{-1/3}$, see [144, p. 635]. Lieb [144, Theorem 7.30] also shows that the correction is independent of the electron number, i.e., it also holds when comparing the TF and TFW energies for ions with fixed ratio N/Z.

Let us return to the general, multi-center case. To describe TFW theory on the length scale Z^{-1} more precisely, we consider the *atomic TFW functional without electron repulsion*. After a 'renormalization' (that is, formally subtracting the integral of

$$\frac{2}{5}\gamma_{\mathrm{TF}}\left(\frac{Z}{\gamma_{\mathrm{TF}}|x|}\right)^{5/2}$$

from the right side of (2.23)) one can show that the resulting functional has a unique minimizer and that this minimizer solves the Euler–Lagrange equation

$$\left(-\frac{A}{2}\Delta + \gamma_{\mathrm{TF}}\rho^{2/3} - \frac{Z}{|x|}\right)\sqrt{\rho} = 0; \tag{2.33}$$

see [144, Theorem 7.29]. By scaling, one has $\rho(x) = (2Z^2/(A\gamma_{\mathrm{TF}}))^{3/2}\rho_\infty(2Zx/A)$, where ρ_∞ is the solution corresponding to $Z = A/2 = \gamma_{\mathrm{TF}}$.

Then we have the following results on the hydrogenic energy and length scales.

Theorem 2.10 ([144, Theorem 7.30], [146, (2.26)]) *Let $A > 0$, $\underline{Z} = (Z_1, \dots, Z_K) \in (0,\infty)^K$, $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, and $N > 0$ so that $\lambda := N/|\underline{Z}|$ is fixed.*

(1) (Energy) We have

$$E^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}) = E^{\mathrm{TF}}(N, \underline{Z}, \underline{R}) + D^{\mathrm{TFW}} \sum_{\kappa=1}^{K} Z_\kappa^2 + o(|\underline{Z}|^2) \tag{2.34}$$

with $D^{\mathrm{TFW}} := 2^{1/2} A^{1/2} \gamma_{\mathrm{TF}}^{-3/2} \cdot \int_{\mathbb{R}^3} |\nabla \sqrt{\rho_\infty}|^2 \, \mathrm{d}x$.

(2) (Density) Define $\underline{z}$ *and* $\underline{r}$ *by* $\underline{Z} = |\underline{Z}|\underline{z}$ *and* $\underline{R} = |\underline{Z}|^{-1/3}\underline{r}$*, respectively. Then, the solution* ρ^{TFW} *of the problem* (2.30) *converges to that of* (2.33) *in the sense that for each* $\kappa \in \{1, \dots, K\}$*,*

$$\lim_{N\to\infty} Z_\kappa^{-3} \rho^{\mathrm{TFW}}(N, \underline{Z}, \underline{R}, R_\kappa + Z_\kappa^{-1} x) = (A\gamma_{\mathrm{TF}}/2)^{-3/2} \rho_\infty(2x/A) \tag{2.35}$$

both pointwise and in L^1_{loc}.

As emphasized by Lieb and Liberman in [146, Section 2.C], the second term in (2.34) has the following properties, which allows one to think of it as a "core effect":

- It is independent of $\lambda = N/|\underline{Z}|$.
- It is additive in the nuclei, that is, it is a sum of terms corresponding to each atom in the molecule.
- The constant D^{TFW} does not change if the electron–electron repulsion is removed.

By the last point, we mean that (2.34) remains true, with the same constant D^{TFW}, if in the definitions of both $E^{\mathrm{TFW}}(N, \underline{Z}, \underline{R})$ and $E^{\mathrm{TF}}(N, \underline{Z}, \underline{R})$ the term $D(\rho, \rho)$ is dropped. This is proved in [144].

The asymptotics (2.34) and the convergence in (2.35) suggest a discussion of the parameter A in (2.23). By Theorem 2.10, it suffices to discuss the atomic case $K = 1$. While Weizsäcker initially chose A to be one, other values have been suggested. For instance, Kirzhnits [132] suggested $A \approx 1/9$ based on the gradient expansion of the Hohenberg–Kohn functional, assuming the Coulomb potential was replaced by a "weak perturbing potential" ([146, p. 12]). However, due to the local singularity, the Coulomb potential cannot be regarded as such a weak perturbing potential.

More than 15 years before Theorem 2.10 was proved, Yonei and Tomishima [250] analyzed (2.33) with μ such that the solution ρ_∞ obeys $\int \rho_\infty = Z$. From a numerical analysis, they concluded $A \approx 1/5$ (especially when $Z > 25$) leads to good agreement with the energy obtained from summing up the first Z eigenvalues of the hydrogen operator (1.9) (Bohr atom, cf. Remark 2.5 and Sect. 3.1.4).

Possibly inspired by Yonei's and Tomishima's work, Lieb and Liberman [146, (2.32)] chose A such that the Z^2-correction in the TFW model agrees with that of the quantum model, i.e., $D^{\mathrm{TFW}} = q/4$. This choice leads to $A = 0.1859$.

Another choice for A is motivated by comparing the densities ρ_Z^{TFW} and the one-particle ground state density ρ_{S} in (1.5) on the length scale Z^{-1}. As indicated in (1.14), the spherical average over ρ_{S} tends to the hydrogenic density ρ_{S}^H (cf. (1.12)) on the length scale Z^{-1} *pointwise* as $Z \to \infty$. Recall that all hydrogenic eigenfunctions of (1.13) are finite at the origin with only eigenfunctions with $\ell = 0$ being nonzero. (For a detailed analysis of ρ_{S}^H, we refer to Theorem 3.11 by Heilmann and Lieb [104].)

Thus, the limiting value of $Z^{-3}\rho_{\mathrm{S}}(Z^{-1}\cdot(0+))$ as $Z\to\infty$ is well-defined and can be computed explicitly thanks to the explicit knowledge of hydrogen eigenfunctions. At the same time, the convergence in (2.35) is pointwise as well, so $Z^{-3}\rho_Z^{\mathrm{TFW}}(Z^{-1}\cdot)$ is also accessible and can be computed numerically. Thus, to have agreement of the quantum density ρ_{S} and the TFW density on the scale Z^{-1}, one may choose Weizsäcker's parameter A so that one has the equality

$$\rho_{\mathrm{S}}^{H}(0)=(A\gamma_{\mathrm{TF}}/2)^{-3/2}\rho_{\infty}(0). \tag{2.36}$$

This led Lieb and Liberman to the numerical value $A\approx 0.4798$, cf. [146, (2.33)].

The following table summarizes plausible choices for Weizsäcker's coefficient A.

	A
Weizsäcker (mass defect theory)	$=1$
Kirzhnits (gradient expansion)	≈ 0.11
Yonei–Tomishima (numerical computations, Bohr atom)	≈ 0.2
Lieb–Liberman (energy agreement)	≈ 0.1859
Lieb–Liberman (density agreement)	≈ 0.4798

In conclusion, one may regard the proof of the Scott conjecture in TFW theory as a warm-up problem for its proof in the full quantum problem. (One may wonder whether Scott was aware of Weizsäcker's extension [240] at the time of writing his work [200].)

2.3 Hellmann–Weizsäcker functional

In this subsection, we discuss the so-called *Hellmann–Weizsäcker functional*, which plays an important role in the proof of the Scott conjecture by Siedentop and Weikard, as we will discuss in Sect. 3.1.4 below.

We first introduce the Hellmann–Weizsäcker functional for fixed angular momentum $\ell\in\mathbb{N}_0$. We work on $\mathbb{R}_+$ with the measure $\mathrm{d}r$. Here and in the following, we use the letter $\varrho:\mathbb{R}_+\to\mathbb{R}_+$ to denote one-dimensional, radial densities with particle number $\int_0^\infty\varrho(r)\mathrm{d}r$, i.e., we integrate with respect to $\mathrm{d}r$ and not $r^2\mathrm{d}r$. Three-dimensional densities are denoted by the letter $\rho:\mathbb{R}^3\to\mathbb{R}_+$. We set

$$\mathcal{G}^{\mathrm{W}}:=\left\{\varrho\in L^3(\mathbb{R}_+):\ \varrho\geq 0,\ \sqrt{\varrho}'\in L^2(\mathbb{R}_+),\ \varrho(0)=0\right\}.$$

Here, the derivative of $\sqrt{\varrho}'$ is understood in the sense of distributions and we recall that the square integrability of this derivative implies that $\sqrt{\varrho}$ is continuous on $\mathbb{R}_+$ and has a boundary value $\sqrt{\varrho}(0)$. In particular, the last condition in the definition of $\mathcal{G}^{\mathrm{W}}$ is well-defined. Let

$$\alpha_\ell := \left(\frac{\pi}{q(2\ell+1)}\right)^2$$

and define, for $Z > 0$ and $\varrho \in \mathcal{G}^{\mathrm{W}}$,

$$\mathcal{E}^{\mathrm{HW}}_{\ell,Z}(\varrho) := \frac{1}{2}\int_0^\infty \left(((\sqrt{\varrho})'(r))^2 + \frac{\ell(\ell+1)}{r^2}\varrho(r) + \frac{\alpha_\ell}{3}\varrho(r)^3\right) \mathrm{d}r - \int_0^\infty \frac{Z}{r}\varrho(r)\,\mathrm{d}r. \tag{2.37}$$

The second term is finite by Hardy's inequality and so is the last term, since, for any $R > 0$,

$$\int_0^\infty \frac{\varrho_\ell(r)}{r}\,\mathrm{d}r \leq R\int_0^R \frac{\varrho_\ell(r)}{r^2}\,\mathrm{d}r + \left(\int_R^\infty \varrho_\ell(r)^3\,\mathrm{d}r\right)^{1/3}\left(\int_R^\infty r^{-3/2}\,\mathrm{d}r\right)^{2/3}.$$

Thus, $\mathcal{E}^{\mathrm{HW}}_{\ell,Z}$ is well-defined on $\mathcal{G}^{\mathrm{W}}$.

Next, we introduce the full Hellmann–Weizsäcker functional. It is defined on sequences $\underline{\varrho} := (\varrho_0, \varrho_1, ...)$ with $\varrho_\ell \in \mathcal{G}^{\mathrm{W}}$ for all $\ell \in \mathbb{N}_0$. For such a sequence, we set

$$\tilde{D}(\underline{\varrho}, \underline{\varrho}) := \frac{1}{2}\sum_{\ell,\ell'\geq 0}\iint_{\mathbb{R}_+\times\mathbb{R}_+} \mathrm{d}r\,\mathrm{d}r'\,\frac{\varrho_\ell(r)\varrho_{\ell'}(r')}{\max\{r, r'\}}.$$

Let

$$\mathcal{M}^{\mathrm{W}} := \left\{\underline{\varrho} \in (\mathcal{G}^{\mathrm{W}})^{\mathbb{N}_0} : \sum_{\ell\geq 0}\int_0^\infty \left(((\sqrt{\varrho_\ell})'(r))^2 + \frac{\ell(\ell+1)}{r^2}\varrho_\ell(r) + \frac{\alpha_\ell}{3}\varrho_\ell(r)^3\right)\mathrm{d}r < \infty,\right.$$
$$\left.\tilde{D}(\underline{\varrho}, \underline{\varrho}) < \infty\right\} \tag{2.38}$$

The *Hellmann–Weizsäcker functional* [108] is defined, for $\underline{\varrho} \in \mathcal{M}^{\mathrm{W}}$, by

$$\mathcal{E}^{\mathrm{HW}}_Z(\underline{\varrho}) := \sum_{\ell\geq 0}\mathcal{E}^{\mathrm{HW}}_{\ell,Z}(\varrho_\ell) + \tilde{D}(\underline{\varrho}, \underline{\varrho}). \tag{2.39}$$

One can prove that $\mathcal{E}^{\mathrm{HW}}_Z$ is well-defined on $\underline{\varrho} \in \mathcal{M}^{\mathrm{W}}$. This functional is studied in detail in [207]; see also Hoops [112]. Finally, for $N > 0$, we set

$$\mathcal{M}^{\mathrm{W}}_N := \left\{\underline{\varrho} \in \mathcal{M}^{\mathrm{W}} : \sum_{\ell\geq 0}\int_0^\infty \varrho_\ell(r)\,\mathrm{d}r = N\right\}.$$

The following theorem shows how the terms $(\alpha_\ell/3)\varrho_\ell^3$ in the Hellmann–Weizsäcker functional are related to the term $(3/5)\gamma_{\mathrm{TF}}\rho^{5/3}$ in the TF functional.

Theorem 2.11 *Let $E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z)$ be the Thomas–Fermi energy of the constrained problem without electron–electron repulsion; see Remark 2.5. Then, if $N = \alpha Z$ and $Z \to \infty$,*

$$\inf\left\{\mathcal{E}^{\mathrm{HW}}_Z(\underline{\varrho}) - \tilde{D}(\underline{\varrho},\underline{\varrho}) : \underline{\varrho} \in \mathcal{M}^{\mathrm{W}}_N\right\} = E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z) + \mathcal{O}_\alpha(Z^2). \tag{2.40}$$

Remark 2.12 (1) If one replaces Weizsäcker's gradient term in the definition of $\mathcal{E}^{\mathrm{HW}}_Z$ by $(4r^2)^{-1}\varrho_\ell$ (which is a lower bound by Hardy's inequality), one is led to the *Hellmann functional*

$$\mathcal{E}^{\mathrm{H}}_Z(\underline{\varrho}) := \sum_{\ell\geq 0} \mathcal{E}^{\mathrm{H}}_{\ell,Z}(\varrho_\ell), \tag{2.41}$$

$$\mathcal{E}^{\mathrm{H}}_{\ell,Z}(\varrho_\ell) := \frac{1}{2}\int_0^\infty \left(\frac{\alpha_\ell}{3}\varrho_\ell(r)^3 + \frac{(\ell+1/2)^2}{r^2}\varrho_\ell(r)\right)\mathrm{d}r - \int_0^\infty \frac{Z}{r}\varrho_\ell(r)\,\mathrm{d}r. \tag{2.42}$$

These functionals are well-defined on sets $\mathcal{G}$ and $\mathcal{M}$ that are defined in a similar manner as $\mathcal{G}^{\mathrm{W}}$ and $\mathcal{M}^{\mathrm{W}}$. A straightforward computation [213, Theorem 1] shows

$$\inf\{\mathcal{E}^{\mathrm{H}}_Z(\underline{\varrho}) : \underline{\varrho} \in \mathcal{M}_N\} = E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z) + \mathcal{O}(Z^2N^{-1/3}). \tag{2.43}$$

This is one step in the proof of Theorem 2.11.

(2) Hoops [112, Theorem 4.5] showed that the electron–electron repulsion does not alter (2.40) significantly. Moreover, he computed the coefficient of the Z^2-term in this case. If $Z - \alpha Z^\beta \leq N \leq Z + Q_c$, where $\alpha > 0$, $0 \leq \beta < 2/3$, and $Q_c \geq 0$ is the Z-independent number specified in [112, Theorem 3.3], then one has

$$\inf\{\mathcal{E}^{\mathrm{HW}}_Z(\underline{\varrho}) : \underline{\varrho} \in \mathcal{M}^{\mathrm{W}}_N\} = E^{\mathrm{TF}}(Z) + qGZ^2 + o(Z^2), \tag{2.44}$$

where G is the infimum of another explicit functional defined in [112, (4.15)–(4.16)] and obeys the numerical bounds $2\cdot 0.388 \leq G \leq 2\cdot 0.417$, see [112, p. 58]. The coefficient G is about three times bigger than Scott's coefficient $1/4$. As Hoops puts it [112, p. 58]: *"To have such a big discrepancy suggests that the Hellmann–Weizsäcker functional does not treat the innermost electrons sufficiently accurate to get the same behavior as the quantum mechanical ground state. That means that Weizsäcker's gradient term is a major correction (it creates a Z^2-order term) at places where we have strong varying potentials but it does not suffice to give the right coefficient."*

2.4 Relativistic TFW functional by Engel and Dreizler

As discussed in the introduction, a relativistic description of large Coulomb systems is mandatory. This suggests to consider relativistic density functionals. A particularly simple one can be traced back at least to Vallarta and Rosen [241] and Jensen [124], who mimicked the steps (2.2)–(2.4) with the kinetic energy $p^2/2$ replaced by $\sqrt{c^2p^2+c^4}-c^2$ to derive a relativistic Thomas–Fermi theory. For $q = 2$ and nuclear configuration

$\underline{Z} = (Z_1, \dots, Z_K) \in (0,\infty)^K$, $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, the resulting functional is

$$\mathcal{E}^{\mathrm{rTF}}_{c,V}(\rho) := \mathcal{T}^{\mathrm{rTF}}(\rho) - \int_{\mathbb{R}^3} V(x)\rho(x)\,\mathrm{d}x + D(\rho,\rho) + U \tag{2.45}$$

with

$$\mathcal{T}^{\mathrm{rTF}}(\rho) := \int_{\mathbb{R}^3} \frac{c^5}{8\pi^2} T^{\mathrm{rTF}}\left(\frac{p(x)}{c}\right) \mathrm{d}x, \tag{2.46}$$

$T^{\mathrm{rTF}}(t) := t(t^2+1)^{3/2} + t^3(t^2+1)^{1/2} - \operatorname{arsinh}(t) - \frac{8}{3}t^3$, and the Fermi momentum

$$p(x) := (3\pi^2\rho(x))^{1/3}. \tag{2.47}$$

This functional is unbounded from below since the relativistic kinetic energy cannot control the Coulomb singularity. This was already anticipated by Jensen, see also Gombás [94, §14], [95, Chapter III, Section 16] for a review of these facts. Gombás also suggested that Weizsäcker's (non-relativistic) inhomogeneity correction would prevent the unboundedness from below. His suggestion was first carried out by Tomishima [238], who showed, among other things, the finiteness of the energy and the electron density at the nucleus.

While Gombás introduced the Weizsäcker term ad hoc, Engel and Dreizler [43] offered a (formal) derivation from quantum electrodynamics. The Engel–Dreizler derivation also yields an exchange term. In total, their functional reads

$$\mathcal{E}^{\mathrm{rTFWD}}_{c,V}(\rho) := \mathcal{E}^{\mathrm{rTF}}_{c,V}(\rho) + \mathcal{T}^{\mathrm{W}}(\rho) - \mathcal{X}(\rho). \tag{2.48}$$

The Weizsäcker term is

$$\mathcal{T}^{\mathrm{W}}(\rho) := \int_{\mathbb{R}^3} \frac{3A}{8\pi^2} (\nabla p)^2(x) \cdot c \cdot f\left(\frac{p(x)}{c}\right)^2 \mathrm{d}x \tag{2.49}$$

with $f(t)^2 := t(1+t^2)^{-1/2} + 2t^2(1+t^2)^{-1} \operatorname{arsinh}(t)$ and an adjustable parameter $A > 0$. The exchange term is

$$\mathcal{X}(\rho) := \int_{\mathbb{R}^3} \frac{c^4}{8\pi^3} X\left(\frac{p(x)}{c}\right) \mathrm{d}x \tag{2.50}$$

with $X(t) := 2t^4 - 3[t(1+t^2)^{1/2} - \operatorname{arsinh}(t)]^2$.

The analysis of $\mathcal{E}^{\mathrm{rTFWD}}_{c,V}$ started with Chen [25] and was continued in the works [26, 27]. In the ultrarelativistic limit, i.e., in absence of the arsinh function in the Weizsäcker term, it had been investigated earlier in [16]. The functional $\mathcal{E}^{\mathrm{rTFWD}}_{c,V}$ is naturally defined on

$$P := \{\rho \in L^{4/3}(\mathbb{R}^3) : \rho \geq 0,\ D(\rho,\rho) < \infty,\ \nabla(F \circ p) \in L^2(\mathbb{R}^3)\}, \tag{2.51}$$

$$P_N := \left\{\rho \in P : \int_{\mathbb{R}^3} \rho \leq N\right\} \tag{2.52}$$

where $F(t) := \int_0^t f(s)\,\mathrm{d}s$. In the absence of the exchange term $\mathcal{X}(\rho)$, Chen [25, p. 39] proved the existence of minimizers of $\mathcal{E}^{\mathrm{rTFWD}}_{c,V}$.

As we shall discuss in Sect. 4.1, *non-renormalized* relativistic quantum models for Coulomb systems are not expected to be well-defined for arbitrary large nuclear charges, since the Coulomb potential and the kinetic energy have the same scaling behavior, at least for high momenta. The renormalization in Engel's and Dreizler's derivation leads to the arsinh function in Weizsäcker's term, which ensures the lower boundedness of $\mathcal{E}^{\mathrm{rTFWD}}_{c,V}(\rho)$ for all nuclear charges $\underline{Z}$. The necessity of renormalization was realized early, see, e.g., Heisenberg and Euler [107].

Theorem 2.13 ([26, Theorem 1]) *For $K = 1$ and given $c, Z, A > 0$ let $\kappa := Z/(c\sqrt{A})$. Let $\xi := (4\pi)^{-1}\max\{X(t)/t^3 : t > 0\}$ and $s_0 : \mathbb{R}_+ \to \mathbb{R}_+$ be the explicit function given in* [26, (16)]*, which is strictly monotone increasing and satisfies $s_0(0) = 0$ and $\lim_{\kappa\to\infty} s_0(\kappa) = \infty$. Then for all $\rho \in P$ with $\int \rho = N$ one has*

$$\mathcal{E}^{\mathrm{rTFWD}}_{c,V}(\rho) \geq -\frac{4s_0(\kappa)^5}{5T^{\mathrm{rTF}}(s_0(\kappa))} E^{\mathrm{TF}}_{Z=1}(1) Z^{7/3} - \xi cN. \tag{2.53}$$

In the absence of the Dirac term, an analogous result was proved in [27, Theorem 1]. In fact, their result also holds in the molecular case.

The existence of minimizers and bounds for the excess charge (in absence or presence of the Dirac term) were proved by Chen [25, p. 39] and in [27, Theorem 2] and [26, Theorem 2]. In passing, we mention that bounds on the excess charge are available in many non-relativistic models; see, e.g., Lieb [144], as well as Benguria and Lieb [15], Solovej [222], and the more recent work [88].

The following result concerns the energy asymptotics in the atomic case.

Theorem 2.14 ([205, Theorem 1]) *Let $K = 1$ and $Z/c > 0$ be fixed. Then*

$$\inf_{\rho\in P_Z} \mathcal{E}^{\mathrm{rTFWD}}_{c,Z/|x|}(\rho) = E^{\mathrm{TF}}(Z) + \mathcal{O}(Z^2) \quad \text{as } Z \to \infty, \tag{2.54}$$

where P_Z is defined in (2.52) *with $N = Z$.*

The core elements of the proof are the facts that the relativistic kinetic energy is dominated by the non-relativistic one, that relativistically described electrons far away from the nucleus behave non-relativistically, and that the TFW functional provides a Z^2-correction to the Thomas–Fermi energy. One may argue that Theorem 2.14 is expected in view of the heuristics explained in Sect. 4.3.1. Still, it is quite surprising that a formally derived functional correctly yields a fundamental feature like the ground state energy of large atoms.

3 Quantum mechanics of non-relativistic Coulomb systems

In this section, we review results for the energy and density of non-relativistic systems with one or several nuclei. These are described by the Hamilton operator $H_{N,V}$ in (1.1). Recall that the ground state energy $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ is defined in (1.4).

3.1 Atoms without magnetic fields

3.1.1 Thomas–Fermi scale

One of the main results of the work [152] of Lieb and Simon is that TF theory correctly describes both the leading order of the quantum mechanical ground state energy of large atoms, and the one-particle electron distribution on the length scale $Z^{-1/3}$ in the limit $Z \to \infty$. This is summarized in the following theorem.

Theorem 3.1 *Let $E^{\mathrm{S}}(N, Z) = \inf \operatorname{spec}(H_{N,Z})$ be the ground state energy of $H_{N,Z}$. Fix $\alpha = N/Z$. Then,*

$$\lim_{Z\to\infty} \frac{E^{\mathrm{S}}(N, Z)}{Z^{7/3}} = E^{\mathrm{TF}}(\alpha, 1). \tag{3.1}$$

If $E^{\mathrm{S}}(N, Z)$ is an eigenvalue of $H_{N,Z}$ and ρ_{S} is the one-particle density of any of its associated normalized eigenfunctions, then one has

$$\lim_{Z\to\infty} \|Z^{-2}\rho_{\mathrm{S}}(Z^{-1/3}\cdot) - \rho^{\mathrm{TF}}_{Z=1}(\alpha, \cdot)\|_{\mathrm{C}} = 0, \tag{3.2}$$

$$\lim_{Z\to\infty} \int_{\mathbb{R}^3} U(x) Z^{-2}\rho_{\mathrm{S}}(Z^{-1/3}x)\,\mathrm{d}x = \int_{\mathbb{R}^3} U(x)\rho^{\mathrm{TF}}_{Z=1}(\alpha, x)\,\mathrm{d}x \tag{3.3}$$

for all $U \in L^{5/2}(\mathbb{R}^3)$. Finally, if $N \leq Z$, then the convergence $Z^{-2}\rho_{\mathrm{S}}(Z^{-1/3}\cdot) \to \rho^{\mathrm{TF}}_{Z=1}(\alpha, \cdot)$ also holds in the weak L^1-sense.

Remark 3.2 As mentioned before, $E^{\mathrm{S}}(N, Z)$ is indeed an eigenvalue of $H_{N,Z}$ in the most relevant case $N = Z$. However, there are generalizations of the convergence statements (3.2)–(3.3) that remain valid even if $E^{\mathrm{S}}(N, Z)$ is not an eigenvalue. Namely, one can take ρ_{S} to be the one-particle density of elements in any sequence of normalized functions ψ_N, $N = 1, 2, \ldots$ in the form domain of $H_{N,Z}$ satisfying

$$\lim_{N\to\infty} \frac{\langle \psi_N, H_{N,Z}\psi_N\rangle - E^{\mathrm{S}}(N, Z)}{Z^{7/3}} = 0. \tag{3.4}$$

Such a sequence $(\psi_N)_{N\in\mathbb{N}}$ is sometimes called an approximate ground state of $H_{N,Z}$ on the Thomas–Fermi scale.

Asymptotics (3.1) and (3.3) (the latter for characteristic functions of bounded, measurable sets) are due to Lieb and Simon [152, Theorems III.1, III.3]. In the context of a proof of stability of matter, Thirring [234] found a substantially simpler proof of the lower bound in (3.1) that used coherent states involving Gaussians. Lieb slightly generalized these coherent states and found a shorter proof for the upper bound in (3.1), see [144, Theorem 5.1] (where also an adaption of Thirring's proof of the lower bound is reported). Formula (3.3) (for certain characteristic functions) is also due to Baumgartner [12], while the convergence (3.2) of ρ_{S} in Coulomb norm was proved by Fefferman and Seco [66]. (Note that the Scott correction with error bound $\mathcal{O}(Z^{47/24})$

(see [1, 2, 208, 209]) actually implies the quantitative bound $\|Z^{-2}\rho_S(Z^{-1/3}\cdot) - \rho^{\mathrm{TF}}_{Z=1}(\alpha,\cdot)\|_C \lesssim Z^{-3/16}$.) Asymptotics (3.3) for general $U \in L^{5/2}(\mathbb{R}^3)$ follow from the fact that finite sums of characteristic functions of bounded measurable sets are dense in $L^{5/2}$, together with the uniform boundedness $\int_{\mathbb{R}^3}\left(Z^{-2}\rho_S(Z^{-1/3}x)\right)^{5/3} = \mathcal{O}(1)$, which in turn follows from the kinetic Lieb–Thirring inequality.

Remark 3.3 (The Bohr atom) Let $E_{\mathrm{Bohr}}(N,Z)$ be the ground state energy of $H_{N,V}$ in the atomic case ($K = 1$, $\underline{R} = 0$, $\underline{Z} = Z$) and without electron–electron repulsion, that is, without the double sum in (1.1). Let $E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z)$ be the corresponding quantity in TF theory, defined in Remark 2.5. Note that, by scaling, $E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z) = E^{\mathrm{TF}}_{\mathrm{Bohr}}(N/Z,1)\cdot Z^{7/3}$. We claim that, for any fixed $\alpha = N/Z$,

$$\lim_{Z\to\infty}\frac{E_{\mathrm{Bohr}}(N,Z)}{Z^{7/3}} = E^{\mathrm{TF}}_{\mathrm{Bohr}}(\alpha,1).$$

Indeed, this can either be proved by following the proof of Theorem 3.1 or, much more directly, by using the explicit formula for the eigenvalue $E_{\mathrm{Bohr}}(N,Z)$ and the explicit formula for $E^{\mathrm{TF}}_{\mathrm{Bohr}}(N,Z)$ in (2.22).

Let us return to the situation of Theorem 3.1. Recall that the TF minimizer satisfies $\rho^{\mathrm{TF}}_{Z=1}(x) \sim \mathrm{const}\ |x|^{-3/2}$ as $x \to 0$ (see Theorem 2.3). Thus, Theorem 3.1 implies that the ground state density develops a singularity on the scale $Z^{-1/3}$. This is not surprising, since the electrons in a Bohr atom have a density proportional to Z^3, which tends to infinity relative to the TF magnitude Z^2. Thus, TF theory is not expected to provide a complete description of large atoms, especially on scales Z^{-1} close to the nucleus. For this reason, we now look closer at the electrons on the shorter, hydrogenic length scale Z^{-1}.

3.1.2 Scott scale

As explained in the introduction, Scott's idea is that the leading correction to TF theory stems from the few innermost high-energy electrons on distances Z^{-1} from the nucleus, i.e., on the natural length scale of the hydrogen operator S^H_Z (see (1.9)). Recall also that the eigenvalues of this operator have magnitude $\mathcal{O}(Z^2)$.

The following theorem states that *Scott's conjecture is indeed true*. Hughes [113, 114] (lower bound) and the works [208, 209] (upper and lower bound) proved this conjecture for neutrally charged atoms. Since the Scott correction should not depend on "electrons on the outermost shells", it was believed that the conjecture also holds for ions. Indeed, Bach [1, 2] showed that also this intuition is correct and proved Scott's conjecture for (positive and negative) ions.

Theorem 3.4 ([1, 2, 113, 114, 208, 209]) *Let $\alpha > 0$ and $N = \alpha Z$ with $N \in \mathbb{N}$. Then, the ground state energy $E^{\mathrm{S}}(N,Z)$ of $H_{N,Z}$ in (1.1) satisfies*

$$E^{\mathrm{S}}(N,Z) = E^{\mathrm{TF}}(\alpha,1)\cdot Z^{7/3} + \frac{q}{4}\cdot Z^2 + \mathcal{O}(Z^{47/24}). \tag{3.5}$$

We will give a heuristic argument in favor of Theorem 3.4 later in Sect. 3.1.4. At this point, we would also like to mention two alternative and interesting proofs of Theorem 3.4 by Ivrii and Sigal [119] and by Solovej and Spitzer [225], which do not use the spherical symmetry of the atomic case (see Theorem 3.15). Both used them to prove the Scott conjecture for clamped nuclei whose distances are scaled by $Z^{-1/3}$.

Next, we turn to the strong Scott conjecture. Scott's heuristics led Lieb [144, p. 623] to the belief that for large Z the suitably rescaled electron density ρ_{S} on distances Z^{-1} from the nucleus converges to the hydrogenic density ρ_{S}^H (see (1.12)). Since the magnitude of the total electronic density of a Bohr atom is proportional to Z^3, one suspects that the correct object to study is the scaled density $Z^{-3}\rho_{\mathrm{S}}(Z^{-1}x)$. A step towards the proof of the strong Scott conjecture in the full N-particle setting was taken in [202], where the following upper bound was shown:

$$\limsup_{Z\to\infty} \frac{\rho_{\mathrm{S}}(0)}{Z^3} \leq \frac{\pi}{24} q; \tag{3.6}$$

see also Theorem 3.8 for a more general statement. Interestingly, the numerical value $\pi/24$ is quite close to $q^{-1}\cdot\rho_{\mathrm{S}}^H(0) = \pi^{-1}\zeta(3)$ (see Theorem 3.11). Motivated by this strong numerical evidence, Iantchenko et al. [117] eventually proved *Lieb's strong Scott conjecture*.

In fact, in [117] also an angular-momentum-resolved version of this conjecture is proved. To formulate this result, for $\ell \in \mathbb{N}_0$, we let $Y_{\ell,m}$, $m \in \{-\ell, \dots, \ell\}$, be $L^2(\mathbb{S}^2)$-orthonormal spherical harmonics of degree ℓ. We then define one-dimensional, radial, angular-momentum-resolved densities of $\psi \in \bigwedge_{\nu=1}^N L^2(\mathbb{R}^3 : \mathbb{C}^q)$ by

$$\varrho_\ell(r) := Nr^2 \sum_{m=-\ell}^{\ell} \sum_{\sigma=1}^{q} \int_{\Gamma^{N-1}} \left| \int_{\mathbb{S}^2} \mathrm{d}\omega\, \overline{Y_{\ell,m}(\omega)} \psi(r\omega, \sigma; y_2, \dots, y_N) \right|^2 \mathrm{d}y_2 \cdots \mathrm{d}y_N \tag{3.7}$$

for $\ell \in \mathbb{N}_0$ and $r > 0$. We recall that we use the letter $\varrho : \mathbb{R}_+ \to \mathbb{R}_+$ to denote one-dimensional, radial densities with particle number $\int_0^\infty \varrho(r)\mathrm{d}r$, i.e., we integrate with respect to $\mathrm{d}r$ and not $r^2\mathrm{d}r$. Three-dimensional densities are denoted by the letter $\rho : \mathbb{R}^3 \to \mathbb{R}_+$. The densities ϱ_ℓ in (3.7) are related to the total density ρ in (1.5) by

$$\int_{\mathbb{S}^2} \rho(r\omega)\, \mathrm{d}\omega = r^{-2} \sum_{\ell=0}^{\infty} \varrho_\ell(r) \tag{3.8}$$

for $r > 0$. If ψ in (3.7) is an eigenfunction of $H_{N,V}$ with eigenvalue $E^{\mathrm{S}}(N, Z, R)$, we write

$$\varrho_{\ell,\mathrm{S}} \tag{3.9}$$

for (3.7) and analogously for other Hamiltonians that we discuss later.

Recall that the (spinless) hydrogen Hamiltonian S^H was defined in (1.13). Due to the spherical symmetry of S^H, one can consider its parts in a fixed angular momentum channel $\ell \in \mathbb{N}_0$, i.e.,

$$\frac{1}{2}\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\ell(\ell+1)}{r^2}\right)-\frac{1}{r} \quad \text{in } L^2(\mathbb{R}_+,\mathrm{d}r:\mathbb{C}). \tag{3.10}$$

The eigenfunctions $\psi^{\mathrm{S}}_{n,\ell,m}$ of S^H are then of the form

$$\psi^{\mathrm{S}}_{n,\ell,m}(x)=\frac{\psi^{\mathrm{S}}_{n,\ell}(|x|)}{|x|}Y_{\ell,m}\left(\frac{x}{|x|}\right), \tag{3.11}$$

where $\psi^{\mathrm{S}}_{n,\ell}\in L^2(\mathbb{R}_+,\mathrm{d}r)$ are normalized eigenfunctions of (3.10). Unsöld's theorem (cf. [239, p. 377], [247, Section 18.4]) states that $\sum_{m=-\ell}^{\ell}Y_{\ell,m}(\omega)\overline{Y_{\ell,m}(\sigma)}=\frac{2\ell+1}{4\pi}P_\ell(\omega\cdot\sigma)$ for $\omega,\sigma\in\mathbb{S}^2$ and the ℓ-th Legendre polynomial P_ℓ, which obeys $P_\ell(1)=1$. Using this, one can carry out the m-summation in the definition of the hydrogenic density ρ_S^H in (1.12) and obtains

$$\rho^H_{\mathrm{S}}(x)=\frac{1}{4\pi|x|^2}\sum_{\ell=0}^{\infty}\varrho^H_{\ell,\mathrm{S}}(|x|),\quad x\in\mathbb{R}^3 \tag{3.12}$$

with the one-dimensional, angular-momentum-resolved hydrogenic densities

$$\varrho^H_{\ell,\mathrm{S}}(r):=q(2\ell+1)\sum_{n=0}^{\infty}|\psi^{\mathrm{S}}_{n,\ell}(r)|^2,\quad r>0. \tag{3.13}$$

Formula (3.12) implies, in particular, that ρ_S^H is spherically symmetric, as mentioned in the introduction. The right sides of (3.12) and (3.13) converge; see Theorem 3.11 for details.

The following theorem states the validity of the strong Scott conjecture.

Theorem 3.5 ([117]) *Let $\ell\in\mathbb{N}_0$, $E^{\mathrm{S}}(N,Z)$ be an eigenvalue of $H_{N,Z}$, and ρ_{S} and let $\varrho_{\ell,\mathrm{S}}$ be the total and angular-momentum-resolved one-particle densities associated with any of its eigenfunctions, respectively. Then, the following statements hold.*

(1) (Convergence of angular momentum density). For all $r>0$, one has pointwise convergence

$$\lim_{Z\to\infty}Z^{-3}\varrho_{\ell,\mathrm{S}}(r/Z)=\varrho^H_{\ell,\mathrm{S}}(r). \tag{3.14}$$

Moreover, for $v\in L^1(\mathbb{R}_+,\mathrm{d}r)$ one has

$$\lim_{Z\to\infty}\int_0^\infty r^{-1}v(r)Z^{-3}\varrho_{\ell,\mathrm{S}}(r/Z)\,\mathrm{d}r=\int_0^\infty r^{-1}v(r)\varrho^H_{\ell,\mathrm{S}}(r)\,\mathrm{d}r. \tag{3.15}$$

(2) *(Convergence of total density) Let $W \in L^\infty(\mathbb{S}^2)$ and $r > 0$. Then the total density, when spherically averaged, converges pointwise to the hydrogenic density, i.e.,*

$$\lim_{Z\to\infty} \int_{\mathbb{S}^2} W(\omega) Z^{-3} \rho_{\mathrm{S}}(r\omega/Z)\, \mathrm{d}\omega = \rho_{\mathrm{S}}^H(r\sigma) \int_{\mathbb{S}^2} W(\omega)\, \mathrm{d}\omega \quad \text{for all } \sigma \in \mathbb{S}^2. \tag{3.16}$$

Moreover, for any locally bounded $v \in L^1(\mathbb{R}^3)$, one has

$$\lim_{Z\to\infty} \int_{\mathbb{R}^3} |x| v(x) Z^{-3} \rho_{\mathrm{S}}(x/Z)\, \mathrm{d}x = \int_{\mathbb{R}^3} |x| v(x) \rho_{\mathrm{S}}^H(x)\, \mathrm{d}x. \tag{3.17}$$

Remark 3.6 Theorem 3.5 remains valid for the total and angular-momentum-resolved one-particle densities ρ_{S} and $\varrho_{\ell,\mathrm{S}}$ of elements in any sequence of normalized functions ψ_N, $N = 1, 2, \ldots$ in the form domain of $H_{N,Z}$ satisfying

$$\lim_{N\to\infty} \frac{\langle \psi_N, H_{N,Z}\psi_N\rangle - E^{\mathrm{S}}(N,Z)}{Z^2} = 0. \tag{3.18}$$

Such a sequence $(\psi_N)_{N\in\mathbb{N}}$ is sometimes called approximate ground state of $H_{N,Z}$ on the Scott scale.

Later, we shall see that the hydrogenic density obeys

$$\rho_{\mathrm{S}}^H(x) = \left(\frac{1}{\gamma_{\mathrm{TF}}}\right)^{3/2} |x|^{-3/2} + o(|x|^{-3/2}) \tag{3.19}$$

as $|x| \to \infty$. Since Theorem 2.3 asserts that the TF density has the exact same asymptotic behavior, but for small $|x|$ (on the scale $Z^{-\frac{1}{3}}$), Theorem 3.5 shows that there is a smooth transition of ρ_{S} between the length scales Z^{-1} and $Z^{-\frac{1}{3}}$.

Remark 3.7 (More results on the quantum density) We summarize some further results for the many-particle ground state density.

(1) Recall that Theorem 3.5 does not say anything yet about the quantum density at the origin $r = 0$. Therefore, it is of interest to find quantitative upper bounds on $\rho_{\mathrm{S}}(0)$. We record the following theorem.

Theorem 3.8 ([187, 188, 202]) *Let $(\psi_N)_{N\in\mathbb{N}}$ be an approximate ground state of $H_{N,Z}$ on the Scott scale in the sense of Remark 3.6, and let ρ_{S} be the one-particle density of the element ψ_N of that sequence. Fix any $c > 0$ and assume that $N/Z > 0$ is fixed or that $N > Z - cZ^{1/2}$. Then one has*

$$\limsup_{Z\to\infty} \frac{\rho_{\mathrm{S}}(0)}{Z^3} \leq \frac{\pi}{24} q. \tag{3.20}$$

For $N = Z$, this was shown in [202] before the strong Scott conjecture [117] was proved. The result for ions is due to Rakowsky [187] and [188]. At the core of the proof of Theorem 3.8 lies a linear response argument and the inequality

$$\rho_{\mathrm{S}}(0) \leq \frac{Z}{2\pi} \int_{\mathbb{R}^3} \frac{\rho_{\mathrm{S}}(x)}{|x|^2} \, \mathrm{d}x \tag{3.21}$$

due to Hoffmann–Ostenhof et al. [110]. Theorem 3.8 supports the belief that the strong Scott conjecture holds for ions as well.

(2) The work [118] proved the convergence of the one-particle ground state density matrix on Scott's scale. Consider an approximate ground state $(\psi_N)_{N\in\mathbb{N}}$ of $H_{N,Z}$ on the Scott scale. For $x, y \in \mathbb{R}^3$, let

$$\begin{aligned} \gamma_S(x,y) := \sum_{\sigma_1,\ldots,\sigma_N=1}^{q} \sum_{\nu=1}^{N} \int_{\mathbb{R}^{3(N-1)}} \mathrm{d}x_1 \cdots \mathrm{d}x_{\nu-1} \, \mathrm{d}x_{\nu+1} \cdots \mathrm{d}x_N \\ \psi_N(x_1,\sigma_1;\ldots;x_{\nu-1},\sigma_{\nu-1};x,\sigma_\nu;x_{\nu+1},\sigma_{\nu+1};\ldots;x_N,\sigma_N) \\ \times \overline{\psi_N(x_1,\sigma_1;\ldots;x_{\nu-1},\sigma_{\nu-1};y,\sigma_\nu;x_{\nu+1},\sigma_{\nu+1};\ldots;x_N,\sigma_N)} \end{aligned} \tag{3.22}$$

be the kernel of the associated approximate one-particle ground state density matrix γ_S. Observe that $0 \leq \gamma_S \leq q$ is a trace class operator. Recall the $L^2(\mathbb{R}^3)$-normalized eigenfunctions $\psi^{\mathrm{S}}_{n,\ell,m}$ of the hydrogen operator (1.13). Define the orthogonal projection onto the negative (purely discrete) spectral subspace of this operator by

$$\gamma_S^H := q \cdot \sum_{n\geq 0} \sum_{\ell\geq 0} \sum_{m=-\ell}^{\ell} |\psi^{\mathrm{S}}_{n,\ell,m}\rangle\langle\psi^{\mathrm{S}}_{n,\ell,m}|, \tag{3.23}$$

where the series is pointwise convergent (see Theorem 3.11 by Heilmann and Lieb [104]). Then, the following result holds.

Theorem 3.9 ([118, Theorem 1]) *Let K be a trace-class operator, and let γ_S be an approximate one-particle ground state density matrix of $H_{N,Z}$ on the Scott scale in the sense of Remark 3.6. Then, one has the weak convergence*

$$\lim_{Z\to\infty} \mathrm{Tr}\left(K \cdot Z^{-3} \gamma_S\left(\frac{\cdot}{Z}, \frac{\cdot}{Z}\right)\right) = \mathrm{Tr}(K\gamma_S^H). \tag{3.24}$$

(3) As already indicated, there is a smooth transition of ρ_{S} between the scales Z^{-1} and $Z^{-1/3}$ (in view of Theorems 2.3 and 3.5, and Formula (3.19)). This may have led to Lieb's belief [144] that $Z^{-3/2-3/(2\delta)}\rho_{\mathrm{S}}(x/Z^\delta)$ should also behave like $(1/\gamma_{\mathrm{TF}})^{3/2}|x|^{-3/2}$ when $\delta \in (1/3, 1)$. In [116], Iantchenko succeeded in proving this conjecture using some of Ivrii's and Sigal's methods [119] adapted to the case of (neutral) atoms.

Theorem 3.10 ([116, Theorem 2]) *Let $(\psi_N)_{N\in\mathbb{N}}$ be an approximate ground state of $H_{N,Z}$ (in (1.1)) on the Scott scale in the sense of Remark 3.6, and let ρ_{S} be the one-particle density associated with ψ_N. Let $U \in C^\infty(\mathbb{R}^3 \setminus \{0\}) \cap L^\infty(\mathbb{R}^3)$, and assume*

$$|\partial^\nu U(x)| \lesssim_\nu |x|^{-|\nu|-1}\langle x\rangle^{-3}, \quad |x| \geq 2, |\nu| \geq 0, \tag{3.25}$$

$$|\partial^\nu U(x)| \lesssim_\nu |x|^{-|\nu|}, \quad |x| \leq 2, |\nu| \geq 0. \tag{3.26}$$

(Here $\nu = (\nu_1, \nu_2, \nu_3) \in (\mathbb{N}_0)^3$ and $|\nu| = \nu_1 + \nu_2 + \nu_3$. We also use the notation $\langle x\rangle := \sqrt{1+|x|^2}$ for $x \in \mathbb{R}^d$.) Then for any $\delta \in (1/3, 1)$, one has

$$\lim_{Z\to\infty} \int_{\mathbb{R}^3} U(x) Z^{-3/2-3/(2\delta)} \rho_{\mathrm{S}}(x/Z^\delta)\,\mathrm{d}x = \int_{\mathbb{R}^3} U(x) \left(\frac{1}{\gamma_{\mathrm{TF}}}\right)^{3/2} |x|^{-3/2}\,\mathrm{d}x. \tag{3.27}$$

It may very well be true that Theorem 3.10 also holds under less severe assumptions on the test function U. Theorem 3.10 can also be generalized to the molecular case, see [116, Theorem 7] for details. Further extensions were recently outlined by Ivrii [120–122].

Some elements of the proof of Theorem 3.5 will be given in the relativistic case, which is in spirit the same but technically more elaborate (Sect. 4.3.3). Here we just mention that all known proofs for the convergence of the density (as of this writing) rely on energetic results. It would be interesting to see if this scheme could be reversed.

Before we come to the arguments in favor of Theorem 3.4, we collect some properties of the hydrogenic density ρ_{S}^H.

3.1.3 Hydrogenic density

Recall the normalized eigenfunctions $\psi^{\mathrm{S}}_{n,\ell,m}$ of the hydrogen operator (1.13) acting in $L^2(\mathbb{R}^3 : \mathbb{C})$. Recall also the definition of the hydrogenic densities ρ_{S}^H and, for $\ell \in \mathbb{N}_0$, the angular-momentum-resolved version $\varrho^H_{\ell,\mathrm{S}}$ in (1.12) and (3.12)–(3.13), respectively. The specific knowledge of the $\psi^{\mathrm{S}}_{n,\ell,m}$ allowed Heilmann and Lieb [104] to analyze ρ_{S}^H and $\varrho^H_{\ell,\mathrm{S}}$ in great detail. For $n \in \mathbb{N}_0$, $\ell \in \mathbb{N}_0$, and $m \in \{-\ell, \dots, \ell\}$, they are

$$\psi^{\mathrm{S}}_{n,\ell,m}(x) = R_{n,\ell}(r) Y_{\ell,m}\left(\frac{x}{|x|}\right), \tag{3.28}$$

where the $R_{n,\ell}$ are explicitly known [104, p. 3630]. Thus, by Unsöld's theorem,

$$\rho_{\mathrm{S}}^H(x) = \frac{q}{4\pi} \sum_{n\geq 0} \sum_{\ell\geq 0} (2\ell+1) R_{n,\ell}(|x|)^2. \tag{3.29}$$

Making heavy use of properties of special functions, they carried out the ℓ- and n-summations (in that order) and proved the following theorem.

Theorem 3.11 ([104, Theorem 1, p. 3631])

(1) The series on the right side of (3.29) *converges pointwise.*
(2) One has the asymptotic expansion, as $r \to \infty$,

$$\rho_{\mathrm{S}}^{H}(r) = \frac{q}{\sqrt{2}\pi^2} r^{-3/2} \left[\sum_{j\geq 0} a_j (8r)^{-j} - \sin(\sqrt{32r}) \sum_{j\geq 1} b_j (8r)^{-j} + \cos(\sqrt{32r}) \sum_{j\geq 1} c_j (8r)^{-j-1/2} \right]. \tag{3.30}$$

The first few coefficients are:

$$a_0 = 2/3 \quad a_1 = -1/12 \quad a_2 = 79/960,$$
$$b_1 = 3/2 \quad b_2 = -140\,589/11\,200,$$
$$c_1 = 141/40 \quad c_2 = -2\,028\,627/44\,800.$$

(3) Let $\lambda \in (0, 1]$ *and let* $\rho_{Z=1}^{\mathrm{TF}}(\lambda, x)$ *be the TF minimizer of* $\mathcal{E}_{Z=1}^{\mathrm{TF}}$ *on* $\mathcal{I}_\lambda$. *Then for any* $\lambda \in (0, 1]$,

$$\lim_{|x|\to\infty} |x|^{3/2} \rho_{\mathrm{S}}^{H}(|x|) = \lim_{|x|\to 0} |x|^{3/2} \rho_{Z=1}^{\mathrm{TF}}(\lambda, x). \tag{3.31}$$

(4) $\rho_{\mathrm{S}}^{H}(r)$ *is monotone decreasing and achieves its maximum at* $r = 0$ *with*

$$\rho_{\mathrm{S}}^{H}(r) \leq \rho_{\mathrm{S}}^{H}(0) = \frac{q}{\pi} \sum_{n\geq 0} (n+1)^{-3} \approx q \cdot 0.383. \tag{3.32}$$

Remark 3.12 The "shell structure", i.e., the oscillations of $\rho_{\mathrm{S}}^{H}(r)$, is barely visible. As Heilmann and Lieb put it [104, p. 3633]: "*In fact, it is necessary to take two derivatives with respect to r in order to make the oscillatory terms as large as the nonoscillatory ones. In short, shell structure is not a prominent property of this universal atomic function.*" For graphical illustrations, see, e.g., [104, p. 3633].

3.1.4 Scott's derivation of the Z^2-correction and ideas of Siedentop and Weikard

We first present Scott's [200] heuristic derivation of the Z^2-correction to TF theory. For simplicity, we restrict ourselves to the neutral case $N = Z$. Our exposition follows March [161, pp. 8–11]. Afterward, we present the ideas in [208] to prove the upper bound (3.5).

Scott's idea is that the Z^2-correction stems from the innermost electrons, which live roughly a distance Z^{-1} away from the nucleus. Since there are only "few" electrons

on this scale, one expects the electron–electron repulsion to be irrelevant there, i.e., the electrons should be described by the hydrogen operator S_Z^H.

These heuristics suggest that the first correction of the Thomas–Fermi energy for a large atom should be the difference between the "Bohr energy" (i.e., the sum over all hydrogen eigenvalues) and the Thomas–Fermi Bohr energy. We computed the latter in (2.22). In the neutral case, we obtain

$$E^{\mathrm{TF}}_{\mathrm{Bohr}}(Z) = -(3^{1/3}/2)q^{2/3}Z^{7/3}. \tag{3.33}$$

On the other hand, in the Bohr atom, each shell (indexed by $n \in \mathbb{N}$) of energy $-Z^2/(2n^2)$ has qn^2 states. Thus, the $N = Z$ many electrons occupy k shells, where k is determined by

$$Z = N = q\left(\sum_{n=1}^{k} n^2 + (k+1)^2\varepsilon\right) = q\left(\frac{k^3}{3} + \frac{k^2}{2} + \frac{k}{6} + (k+1)^2\varepsilon\right) \tag{3.34}$$

and where $0 \leq \varepsilon < 1$ is the fraction of the $(k+1)$-st shell that is filled. One finds $k = (3Z/q)^{1/3} - \frac{1}{2} - \varepsilon + o(1)$ as $Z \to \infty$. Thus, the energy of the Bohr atom is

$$E_{\mathrm{Bohr}}(Z) = -\frac{Z^2}{2}q\left(\varepsilon + \sum_{n=1}^{k} 1\right) = E^{\mathrm{TF}}_{\mathrm{Bohr}}(Z) + \frac{q}{4}Z^2 + o(Z^2). \tag{3.35}$$

The second term here is exactly the Scott correction.

We now present some ideas from [208] that enter into the proof of the upper bound in (3.5). As usual, an upper bound will be derived using a suitable trial state. As we will describe later in more detail, this trial state contains, in addition to hydrogen orbitals, also so-called Macke orbitals. It is in connection with these Macke orbitals that the Hellmann–Weizsäcker functional defined in Sect. 2.3 comes into play [212].

To motivate why this functional is relevant, we recall that the TFW energy has an asymptotic expansion whose first term coincides with the TF energy and whose second term behaves like Z^2. If one could show that the TFW functional (with some choice of A) provides an upper bound for the ground state energy $E^{\mathrm{S}}(N, Z)$, then there might be a chance that this functional can be used to prove the upper bound in (3.5). Apart from a factor that decreases like N^{-2} and is irrelevant in the limit $N \to \infty$, this was indeed proved in *one spatial dimension* by March [162] and March and Young [163]. They showed that the sum of the first N eigenvalues of $-\frac{d^2}{dx^2} - v$ in $L^2(\mathbb{R})$ is bounded from above by

$$\inf\left\{\int_{\mathbb{R}}\left[\frac{1}{2}((\sqrt{\rho})')^2 + \frac{1}{2}\cdot\frac{\pi^2}{3}\left(1 - \frac{1}{N^2}\right)\rho(x)^3 - v(x)\rho(x)\right]\mathrm{d}x \;:\; \rho \in \mathcal{A}_N\right\}, \tag{3.36}$$

where $\mathcal{A}_N$ is the one-dimensional analog of (2.25); see also [206, Section 3] or Müller [176, pp. 114–139]. To prove this, March and Young used cleverly constructed trial

functions by Macke [158, 159]. These so-called Macke orbitals may be seen as a (finer) analogue of coherent states. March and Young also proposed d-dimensional versions of Macke's orbitals, which, however, lead to a contradiction, as was pointed out by Müller [176, pp. 131–134], Lieb [143, p. 96], and the author of [212, p. 213]; see also Dietze [36] for a closer inspection.

Let us return to the three-dimensional case. In [207, Theorem 5.2] and [213, (4.1)] (see also Ladányi [136] and [212] for precursors), the following upper bound was proved in the atomic case:

$$E^{\mathrm{S}}(N,Z) \leq \inf\left\{\mathcal{E}^{\mathrm{HW}}_Z(\underline{\varrho}) + \mathcal{R}(\underline{\varrho}) : \underline{\varrho} \in \mathcal{M}^{\mathrm{W}}_N\right\} \tag{3.37}$$

with an (unimportant) remainder term

$$\mathcal{R}(\underline{\varrho}) := \sum_{\ell\geq 0, n_\ell\neq 0} \frac{\alpha_\ell}{3}\left(\frac{-1+6\varepsilon_\ell-3\varepsilon_\ell^2}{n_\ell^2} + \frac{2\varepsilon_\ell^3-6\varepsilon_\ell^2+4\varepsilon_\ell}{n_\ell^3}\right)\int_0^\infty \varrho_\ell(r)^3\,\mathrm{d}r. \tag{3.38}$$

Here $n_\ell = (q(2\ell+1))^{-1}\int_0^\infty \varrho_\ell(r)\,\mathrm{d}r$ and $\varepsilon_\ell := n_\ell - [n_\ell] \in [0,1)$. Physically, n_ℓ has the interpretation as the number of electrons in the sector of angular momentum ℓ corresponding to fixed magnetic quantum number m and spin s. (In [207, 208, 213], this number is denoted by $N_{\ell,m,s}$.) The total number of electrons in the angular momentum channel ℓ is therefore $q(2\ell+1)n_\ell$. Note that, if n_ℓ is integer, then $\mathcal{R}(\underline{\varrho}) \leq 0$ and the term can be dropped. For general n_ℓ, this term has the effect of slightly modifying the prefactor of the term involving ϱ_ℓ^3 in the Hellmann–Weizsäcker functional. For properly chosen $\underline{\varrho}$, it is $\mathcal{O}(Z^{5/3})$, cf. [208, pp. 472–473, Proposition 3.6]. In this way, one can obtain from (3.37) the bound

$$E^{\mathrm{S}}(N,Z) \leq E^{\mathrm{TF}}(N,Z) + \mathrm{const}\ Z^2. \tag{3.39}$$

This contains an error term of the correct order and is the 'interacting analogue' of the upper bound in Theorem 2.11. The proof also reveals that Weizsäcker's correction is $o(Z^2)$ when the ℓ-summation starts at $L = [Z^{1/12}]$, cf. [208, Proposition 3.3]. Thus, we have obtained an upper bound of the correct order, but not yet with the correct coefficient. In order to obtain the correct coefficient, we need one more modification of the above strategy.

After this preparation, we can give a brief outline of the proof in [208] of the upper bound in (3.5). The basic idea is to describe electrons close to the nucleus using hydrogen eigenfunctions, and electrons far from the nucleus using the Hellmann–Weizsäcker functional. The distinction between "close" and "far" electrons is implemented by an angular momentum cutoff $L = [Z^\delta]$ for an appropriate $\delta \in (0,1)$. This is suggested by the solution of Kepler's problem, where the perihelion of a planet grows like the square of its angular momentum. For the hydrogen atom, this is reflected by the explicitly computable expectation values of powers of $|x|$ in their eigenfunctions, see, e.g., Bethe [17, (3.19)–(3.27)].

In the following outline, we disregard the electron–electron repulsion. Treating this term requires some effort, but it does not affect the Scott correction and, therefore, ignoring this term helps to clarify the basic steps in the proof.

(1) Use the variational principle with a trial state that is made up of hydrogen eigenfunctions for angular momenta $0 \leq \ell < [Z^{\frac{1}{12}}]$ and Macke orbitals for $\ell \geq [Z^{\frac{1}{12}}]$. For the precise form of the resulting upper bound, see [208, (2.3)].
(2) The Macke orbitals for large ℓ lead to the Hellmann–Weizsäcker functionals $\mathcal{E}^{\mathrm{HW}}_{\ell,Z}$ (see (2.37)). These functionals are summed starting from $\ell \geq [Z^{1/12}]$. As remarked after (3.39), the Weizsäcker term is $o(Z^2)$; see [208, Proposition 3.3]. Thus, $\sum_{\ell \geq [Z^{1/12}]} \mathcal{E}^{\mathrm{HW}}_{\ell,Z}[\varrho_\ell] \leq \sum_{\ell \geq [Z^{1/12}]} \mathcal{E}^{\mathrm{H}}_{\ell,Z}[\varrho^{\mathrm{H}}_\ell] + o(Z^2)$ in terms of the Hellmann functionals $\mathcal{E}^{\mathrm{H}}_{\ell,Z}$ in (2.42) and their minimizers $\varrho^{\mathrm{H}}_\ell$.
(3) The summation of the hydrogen eigenvalues up to angular momentum $\ell < [Z^{1/12}]$ leads to $\sum_{\ell < [Z^{1/12}]} \mathcal{E}^{\mathrm{H}}_{\ell,Z}[\varrho^{\mathrm{H}}_\ell]$ plus Scott's correction $\frac{q}{4} Z^2$ plus $\mathcal{O}(Z^{23/12})$; see [208, Propositions 3.1 and 3.2].
(4) By (2.43), the leading order of the Hellmann functional is the TF energy modulo $\mathcal{O}(Z^{5/3})$-errors; see [208, Lemma 4.1].

This concludes our sketch of the upper bound in (3.5). We mention that Macke orbitals and the Hellmann–Weizsäcker functional can also be used to give a proof of the lower bound of (1.10); see [210] and, for an exposition of the basic ideas, [211]. Both in the proof of the upper and lower bound, the use of Macke orbitals is reminiscent of the use of coherent states by Thirring and Lieb in their proofs of the asymptotic exactness of TF theory.

3.2 Molecules without magnetic fields

3.2.1 Thomas–Fermi scale

As in the atomic case, TF theory predicts the leading term of $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ and the density ρ_{S} on the TF length scale correctly. More precisely, fix $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$, $\underline{Z} = (Z_1, \dots, Z_K) \in (0, \infty)^K$, $|\underline{Z}| = \sum_{\kappa=1}^K Z_\kappa$, and the TF electron number λ. It is not necessary to assume $\lambda \leq |\underline{Z}|$. For each $N = 1, 2, \dots$, define $a_N = N/\lambda$. In $H_{N,V}$ in (1.1) replace each Z_κ by $a_N \cdot Z_\kappa$ and each R_κ by $a_N^{-1/3} R_\kappa$. This means that the nuclei come together at the rate $a_N^{-1/3} \sim |\underline{Z}|^{-1/3}$ as $N \to \infty$ when $N/|\underline{Z}|$ is kept constant. At this point we want to emphasize that this scaling of R_κ, which has become customary in the mathematical literature, is motivated by mathematical considerations rather than by physical reality. However, neither the energy nor the density is expected to be close to the molecular ground state energy or ground state density. In fact, the two energies are expected to differ already to leading order, since the minimal positions of the nuclei do not scale in this way.

In case $E^{\mathrm{S}}(N, a_N \underline{Z}, a_N^{-1/3} \underline{R})$ is an eigenvalue, let ψ_N be an associated eigenfunction with corresponding one-particle density ρ_{S}. If not, ρ_{S} shall denote the one-particle density associated with the element ψ_N of an approximate ground state $(\psi_N)_{N \in \mathbb{N}}$ on the Thomas–Fermi scale in the sense of Remark 3.2.

By the scaling relations (2.13) for TF theory, we have

$$\rho^{\mathrm{TF}}(\lambda, \underline{Z}, \underline{R}, x) = a_N^{-2}\rho^{\mathrm{TF}}(N, a_N\underline{Z}, a_N^{-1/3}\underline{R}, a_N^{-1/3}x) \tag{3.40a}$$

$$E^{\mathrm{TF}}(\lambda, \underline{Z}, \underline{R}) = a_N^{-7/3}E^{\mathrm{TF}}(N, a_N\underline{Z}, a_N^{-1/3}\underline{R}). \tag{3.40b}$$

We now make the connection between the full quantum problem (1.4) with frozen nuclear positions associated to $H_{N,V}$, and TF theory by letting the total nuclear charge $|\underline{Z}|$ and the electron number N tend to infinity in such a way that the ionization degree $N/|\underline{Z}|$ is kept constant. The following theorem due to Lieb and Simon [152] generalizes Theorem 3.1.

Theorem 3.13 ([152, Section III], [141, Theorem 5]) *Fix $\lambda > 0$ and let $a_N = N/\lambda$, $\underline{z} = (z_1, \ldots, z_K) \in (0, \infty)^K$, and $\underline{R} = (R_1, \ldots, R_K) \in \mathbb{R}^{3K}$. Let $H_{N,V}$ be as in (1.1) with nuclear configuration $\{a_N\underline{z}, a_N^{-1/3}\underline{R}\}$. Then, the following statements hold:*

(1) The quantity $a_N^{-7/3}E^{\mathrm{S}}(N, a_N\underline{z}, a_N^{-1/3}\underline{R})$ has a limit as $N \to \infty$ and this limit coincides with $E^{\mathrm{TF}}(\lambda, \underline{z}, \underline{R})$.

(2) The scaled one-particle density $a_N^{-2}\rho_{\mathrm{S}}(a_N^{-1/3}x)$ associated with a (possibly approximate) ground state on the TF scale has a limit as $N \to \infty$. If $\lambda \leq |\underline{z}|$, then the convergence is weakly in L^1 and the limit is $\rho^{\mathrm{TF}}(\lambda, |\underline{z}|, \underline{R}, x)$. If $\lambda > |\underline{z}|$, then the convergence is weakly in L^1_{loc} and the limit is $\rho^{\mathrm{TF}}(|\underline{z}|, |\underline{z}|, \underline{R}, x)$.

As Lieb [141, p. 560] notices: "*Note that if $\lambda > |\underline{z}|$, then this result says that the surplus charge moves off to infinity and the result is a neutral molecule. This means that large atoms or molecules cannot have a negative ionization proportional to the total nuclear charge; at best they can have a negative ionization which is a vanishingly small fraction of the total charge.*"

Remark 3.14 Note that, if the R_κ are kept *fixed and unscaled*, one ends up with isolated atoms in the limit $N \to \infty$, see Lieb [141, pp. 559–560] for the precise statements.

3.2.2 Scott scale

In addition to being independent of the absence or presence of the electron–electron repulsion and of the ionization degree, one expects the Z^2-correction to be the sum of the Scott corrections of the atoms constituting the molecule, as long as the minimal internuclear distance is not too close to the Scott scale. In particular, this is expected for ground states of molecules where the interatomic distance is expected to be of order one in the scaling parameter of the nuclear charges.

The Scott conjecture for molecules with frozen nuclear positions was first proved by Ivrii and Sigal [119] using a multiscale analysis and microlocal techniques. Later, Solovej and Spitzer [225] found a proof that is partly similar to the multi-scale analysis in [119] using an interesting new coherent states method. Around the same time, Balodis [8] proved the Scott correction uniformly in K. The following theorem is the content of [225, Theorem 1].

Theorem 3.15 *Let $\underline{Z} = (Z_1, \dots, Z_K) \in (0,\infty)^K$ and $\underline{R} = |\underline{Z}|^{-1/3}(r_1, \dots, r_K) \in \mathbb{R}^{3K}$ with $\min_{k\neq\ell} |r_k - r_\ell| > r_0$ for some $r_0 > 0$. Define $\underline{z} = (z_1, \dots, z_K) := |\underline{Z}|^{-1}\underline{Z}$. Let $E^{\mathrm{TF}}(\underline{z}, \underline{r})$ be the Thomas–Fermi energy of the unconstrained problem (2.9) and let $E^{\mathrm{S}}(N, \underline{Z}, \underline{R})$ be the ground state energy of $H_{|\underline{Z}|,V}$ with nuclear configuration $\underline{Z}$ and $\underline{R}$. Then*

$$E^{\mathrm{S}}(|\underline{Z}|, \underline{Z}, \underline{R}) = E^{\mathrm{TF}}(\underline{z}, \underline{r}) \cdot |\underline{Z}|^{7/3} + \frac{q}{4} \sum_{\kappa=1}^{K} Z_\kappa^2 + \mathcal{O}(|\underline{Z}|^{2-1/30}) \tag{3.41}$$

as $|\underline{Z}| \to \infty$, where the error term $\mathcal{O}(|\underline{Z}|^{2-1/30})$ besides $|\underline{Z}|$ depends only on $Z_1, \dots, Z_K$ and r_0.

3.3 Molecules with self-generated magnetic fields

In this subsection, we consider molecules in the presence of a classical magnetic field. Quoting Erdős and Solovej [53, p. 229]: "*External magnetic fields were taken into account in* [153, 154] *(homogeneous) and* [52] *(inhomogeneous), but subject to certain regularity conditions. Self-generated magnetic fields, obtained from Maxwell's equation, are not known to satisfy these conditions.*" For this reason, we shall consider self-generated magnetic fields here. (See (2) in Remark 3.16 below for an explanation of the word "self-generated".)

To introduce the setting precisely, let

$$\mathfrak{A} := \left\{ \underline{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3 : \mathbb{R}^3) : \nabla \otimes \underline{A} \in L^2(\mathbb{R}^3, \mathbb{R}^{3\times 3}),\ \mathrm{div}(\underline{A}) = 0 \right\}, \tag{3.42}$$

where all derivatives are understood in the sense of distributions and where $\nabla \otimes \underline{A}$ denotes the 3×3 matrix of all derivatives $\partial_i A_j$. We set $|\nabla \otimes \underline{A}|^2 = \sum_{i,j=1}^3 |\partial_i A_j|^2$ and, with $c > 0$ denoting the velocity of light, consider the magnetic field energy

$$\frac{c^2}{8\pi} \int_{\mathbb{R}^3} |(\nabla \times \underline{A})(x)|^2 \, \mathrm{d}x = \frac{c^2}{8\pi} \int_{\mathbb{R}^3} |(\nabla \otimes \underline{A})(x)|^2 \, \mathrm{d}x. \tag{3.43}$$

The identity here is a consequence of the Coulomb gauge.

In the non-relativistic approximation, the one-particle kinetic energy is the *magnetic Schrödinger* or *Pauli operator*

$$T(\underline{A}) = \frac{1}{2} \left(-i\nabla + \underline{A}(x)\right)^2 \quad \text{or} \quad T(\underline{A}) = \frac{1}{2} \left[\underline{\sigma} \cdot \left(-i\nabla + \underline{A}(x)\right)\right]^2 \tag{3.44}$$

in $L^2(\mathbb{R}^3 : \mathbb{C}^2)$ depending on whether the particles are (effectively) considered spinless, or have spin-$\frac{1}{2}$. Here $\underline{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ is the vector of Pauli matrices.

The total energy of a non-relativistic molecule with charges $\underline{Z} = (Z_1, \dots, Z_K) \in (0, \infty)^K$ fixed at positions $\underline{R} = (R_1, \dots, R_K) \in \mathbb{R}^{3K}$ in a classical magnetic vector potential $\underline{A} \in \mathfrak{A}$ is then described by the Hamilton operator

$$H_{N,V,\underline{A}} = \sum_{\nu=1}^{N} \left(T^{(\nu)}(\underline{A}) - V(x_\nu) \right) + \sum_{1 \le \nu < \mu \le N} \frac{1}{|x_\nu - x_\mu|} + U \quad \text{in} \bigwedge_{\nu=1}^{N} (L^2(\mathbb{R}^3 : \mathbb{C}^2)), \tag{3.45}$$

where V is the electron–nucleus interaction as in (1.2).

In case the kinetic energy is described by the Pauli operator, we will need to impose an additional restriction on the quotient $|\underline{Z}|/c^2$. Indeed, if $|\underline{Z}|/c^2$ is sufficiently small, then the quadratic form associated with (3.45) is bounded from below uniformly in $\underline{A}$, see, e.g., [69, 92, 147, 148]. Crucially, however, stability fails, if $|\underline{Z}|/c^2$ is too large, see [48, 157].

For both choices of the magnetic kinetic energy $T(\underline{A})$ and each fixed $\underline{A} \in \mathfrak{A}$, the operator $H_{N,V,\underline{A}}$ is defined as the Friedrichs extension of the corresponding quadratic form defined on $\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^2)$.

For fixed magnetic potential $\underline{A} \in \mathfrak{A}$ and fixed nuclear positions, the electronic ground state energy is

$$E(N, \underline{Z}, \underline{R}, \underline{A}) := \inf \operatorname{spec}(H_{N,V,\underline{A}}). \tag{3.46}$$

The total ground state energy with fixed nuclear positions arises from minimizing this energy with respect to $\underline{A} \in \mathfrak{A}$, i.e.,

$$E^{\mathrm{S,mag}}(N, \underline{Z}, \underline{R}, c) := \inf_{\underline{A} \in \mathfrak{A}} \left(E(N, \underline{Z}, \underline{R}, \underline{A}) + \frac{c^2}{8\pi} \int_{\mathbb{R}^3} |(\nabla \times \underline{A})(x)|^2 \, \mathrm{d}x \right). \tag{3.47}$$

Remark 3.16 (1) In (3.47), it suffices to minimize over all compactly supported $\underline{A} \in \mathfrak{A}$.

(2) As remarked in [53, p. 231], the Euler–Lagrange equation that arises from minimizing $\left\langle \Psi, \left(H_{N,V,\underline{A}} + \frac{c^2}{8\pi} \int_{\mathbb{R}^3} |(\nabla \times \underline{A})(x)|^2 \, \mathrm{d}x \right) \Psi \right\rangle$ over Ψ and $\underline{A}$, corresponds to the stationary version of the coupled Maxwell–Pauli system, i.e., the eigenvalue problem $H_{N,V,\underline{A}} \Psi = E^{\mathrm{S,mag}}(N, \underline{Z}, \underline{R}, c) \Psi$ together with the Maxwell equation for the magnetic field, i.e., $\nabla \times \underline{B} = 4\pi c^{-2} \underline{J}_\Psi$; here $\underline{J}_\Psi$ is the current of the wave function Ψ. This explains why $\underline{B}$ is called a self-generated magnetic field.

3.3.1 Thomas–Fermi scale

On the Thomas–Fermi scale, it turns out—as the semiclassical picture suggests—that the magnetic field does not change the leading order of the energetic expansion as $Z \to \infty$. To make this precise, define

$$E^{\mathrm{S,mag}}(\underline{Z}, \underline{R}, c) := \inf_{N \in \mathbb{N}} E^{\mathrm{S,mag}}(N, \underline{Z}, \underline{R}, c), \tag{3.48}$$

$$E^{\mathrm{S,nonmag}}(\underline{Z},\underline{R},c) := \inf_{N\in\mathbb{N}} \inf \operatorname{spec}(H_{N,V,0}). \tag{3.49}$$

Erdős and Solovej [53] proved the following theorem.

Theorem 3.17 ([53, Theorem 1.1]) *Suppose that $T(\underline{A})$ is either the Pauli or the magnetic Schrödinger operator (see (3.44)) and assume (for simplicity) $Z := Z_1 = Z_2 = \ldots = Z_K$ and $|R_i - R_j| \geq c_1 Z^{-1/3}$ for all $i \neq j$. Then, there is a positive constant κ_0 such that if $Z/c^2 \leq \kappa_0$, then*

$$E^{\mathrm{S,nonmag}}(\underline{Z},\underline{R},c) \geq E^{\mathrm{S,mag}}(\underline{Z},\underline{R},c) \geq E^{\mathrm{S,nonmag}}(\underline{Z},\underline{R},c) - c_2 Z^{\frac{7}{3}-\frac{1}{63}}. \tag{3.50}$$

3.3.2 Scott scale

The following theorem due to Erdős et al. [50, 51] characterizes the Scott correction in the presence of a self-generated magnetic field.

Theorem 3.18 ([50, Theorem 1.1]) *Suppose that $T(\underline{A})$ is either the Pauli or the magnetic Schrödinger operator (see (3.44)). Let $\underline{z} = (z_1,\ldots,z_K) \in (0,\infty)^K$ with $\sum_{\kappa=1}^K z_k = 1$ and $\underline{r} = (r_1,\ldots,r_K) \in \mathbb{R}^{3K}$ with $\min_{k\neq\ell} |r_k - r_\ell| \geq r_0$ for some $r_0 > 0$ be given. Let $\underline{Z} = (Z_1,\ldots,Z_K) = |\underline{Z}|(z_1,\ldots z_K) \in (0,\infty)^K$ for some $|\underline{Z}| > 0$ and $\underline{R} = |\underline{Z}|^{-1/3}\underline{r}$ be the charges and the positions of the nuclei of the operator $H_{N,V,\underline{A}}$ in (3.45). Then there is a universal (independent of $\underline{z}$, $\underline{r}$, K), continuous, monotone non-increasing function $S : (0,\kappa_0] \to \mathbb{R}$ with some universal $\kappa_0 > 0$ and with $\lim_{\kappa\searrow 0} S(\kappa) = \frac{1}{4}$ such that, as $|\underline{Z}| = \sum_{\kappa=1}^K Z_\kappa \to \infty$ and $c \to \infty$ with $\max_\kappa 8\pi Z_\kappa/c^2 \leq \kappa_0$, one has*

$$E^{\mathrm{S,mag}}(|\underline{Z}|,\underline{Z},\underline{R},c) = E^{\mathrm{TF}}(\underline{z},\underline{r})|\underline{Z}|^{7/3} + 2\cdot|\underline{Z}|^2 \sum_{\kappa=1}^K z_\kappa^2 \cdot S(8\pi Z_\kappa/c^2) + o(|\underline{Z}|^2). \tag{3.51}$$

Remark 3.19 (1) The theorem is independent of the existence and uniqueness (modulo gauge freedom) of the minimizer $\underline{A}$. In fact, it is not clear whether the infimum is attained at $\underline{A} = 0$ or at a non-trivial magnetic field.

(2) The threshold κ_0 for which the assertion of Theorem 3.18 is shown to hold is less than the number κ_{cr} above which $H_{N,V,\underline{A}}$ fails to be bounded from below.

(3) The theorem does not assert that $S(\kappa)$ is *strictly* decreasing, although this is believed to be the case. In fact, it is conceivable that $S(\kappa)$ is constant equal to $1/4$ for all κ up to the critical value κ_{cr} beyond which it is minus infinity.

Remark 3.20 Theorem 3.17 concerning the leading order holds also in the case where the $\underline{A}$-field is quantized [53]. So far, the Scott correction for quantized $\underline{A}$-fields—both in the non-relativistic setting of Theorem 3.18 and in the relativistic one of Theorem 4.21 below—can only be proved with a low ultraviolet cutoff of the magnetic field which corresponds to a length scale that is longer than the Scott scale, i.e., would be of limited physical meaning.

We emphasize that all results in this subsection concern the energy. We are not aware of results concerning the density.

4 Relativistic Coulomb systems

In this section, we discuss relativistic models of large Coulomb systems and begin with an overview of the relevant underlying one-particle operators.

4.1 One-particle operators

We first introduce the relativistic one-particle operators that will later be used to construct the many-particle operators that we are mostly interested in. We state conditions on the coupling constants of the Coulomb potential for which the operators can be defined and recall some of their spectral properties. More detailed treatments are contained, e.g., in the textbooks by Balinsky and Evans [7] and Thaller [232], as well as in the paper by Matte and Stockmeyer [166] and the references therein.

4.1.1 Chandrasekhar operator

Definition

The Chandrasekhar operator is the simplest relativistic operator discussed here. In the literature, this operator is sometimes referred to as Herbst operator or pseudorelativistic operator. Its origins can be traced back at least to Chandrasekhar in the context of (in)stability of neutron stars [24] (see also [155, 156]). The mathematical investigation of this operator started with the work of Herbst [109]; see also Weder [244] for electric potentials $V(x) = |x|^{-\beta}$ with $\beta \in (0, 1)$. The operator is defined as the Friedrichs extension of the quadratic form—whenever it is bounded from below (see (4.3))—associated with

$$C^H_{c,Z} := \sqrt{-c^2\Delta + c^4} - c^2 - \frac{Z}{|x|} \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}) \tag{4.1}$$

with form domain being the Schwartz space $\mathcal{S}(\mathbb{R}^3 : \mathbb{C})$. In the following, we abbreviate the fractional Laplace operator by $|p| := \sqrt{-\Delta}$.

Scaling

The operator has a natural length scale, namely c^{-1}. Indeed, scaling $x \mapsto x/c$ and writing $\gamma := Z/c$ shows that $C^H_{c,Z}$ is unitarily equivalent to $c^2 C^H_{1,\gamma} =: c^2 C^H_\gamma$ with

$$C^H_\gamma := \sqrt{-\Delta + 1} - 1 - \frac{\gamma}{|x|} \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}). \tag{4.2}$$

Kato's inequality

The sharp Hardy–Kato–Herbst inequality—for short Kato's inequality—states that

$$\frac{2}{\pi}\int_{\mathbb{R}^3}\frac{|u(x)|^2}{|x|}\,\mathrm{d}x \le \int_{\mathbb{R}^3}|\xi||\hat{u}(\xi)|^2\,\mathrm{d}\xi, \quad u\in\mathcal{S}(\mathbb{R}^3), \tag{4.3}$$

where $\hat{u}(\xi) := (2\pi)^{-3/2}\int_{\mathbb{R}^3}\mathrm{e}^{-ix\cdot\xi}u(x)\,\mathrm{d}x$; see Kato [130, Chapter 5, Formula (5.33)] (without proof) and Herbst [109, Theorem 2.5]. It follows from Kato's inequality and the inequalities $|p| \ge \sqrt{p^2+1}-1 \ge |p|-1$ that the quadratic form associated with C_γ^H is bounded from below if and only if $\gamma \le \gamma_{\mathrm{C}}$ with

$$\gamma_{\mathrm{C}} := \frac{2}{\pi}. \tag{4.4}$$

In fact, Raynal et al. [189] showed that the form is strictly greater than -1, even if $\gamma = 2/\pi$. Numerical evidence for this fact had been provided by Hardekopf and Sucher [101].

Domain considerations

The quadratic form domain of C_γ^H is $H^{1/2}(\mathbb{R}^3)$ when $\gamma < 2/\pi$. For $\gamma = 2/\pi$, the form domain is the closure of $\mathcal{S}(\mathbb{R}^3)$ with respect to the norm $(\langle u, C_\gamma^H u\rangle + \|u\|^2)^{1/2}$. In analogy to the local case, we believe that there are functions in the form domain of $C_{2/\pi}^H$ for which both sides of Kato's inequality are infinite and, therefore, that this form domain strictly contains $H^{1/2}(\mathbb{R}^3)$. For domain considerations, see also Le Yaouanc et al. [137].

Decomposition into angular momenta

The spherical symmetry allows to decompose C_γ^H into angular momentum channels. Decomposing $L^2(\mathbb{R}^3)$ into the direct sum

$$L^2(\mathbb{R}^3) = L^2(\mathbb{R}_+, r^2\,\mathrm{d}r)\otimes L^2(\mathbb{S}^2,\mathrm{d}\omega) = \bigoplus_{\ell\in\mathbb{N}_0}\mathcal{H}_\ell,$$

induces the decomposition

$$C_\gamma^H = \bigoplus_{\ell\in\mathbb{N}_0}\tilde{C}_{\ell,\gamma}^H\otimes\mathbf{1}_{K_\ell}, \tag{4.5}$$

where $\tilde{C}_{\ell,\gamma}^H$ acts in $L^2(\mathbb{R}_+, r^2\,\mathrm{d}r)$. Here $\mathcal{H}_\ell = L^2(\mathbb{R}_+, r^2\,\mathrm{d}r)\otimes K_\ell$ with K_ℓ being the eigenspace associated with the ℓ-th eigenvalue $\ell(\ell+1)$ of the Laplace–Beltrami

operator on $\mathbb{S}^2$. Defining $U : L^2(\mathbb{R}_+, r^2\,\mathrm{d}r) \to L^2(\mathbb{R}_+, \mathrm{d}r)$ by $(Uf)(r) = rf(r)$ for $f \in L^2(\mathbb{R}_+, r^2\,\mathrm{d}r)$, we may introduce

$$C^H_{\ell,\gamma} := U\tilde{C}^H_{\ell,\gamma}U^* = \sqrt{-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{r^2} + 1} - 1 - \frac{\gamma}{r} \quad \text{in } L^2(\mathbb{R}_+, \mathrm{d}r). \tag{4.6}$$

Fourier–Bessel transform

The kinetic energy operator

$$C_\ell := \sqrt{-\frac{\mathrm{d}^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + 1} - 1 \quad \text{in } L^2(\mathbb{R}_+, \mathrm{d}r) \tag{4.7}$$

can be diagonalized by the Fourier–Bessel transform $\Phi_\ell : L^2(\mathbb{R}_+, \mathrm{d}r) \to L^2(\mathbb{R}_+, \mathrm{d}r)$. For $u \in \mathcal{S}(\mathbb{R}_+)$, it acts as

$$u \mapsto (\Phi_\ell u)(k) := \int_0^\infty \mathrm{d}r\, \sqrt{kr} J_{\frac{1}{2}+\ell}(kr)u(r), \quad k \in \mathbb{R}_+. \tag{4.8}$$

Note that $\Phi_\ell = \Phi_\ell^*$ is unitary on $L^2(\mathbb{R}_+, \mathrm{d}r)$. Just as the Fourier transform diagonalizes translation invariant operators, the Fourier–Bessel transform diagonalizes translation invariant, spherically symmetric operators when restricted to a specific angular momentum channel ℓ. Define the operator p_ℓ in $L^2(\mathbb{R}_+, \mathrm{d}r)$ by the equality

$$\langle u, p_\ell u\rangle_{L^2(\mathbb{R}_+,\mathrm{d}r)} = \langle f, (-\Delta)^{1/2} f\rangle_{L^2(\mathbb{R}^3)} \tag{4.9}$$

for any $f(x) = |x|^{-1}u(|x|)Y_{\ell,m}(x/|x|)$ with $u \in \mathcal{S}$. Formally, we have

$$p_\ell = \sqrt{-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{r^2}}.$$

Then, for any spectral multiplier $F \in L^1_{\mathrm{loc}}(\mathbb{R}_+)$ of p_ℓ, one has

$$(\Phi_\ell(F(p_\ell)f))(k) = F(k) \cdot (\Phi_\ell f)(k), \quad k > 0, \tag{4.10}$$

and (in weak sense) the kernel of $F(p_\ell)$ is

$$(F(p_\ell))(r,s) = \int_0^\infty \mathrm{d}k\, F(k)\sqrt{kr}J_{\frac{1}{2}+\ell}(kr)\sqrt{ks}J_{\frac{1}{2}+\ell}(ks), \quad r,s > 0. \tag{4.11}$$

Hydrogen eigenvectors and density

Let $\psi^{\mathrm{C}}_{n,\ell,m}$ denote the $L^2(\mathbb{R}^3)$-normalized eigenvectors of C^H_γ. Due to the spherical symmetry of C^H_γ, we have

$$\psi^{\mathrm{C}}_{n,\ell,m}(x) = \frac{\psi^{\mathrm{C}}_{n,\ell}(|x|)}{|x|} Y_{\ell,m}\left(\frac{x}{|x|}\right), \tag{4.12}$$

where $\psi^{\mathrm{C}}_{n,\ell}$ are the $L^2(\mathbb{R}_+, \mathrm{d}r)$-normalized eigenvectors of $C^H_{\ell,\gamma}$. The radial, one-dimensional hydrogenic density in angular momentum channel $\ell \in \mathbb{N}_0$ is

$$\varrho^H_{\ell,\mathrm{C}}(r) := q(2\ell+1) \sum_{n\geq 0} |\psi^{\mathrm{C}}_{n,\ell}(r)|^2, \quad r > 0, \tag{4.13}$$

and the (spherically symmetric) total, three-dimensional density is

$$\rho^H_{\mathrm{C}}(x) = \frac{1}{4\pi|x|^2} \sum_{\ell\geq 0} \varrho^H_{\ell,\mathrm{C}}(|x|), \quad x \in \mathbb{R}^3. \tag{4.14}$$

These quantities are indeed well-defined as the following theorem due to [87, Theorem 1.4] shows. To state it, we define

$$\begin{aligned} \Phi : (-1,1] &\to (-\infty, 2/\pi] \\ \sigma &\mapsto \frac{2\Gamma\left(\frac{1}{2}(3-\sigma)\right)\Gamma\left(\frac{1}{2}(1+\sigma)\right)}{\Gamma\left(\frac{\sigma}{2}\right)\Gamma\left(\frac{1}{2}(2-\sigma)\right)} = (1-\sigma)\tan\left(\frac{\pi\sigma}{2}\right). \end{aligned} \tag{4.15}$$

This is a monotone increasing function, which satisfies $\lim_{\sigma\searrow -1}\Phi(\sigma) = -\infty$ and $\Phi(0) = 0$, and whose maximal value is $2/\pi = \Phi(1)$. Consequently, for any $\gamma \in [0, 2/\pi]$ there is a unique $\sigma_\gamma \in [0,1]$ such that $\Phi(\sigma_\gamma) = \gamma$ for $\gamma \in [0, 2/\pi]$, i.e.,

$$\sigma_\gamma = \Phi^{-1}(\gamma) \in [0,1] \quad \text{for } \gamma \in [0, 2/\pi]. \tag{4.16}$$

Theorem 4.1 ([87, Theorem 1.4]) *Let $1/2 < s \leq 3/4$ if $0 < \gamma < (1+\sqrt{2})/4$ and $1/2 < s < 3/2 - \sigma_\gamma$ if $(1+\sqrt{2})/4 \leq \gamma < 2/\pi$. Then for all $\ell \in \mathbb{N}_0$ there is a constant $A_{s,\gamma} > 0$ such that for all $r \in \mathbb{R}_+$ one has*

$$\begin{aligned} \varrho^H_{\ell,\mathrm{C}}(r) \leq q \cdot A_{s,\gamma} \left(\ell+\tfrac{1}{2}\right)^{-4s+1} \\ \times \left[\left(\frac{r}{\ell+\frac{1}{2}}\right)^{2s-1} \mathbf{1}_{\{r\leq \ell+\frac{1}{2}\}} + \left(\frac{r}{\ell+\frac{1}{2}}\right)^{4s-1} \mathbf{1}_{\{\ell+\frac{1}{2} < r \leq (\ell+\frac{1}{2})^2\}} \right. \\ \left. + \left(\ell+\tfrac{1}{2}\right)^{4s-1} \mathbf{1}_{\{r > (\ell+\frac{1}{2})^2\}} \right]. \end{aligned} \tag{4.17}$$

Moreover, for any $\varepsilon > 0$, there are constants A_γ, $A_{\gamma,\varepsilon} > 0$ such that for all $r \in \mathbb{R}_+$ one has

$$\rho_{\mathrm{C}}^H(r) \leq \begin{cases} q \cdot A_\gamma \, r^{-\frac{3}{2}} & \text{if } 0 < \gamma < (1+\sqrt{2})/4, \\ q \cdot A_{\gamma,\varepsilon} \left(r^{-2\sigma_\gamma - \varepsilon} \mathbf{1}_{\{r \leq 1\}} + r^{-\frac{3}{2}} \mathbf{1}_{\{r>1\}} \right) & \text{if } (1+\sqrt{2})/4 \leq \gamma < 2/\pi. \end{cases} \tag{4.18}$$

Remark 4.2 (1) The proof of (4.17) uses Bessel kernel bounds for $C_{\ell,\gamma}^H$, i.e., bounds for the integral kernel

$$(C_{\ell,\gamma}^H + a_\ell)^{-t}(r,s) \tag{4.19}$$

with $a_\ell = a_\gamma(\ell+1/2)^{-2}$, $r, s > 0$, and $t \in (1, \min\{3-2\sigma_\gamma, 3\})$. For $\gamma < 1/2$, the Hardy potential γ/r is an *operator perturbation* for $p_{\ell=0}$ by Hardy's inequality. Hence, the proof in this case effectively only uses Bessel kernel bounds for C_ℓ (recall (4.7)), which can be obtained using the Fourier–Bessel transform. On the other hand, if $\gamma \geq 1/2$, a comparison between powers of $C_{\ell,\gamma}^H$ and p_ℓ is not straightforward. In this case, the proof of [87, Theorem 1.4] used the comparison result in [86] (see Theorem 4.17 later). This is the reason for the assumption $s < 3/2 - \sigma_\gamma$ and the appearance of $\varepsilon > 0$ in (4.18).

(2) Instead of comparing Bessel kernels of $C_{\ell,\gamma}^H$ and p_ℓ, one can compare the Bessel kernels of $C_{\ell,\gamma}^H$ and $p_\ell - \gamma/r$. For $\ell = 0$, the latter can immediately be derived using the spectral theorem and recent heat kernel bounds for $|p| - \gamma/|x|$ by Bogdan et al. [18]. Since for $\ell \geq 1$ the Hardy potential is again an operator perturbation for $\gamma < 1/2$ (by Hardy's inequality), Bessel kernel bounds for $p_\ell - \gamma/r$ are similar to those for p_ℓ. We expect that this strategy allows to remove the $\varepsilon > 0$ in (4.18) when $\gamma > (1+\sqrt{2})/4$. It is an open problem to prove that the behavior of $\varrho_{\ell,\mathrm{C}}^H$ and ρ_{C}^H at $r = 0$ for $\gamma > (1+\sqrt{2})/4$ is optimal.

(3) We do not expect Bessel kernel bounds for $p_\ell - \gamma/r$ to yield precise (probably γ-dependent) bounds for $\varrho_{\ell,\mathrm{C}}^H$ at the origin in the cases $\ell = 0$ and $\gamma \leq 1/2$, and $\ell \geq 1$ and $\gamma \leq 2/\pi$, because the Bessel kernel bounds for $p_\ell - \gamma/r$ are similar to those for p_ℓ.

(4) The appearance of $\gamma = (1+\sqrt{2})/4$ is technical and comes from the restriction $\sigma \leq 3/4$ together with the fact that $\sigma_{(1+\sqrt{2})/4} = 3/4$.

Larger coupling constants for higher angular momenta

Using a relative to the Fourier–Bessel transform, namely the Mellin transform, Le Yaouanc et al. [137] showed that the largest admissible coupling constant associated with $C_{\ell,\gamma}^H$ increases as ℓ increases. Independently, Yafaev [249, (2.4), (2.26)] gave an alternative proof of this fact and proved

$$\int_0^\infty \mathrm{d}k \, k |(\Phi_\ell u)(k)|^2 \geq \frac{2\Gamma\left(\frac{1}{4}(4+2\ell)\right)^2}{\Gamma\left(\frac{1}{4}(2+2\ell)\right)^2} \int_0^\infty \frac{|u(r)|^2}{r} \, \mathrm{d}r. \tag{4.20}$$

For $d = 3$ and $\ell = 1$, the largest admissible coupling constant is $\pi/2$, which compares to the critical value $2/\pi$ when $\ell = 0$. We note that similar inequalities hold in dimensions d other then three and powers $\alpha \in (0, \min\{2, d\})$ of the square root of the Laplacian.

Ground state transform

An alternative representation of the operator $(-\Delta)^{1/2} - \gamma/|x|$ in $L^2(\mathbb{R}^3)$ proceeds via the *ground state transform*. To that end, recall (4.15). The ground state transform makes use of the fact that the radial function $x \mapsto |x|^{-\sigma}$ is a *(generalized) ground state* for $|p| - \Phi(\sigma)|x|^{-1}$. It states that

$$\langle u, (|p| - \Phi(\sigma)|x|^{-1})u\rangle = \frac{1}{2\pi^2}\int_{\mathbb{R}^3} \frac{|v(x) - v(y)|^2}{|x-y|^4} \cdot (|x||y|)^{-\sigma}\, \mathrm{d}x\, \mathrm{d}y \tag{4.21}$$

where $\sigma \in [0, 1]$, $u(x) = |x|^{-\sigma} v(x)$ with $v \in \mathcal{S}(\mathbb{R}^3\backslash\{0\})$, cf. [83, Proposition 4.1]. Note that for the ordinary Hardy operator with inverse-square potential the ground state transform has been known long before, see, e.g., [190, p. 169] for a textbook treatment when $d = 3$. For a further study of the ground state transform in the fractional case, see [89].

Spectrum

Although the eigenvalues $\lambda_{Z,n,\ell}$ ($n \in \mathbb{N}_0$) of $C^H_{c,Z}$ are not explicitly known, the inequality $\sqrt{p^2+1} - 1 \leq p^2/2$ and the lower bound of [91, Theorem 2.2] imply the inequalities

$$-\frac{Z^2}{2(n+\ell+1)^2} \geq \lambda_{Z,n,\ell} \geq -\text{const} \cdot \frac{Z^2}{(n+\ell+1)^2}, \tag{4.22}$$

where the constant in the second inequality can be chosen independently of $\gamma \in [0, 2/\pi]$. The expression on the left side is just the n-th eigenvalue of the hydrogen operator (1.9) in angular momentum channel ℓ. Thus, although the relativistic eigenvalues are smaller than the non-relativistic ones, their magnitudes in Z are the same and many of their summability properties with respect to n are similar.

Finally, the spectrum of C^H_γ in $[0, \infty)$ is purely absolutely continuous, the singular continuous spectrum is empty, and there are no embedded eigenvalues [109, Theorem 2.3]. In particular, there is no zero eigenvalue, a fact that we will use later.

Physical shortfalls

Although C^H_γ is mathematically well understood, it has a number of physical deficits. For instance, the restriction $\gamma \leq 2/\pi$ implies that only atoms with nuclear charge < 88 can be described. Moreover, the predicted ground state energies for heavy atoms are much too low. This can already be anticipated by comparing the ground state

energies for hydrogen with $c = 1$ and coupling γ close to $2/\pi$, which are ≈ -0.5 in the Chandrasekhar model [189, p. 106] and ≈ -0.06 (cf. (4.35)) in the Dirac model, respectively.

Although the model is unsuitable for the quantitative description of systems with strong attractive external Coulomb forces, Chandrasekhar [24] used it successfully for attractive two-particle Coulomb forces in his Nobel prize winning estimate on the mass necessary to collapse a star to a white dwarf. Despite its mathematical simplicity and its success in correctly describing some qualitative features of relativistic Coulomb systems, it is desirable to examine models that also lead to quantitatively correct predictions for ground state properties. Such models are, e.g., based on the Coulomb–Dirac operator, which we discuss next.

4.1.2 Coulomb–Dirac operator

Free Dirac operator

In 1928, Dirac [37, 38] derived a Lorentz invariant equation of motion for quantum mechanical particles with spin moving in an external electromagnetic field, the so-called Dirac equation. We refer to [17, 232] for comprehensive treatments. For a free particle, the equation reads

$$i\,\partial_t \psi(t,x) = \left(-ic\underline{\alpha}\cdot\nabla + \beta c^2\right)\psi(t,x) \tag{4.23}$$

with the Dirac matrices $\underline{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$,

$$\alpha_j = \begin{pmatrix} 0_{\mathbb{C}^2} & \sigma_j \\ \sigma_j & 0_{\mathbb{C}^2} \end{pmatrix},$$

the Pauli matrices $\underline{\sigma} := (\sigma_1, \sigma_2, \sigma_3)$, and $\beta = \mathrm{diag}(1, 1, -1, -1)$. The operator on the right side of (4.23) is called the free Dirac operator. It acts on states $\psi(t,x) \in \mathbb{C}^4$, called Dirac spinors. The underlying Hilbert space is $L^2(\mathbb{R}^3 : \mathbb{C}^4)$. The domain on which the free Dirac operator can be realized as a self-adjoint operator is $H^1(\mathbb{R}^3 : \mathbb{C}^4)$. The Foldy–Wouthuysen transform U_{FW} allows to perform a block diagonalization, whereby the free Dirac operator takes the form

$$U_{\mathrm{FW}}\left(-ic\underline{\alpha}\cdot\nabla + \beta c^2\right)U_{\mathrm{FW}}^* = \begin{pmatrix} \sqrt{-c^2\Delta + c^4} & 0 \\ 0 & -\sqrt{-c^2\Delta + c^4} \end{pmatrix}. \tag{4.24}$$

This shows that the spectrum equals $(-\infty, -c^2] \cup [c^2, \infty)$. Physically, this means that states can possess "negative energy" and that there is an infinitely deep energy reservoir, the so-called Dirac sea. By adding electromagnetic fields and the charge conjugation operator, one can interpret states with negative energy as "antiparticles", i.e., particles with same mass but opposite charge. Such particles are called positrons.

Self-adjoint extensions of the Coulomb–Dirac operator

The one-particle Dirac operator describing the hydrogen atom can initially be defined on $\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)$ and is formally given by the differential operator

$$D^H_{c,Z} := -ic\underline{\alpha} \cdot \nabla + c^2\beta - \frac{Z}{|x|} \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}^4). \tag{4.25}$$

Scaling $x \mapsto x/c$ and writing $\gamma := Z/c$ shows that $D^H_{c,Z}$ is unitarily equivalent to

$$c^2 \left[-i\underline{\alpha} \cdot \nabla + \beta - \frac{\gamma}{|x|} \right] =: c^2 D^H_{1,\gamma} =: c^2 D^H_\gamma . \tag{4.26}$$

Weidmann [245] showed that D^H_γ is essentially self-adjoint on $\mathcal{S}(\mathbb{R}^3 \setminus \{0\} : \mathbb{C}^4)$ if and only if $|\gamma| < \sqrt{3}/2$, see also [232, Theorem 4.4]. For $\gamma \in [\sqrt{3}/2, 1]$, there is a "distinguished" (sometimes called "physically relevant") self-adjoint extension of D^H_γ. For $\gamma \in (\sqrt{3}/2, 1)$, this extension was established by Schmincke [197], Wüst [248] (see also Kalf, Schmincke, Walter, and Wüst [128] for a review of these results), Nenciu [181], and Klaus and Wüst [133]. According to Schmincke and Wüst, this realization stands out by the property that all states in the domain of the Coulomb–Dirac operator have finite potential energy. On the other hand, Nenciu's realization is distinguished by the fact that states have finite kinetic energy. Klaus and Wüst showed that both realizations coincide and that the essential spectrum is $(-\infty, 1] \cup [1, \infty)$, see [134] (or [232, p. 117] for a textbook treatment). In summary, the domain $\mathrm{dom}(D^H_\gamma)$ of the distinguished realization satisfies $H^1(\mathbb{R}^3 : \mathbb{C}^4) \subset \mathrm{dom}(D^H_\gamma) \subset H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$, and the quadratic form domain is $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$. In particular, the expectation values of both kinetic and potential energy are finite in $\mathrm{dom}(D^H_\gamma)$; this motivates the term "physically relevant extension". With the help of the sharp Hardy–Dirac inequality [42],

$$\int_{\mathbb{R}^3} \frac{|\varphi(x)|^2}{|x|}\, \mathrm{d}x \le \int_{\mathbb{R}^3} \left(\frac{|(\underline{\sigma} \cdot \nabla\varphi)(x)|^2}{1 + |x|^{-1}} + |\varphi(x)|^2 \right) \mathrm{d}x, \quad \varphi \in H^1(\mathbb{R}^3 : \mathbb{C}^2), \tag{4.27}$$

Esteban and Loss [57] constructed a distinguished self-adjoint extension for $\gamma = 1$. States in the domain of this operator need not have finite kinetic and potential energy separately. We remark that similar results in two dimensions (where the critical coupling is $\gamma = 1/2$) were proved by Warmt [243]. In this review, we will only focus on the three-dimensional case and $\gamma < 1$.

Partial wave analysis

Since D^H_γ is spherically symmetric, one can, analogously to the angular momentum decomposition for spherically symmetric scalar operators, perform a partial wave

decomposition, see, e.g., [59], [7, Section 2.1], [232, Sections 4.6.3–4.6.5], and [170, Appendix A]. We begin by observing that those of the spherical $\mathbb{C}^2$-spinors

$$\Omega_{\ell,m,s}(\omega) := \begin{pmatrix} 2s\sqrt{\frac{\ell+\frac{1}{2}+2sm}{2\ell+1}}\, Y_{\ell,m-\frac{1}{2}}(\omega) \\ \sqrt{\frac{\ell+\frac{1}{2}-2sm}{2\ell+1}}\, Y_{\ell,m+\frac{1}{2}}(\omega) \end{pmatrix} \tag{4.28}$$

with $\ell = 0, 1, 2, \ldots$ and $m = -\ell - \frac{1}{2}, \ldots, \ell + \frac{1}{2}$, that do not vanish, form an orthonormal basis of $L^2(\mathbb{S}^2 : \mathbb{C}^2)$, see, e.g., [59, (7)]. Moreover, they are joint eigenfunctions of L^2, J^2 ($J = L + S$ being the total angular momentum), and J_3 with respective eigenvalues $\ell(\ell+1)$, $(\ell+s)(\ell+s+1)$, and m.

Introducing the spin-orbit operator $K = \beta(J^2 - L^2 + 1/4)$, there is an orthonormal basis of eigenvectors $\Phi^\sigma_{\kappa,m}$ of $L^2(\mathbb{S}^2 : \mathbb{C}^4)$ such that $J^2\Phi^\sigma_{\kappa,m} = j_\kappa(j_\kappa+1)\Phi^\sigma_{\kappa,m}$, $J_3\Phi^\sigma_{\kappa,m} = m\Phi^\sigma_{\kappa,m}$, and $K\Phi^\sigma_{\kappa,m} = \kappa\Phi^\sigma_{\kappa,m}$ with the total angular momentum j_κ and orbital angular momentum ℓ_κ defined as

$$j_\kappa := |\kappa| - \tfrac{1}{2} \text{ and } \ell_\kappa := j_\kappa - \tfrac{1}{2}\operatorname{sgn}(\kappa) = |\kappa| - \theta(\kappa), \tag{4.29}$$

the magnetic quantum numbers $m \in \{-j_\kappa, \ldots, j_\kappa\}$, the spin–orbit coupling

$$\kappa \in \dot{\mathbb{Z}} := \mathbb{Z} \setminus \{0\}, \tag{4.30}$$

and $\sigma \in \{+, -\}$. A standard choice is

$$\Phi^+_{\kappa,m} := \begin{pmatrix} \mathrm{i}\operatorname{sgn}(\kappa)\Omega_{\ell_\kappa,m,\frac{1}{2}\operatorname{sgn}(\kappa)} \\ 0 \end{pmatrix}, \quad \Phi^-_{\kappa,m} := \begin{pmatrix} 0 \\ -\operatorname{sgn}(\kappa)\Omega_{\ell_\kappa+\operatorname{sgn}(\kappa),m,-\frac{1}{2}\operatorname{sgn}(\kappa)} \end{pmatrix}. \tag{4.31}$$

Using these spinors, we introduce the spaces

$$\mathfrak{h}_{\kappa,m} := \operatorname{span}\{x \mapsto \tfrac{f^+(|x|)}{|x|}\Phi^+_{\kappa,m}(\tfrac{x}{|x|}) + \tfrac{f^-(|x|)}{|x|}\Phi^-_{\kappa,m}(\tfrac{x}{|x|}) : f^+, f^- \in L^2(\mathbb{R}_+)\}, \tag{4.32}$$

$$\mathfrak{h}_\kappa := \bigoplus_{m=-j_\kappa}^{j_\kappa} \mathfrak{h}_{\kappa,m}. \tag{4.33}$$

These spaces form an orthogonal decomposition of $L^2(\mathbb{R}^3 : \mathbb{C}^4)$. Note that Dirac operators with radial potentials leave the spaces $\mathfrak{h}_{\kappa,m}$ invariant. To see this, let $f \in$

$\mathfrak{h}_{\kappa,m} \cap H^1(\mathbb{R}^3 : \mathbb{C}^4)$ and $g \in \mathfrak{h}_{\kappa',m'} \cap H^1(\mathbb{R}^3 : \mathbb{C}^4)$. Then, one has that

$$\begin{aligned}\langle f, D_\gamma^H g\rangle_{L^2(\mathbb{R}^3:\mathbb{C}^4)} \\ = \left\langle \begin{pmatrix} f^+ \\ f^- \end{pmatrix}, \begin{pmatrix} 1-\frac{\gamma}{r} & -\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r} \\ \frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r} & -1 - \frac{\gamma}{r} \end{pmatrix} \begin{pmatrix} g^+ \\ g^- \end{pmatrix} \right\rangle_{L^2(\mathbb{R}_+:\mathbb{C}^2)} \delta_{\kappa\kappa'}\delta_{mm'},\end{aligned} \tag{4.34}$$

see also [232, (7.105)].

Spectrum

The Coulomb–Dirac operator D_γ^H has no embedded eigenvalues (Kalf [129]) and no singular continuous spectrum in $[0, \infty)$ (Vogelsang [242], and Richard and Tiedra de Aldecoa [193]). The lowest eigenvalue is $\lambda_1 = \sqrt{1-\gamma^2}$ and one has $\lim_{k\to\infty} \lambda_k = 1$. The eigenvalues of D_γ^H are explicitly known and given by

$$\lambda_{n,\kappa} = \left(1 + \frac{\gamma^2}{\left(n + \sqrt{\kappa^2 - \gamma^2}\right)^2}\right)^{-1/2}. \tag{4.35}$$

They only depend on $(\kappa, n) \in (-\mathbb{N} \times \mathbb{N}) \cup (\mathbb{N} \times \mathbb{N}_0)$. Sommerfeld [226] anticipated these eigenvalues in the framework of the old relativistic theory of quanta even before the Coulomb–Dirac operator was written down. Darwin [32], Gordon [96], and Pidduck [185] solved the eigenvalue equation for the Coulomb–Dirac operator only 12 years later; see also Bethe's [17] or Thaller's [232, Section 7.4] textbooks for comprehensive treatments and Mawhin and Ronveaux [167] for interesting historical comments. In particular, one has the bounds

$$-\frac{\gamma^2}{2(n+\ell+1)^2} \geq \lambda_{n,\kappa} - 1 \geq -\text{const} \cdot \frac{\gamma^2}{(n+\ell+1)^2},$$

see also [100, Lemma 1].

Remark 4.3 If the Coulomb potential $\gamma/|x|$ is replaced by a more general measurable Hermitian 4×4-matrix-valued function $V : \mathbb{R}^3 \to \mathbb{C}^{4\times 4}$ with $0 \leq V(x) \leq \gamma/|x| \otimes \mathbf{1}_{\mathbb{C}^4}$, then the eigenvalues of $-i\underline{\alpha}\cdot\nabla + \beta - V$ can be computed using analogues of the classical Courant–Fischer min-max principle, (cf. [191, Theorems XIII.1-2]) originally written down by Talman [231] and Datta and Devaiah [33], mathematically established by Esteban and Séré [58] and by [98, 99], and further developed by Dolbeault et al. [41, 42], Morozov and Müller [173], Müller [177], Esteban et al. [55, 56], and Schimmer et al. [196]. The latter turned the principle around and used it to define the Hamiltonian, since the maximization leads to the Hardy type inequality (4.27).

Hydrogen eigenvectors and density

Similarly, the eigenvectors $\psi^{\mathrm{D}}_{n,\kappa,m}$ of the eigenvalue equation $D^H_\gamma \psi^{\mathrm{D}}_{n,\kappa,m} = \lambda_{n,\kappa}\psi^{\mathrm{D}}_{n,\kappa,m}$ are also well-known, see, e.g., Pidduck [185] (in terms of Laguerre polynomials) or Gordon [96] and Darwin [32] (in terms of hypergeometric confluent functions). For nice pictorial representations, see, e.g., White [246] and, for textbook references, see Bethe [17, Formula (9.37)] and Thaller [233, p. 427]. The *three-dimensional* density for a Bohr atom for a given $\gamma \in (0, 1)$ in spin–orbit channel $\kappa \in \dot{\mathbb{Z}}$ is

$$\rho^H_{\kappa,\mathrm{D}}(x) := \sum_{n=\theta(-\kappa)}^{\infty} \sum_{m=-j_\kappa}^{j_\kappa} \sum_{\sigma=1}^{4} |\psi^{\mathrm{D}}_{n,\kappa,m}(x,\sigma)|^2, \quad x \in \mathbb{R}^3, \tag{4.36}$$

and the total, three-dimensional hydrogenic density is

$$\rho^H_{\mathrm{D}}(x) := \sum_{\kappa\in\dot{\mathbb{Z}}} \rho^H_{\kappa,\mathrm{D}}(x), \quad x \in \mathbb{R}^3. \tag{4.37}$$

These quantities are indeed well-defined, as the following theorem demonstrates. To state it, let

$$\Sigma_\gamma := 1 - \sqrt{1-\gamma^2} \in [0,1] \quad \text{for } \gamma \in [0,1]. \tag{4.38}$$

Theorem 4.4 ([170, Theorem 2.3]) *Let $1/2 < s \le 3/4$, if $\gamma \in (0, \sqrt{15}/4)$ and $1/2 < s < 3/2 - \Sigma_\gamma$, if $\gamma \in [\sqrt{15}/4, 1)$. Then for all $\kappa \in \dot{\mathbb{Z}}$ there is a constant $A_{s,\gamma} > 0$ such that for all $x \in \mathbb{R}^3 \setminus \{0\}$ one has*

$$\rho^H_{\kappa,\mathrm{D}}(x) \le A_{s,\gamma} \frac{|\kappa|^{1-4s}}{|x|^2} \times \left[\left(\frac{|x|}{|\kappa|}\right)^{2s-1} \mathbf{1}_{\{|x|\le|\kappa|\}} + \left(\frac{|x|}{|\kappa|}\right)^{4s-1} \mathbf{1}_{\{|\kappa|\le|x|\le|\kappa|^2\}} + |\kappa|^{4s-1}\mathbf{1}_{\{|x|\ge|\kappa|^2\}} \right].$$

Moreover, for any $\varepsilon > 0$ there are constants $A_{\gamma,\varepsilon}, A_\gamma > 0$ such that for all $x \in \mathbb{R}^3\setminus\{0\}$ one has

$$\rho^H_{\mathrm{D}}(x) \le \begin{cases} A_\gamma |x|^{-3/2} & \text{if } \gamma \in (0, \sqrt{15}/4] \\ A_{\gamma,\varepsilon}\left(|x|^{-2\Sigma_\gamma-\varepsilon}\mathbf{1}_{\{|x|\le 1\}} + |x|^{-3/2}\mathbf{1}_{\{|x|>1\}}\right) & \text{if } \gamma \in (\sqrt{15}/4, 1) \end{cases}. \tag{4.39}$$

The proof of this theorem is similar to that of Theorem 4.1.

Instability

In the Chandrasekhar model, we call an atom "unstable", if the coupling constant is so large that the operator is unbounded from below. Recall that for $\gamma < 1$ the Coulomb–Dirac operator D_γ^H has a "distinguished" self-adjoint extension with the property that the expectation values of both kinetic and potential energy are finite in $\mathrm{dom}(D_\gamma^H)$. *Instability* for the Coulomb–Dirac operator refers to the fact that all self-adjoint extensions of the Coulomb–Dirac operator have infinitely many eigenfunctions with infinite expectation value of the potential energy. This situation occurs when $\gamma > 1$, i.e., in the case when the lowest eigenvalue of D_γ^H has hit zero. See, e.g., Hogreve [111, Theorem 2.1.(iii)] and the references therein for details and Thaller [232, p. 218] for an overview.

Brown–Ravenhall operator

According to Dirac, the "vacuum", i.e., the situation in which no (negatively charged) electrons with positive energies are present, is described by a completely filled negative energy continuum of the Dirac operator (the so-called Dirac sea), whereas only solutions to the free Dirac equation with positive kinetic energy should be regarded as "physical electrons". Dirac proposed the following interpretation [40, p. 362]:

> "*The most stable states for an electron (the states of lowest energy) are those with negative energy and very high velocity. All the electrons in the world will tend to fall into these states with emission of radiation. The Pauli exclusion principle, however, will come into play and prevent more than one electron going into any one state. Let us assume there are so many electrons in the world that all the most stable states are occupied, or, more accurately, that all the states of negative energy are occupied except perhaps a few of small velocity. Any electrons with positive energy will now have very little chance of jumping into negative-energy states and will therefore behave like electrons are observed to behave in the laboratory. We shall have an infinite number of electrons in negative-energy states, and indeed an infinite number per unit volume all over the world, but if their distribution is exactly uniform we should expect them to be completely unobservable. Only the small departures from exact uniformity, brought about by some of the negative-energy states being unoccupied, can we hope to observe.*"

Shortly after Dirac's equation was formulated, Breit [19–21] derived a relativistic wave equation for helium using the quantum electrodynamics of Heisenberg and Pauli, which reads

$$i\frac{\partial\psi(x_1,x_2)}{\partial t} = \Bigg[(-i\underline{\alpha}\cdot\nabla+\beta)^{(1)} + (-i\underline{\alpha}\cdot\nabla+\beta)^{(2)} - \frac{\gamma}{|x_1|} - \frac{\gamma}{|x_2|} + \frac{1}{|x_1-x_2|} \tag{4.40a}$$

$$-\frac{1}{2|x_1-x_2|}\left(\underline{\alpha}^{(1)}\cdot\underline{\alpha}^{(2)} + \frac{\underline{\alpha}^{(1)}\cdot(x_1-x_2)\cdot\underline{\alpha}^{(2)}\cdot(x_1-x_2)}{|x_1-x_2|^2}\right)\Bigg]\psi(x_1,x_2). \tag{4.40b}$$

As is explained in [22, p. 552], "the superscripts (1) and (2) indicate operation on the coordinate or spinor components of the first or second electron, respectively, in the sixteen-component wave function $\psi(x_1, x_2)$". Up to the single term in (4.40b), Breit's equation coincides with the naive extension of Dirac's equation for two particles. Brown and Ravenhall [22] observed that the energies predicted by Breit's equation did not match the experimentally measured values very well and explained their observation as follows [22, pp. 552–553]:

> "*Because of the negative-energy states, equation* (4.40) *is in fact meaningless. This can be seen by constructing a solution of [the Dirac equation for two electrons in absence of electron-electron repulsion] and then turning on the inter-electron interaction slowly. The system can make real transitions to states where one electron has a large negative energy and the other electron is in the positive-energy continuum; thus equation* (4.40) *has no stationary solutions if interpreted in this way.*"

In the language of spectral theory, the spectrum of a two-particle Coulomb–Dirac operator occupies the whole real axis (already without electron–electron repulsion), and all eigenvalues are embedded. This phenomenon is sometimes called *Brown–Ravenhall disease* [186, 192, 230]. As is well-known from the non-relativistic theory, these are likely to turn into resonances when the electron–electron repulsion is turned on, which leads to unphysical consequences, such as the instability of the atom. We conclude this discussion by mentioning that despite these physical deficits, Oelker [182] recently showed that the single-particle Dirac operator may be extended to a self-adjoint multi-particle operator.

To remedy the above serious defects, Brown and Ravenhall proposed to only allow states with positive energy with respect to the free Dirac operator, i.e., they restricted the Hilbert space of admissible states to

$$\mathfrak{h}_{c,0} := \Lambda_{c,0}(L^2(\mathbb{R}^3 : \mathbb{C}^4)) := \mathbf{1}_{(0,\infty)}(-ic\underline{\alpha} \cdot \nabla + c^2\beta)(L^2(\mathbb{R}^3 : \mathbb{C}^4)). \tag{4.41}$$

The energy of an electron in the Brown–Ravenhall picture is then given by

$$\langle \psi, (D^H_{c,Z} - c^2)\psi \rangle, \quad \psi \in \Lambda_{c,0}\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4). \tag{4.42}$$

The work [59] showed that this energy is bounded from below, if and only if $\gamma = Z/c \leq \gamma_{\mathrm{B}}$ with

$$\gamma_{\mathrm{B}} := \frac{2}{\pi/2 + 2/\pi}, \tag{4.43}$$

which implies $Z < 125$. For such γ, the energy form can be extended to a closed quadratic form in $\mathfrak{h}_{c,0}$ with form domain $\mathfrak{h}_{c,0} \cap \mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)$. The resulting self-adjoint operator constructed according to Friedrichs is called the Brown–Ravenhall operator and is denoted by $B_{c,Z}$. By scaling $x \mapsto x/c$, the Brown–Ravenhall operator is seen to be unitarily equivalent to $c^2 B_{1,\gamma}$ with $\gamma = Z/c$. We write $B_\gamma := B_{1,\gamma}$.

Although we will not use it in this review, we record the following convenient representation of the Brown–Ravenhall operator as a self-adjoint operator in $L^2(\mathbb{R}^3 : \mathbb{C}^2)$: for $E_c(\xi) := \sqrt{c^2|\xi|^2 + c^4}$ with $\xi \in \mathbb{R}^3$ and

$$\varphi_j(\xi) := \sqrt{\frac{E_1(\xi) + (-1)^j}{2E_1(\xi)}}, \quad j \in \{0, 1\}, \quad \xi \in \mathbb{R}^3, \tag{4.44}$$

we define the $\mathbb{C}^{2\times 2}$-valued functions

$$\Phi_0(\xi) := \varphi_0(|\xi|)\mathbf{1}_{\mathbb{C}^2}, \quad \Phi_1(\xi) := \varphi_1(|\xi|)\frac{\sigma \cdot \xi}{|\xi|}, \quad \xi \in \mathbb{R}^3. \tag{4.45}$$

Then, the map

$$\mathbf{\Phi}_c : L^2(\mathbb{R}^3 : \mathbb{C}^2) \to L^2(\mathbb{R}^3 : \mathbb{C}^4), \quad u \mapsto \begin{pmatrix} \Phi_0(-i\nabla/c)u \\ \Phi_1(-i\nabla/c)u \end{pmatrix} \tag{4.46}$$

maps $L^2(\mathbb{R}^3 : \mathbb{C}^2)$ unitarily onto $\mathfrak{h}_{c,0}$, cf. [59]. Therefore, B_γ in $\mathfrak{h}_{c,0}$ is unitarily equivalent to the operator

$$E_c(-i\nabla) - c^2 - \mathcal{T}_c\left(\frac{Z}{|x|}\right) \quad \text{in } L^2(\mathbb{R}^3 : \mathbb{C}^2) \tag{4.47}$$

with the "twisted potential"

$$\begin{aligned} \mathcal{T}_c(V) :&= \begin{pmatrix} \Phi_0(-i\nabla/c) \\ \Phi_1(-i\nabla/c) \end{pmatrix} V \begin{pmatrix} \Phi_0(-i\nabla/c) \\ \Phi_1(-i\nabla/c) \end{pmatrix} \\ &= \Phi_0\left(\frac{-i\nabla}{c}\right) V \Phi_0\left(\frac{-i\nabla}{c}\right) + \Phi_1\left(\frac{-i\nabla}{c}\right) V \Phi_1\left(\frac{-i\nabla}{c}\right) \end{aligned} \tag{4.48}$$

for any $V : \mathbb{R}^3 \to \mathbb{C}^4$, whenever meaningfully defined. From a technical point of view, the representation (4.47) is important, e.g., in [23, 59, 91, 168]. (Figuratively speaking, the transformation $\mathcal{T}_c$ mollifies the Coulomb singularity and ensures the lower boundedness of B_γ for coupling constants greater than $2/\pi$. This transpires, e.g., in [91, Lemma 2.7] and [82, Lemma 5.2].)

In [59], the authors showed that the Brown–Ravenhall operator B_γ is bounded from below by $-\gamma(\pi/4 - 1/\pi) - 1$ when $\gamma \leq \gamma_{\mathrm{B}}$. In fact, Tix [236, 237] proved the stronger lower bound $-\gamma_{\mathrm{B}}$.

If $\gamma < \gamma_{\mathrm{B}}$, the essential spectrum of the Brown–Ravenhall operator B_γ is $[0, \infty)$ and the singular continuous spectrum is empty [59, Theorem 2]. Moreover, there are no embedded eigenvalues, and the spectrum in $[0, \infty)$ is purely absolutely continuous [7, Theorem 3.4.1]. As in the Chandrasekhar case, the eigenvalues $\lambda_{Z,n,j,\ell}$ of $B_{c,Z}$ in channel (j, ℓ) satisfy the bounds

$$-\frac{Z^2}{2(n+\ell+1)^2} \geq \lambda_{Z,n,j,\ell} \geq -\text{const} \cdot \frac{Z^2}{(n+\ell+1)^2},$$

where the constant in the second inequality can be chosen independently of γ. The lower bound is due to [91, Theorem 2.1], while the upper bound follows from the fact that the non-relativistic kinetic energy dominates the relativistic one. In particular, the Brown–Ravenhall eigenvalues are smaller than those of $D^H_{c,Z} - c^2$ due to the min–max principle for operators with spectral gaps, cf. [98, 99].

Furry operator

Naturally, the projection onto the positive spectral subspace of the free Dirac operator is not the only possibility to get rid of the positronic part of the wave functions. Furry and Oppenheimer [93] proposed rather to project onto the positive spectral subspace of the Coulomb–Dirac operator, i.e., the Hilbert space of admissible states is

$$\mathfrak{h}_{c,Z} := \Lambda_{c,Z}(L^2(\mathbb{R}^3 : \mathbb{C}^4)) := \mathbf{1}_{(0,\infty)}(D^H_{c,Z})(L^2(\mathbb{R}^3 : \mathbb{C}^4)).$$

Since D^H_γ can be realized as a self-adjoint operator with form domain $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$ by Nenciu's method [181] when $Z/c = \gamma < \gamma_{\mathrm{F}}$ with

$$\gamma_{\mathrm{F}} := 1, \tag{4.49}$$

we have

$$\Lambda_{c,Z}(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)) \subseteq H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$$

and dense in $\mathfrak{h}_{c,Z}$. Therefore, the quadratic form

$$\langle \psi, (D^H_{c,Z} - c^2)\psi \rangle, \quad \psi \in \Lambda_{c,Z}\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4) \tag{4.50}$$

is well-defined and bounded from below when $\gamma \in (0, \gamma_{\mathrm{F}})$. According to Friedrichs, the form gives rise to a corresponding self-adjoint operator. The quadratic form domain of this operator is $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4) \cap \mathfrak{h}_{c,Z}$. This operator is called the Furry operator and denoted by $F_{c,Z}$. Scaling $x \mapsto x/c$ shows that the Furry operator is unitarily equivalent to $c^2 F_{1,\gamma}$ with $\gamma = Z/c$ and we write $F_\gamma := F_{1,\gamma}$ in the rescaled picture.

Mittleman operator

Although, at this point, the choice of the projections seems to be arbitrary and only justifiable by the comparison of the results with the measured quantities this is—according to Mittleman [171]—not the case: the optimal projection and optimal ground state should be obtained by a mini–max principle, namely the infimum over the states in a class of fermionic Hilbert spaces defined by the positive spectral subspace of some Dirac operator $-i\underline{\alpha} \cdot \nabla + mc^2\beta - \varphi$ followed by a supremum over a suitable

class of potentials φ. However, this has not been implemented on a mathematical level. In fact, there some elementary no-go results [9, 11] that a potential mathematical implementation has to circumvent. For a more detailed review of Mittleman's principle and references, see, e.g., [54, Section 4.5].

For a variational principle inspired by Mittleman, see, e.g., [5], and for works connecting Mittleman's principle and the Dirac–Fock equations, see, e.g., [9–11].

4.2 Many-particle operators

The results for the above-discussed single-particle operators allow to define many-particle operators.

4.2.1 Chandrasekhar operator

Chandrasekhar molecules with $q = 2$ are described by

$$C_{N,V} := \sum_{\nu=1}^{N} \left(\sqrt{-c^2\Delta_\nu + c^4} - c^2 - V(x_\nu) \right) + \sum_{1\leq \nu<\mu\leq N} \frac{1}{|x_\nu - x_\mu|} + U \tag{4.51}$$

for $\gamma \leq \gamma_{\mathrm{C}} = 2/\pi$ and V and U as in (1.2) and (1.3), respectively. Technically, $C_{N,V}$ is defined as the Friedrichs extension of the corresponding quadratic form with form domain consisting of finite linear combinations of N-particle Slater determinants with entries in $\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^2)$.

The ground state energy of a Chandrasekhar molecule is:

$$E_c^{\mathrm{C}}(N, \underline{Z}, \underline{R}) := \inf \operatorname{spec}(C_{N,V}). \tag{4.52}$$

In the neutral, atomic case ($K = 1$, $\underline{R} = 0$, $\underline{Z} = Z = N$), the ground state energy $E_c^{\mathrm{C}}(Z) := E_c^{\mathrm{C}}(Z, Z, 0)$ is an eigenvalue [139].

For an associated ground state ψ of $C_{N,V}$ (or an approximate ground state on the Thomas–Fermi or Scott scale), we define the associated three-dimensional one-particle ground state densities

$$\rho_{\mathrm{C}}(x) := N \sum_{\sigma=1}^{2} \int_{\Gamma^{N-1}} |\psi(x, \sigma; y_2, \dots, y_N)|^2 \, \mathrm{d}y_2 \cdots \mathrm{d}y_N, \quad x \in \mathbb{R}^3. \tag{4.53}$$

Similarly as in the Schrödinger case, we define the one-dimensional angular-momentum-resolved version of ρ_{C} for any $\ell \in \mathbb{N}_0$ by

$$\varrho_{\ell,\mathrm{C}}(r) := Nr^2 \sum_{\sigma=1}^{2} \sum_{m=-\ell}^{\ell} \int_{\Gamma^{N-1}} \left| \int_{\mathbb{S}^2} \overline{Y_{\ell,m}(\omega)} \psi(r\omega, \sigma; y_2, \dots, y_N) \right|^2 \mathrm{d}y_2 \cdots \mathrm{d}y_N \tag{4.54}$$

for $r > 0$. Note that

$$\int_{\mathbb{S}^2} \rho_{\mathrm{C}}(r\omega)\,\mathrm{d}\omega = r^{-2} \sum_{\ell \geq 0} \varrho_{\ell,\mathrm{C}}(r), \quad r > 0. \tag{4.55}$$

4.2.2 Brown–Ravenhall and Furry operators

The energy of an atom in the Brown–Ravenhall or Furry pictures is given by:

$$\mathcal{E}_{c,Z,N}[\psi] := \left\langle \psi, \left(\sum_{\nu=1}^{N} \left(D_{c,Z} - c^2 \right)_{\nu} + \sum_{1 \leq \nu < \mu \leq N} \frac{1}{|x_\nu - x_\mu|} \right) \psi \right\rangle, \tag{4.56}$$

whenever ψ belongs to the space of finite linear combinations of N-particle Slater determinants with entries in $\Lambda_{c,\#}\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)$ where $\# \in \{0, Z\}$. The quadratic form is bounded from below if $\gamma \leq \gamma_{\mathrm{B}}$ in the Brown–Ravenhall case and if $\gamma \leq 1$ in the Furry case by the previous discussion of the one-particle operators. The resulting self-adjoint operators constructed according to Friedrichs are called the Brown–Ravenhall and Furry operators, respectively. If $N = Z$, we drop the third index in the above energy form and write $\mathcal{E}_{c,Z}[\psi] := \mathcal{E}_{c,Z,Z}$.

The ground state energy of a Brown–Ravenhall or Furry atom is

$$E_c^{\mathrm{B}}(N, Z) := \inf \left\{ \mathcal{E}_{c,Z,N}[\psi] : \psi \in \bigwedge_{\nu=1}^{N} \Lambda_{c,0}\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4) \right\}, \tag{4.57}$$

$$E_c^{\mathrm{F}}(N, Z) := \inf \left\{ \mathcal{E}_{c,Z,N}[\psi] : \psi \in \bigwedge_{\nu=1}^{N} \Lambda_{c,Z}\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4) \right\}. \tag{4.58}$$

We record that Morozov and Vugalter [174] (see also Morozov [172], Jakubaßa-Amundsen [123] for HVZ theorems), and Matte and Stockmeyer [166] proved that for $N = Z$, the Brown–Ravenhall and Furry ground state energies $E_c^{\mathrm{B/F}}(Z) := E_c^{\mathrm{B/F}}(Z, Z)$ are eigenvalues.

For an associated ground state ψ of $\mathcal{E}_{c,Z,N}$ (or an approximate ground state on the Thomas–Fermi or Scott scale) in either the Brown–Ravenhall or Furry picture, we define the associated one-particle ground state densities

$$\rho_{\mathrm{B/F}}(x) := N \sum_{\sigma=1}^{4} \int_{\Gamma^{N-1}} |\psi(x, \sigma; y_2, \ldots, y_N)|^2 \,\mathrm{d}y_2 \cdots \mathrm{d}y_N, \quad x \in \mathbb{R}^3. \tag{4.59}$$

As in the Chandrasekhar case, we define a spin-orbit resolved version of $\rho_{\mathrm{B/F}}$. More precisely, for given spin–orbit coupling $\kappa \in \dot{\mathbb{Z}}$ (recall (4.29)–(4.30)), we define

$$\rho_{\kappa,\mathrm{B/F}}(x) := \frac{N}{4\pi} \sum_{\sigma\in\{+,-\}} \sum_{m=-j_\kappa}^{j_\kappa} \int_{\Gamma^{N-1}} \mathrm{d}y \left| \sum_{\tau=1}^{4} \int_{\mathbb{S}^2} \mathrm{d}\omega\, \overline{\Phi^\sigma_{\kappa,m}(\omega,\tau)} \psi(|x|\omega,\tau,y) \right|^2 \tag{4.60}$$

for $x \in \mathbb{R}^3$. Here $\Phi^\sigma_{\kappa,m}$ are the spherical Dirac spinors (4.31). Note that

$$\frac{1}{4\pi} \int_{\mathbb{S}^2} \rho_{\mathrm{B/F}}(|x|\omega)\mathrm{d}\omega = \sum_{\kappa\in\dot{\mathbb{Z}}} \rho_{\kappa,\mathrm{B/F}}(x), \quad x \in \mathbb{R}^3. \tag{4.61}$$

Remark 4.5 (1) The Brown–Ravenhall and Furry operators are examples of so-called "no-pair" operators, i.e., Schrödinger operators that can *formally* be derived from quantum electrodynamics by *neglecting the creation of electron-positron pairs* [229]. These operators are popular among quantum chemists, as they provide decent numerical results which are in good accordance with experimentally measured data. For instance, the Scott correction in the Furry picture (Formula (4.78) in Theorem 4.11) coincides astonishingly well with experimental data (see, e.g., [135]), see [100, Section 6], and [186, 192] for textbook treatments.

(2) The Scott correction is also believed to be true when the mean field in the sense of Mittleman [171] is taken into account.

However, this is so far only known in the Hartree–Fock approximation when the involved projection is given by the Dirac–Fock operator, see Fournais et al. [79].

In the following subsections, we summarize results concerning the asymptotic expansion of the ground state energies and convergence of the one-particle ground state densities for the above-introduced models in the atomic and molecular cases. In particular, we review the elements of the proof of the *relativistic strong Scott conjecture* for Chandrasekhar atoms in [85, 87].

4.3 Atoms without magnetic fields

As far as we know, the results below have only been proved in the neutral case $N = Z$. We believe that they also hold for ions.

4.3.1 Thomas–Fermi scale

In all of the above relativistic models, the leading order of the asymptotic expansion of the ground state energy is non-relativistic. These results indicate that electrons whose distances to the nucleus are of order $Z^{-1/3}$ still behave non-relativistically, although they are being sucked into the nucleus. The following theorem was proved by Sørensen [184] (Chandrasekhar), by [23] and [91] (Brown–Ravenhall), and by [100] (Furry, as a consequence of the Scott correction). Recall the critical coupling constants γ_{C}, γ_{B}, γ_{F} in (4.4), (4.43), (4.49).

Theorem 4.6 *Let $N = Z$ and $E^{\mathrm{TF}}(Z)$ denote the Thomas–Fermi energy of a neutral Thomas–Fermi atom with $q = 2$. Then,*

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{C}}(Z) - E^{\mathrm{TF}}(Z)}{Z^{7/3}} = 0 \quad \textit{for fixed } \frac{Z}{c} \leq \gamma_{\mathrm{C}}, \tag{4.62}$$

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{B}}(Z) - E^{\mathrm{TF}}(Z)}{Z^{7/3}} = 0 \quad \textit{for fixed } \frac{Z}{c} \leq \gamma_{\mathrm{B}}, \tag{4.63}$$

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{F}}(Z) - E^{\mathrm{TF}}(Z)}{Z^{7/3}} = 0 \quad \textit{for fixed } \frac{Z}{c} < \gamma_{\mathrm{F}}. \tag{4.64}$$

Remark 4.7 (Elements in the proof of Theorem 4.6) We make some remarks on Sørensen's proof [184] for the Chandrasekhar case. Since $\sqrt{p^2+1} - 1 \leq p^2/2$, it suffices to prove the lower bound, whose proof is similar to Lieb's simplified proof of Theorem 3.1, see [144, Theorem 5.1]. It can be split into the following steps.

(1) Reduce the linear many-particle problem to estimating the nonlinear one-particle quadratic form

$$\sum_{\nu=1}^{N} \left\langle m_\nu, \left[\sqrt{-c^2\Delta + c^4} - c^2 - \frac{Z}{|x|} + \rho_Z^{\mathrm{TF}} * \frac{1}{|\cdot|} \right] m_\nu \right\rangle \tag{4.65}$$

with the Thomas–Fermi density ρ_Z^{TF} and orthonormal orbitals $\{m_\nu\}_{\nu=1}^N$ from below with the help of a correlation inequality (e.g., by Lieb and Oxford [142, 149, 183] or that of [160]).

(2) Due to the (non-perturbative) Coulomb singularity at the origin, one localizes position space into the regions $|x| \lesssim Z^{-o}$ and $|x| \gtrsim Z^{-o}$ with $o \in (1/3, 2/3)$. Guided by the proof of Theorem 3.1 (Lieb [144, Theorem 5.1]) and the intuition that electrons on distances Z^{-o} behave non-relativistically, it is expected that the electrons in the region $|x| \gtrsim Z^{-o}$ lead to the TF energy, while the contribution from $|x| \lesssim Z^{-o}$ is $o(Z^{7/3})$. The localization errors can be controlled at the end of the argument with the help of an arbitrarily small amount ($Z^{-\varepsilon}$) of kinetic energy.

(3) The contribution of the electrons in $\{|x| \lesssim Z^{-o}\}$, where the Coulomb singularity is located, can be controlled with the help of the following strengthening of one of Daubechies' inequalities [34],

$$\mathrm{Tr}\left(|p| - \frac{2/\pi}{|x|} - V \right)_- \lesssim \int_{\mathbb{R}^3} V(x)_+^4 \, \mathrm{d}x \tag{4.66}$$

by [83] and the inequality $\sqrt{p^2+1} - 1 \geq |p| - 1$. (Inequality (4.66) is often called Hardy–Lieb–Thirring inequality because of the homogeneity of the "unperturbed Hardy operator" $|p| - \frac{2/\pi}{|x|}$.) Here, V is a bounded function, supported on $\{|x| \lesssim Z^{-o}\}$. Using (4.66) one computes the contribution to the energy to be $\mathcal{O}(Z^{2+3(1-o)})$, which is more than $Z^{7/3}$. For this reason another localization on the length scale Z^{-i} is necessary. The Hardy–Lieb–Thirring inequality for V being

supported on $\{|x| \lesssim Z^{-i}\}$ then produces an $o(Z^{7/3})$ error when $i \in (8/9, 1)$. The additionally introduced localization error can be controlled by an ε of kinetic energy, too.

(4) The energy contribution of electrons located in the intermediate region $\{Z^{-i} \lesssim |x| \lesssim Z^{-o}\}$ can be controlled using Daubechies' inequality,

$$\mathrm{Tr}\left(\sqrt{-\Delta+1}-1-V(x)\right)_- \lesssim \int_{\mathbb{R}^3} (V_+^{5/2}(x)+V_+^4(x))\,\mathrm{d}x. \tag{4.67}$$

Note that $|x|^{-1} \notin L^4(\mathbb{R}^3)$.

(5) Electrons in the region $\{|x| \gtrsim Z^{-o}\}$ are expected to generate the TF energy. Here semiclassical analysis is used. Roughly speaking, one compares the quantum energy

$$\sum_{\nu=1}^{N} \langle m_\nu, \mathbf{1}_{\{|x|\gtrsim Z^{-o}\}} \left[\sqrt{-c^2\Delta+c^4}-c^2-\frac{Z}{|x|}+\rho_Z^{\mathrm{TF}} * \frac{1}{|\cdot|}\right] \mathbf{1}_{\{|x|\gtrsim Z^{-o}\}} m_\nu\rangle \tag{4.68}$$

to the classically expected energy

$$\iint_{|q|\gtrsim Z^{-o}} \left(\sqrt{c^2p^2+c^4}-c^2-\frac{Z}{|q|}+\rho_Z^{\mathrm{TF}} * \frac{1}{|\cdot|}(q)\right)_- \frac{\mathrm{d}p\,\mathrm{d}q}{(2\pi)^3}. \tag{4.69}$$

The latter leads to the *non-relativistic* TF energy, since $\sqrt{c^2p^2+c^4}-c^2 \sim p^2/2$ for $|p| \lesssim Z^o \ll Z$ (since $|x| \gtrsim Z^{-o}$ with $o \in (1/3, 2/3)$). To that end, a phase-space localization using coherent states [144, Theorem 5.1] is used. In fact, merely the localization errors coming from the phase-space localization force the position localization to the scale $\lesssim Z^{-1/3}$.

Theorem 4.6 is accompanied by the following convergence results for the ground state densities.

Theorem 4.8 ([168, 169]) *Let $N = Z$ and let ρ_1^{TF} denote the hydrogenic Thomas–Fermi minimizer with $\int \rho_1^{\mathrm{TF}}(x)\,\mathrm{d}x = 1$ and $q = 2$. Then*

$$\lim_{Z,c\to\infty} Z^{-2}\rho_{\mathrm{C}}(Z^{-1/3}\cdot) = \rho_1^{\mathrm{TF}} \quad \textit{for fixed } \frac{Z}{c} \le \gamma_{\mathrm{C}}, \tag{4.70}$$

$$\lim_{Z,c\to\infty} Z^{-2}\rho_{\mathrm{B}}(Z^{-1/3}\cdot) = \rho_1^{\mathrm{TF}} \quad \textit{for fixed } \frac{Z}{c} \le \gamma_{\mathrm{B}}, \tag{4.71}$$

$$\lim_{Z,c\to\infty} Z^{-2}\rho_{\mathrm{F}}(Z^{-1/3}\cdot) = \rho_1^{\mathrm{TF}} \quad \textit{for fixed } \frac{Z}{c} < \gamma_{\mathrm{F}}. \tag{4.72}$$

In all three formulae, the convergence holds in Coulomb norm (see (2.5)–(2.6)) with convergence rate $\mathcal{O}(Z^{-3/16})$. In the Chandrasekhar case, the convergence also holds

when both sides are integrated against any $U \in L^{5/2} \cap L^4(\mathbb{R}^3)$ *and in the Brown–Ravenhall case when in addition* $U \in |\cdot|^{-1} L^\infty$ *is Lipschitz.*

Remark 4.9 (1) The proof of the convergence in Coulomb norm uses an observation of Fefferman and Seco [66], together with the energetic expansion of the ground state energy. For an error term $\mathcal{O}(Z^a)$ to the leading TF energy with $a < 7/3$, the convergence rate is $\mathcal{O}(Z^{(a-7/3)/2})$. In view of the energetic results [90, 91, 100, 224] (Scott correction), we have $a = 47/24$.

(2) The proof of weak convergence uses the proof of the energetic results (Theorem 4.6) together with a linear response argument. We will flesh out the details in the discussion of the densities on the Scott scale (Sect. 4.3.3).

4.3.2 Scott scale

As explained in the introduction, electrons in proximity of the nucleus are expected to generate relativistic effects that should be visible in the ground state energy and density on the spatial scale Z^{-1}. In fact, the Scott correction is relativistically lowered. The precise amount depends on the sum of the differences of the non-relativistic and the relativistic hydrogen eigenvalues. To that end, let λ_n^{S}, λ_n^{C}, λ_n^{B}, and λ_n^{F} denote the γ-dependent eigenvalues of the non-relativistic operator S_γ^H in (1.9), of the Chandrasekhar operator C_γ^H in (4.2) (with $q = 2$), of the Brown–Ravenhall operator B_γ, and of the Furry operator F_γ. (The Furry eigenvalues coincide of course with those (4.35) of $D_\gamma^H - 1$.) We introduce the spectral shifts

$$[0, \gamma_{\mathrm{C}}] \ni \gamma \mapsto s_{\mathrm{C}}(\gamma) := \gamma^{-2} \sum_{n \geq 0} \left(\lambda_n^{\mathrm{S}} - \lambda_n^{\mathrm{C}} \right) \geq 0, \tag{4.73}$$

$$[0, \gamma_{\mathrm{B}}] \ni \gamma \mapsto s_{\mathrm{B}}(\gamma) := \gamma^{-2} \sum_{n \geq 0} \left(\lambda_n^{\mathrm{S}} - \lambda_n^{\mathrm{B}} \right) \geq 0, \tag{4.74}$$

$$[0, \gamma_{\mathrm{F}}] \ni \gamma \mapsto s_{\mathrm{F}}(\gamma) := \gamma^{-2} \sum_{n \geq 0} \left(\lambda_n^{\mathrm{S}} - \lambda_n^{\mathrm{F}} \right) \geq 0, \tag{4.75}$$

and record the following observation.

Proposition 4.10 *Let* $\# \in \{\mathrm{C}, \mathrm{B}, \mathrm{F}\}$. *Then, the functions* $s_\#$ *on their respective domains are continuous and monotone decreasing and obey* $s_\#(0) = 0$.

Proof For s_{C}, this is proved in [224, Theorems 1.1, 1.4, Corollary 1.6]. See also [90, p. 552], where it is shown that s_{C} is monotone decreasing and finite. For s_{F}, the claim can be inferred from the explicitly known eigenvalues λ_n^{S} and λ_n^{F}, respectively. The continuity and monotonicity of s_{B} follow from the explicit knowledge of the Schrödinger and Coulomb–Dirac eigenvalues, and the inequality $\lambda_n^{\mathrm{F}} \geq \lambda_n^{\mathrm{B}}$. □

The following theorem concerning the energy asymptotics of Chandrasekhar atoms was proved independently by Solovej et al. [224], and the work [90] using different techniques. The result for Brown–Ravenhall atoms was proved by [91], and that for Furry atoms by [100].

Theorem 4.11 *Let $N = Z$ and let $E^{\mathrm{TF}}(Z)$ denote the Thomas–Fermi energy of a neutral Thomas–Fermi atom with $q = 2$. Then*

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{C}}(Z) - \left[E^{\mathrm{TF}}(Z) + \left(\frac{1}{2} - s_{\mathrm{C}}(\gamma)\right) Z^2\right]}{Z^2} = 0 \quad \text{for fixed } \frac{Z}{c} \leq \gamma_{\mathrm{C}}, \tag{4.76}$$

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{B}}(Z) - \left[E^{\mathrm{TF}}(Z) + \left(\frac{1}{2} - s_{\mathrm{B}}(\gamma)\right) Z^2\right]}{Z^2} = 0 \quad \text{for fixed } \frac{Z}{c} \leq \gamma_{\mathrm{B}}, \tag{4.77}$$

$$\lim_{Z,c\to\infty} \frac{E_c^{\mathrm{F}}(Z) - \left[E^{\mathrm{TF}}(Z) + \left(\frac{1}{2} - s_{\mathrm{F}}(\gamma)\right) Z^2\right]}{Z^2} = 0 \quad \text{for fixed } \frac{Z}{c} < \gamma_{\mathrm{F}}. \tag{4.78}$$

In all of the above limits, the error term can be quantified and is $\mathcal{O}(Z^{47/24})$.

Remark 4.12 It is believed that these results also hold for ions (at least as long as the ionization degree is sufficiently small), since the electrons on length scales $\mathcal{O}(Z^0)$ should not disturb the energy generated by electrons on length scales $\mathcal{O}(Z^{-1})$. However, a rigorous proof is lacking.

The energetic results on the Scott scale are accompanied by recent results [85, 87, 170] for the density in the Chandrasekhar and Furry cases.

Theorem 4.13 ([85, 87, 170]) *Let*

$$U \in \mathcal{D} := \Big\{ W \in L^1_{\mathrm{loc}}(\mathbb{R}_+) : \forall \varepsilon > 0\, \exists a > 0\, \forall r > 0 : \\ |W(r)| \leq a \left(r^{-1} \mathbf{1}_{\{r\leq 1\}} + r^{-\frac{3}{2}-\varepsilon} \mathbf{1}_{\{r\geq 1\}} \right) \Big\} \tag{4.79}$$

be arbitrary. Then, the following statements hold.

(1) (Convergence for fixed angular momentum/spin-orbit coupling) *Let $\ell \in \mathbb{N}_0$ and $\kappa \in \dot{\mathbb{Z}}$ be fixed. Then*

$$\lim_{Z,c\to\infty} \int_0^\infty c^{-3} \varrho_{\ell,\mathrm{C}}(c^{-1}r) U(r)\, \mathrm{d}r = \int_0^\infty \varrho^H_{\ell,\mathrm{C}}(r) U(r)\, \mathrm{d}r \quad \text{for fixed } \frac{Z}{c} < \gamma_{\mathrm{C}}, \tag{4.80}$$

$$\lim_{Z,c\to\infty} \int_{\mathbb{R}^3} c^{-3} \rho_{\kappa,\mathrm{F}}(c^{-1}x) U(|x|)\, \mathrm{d}x = \int_{\mathbb{R}^3} \rho^H_{\kappa,\mathrm{D}}(x) U(|x|)\, \mathrm{d}x \quad \text{for fixed } \frac{Z}{c} < \gamma_{\mathrm{F}}. \tag{4.81}$$

(2) (Convergence of total density) *We have*

$$\lim_{Z,c\to\infty} \int_{\mathbb{R}^3} c^{-3} \rho_{\mathrm{C}}(c^{-1}x) U(|x|)\, \mathrm{d}x = \int_{\mathbb{R}^3} \rho^H_{\mathrm{C}}(x) U(|x|)\, \mathrm{d}x \quad \text{for fixed } \frac{Z}{c} < \gamma_{\mathrm{C}}, \tag{4.82}$$

$$\lim_{Z,c\to\infty} \int_{\mathbb{R}^3} c^{-3} \rho_{\mathrm{F}}(c^{-1}x) U(|x|)\, \mathrm{d}x = \int_{\mathbb{R}^3} \rho^H_{\mathrm{D}}(x) U(|x|)\, \mathrm{d}x \quad \text{for fixed } \frac{Z}{c} < \gamma_{\mathrm{F}}. \tag{4.83}$$

Remark 4.14 (1) For the sake of clarity, we restricted attention to the above class $\mathcal{D}$ of test functions, although the results actually hold for a substantially larger class.
(2) However, the exemplary test function class (4.79) is believed to be optimal.
   (a) Due to Kato's inequality, we cannot expect (at least not for $\ell = 0$) (4.80)–(4.83) to hold for test functions, whose singularity is worse than $|x|^{-1}$.
   (b) The $|x|^{-3/2-\varepsilon}$ decay seems optimal in view of the $|x|^{-3/2}$-decay of $\rho^H_{\mathrm{C/F}}$, see Theorems 4.1 and 4.4.
(3) In view of Theorems 4.1 and 4.4, a transition between the length scales Z^{-1} and $Z^{-1/3}$ is again clearly visible.

4.3.3 Elements in the proof of Theorem 4.13

The rest of this subsection is concerned with explaining the key elements of the proof of Theorem 4.13 in the Chandrasekhar case, i.e., the limits (4.80) and (4.82). For simplicity we set $q = 1$ here. We begin with the argument to prove (4.80) for a fixed angular momentum channel.

We follow the lines of Lieb and Simon [152], Baumgartner [12], and [117] by employing a linear-response argument. Let $|\psi\rangle\langle\psi|$ be a ground state density matrix of the atomic many-particle operator C_Z (see (4.51)), and define, for $U \in \mathcal{D}$ and in slight abuse of notation, the perturbed operator

$$C_{Z,\lambda} := C_Z - \lambda \sum_{\nu=1}^{Z} c^2 U(c|x_\nu|)\Pi_{\ell,\nu} \quad \text{in} \quad \bigwedge_{\nu=1}^{Z} L^2(\mathbb{R}^3). \tag{4.84}$$

Here Π_ℓ is the orthogonal projection in $L^2(\mathbb{R}^3)$ onto the ℓ-th angular momentum channel defined by

$$\Pi_\ell := \sum_{m=-\ell}^{\ell} |Y_{\ell,m}\rangle\langle Y_{\ell,m}|,$$

and $\Pi_{\ell,\nu}$ acts as Π_ℓ with respect to the ν-th particle. Since the singularity of U is Coulombic, $C_{Z,\lambda}$ is realized as a self-adjoint operator by Kato's inequality if $\gamma < 2/\pi$ and $|\lambda|$ is sufficiently small. Moreover, since (4.80) is linear in U we may assume $U \geq 0$ and $\lambda > 0$ without loss of generality.

By the linear response argument, the Scott correction (Theorem 4.11), and scaling $x \mapsto x/c$, we have

$$\begin{aligned}
&\overline{\lim_{Z\to\infty}} \int_0^\infty c^{-3} \varrho_{\ell,\mathrm{C}}(r/c) U(r)\, \mathrm{d}r \\
&= \lim_{\lambda \searrow 0} \overline{\lim_{Z\to\infty}} \operatorname{Tr}_{\bigwedge_{\nu=1}^{Z} L^2(\mathbb{R}^3)} \left[\frac{|\psi\rangle\langle\psi|(C_Z - C_{Z,\lambda})}{\lambda c^2} \right] \\
&\leq (2\ell+1) \cdot \lim_{\lambda \searrow 0} \frac{\operatorname{Tr}_{L^2(\mathbb{R}_+)}(C^H_{\ell,\gamma} - \lambda U(r))_- - \operatorname{Tr}_{L^2(\mathbb{R}_+)}(C^H_{\ell,\gamma})_-}{\lambda}
\end{aligned} \tag{4.85}$$

with $C^H_{\ell,\gamma}$ as in (4.6). To compute the right side of (4.85), we have two options.

(1) Find a majorant to apply the dominated convergence theorem to interchange $\liminf_{\lambda\searrow 0}$ and Tr. Then apply standard perturbation theory, i.e., the classical Hellmann–Feynman theorem for a single eigenvalue. This leads to the shorter proof in [85].
(2) Compute the derivative with respect to λ directly. This lead to the longer, original proof in [87].

Here we shall present the arguments of the longer proof, as we believe that it better unearths the involved mathematics of the relativistic strong Scott conjecture. Besides, it allows us to popularize a generalization of the classical Hellmann–Feynman theorem that may be of independent interest in the analysis of many-particle problems.

First we state this generalized Hellmann–Feynman theorem with "natural" assumptions on the perturbation. However, this version is not applicable to our problem. Afterward, we state a generalization with weaker assumptions, which suffices for our purposes. Recall that an operator B is called *relatively form trace class* with respect to a self-adjoint operator A that is bounded from below, if $(A+M)^{-1/2}B(A+M)^{-1/2}$ is trace class for some (and hence any) large enough $M > 0$.

Theorem 4.15 ([87, Theorem 3.1]) *Assume that A is a self-adjoint operator in some Hilbert space with A_- trace class. Assume that B is a non-negative operator in the same Hilbert space, and relatively form trace class with respect to A. Then, the one-sided derivatives of*

$$\lambda \mapsto S(\lambda) := \mathrm{Tr}(A-\lambda B)_-$$

satisfy

$$\mathrm{Tr}\, B\mathbf{1}_{(-\infty,0)}(A) = D^- S(0) \leq D^+ S(0) = \mathrm{Tr}\, B\mathbf{1}_{(-\infty,0]}(A). \tag{4.86}$$

In particular, S is differentiable at $\lambda = 0$, if and only if $B|_{\ker A} = 0$.

Remark 4.16 (1) The relative form trace class assumption implies that the expression on the right of (4.86), and consequently also that on the left, is finite.
(2) By the variational principle, it follows that S is convex. Thus, S has left- and right-sided derivatives (cf. [217, Theorem 1.26]).
(3) If $\inf\sigma_{\mathrm{ess}}(A) > 0$ or $A-\lambda B$ has only finitely many negative eigenvalues, then the derivative and the trace can be interchanged and the result follows from the classical Hellman–Feynman theorem. The point is that the formulae remain valid even when the bottom of the essential spectrum is zero, so that perturbation theory is not directly applicable.

In our application, A is the Chandrasekhar operator $C^H_{\ell,\gamma}$ (which has no zero eigenvalue) and $B = U$ in $L^2(\mathbb{R}_+, \mathrm{d}r)$. Thus, (4.80) would follow from Theorem 4.15, if one could verify its assumptions. By Kato's inequality (using $\gamma < 2/\pi$), one can replace A by the kinetic energy C_ℓ. In this case, the relative trace class condition can be formulated explicitly using the Fourier–Bessel transform. But since $(k+1)^{-1} \notin L^1(\mathbb{R}_+, \mathrm{d}k)$,

this shows that $C^H_{\ell,\gamma}$ cannot satisfy the relative trace class assumption, no matter how nice the perturbation $B = U$ is.

For this reason, we proved and used a generalization of Theorem 4.15, where the relative trace class assumption is stated with respect to $(A+M)^{2s}$ for some $s > 1/2$. We will state this generalization in Theorem 4.18 in a moment. Using the following special case of [86, Theorem 1.1], the assumption of Theorem 4.18 can be recast as an assumption involving the kinetic energy C_ℓ (see (4.7)) instead of $C^H_{\ell,\gamma}$.

Theorem 4.17 ([86, Theorem 1.1]) *Let $2/\pi \geq \gamma \geq 0$, $0 < s < 3/2 - \sigma_\gamma$ (with σ_γ as in (4.16)), and assume $V \in L^1_{\mathrm{loc}}(\mathbb{R}^3)$ satisfies $-\gamma/|x| \leq V \leq 0$. Then, we have the quadratic form inequality*

$$|p|^{2s} \lesssim (|p| + V)^{2s}. \tag{4.87}$$

We are now ready to state the generalization of Theorem 4.15.

Theorem 4.18 ([87, Theorem 3.2]) *Assume that A is self-adjoint with A_- trace class. Assume that B is non-negative and relatively form bounded with respect to A. Assume that there are $1/2 < s \leq 1$ such that for some $M > -\inf \operatorname{spec} A$,*

$$(A+M)^{-s} B (A+M)^{-s} \qquad \text{is trace class} \tag{4.88}$$

and

$$\limsup_{\lambda \to 0} \left\| (A+M)^s (A - \lambda B + M)^{-s} \right\| < \infty. \tag{4.89}$$

Then, the conclusions in Theorem 4.15 are valid.

Thus, to conclude the proof of (4.80), we are left with showing the assumptions of Theorem 4.18. Since the test functions U in the above formulation of Theorem 4.13 are bounded by a multiple of the Coulomb potential, the condition (4.89) can be verified easily using Theorem 4.17. We now verify (4.88) with $A = C^H_{\ell,\gamma}$ and $B = U$. Letting $\|\cdot\|_2$ denote the Hilbert–Schmidt norm, we have, for any $1/2 < s \leq 1$,

$$\begin{aligned} \|U^{1/2}(C^H_{\ell,\gamma} + M)^{-s}\|_2^2 &\lesssim \|U^{1/2}(C_\ell + M)^{-s}\|_2^2 \\ &= \int_0^\infty \mathrm{d}r\, U(r) \int_0^\infty \mathrm{d}k\, \frac{kr\, J_{\ell+1/2}(kr)^2}{(\sqrt{k^2+1} - 1 + M)^{2s}} \\ &\lesssim \|U\|_{\mathcal{K}^{(0)}_s}, \end{aligned}$$

where we used Theorem 4.17 and the Fourier–Bessel transform. Here,

$$\|W\|_{\mathcal{K}^{(0)}_s} := \sup_{R \geq 1/2} \left[\int_0^R \left(\frac{r}{R}\right)^{2s-1} |W(r)|\, \mathrm{d}r + \int_R^\infty |W(r)|\, \mathrm{d}r \right].$$

Clearly, functions $U \in \mathcal{D}$, the test function space (4.79), satisfy $\|U\|_{\mathcal{K}^{(0)}_s} < \infty$. This concludes the sketch of the arguments in the proof of (4.80).

To prove the convergence of the total density $c^{-3}\rho_{\mathrm{C}}(x/c)$, we also need to interchange the ℓ-summation with the limits $Z \to \infty$ and $\lambda \to 0$. This is done using the dominated convergence theorem. To apply it, it suffices to prove that there is an $\varepsilon > 0$ such that

$$\mathrm{Tr}(C_\ell - V - \lambda U(r))_- - \mathrm{Tr}(C_\ell - V)_- \lesssim \lambda(\ell + 1/2)^{-2-\varepsilon}, \tag{4.90}$$

whenever $0 \leq V \leq \gamma/r$. In our application, V is closely related to the Thomas–Fermi potential. For the proof of (4.90), see [87, Section 5].

4.4 Molecules without magnetic fields

We immediately present the energetic result for Chandrasekhar molecules on the Scott scale, which was proved by Solovej et al. [224].

Theorem 4.19 *Let $q \in \mathbb{N}$, $\underline{z} = (z_1, \dots, z_K) \in (0,1)^K$ with $\sum_{\kappa=1}^K z_\kappa = 1$ and $\underline{r} = (r_1, \dots, r_K) \in \mathbb{R}^{3K}$ with $\min_{k\neq\ell} |r_k - r_\ell| > r_0$ for some $r_0 > 0$. Define $\underline{Z} = (Z_1, \dots, Z_K) = |\underline{Z}|z$ and $R = |\underline{Z}|^{-1/3} r$ for $|\underline{Z}| > 0$. Let $E^{\mathrm{TF}}(\underline{z}, \underline{r})$ be the Thomas–Fermi energy of the unconstrained problem (2.9) and let $E_c^{\mathrm{C}}(N, \underline{Z}, \underline{R})$ be the ground state energy with nuclear configuration $\underline{Z}$ and $\underline{R}$. Then, the following statements hold:*

(1) The function

$$\left[0, \frac{2}{\pi}\right] \ni \gamma \mapsto \mathcal{S}_{\mathrm{C}}(\gamma) := \lim_{\kappa\to 0} \left(\iint \left[\frac{p^2}{2} - \frac{1}{|v|} + \kappa \right]_- \frac{\mathrm{d}p\,\mathrm{d}v}{(2\pi)^3} - \mathrm{Tr}[H_{\mathrm{C}}(\gamma) + \kappa]_- \right) \tag{4.91}$$

with

$$H_{\mathrm{C}}(\gamma) := \begin{cases} \sqrt{-\gamma^{-2}\Delta + \gamma^{-4}} - \gamma^{-2} - 1/|x| & \text{if } \gamma \in (0, 2/\pi], \\ -\frac{1}{2}\Delta - 1/|x| & \text{if } \gamma = 0 \end{cases} \tag{4.92}$$

is continuous, monotone decreasing, and satisfies $\mathcal{S}_{\mathrm{C}}(0) = 1/4$.

(2) As $|\underline{Z}| = \sum_{\kappa=1}^K Z_\kappa \to \infty$ and $c \to \infty$ with $\max_\kappa\{Z_\kappa/c\} \leq 2/\pi$, one has

$$E_c^{\mathrm{C}}(|\underline{Z}|, \underline{Z}, \underline{R}) = E^{\mathrm{TF}}(\underline{z}, \underline{r})|\underline{Z}|^{7/3} + q \sum_{\kappa=1}^K Z_\kappa^2 \cdot \mathcal{S}_{\mathrm{C}}\left(\frac{Z_\kappa}{c}\right) + \mathcal{O}(|\underline{Z}|^{2-1/30}). \tag{4.93}$$

The error term $\mathcal{O}(|\underline{Z}|^{2-1/30})$ means that $|\mathcal{O}(|\underline{Z}|^{2-1/30})| \lesssim |\underline{Z}|^{2-1/30}$, where the implicit constant depends only on r_0 and K.

Remark 4.20 The convergence of the one-particle ground state density on the Thomas–Fermi scale in Coulomb norm can be proved using the argument in the proof of

Theorem 4.8 together with Theorem 4.19. The convergence of the density on the Scott scale has not been worked out so far.

4.5 Molecules with self-generated magnetic fields

Suppose that the kinetic energy of the electrons is described by the Chandrasekhar operator in the presence of a magnetic vector potential, i.e.,

$$\mathcal{T}^{(c)}(\underline{A}) := \sqrt{c^2 T(\underline{A}) + c^4} - c^2, \tag{4.94}$$

where $T(\underline{A})$ is either the magnetic Schrödinger or Pauli operator as in (3.44). We consider $\underline{A}$-fields in

$$\tilde{\mathfrak{A}} := \{\underline{A} \in L^6(\mathbb{R}^3 : \mathbb{R}^3) : \operatorname{div}(\underline{A}) = 0,\ |\nabla \otimes \underline{A}| \in L^2(\mathbb{R}^3)\}. \tag{4.95}$$

Let

$$C_{N,V,\underline{A}} = \sum_{\nu=1}^{N} \left(\mathcal{T}_{\nu}^{(c)}(\underline{A}) - V(x_\nu)\right) + \sum_{1\le\nu<\mu\le N} \frac{1}{|x_\nu - x_\mu|} + U \quad \text{in} \bigwedge_{\nu=1}^{N} L^2(\mathbb{R}^3 : \mathbb{C}^2) \tag{4.96}$$

be a Hamilton operator for a relativistic molecule with given vector potential $\underline{A}$, and V and U as in (1.2) and (1.3), respectively. (Technically, $C_{N,V,\underline{A}}$ is defined as the Friedrichs extension of the corresponding quadratic form with form domain $\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^2)$, whenever $\max_\kappa Z_\kappa/c \le \gamma_{\mathrm{C}}$.)

For admissible vector potentials $\underline{A} \in \tilde{\mathfrak{A}}$, given nuclear positions $\underline{R}$, and $N = |\underline{Z}|$ the ground state energy is

$$E_c^{\mathrm{C,mag}}(\underline{Z}, \underline{R}, \underline{A}) := \inf \operatorname{spec}(C_{N,V,\underline{A}}), \tag{4.97}$$

and the total energy including the magnetic field energy is

$$E_c^{\mathrm{C,mag}}(\underline{Z}, \underline{R}) := \inf_{\underline{A}\in\tilde{\mathfrak{A}}} \left(E_c^{\mathrm{C,mag}}(\underline{Z}, \underline{R}, \underline{A}) + \frac{c^2}{8\pi^2} \int_{\mathbb{R}^3} |\nabla \times \underline{A}|^2 \right). \tag{4.98}$$

The following energetic result for the Scott scale was proved by Erdős et al. [49].

Theorem 4.21 *Let the notations and assumptions be as in Theorem 4.19. In particular, fix K, $\underline{z} \in (0,1)^K$, and $\underline{r} \in \mathbb{R}^{3K}$. Assume furthermore that there is $\gamma_0 < 2/\pi$ such that $\max_\kappa Z_\kappa/c < \gamma_0$. Then*

$$E_c^{\mathrm{C,mag}}(\underline{Z}, \underline{R}) = E^{\mathrm{TF}}(\underline{z}, \underline{r})|\underline{Z}|^{7/3} + \sum_{\kappa=1}^{K} Z_\kappa^2 \left(\frac{1}{2} - s_{\mathrm{C}}(\gamma)\right) + o(|\underline{Z}|^2) \tag{4.99}$$

in the limits $|\underline{Z}|, c \to \infty$.

Remark 4.22 (1) Since $c^{-1}|\underline{Z}|$ is bounded, the prefactor $c^2/(8\pi^2)$ of the magnetic energy in the relativistic case is of order $|\underline{Z}|^2$ (at least if we assume additionally that $|\underline{Z}|/c$ is kept constant when $|\underline{Z}|, c \to \infty$). This is much larger than in the non-relativistic case (Theorem 3.18), where $c^{-2}|\underline{Z}|$ was bounded. Thus, the self-generated magnetic field has to be much smaller in the relativistic case, which explains why it does not alter the Scott coefficient (contrary to the non-relativistic situation). In fact, the prefactor 8π in front of the field energy is irrelevant and can be replaced by any other fixed constant in the relativistic situation.

(2) The convergence of the density on the Scott scale has not been worked out so far.

5 Open questions

We collect some questions that—at least from our perspective—are interesting both from physical and mathematical points of view.

(1) For $N \in \mathbb{N}$ and $\underline{Z} \in (0, \infty)^K$, we set

$$\mathfrak{E}_S(N, \underline{Z}) := \inf\{E^{\mathrm{S}}(N, \underline{Z}, \underline{R}) : \underline{R} \in \mathbb{R}^{3K}\}. \tag{5.1}$$

This is the ground state energy of a non-relativistic molecule in static approximation, provided there is a state ψ in the form domain of $H_{N,V}$ and nuclear positions $R \in \mathbb{R}^{3K}$ such that $\langle \psi, H_{N,V}\psi\rangle = \mathfrak{E}_S(N, \underline{Z})$. Question: Can one prove the Scott conjecture for $\mathfrak{E}_S(N, \underline{Z})$, i.e., when one minimizes over the nuclear positions? We expect additivity of the energy up to $o(|\underline{Z}|^{\frac{5}{3}})$, i.e.,

$$\mathfrak{E}_S(N, \underline{Z}) = \sum_{\kappa=1}^{K} \left(E^{\mathrm{TF}}(Z_\kappa) + \frac{q}{4} Z_\kappa^2 - C_{\mathrm{DS}} Z_\kappa^{\frac{5}{3}} \right) + o(|\underline{Z}|^{\frac{5}{3}}). \tag{5.2}$$

Even more, one might ask whether the strong Scott conjecture would hold around each of the nuclei if (5.2) is true. A step in this direction was taken by Iantchenko et al. [117, Theorem 3] under the additional hypothesis that the minimal nuclear distance is bounded from below, e.g., by const $|\underline{Z}|^{-\frac{1}{4}}$. The analogue of $\mathfrak{E}_S$ can be defined for other many-particle models discussed in this review, e.g., those in Sect. 4. As far as we know, the Scott conjecture is also open for these problems. Again, we expect additivity of the energy up to order $o(|\underline{Z}|^{5/3})$. One could also consider a variant of this problem, where the kinetic energy of the nuclei is taken into account.

(2) It is folklore in quantum chemistry that chemical accuracy is achieved without taking a self-generated magnetic field into account. Therefore, we ask whether in physical models at least the Scott conjecture does not depend on the self-generated magnetic field.

(3) The Scott conjectures for the energy and the density are open for no-pair operators where a self-consistent mean field is taken into account. In this case, the Hilbert space of admissible one-particle states (in the $x \mapsto x/c$ rescaled picture) is $\Lambda_\chi(L^2(\mathbb{R}^3 : \mathbb{C}^4))$ with $\Lambda_\chi := \mathbf{1}_{(0,\infty)}(D_\gamma^H + \chi)$ with a (not necessary local) mean field χ. The resulting no-pair operator is sometimes called Fuzzy operator. Possible choices for χ are the Thomas–Fermi potential (the right sides of (2.11)–(2.12)), or the Hartree–Fock potential

$$\sum_i \left(|\varphi_i|^2 * \frac{1}{|\cdot|}(x) - \frac{\varphi_i(x)\overline{\varphi_i(\cdot)}}{|x-\cdot|} \right)$$

generated by a set of appropriately chosen orbitals $\{\varphi_i\}_i$. The latter choice is especially popular in quantum chemistry, see, e.g., [125–127, 194]. It turns out, though, that numerically computed values of the ground state energy for all atoms, also heavy ones, in the Fuzzy picture are quite close to those in the Furry picture; see also [100, 171, 192, 195]. Nevertheless, from a mathematical point of view it is interesting to investigate the precise value of the Scott correction for the Fuzzy operator. The following tasks seem natural.

(a) Show that for any (reasonable?) choice of the mean field χ, the leading order of the ground state energy is still the Thomas–Fermi energy.
(b) Show the Scott conjecture for the Fuzzy model defined in the spirit of Mittleman (minimization of the electronic degrees followed by a maximization of the splitting).
(c) Show that, to within the order of accuracy of Scott's correction, the maximization is attained in the Furry picture. (Recall that the Z^2-correction in the Furry picture is exclusively generated by the effective one-particle problem involving the hydrogenic operator D_γ^H. Thus, our intuition is supported by the variational principle for operators with spectral gaps [99, 173], which leads to the largest eigenvalues of $\Lambda_\chi D_\gamma^H \Lambda_\chi$, when one chooses Λ_χ to be the Furry projection. This is also the underlying spirit of Schwinger's derivation [198] of the relativistic Scott correction.)

(4) Can one show first- and second-order asymptotics for the Lieb–Loss model [140]? See Bach and Hach [6] for the first order in the non-relativistic setting.
(5) Let us formulate some questions regarding the hydrogenic densities $\rho_\#^H$ with $\# \in \{\mathrm{C}, \mathrm{B}, \mathrm{F}\}$. For $\# = \mathrm{F}$ one might be able to exploit the explicitly known eigenfunctions of the Coulomb–Dirac operator (cf. [17, 32, 96, 185, 232]) as in Theorem 3.11 by Heilmann and Lieb.

(a) Inspired by Theorems 4.1 and 4.4, we ask whether the densities $\rho_\#^H$ satisfy a power law at the origin, i.e., whether there are model-dependent constants $a_{\gamma,\#}, b_{\gamma,\#} > 0$ such that

$$\lim_{|x|\to 0} \rho_\#^H(x)|x|^{2a_{\gamma,\#}} = b_{\gamma,\#}. \tag{5.3}$$

In view of Theorems 4.1 and 4.4 and the fact $|\psi^{\mathrm{D}}_{n=0,\kappa=\pm1,m}(x)| \sim |x|^{-\Sigma_\gamma}$ for $m = -j_\kappa, \dots, j_\kappa$ and $|x| \ll 1$ (cf. [17, p. 316] or [233, p. 427]), it seems natural to believe that $a_{\sigma,C} = \sigma_\gamma$ (cf. (4.16)) and $a_{\sigma,F} = \Sigma_\gamma$ (cf. (4.38)).

(b) Electrons far away from the nucleus are expected to behave non-relativistically. Can one show

$$\lim_{|x|\to\infty} |x|^{3/2} \rho^H_{\#}(x) = \lim_{|x|\to 0} |x|^{3/2} \rho^{\mathrm{TF}}_{Z=1}(x) \tag{5.4}$$

as in Theorem 3.11? (Here $\rho^{\mathrm{TF}}_{Z=1}$ is the hydrogenic TF density with $q = 2$.) In case $\# = \mathrm{F}$ one might be able to derive an asymptotic expansion as in (3.30) using the explicitly known eigenfunctions.

(c) The non-relativistic density $\rho^H_{\mathrm{S}}(x)$ decreases monotonically in $|x| > 0$. Is this also true for the relativistic hydrogenic densities?

(6) As we have seen in Theorem 2.10 and the ensuing discussion, Weizsäcker's parameter A in the TFW functional (2.23) can be tuned to achieve *either* energy agreement, *or* agreement of the TFW density near the origin. This leads to the following (vague) question of whether one can construct a modification of Weizsäcker's gradient term that gives *simultaneously* the energy and the density at the origin correctly.

Acknowledgements Partial support through U.S. National Science Foundation grant DMS-1954995 (R.L.F.), by the Deutsche Forschungsgemeinschaft through Germany's Excellence Strategy, grant EXC-2111-390814868 (R.L.F.& H.S.), and by the PRIME programme of the German Academic Exchange Service (DAAD) with funds from the German Federal Ministry of Education and Research (BMBF) (K.M.) is acknowledged.

Funding Open Access funding enabled and organized by Projekt DEAL.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest. Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

References

1. Bach, V.: Ein Beweis der Scottschen Vermutung für Ionen. Master's thesis, Institut für Mathematische Physik, Technische Universität Braunschweig, Braunschweig (1989)
2. Bach, V.: A proof of Scott's conjecture for ions. Rep. Math. Phys. **28**(2), 213–248 (1989)

3. Bach, V.: Error bound for the Hartree–Fock energy of atoms and molecules. Commun. Math. Phys. **147**, 527–548 (1992)
4. Bach, V.: Accuracy of mean field approximations for atoms and molecules. Commun. Math. Phys. **155**, 295–310 (1993)
5. Bach, V., Barbaroux, J.-M., Helffer, B., Siedentop, H.: On the stability of the relativistic electron–positron field. Commun. Math. Phys. **201**, 445–460 (1999)
6. Bach, V., Hach, A.: On the ultraviolet limit of the Pauli–Fierz Hamiltonian in the Lieb–Loss model, pp. 1–39 (in print). (2022)
7. Balinsky, A.A., Evans, W.D.: Spectral Analysis of Relativistic Operators. Imperial College Press, London (2011)
8. Balodis, P.: A proof of Scott's correction for matter. Commun. Math. Phys. **249**(1), 79–132 (2004)
9. Barbaroux, J.-M., Esteban, M.J., Séré, E.: Some connections between Dirac–Fock and electron-positron Hartree–Fock. Ann. Henri Poincaré **6**(1), 85–102 (2005)
10. Barbaroux, J.-M., Farkas, W., Helffer, B., Siedentop, H.: On the Hartree–Fock equations of the electron–positron field. Commun. Math. Phys. **255**(1), 131–159 (2005)
11. Barbaroux, J.-M., Helffer, B., Siedentop, H.: Remarks on the Mittleman max–min variational method for the electron–positron field. J. Phys. A Math. Gen. **39**(1), 85–98 (2006)
12. Baumgartner, B.: The Thomas–Fermi-theory as result of a strong-coupling-limit. Commun. Math. Phys. **47**(3), 215–219 (1976)
13. Benguria, R.: The von Weizsäcker and exchange corrections in the Thomas–Fermi theory. PhD thesis, Princeton, Department of Physics (1979)
14. Benguria, R., Brézis, H., Lieb, E.H.: The Thomas–Fermi-von Weizsäcker theory of atoms and molecules. Commun. Math. Phys. **79**(2), 167–180 (1981)
15. Benguria, R., Lieb, E.H.: The most negative ion in the Thomas–Fermi–von Weizsäcker theory of atoms and molecules. J. Phys. B. **18**, 1054–1059 (1985)
16. Benguria, R.D., Loss, M., Siedentop, H.: Stability of atoms and molecules in an ultrarelativistic Thomas–Fermi–Weizsäcker model. J. Math. Phys. **49**(1), 012302, 7, (2008)
17. Bethe, H..: Quantenmechanik der Ein- und Zwei-Elektronenatome. In Geiger, H., Scheel, K. (eds.) Handbuch der Physik, XXIV.1, Buch 2, chapter 3, 2 edition, pp. 273–560. Springer, Berlin (1933)
18. Bogdan, K., Grzywny, T., Jakubowski, T., Pilarczyk, D.: Fractional Laplacian with Hardy potential. Commun. Part. Differ. Equ. **44**(1), 20–50 (2019)
19. Breit, G.: The effect of retardation on the interaction of two electrons. Phys. Rev. **34**(4), 553 (1929)
20. Breit, G.: The fine structure of He as a test of the spin interactions of two electrons. Phys. Rev. **36**(3), 383 (1930)
21. Breit, G.: Dirac's equation and the spin–spin interactions of two electrons. Phys. Rev. **39**(4), 616 (1932)
22. Brown, G.E., Ravenhall, D.G.: On the interaction of two electrons. Proc. Roy. Soc. Lond. Ser. A. **208**, 552–559 (1951)
23. Cassanas, R., Siedentop, H.: The ground-state energy of heavy atoms according to Brown and Ravenhall: absence of relativistic effects in leading order. J. Phys. A **39**(33), 10405–10414 (2006)
24. Chandrasekhar, S.: The maximum mass of ideal white dwarfs. Astrophys. J. **74**, 81–82 (1931)
25. Chen, H..: On the excess charge problem in relativistic quantum mechanics. PhD thesis, Ludwig-Maximilians-Universität München (2019)
26. Chen, H., Frank, R.L., Siedentop, H.: A statistical theory of heavy atoms: energy and excess charge. In: B.-G. Englert, H. Siedentop, and M.-I. Trappe (eds): Density Functionals for Many-Particle Systems: Mathematical Theory and Physical Applications. Lecture Notes Series, Institute of Mathematical Sciences, National University of Singapore, vol. 41, pp. 57–68, World Scientific, Singapore (2023)
27. Chen, H., Siedentop, H.: On the excess charge of a relativistic statistical model of molecules with an inhomogeneity correction. J. Phys. A **53**(39), 395201,19, (2020)
28. Conlon, J.G.: A refinement of the Thomas–Fermi approximation for the N body problem. J. Math. Phys. **24**, 184–192 (1983)
29. Córdoba, A., Fefferman, C., Seco, L.: A trigonometric sum relevant to the nonrelativistic theory of atoms. Proc. Nat. Acad. Sci. U.S.A. **91**(13), 5776–5778 (1994)
30. Córdoba, A., Fefferman, C.L., Seco, L.A.: Weyl sums and atomic energy oscillations. Rev. Mat. Iberoamericana **11**(1), 165–226 (1995)
31. Córdoba, A., Fefferman, C.L., Seco, L.A.: A number-theoretic estimate for the Thomas–Fermi density. Commun. Part. Differ. Equ. **21**(7–8), 1087–1102 (1996)

32. Darwin, C.G.: The wave equation of the electron. Proc. Roy. Soc. (London) **A118**, 654–680 (1928)
33. Datta, S.N., Deviah, G.: The minimax technique in relativistic Hartree–Fock calculations. Pramana **30**(5), 387–405 (1988)
34. Daubechies, I.: An uncertainty principle for fermions with generalized kinetic energy. Commun. Math. Phys. **90**, 511–520 (1983)
35. Dickinson, W.C.: Hartree computation of the internal diamagnetic field for atoms. Phys. Rev. **80**, 563–566 (1950)
36. Dietze, C.I.: On the Thomas–Fermi–von Weizsäcker functional. Bachelor's thesis, Ludwig-Maximilians-Universität München (2018)
37. Dirac, P.A.M.: The quantum theory of the electron. Proc. Roy. Soc. Lond. **117**(A), 610–624 (1928)
38. Dirac, P.A.M.: The quantum theory of the electron II. Proc. Roy. Soc. Lond. **118**(A), 351–361 (1928)
39. Dirac, P.A.M.: Note on exchange phenomena in the Thomas–Fermi atom. Proc. Camb. Philos. Soc. **26**, 376–385 (1931)
40. Dirac, P.A.M.: A theory of electrons and protons. Proc. Roy. Soc. Lond. Ser. A Contain. Pap. Math. Phys. Charact. **126**(801), 360–365 (1930)
41. Dolbeault, J., Esteban, M.J., Séré, E.: On the eigenvalues of operators with gaps. Appl. Dirac Oper. J. Funct. Anal. **174**(1), 208–226 (2000)
42. Dolbeault, J., Esteban, M.J., Séré, E.: Variational characterization for eigenvalues of Dirac operators. Calc. Var. Part. Differ. Equ. **10**(4), 321–347 (2000)
43. Engel, E., Dreizler, R.M.: Field-theoretical approach to a relativistic Thomas–Fermi–Dirac–Weizsäcker model. Phys. Rev. A **35**, 3607–3618 (1987)
44. Englert, B.-G.: Semiclassical Theory of Atoms. Number 300 in Lecture Notes in Physics, 1st edn. Springer, Berlin (1988)
45. Englert, B.-G., Schwinger, J.: Statistical atom: handling the strongly bound electrons. Phys. Rev. A **29**(5), 2331–2338 (1984)
46. Englert, B.-G., Schwinger, J.: Statistical atom: some quantum improvements. Phys. Rev. A **29**(5), 2339–2352 (1984)
47. Englert, B.-G., Schwinger, J.: Atomic-binding-energy oscillations. Phys. Rev. A **32**, 47–63 (1985)
48. Erdős, L., Solovej, J.P.: The kernel of Dirac operators on $\mathbb{S}^3$ and $\mathbb{R}^3$. Rev. Math. Phys. **13**(10), 1247–1280 (2001)
49. Erdős, L., Fournais, S., Solovej, J.P.: Relativistic Scott correction in self-generated magnetic fields. J. Math. Phys. **53**(9), 095202 (2012)
50. Erdős, L., Fournais, S., Solovej, J.P.: Scott correction for large atoms and molecules in a self-generated magnetic field. Commun. Math. Phys. **312**(3), 847–882 (2012)
51. Erdős, L., Fournais, S., Solovej, J.P.: Second order semiclassics with selfgenerated magnetic fields. Ann. Henri Poincaré **13**(4), 671–730 (2012)
52. Erdős, L., Solovej, J.P.: Semiclassical eigenvalue estimates for the Pauli operator with strong non-homogeneous magnetic fields. Commun. Math. Phys. **188**(3), 599–656 (1997)
53. Erdős, L., Solovej, J.P.: Ground state energy of large atoms in a self-generated magnetic field. Commun. Math. Phys. **294**(1), 229–249 (2010)
54. Esteban, M.J., Lewin, M., Séré, E.: Variational methods in relativistic quantum mechanics. Bull. Am. Math. Soc. (N.S.) **45**(4), 535–593 (2008)
55. Esteban, M.J., Lewin, M., Séré, É.: Domains for Dirac–Coulomb min–max levels. Rev. Mat. Iberoam. **35**(3), 877–924 (2019)
56. Esteban, M.J., Lewin, M., Séré, É.: Dirac–Coulomb operators with general charge distribution I. Distinguished extension and min–max formulas. Annales Henri Lebesgue **4**, 1421–1456 (2021)
57. Esteban, M.J., Loss, M.: Self-adjointness for Dirac operators via Hardy–Dirac inequalities. J. Math. Phys. **48**(11), 112107 (2007)
58. Esteban, M.J., Séré, S.: Existence and multiplicity of solutions for linear and nonlinear Dirac operators. In: Partial Differential Equations and Their Applications (Toronto. ON, 1995), pp. 107–118. Amer. Math. Soc, Providence (1997)
59. Evans, W.D., Perry, P., Siedentop, H.: The spectrum of relativistic one-electron atoms according to Bethe and Salpeter. Commun. Math. Phys. **178**(3), 733–746 (1996)
60. Fefferman, C.: Atoms analytic number theory. In: American Mathematical Society Centennial Publications, Vol. II (Providence, RI, 1988), pp. 27–36. Amer. Math. Soc., Providence (1992)
61. Fefferman, C., Seco, L.: Eigenvalues and eigenfunctions of ordinary differential operators. Adv. Math. **95**(2), 145–305 (1992)

62. Fefferman, C., Seco, L.: The density of a one-dimensional potential. Adv. Math. **107**(2), 187–364 (1994)
63. Fefferman, C., Seco, L.: The eigenvalue sum of a one-dimensional potential. Adv. Math. **108**(2), 263–335 (1994)
64. Fefferman, C., Seco, L.: On the Dirac and Schwinger corrections to the ground-state energy of an atom. Adv. Math. **107**(1), 1–188 (1994)
65. Fefferman, C., Seco, L.: The density in a three-dimensional radial potential. Adv. Math. **111**(1), 88–161 (1995)
66. Fefferman, C.L., Seco, L.A.: An upper bound for the number of electrons in a large ion. Proc. Nat. Acad. Sci. USA **86**, 3464–3465 (1989)
67. Fefferman, C.L., Seco, L.A.: Asymptotic neutrality of large ions. Commun. Math. Phys. **128**, 109–130 (1990)
68. Fefferman, C.L., Seco, L.A.: On the energy of a large atom. Bull. AMS **23**(2), 525–530 (1990)
69. Fefferman, C.: Stability of Coulomb systems in a magnetic field. Proc. Nat. Acad. Sci. U.S.A. **92**(11), 5006–5007 (1995)
70. Fefferman, C.L., Seco, L.A.: Aperiodicity of the Hamiltonian flow in the Thomas–Fermi potential. Revista Mathemática Iberoamericana **9**(3), 409–551 (1993)
71. Fermi, E.: Un metodo statistico per la determinazione di alcune proprietá dell'atomo. Atti della Reale Accademia Nazionale dei Lincei, Rendiconti, Classe di Scienze Fisiche, Matematiche e Naturali **6**(12), 602–607 (1927)
72. Fermi, E.: Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente. Z. Phys. **48**, 73–79 (1928)
73. Fock, V.: Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. Z. Phys. **61**, 126–148 (1930)
74. Foldy, L.L.: A note on atomic binding energies. Phys. Rev. **83**, 397–399 (1951)
75. Fournais, S., Hoffmann-Ostenhof, M., Hoffmann-Ostenhof, T., Sørensen, T.Ø.: Sharp regularity results for Coulombic many-electron wave functions. Commun. Math. Phys. **255**(1), 183–227 (2005)
76. Fournais, S., Hoffmann-Ostenhof, M., Hoffmann-Ostenhof, T., Sørensen, T.Ø.: Analytic structure of many-body Coulombic wave functions. Commun. Math. Phys. **289**(1), 291–310 (2009)
77. Fournais, S., Hoffmann-Ostenhof, M., Hoffmann-Ostenhof, T., Sørensen, T.Ø.: Analytic structure of many-body Coulombic wave functions. Commun. Math. Phys. **289**(1), 291–310 (2009)
78. Fournais, S., Hoffmann-Ostenhof, M., Sørensen, T.Ø.: Third derivative of the one-electron density at the nucleus. Ann. Henri Poincaré **9**(7), 1387–1412 (2008)
79. Fournais, S., Lewin, M., Triay, A.: The Scott correction in Dirac–Fock theory. Commun. Math. Phys. **378**(1), 569–600 (2020)
80. Fournais, S., Sørensen, T.Ø.: The electron densities of pseudorelativistic eigenfunctions are smooth away from the nuclei. Commun. Part. Differ. Equ. **35**(7), 1276–1291 (2010)
81. Fournais, S., Sørensen, T.O.: Estimates on derivatives of Coulombic wave functions and their electron densities. J. Reine Angew. Math. **775**, 1–38 (2021)
82. Frank, R.L.: A simple proof of Hardy–Lieb–Thirring inequalities. Commun. Math. Phys. **290**(2), 789–800 (2009)
83. Frank, R.L., Lieb, E.H., Seiringer, R.: Hardy–Lieb–Thirring inequalities for fractional Schrödinger operators. J. Am. Math. Soc. **21**(4), 925–950 (2008)
84. Frank, R.L., Lieb, E.H., Seiringer, R., Siedentop, H.: Müller's exchange-correlation energy in density-matrix-functional theory. Phys. Rev. A **76**, 052517 (2007)
85. Frank, R.L., Merz, K., Siedentop, H.: Relativistic strong Scott conjecture: a short proof. In: B.-G. Englert, H. Siedentop, and M.-I. Trappe (eds): Density Functionals for Many-Particle Systems: Mathematical Theory and Physical Applications. Lecture Notes Series, Institute of Mathematical Sciences, National University of Singapore, vol. 41, pp. 69–79, World Scientific, Singapore (2023)
86. Frank, R.L., Merz, K., Siedentop, H.: Equivalence of Sobolev norms involving generalized Hardy operators. Int. Math. Res. Not. **2021**(3), 2284–2303 (2021)
87. Frank, R.L., Merz, K., Siedentop, H., Simon, B.: Proof of the strong Scott conjecture for Chandrasekhar atoms. Pure Appl. Funct. Anal. **5**(6), 1319–1356 (2020)
88. Frank, R.L., Nam, P.T., Van Den Bosch, H.: The ionization conjecture in Thomas–Fermi–Dirac–von Weizsäcker theory. Commun. Pure Appl. Math. **71**(3), 577–614 (2018)
89. Frank, R.L., Seiringer, R.: Non-linear ground state representations and sharp Hardy inequalities. J. Funct. Anal. **255**(12), 3407–3430 (2008)

90. Frank, R.L., Siedentop, H., Warzel, S.: The ground state energy of heavy atoms: relativistic lowering of the leading energy correction. Commun. Math. Phys. **278**(2), 549–566 (2008)
91. Frank, R.L., Siedentop, H., Warzel, S.: The energy of heavy atoms according to Brown and Ravenhall: the Scott correction. Doc. Math. **14**, 463–516 (2009)
92. Fröhlich, J., Lieb, E.H., Loss, M.: Stability of Coulomb systems with magnetic fields. I. The one-electron atom. Commun. Math. Phys. **104**, 251–270 (1986)
93. Furry, W.H., Oppenheimer, J.R.: On the theory of the electron and positive. Phys. Rev. II. Ser. **45**, 245–262 (1934)
94. Gombás, P.: Die statistische Theorie des Atoms und ihre Anwendungen, 1st edn. Springer, Wien (1949)
95. Gombás, P.: Statistische Behandlung des Atoms. In: Flügge, S. (ed.) Handbuch der Pysik, vol. 36, II, pp. 109–231. Springer, Berlin (1956)
96. Gordon, W.: Die Energieniveaus des Wasserstoffatoms nach der Diracschen Quantentheorie. Z. Phys. **48**, 11–14 (1928)
97. Graf, G.M., Solovej, J.P.: A correlation estimate with applications to quantum systems with Coulomb interactions. Rev. Math. Phys. **6**(5A), 977–997 (1994) (Special issue dedicated to Elliott H. Lieb)
98. Griesemer, M., Lewis, R.T., Siedentop, H.: A minimax principle for eigenvalues in spectral gaps: Dirac operators with Coulomb potentials. Doc. Math. **4**, 275–283 (1999)
99. Griesemer, M., Siedentop, H.: A minimax principle for the eigenvalues in spectral gaps. J. Lond. Math. Soc. (2) **60**(2), 490–500 (1999)
100. Handrek, M., Siedentop, H.: The ground state energy of heavy atoms: the leading correction. Commun. Math. Phys. **339**(2), 589–617 (2015)
101. Hardekopf, G., Sucher, J.: Critical coupling constants for relativistic wave equations and vacuum breakdown in quantum electrodynamics. Phys. Rev. A **31**(4), 2020–2029 (1985)
102. Hartree, D.R.: Wave mechanics of an atom with non-Coulomb central field. Part I. Theory and methods. Proc. Camb. Philos. Soc. **24**, 89–110 (1928)
103. Hartree, D.R.: Wave mechanics of an atom with non-Coulomb central field. Part II. Some results and discussion. Proc. Camb. Philos. Soc. **24**, 111–132 (1928)
104. Heilmann, O.J., Lieb, E.H.: Electron density near the nucleus of a large atom. Phys. Rev. A **52**(5), 3628–3643 (1995)
105. Heisenberg, W.: Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen. Zeitschrift für Physik **33**(1), 879–893 (1925)
106. Heisenberg, W.: Über quantentheoretische Kinematik und Mechanik. Math. Ann. **95**(1), 683–705 (1926)
107. Heisenberg, W., Euler, H.: Folgerungen aus der Diracschen Theorie des Positrons. Zeitschrift für Physik **98**(11), 714–732 (1936)
108. Hellmann, H.: Ein kombiniertes Näherungsverfahren zur Energieberechnung im Vielelektronenproblem II. Acta Physicochim. U.S.S.R. **4**, 225–244 (1936)
109. Herbst, I.W.: Spectral theory of the operator $(p^2 + m^2)^{1/2} - Ze^2/r$. Commun. Math. Phys. **53**, 285–294 (1977)
110. Hoffmann-Ostenhof, M., Hoffmann-Ostenhof, T., Thirring, W.: Simple bounds to the atomic one-electron density at the nucleus and to expectation values of one-electron operators. J. Phys. B **11**(19), L571–L575 (1978)
111. Hogreve, H.: The overcritical Dirac–Coulomb operator. J. Phys. A **46**(2), 025301 (2013)
112. Hoops, S.: The excess charge, the ionization energy, and the Z^2-correction of the Hellmann–Weizsäcker model. PhD thesis, The Norwegian Institute of Technology (1993)
113. Hughes, W.: An atomic energy lower bound that Gives Scott's correction. PhD thesis, Princeton, Department of Mathematics (1986)
114. Hughes, W.: An atomic energy lower bound that agrees with Scott's correction. Adv. Math. **79**, 213–270 (1990)
115. Huxtable, B.D.: Absence of a Scott correction for the total binding energy of noninteracting Fermions in a smooth potential well. PhD thesis, Caltech, Department of Mathematics, Pasadena, CA (1988)
116. Iantchenko, A.: The electron density in intermediate scales. Commun. Math. Phys. **184**(2), 367–385 (1997)
117. Iantchenko, A., Lieb, E.H., Siedentop, H.: Proof of a conjecture about atomic and molecular cores related to Scott's correction. J. Reine Angew. Math. **472**, 177–195 (1996)

118. Iantchenko, A., Siedentop, H.: Asymptotic behavior of the one-particle density matrix of atoms at distances Z^{-1} from the nucleus. Math. Z. **236**(4), 787–796 (2001)
119. Ivrii, J.V., Sigal, I.M.: Asymptotics of the ground state energies of large Coulomb systems. Ann. Math. **138**(2), 243–335 (1993)
120. Ivrii, V.: Strong Scott conjecture. arXiv e-prints arXiv:1908.05478 (2019)
121. Ivrii, V.: Thomas–Fermi approximation to electronic density. arXiv e-prints arXiv:1911.03510 (2019)
122. Ivrii, V.: Upper estimates for electronic density in heavy atoms and molecules. arXiv e-prints arXiv:1906.00611 (2019)
123. Jakubassa-Amundsen, D.: Localization of the essential spectrum for relativistic N-electron ions and atoms. Documenta Mathematica **10**, 417–445 (2005)
124. Jensen, H.: Zur relativistischen Behandlung des Fermiatoms. Zeitschrift für Physik **82**(11–12), 794–802 (1933)
125. Johnson, W.R.: Relativistic many-body theory applied to highly-charged ions. In: Many-Body Theory of Atomic Structure and Photoionization, pp. 19–46 (1993)
126. Johnson, W.R.: Relativistic many-body perturbation theory for highly charged ions. In: Boyle, J.J., Pindzola, M.S. (eds.) Many-Body Atomic Physics, pp. 39–64. Cambridge University Press, Cambridge (1998)
127. Johnson, W.R., Cheng, K.T., Chen, M.H.: Accurate relativistic calculations including QED contributions for few-electron systems. In: Theoretical and Computational Chemistry, vol. 14, pp. 120–187. Elsevier (2004)
128. Kalf, H., Schmincke, U.-W., Walter, J., Wüst, R.: On the spectral theory of Schrödinger and Dirac operators with strongly singular potentials. In: Everitt, W.N. (eds.) Spectral Theory and Differential Equations, Volume 448 of Lecture Notes in Mathematics, Proceeding of the Symposium held at Dundee, Scotland, 1–19 July, pp. 182–226. Springer, Berlin (1974)
129. Kalf, H.: The virial theorem in relativistic quantum mechanics. J. Funct. Anal. **21**(4), 389–396 (1976)
130. Kato, T.: Perturbation Theory for Linear Operators, Volume 132 of Grundlehren der mathematischen Wissenschaften, 1 edn. Springer, Berlin (1966)
131. Kehle, C.: The maximal excess charge for a family of density-matrix-functional theories including Hartree–Fock and Müller theories. J. Math. Phys. **58**(1), 011901, 24, (2017)
132. Kirzhnits, D.A.: Quantum corrections to the Thomas–Fermi equation. Soviet Phys. JETP **5**(1), 64-71,8 (1957)
133. Klaus, M., Wüst, R.: Characterization and uniqueness of distinguished selfadjoint extensions of Dirac operators. Commun. Math. Phys. **64**, 171–176 (1978)
134. Klaus, M., Wüst, R.: Spectral properties of Dirac operators with singular potentials. J. Math. Anal. Appl. **78**, 206–214 (1979)
135. Kramida, A., Ralchenko, Y., Reader, J., NIST ASD Team.: NIST atomic spectra database (ver. 5.2), [Online]. Available: [2014, November 6]. National Institute of Standards and Technology, Gaithersburg (2014) http://physics.nist.gov/asd
136. Ladányi, K.: Variational method of the solution of the quantum mechanical many-body problem. Acta Phys. Hung. **9**, 115–124 (1958)
137. Le Yaouanc, A., Oliver, L., Raynal, J.-C.: The Hamiltonian $(p^2 + m^2)^{1/2} - \alpha/r$ near the critical value $\alpha_c = 2/\pi$. J. Math. Phys. **38**(8), 3997–4012 (1997)
138. Lenz, W.: Über die Anwendbarkeit der statistischen Methode auf Ionengitter. Z. Phys. **77**, 713–721 (1932)
139. Lewis, R.T., Siedentop, H., Vugalter, S.: The essential spectrum of relativistic multi-particle operators. Annales de l'Institut Henri Poincaré **67**(1), 1–28 (1997)
140. Lieb, E.H., Loss, M.: Self-energy of electrons in non-relativistic QED. Preprint, mp-arc, pp. 99–305 (1999)
141. Lieb, E.H.: The stability of matter. Rev. Mod. Phys. **48**, 553–569 (1976)
142. Lieb, E.H.: A lower bound for Coulomb energies. Phys. Lett. **70A**, 444–446 (1979)
143. Lieb, E.H.: Some open problems about Coulomb systems. In: Osterwalder, K., (ed.) Mathematical Problems in Theoretical Physics. Proceedings of the International Conference on Mathematical Physics. Lausanne 1979, pp. 553–569. Springer, Berlin (1980)
144. Lieb, E.H.: Thomas–Fermi and related theories of atoms and molecules. Rev. Mod. Phys. **53**(4), 603–641 (1981)
145. Lieb, E.H.: Bound on the maximum negative ionization of atoms and molecules. Phys. Rev. A **29**(6), 3018–3028 (1984)

146. Lieb, E.H., Liberman, D.A.: Numerical calculation of the Thomas–Fermi–von Weizsäcker function for an infinite atom without electron repulsion. Technical report, Los Alamos National Lab., NM (USA) (1982)
147. Lieb, E.H., Loss, M.: Analysis of Graduate Studies in Mathematics, vol. 4, 2nd edn. American Mathematical Society, Providence (2001)
148. Lieb, E.H., Loss, M., Solovej, J.P.: Stability of matter in magnetic fields. Phys. Rev. Lett. **75**(6), 985–989 (1995)
149. Lieb, E.H., Oxford, S.: Improved lower bound on the indirect Coulomb energy. Intern. J. Quantum Chem. **19**, 427–439 (1981)
150. Lieb, E.H., Simon, B.: On solutions of the Hartree–Fock problem for atoms and molecules. J. Chem. Phys. **61**(2), 735–736 (1974)
151. Lieb, E.H., Simon, B.: The Hartree–Fock theory for Coulomb systems. Commun. Math. Phys. **53**(3), 185–194 (1977)
152. Lieb, E.H., Simon, B.: The Thomas–Fermi theory of atoms, molecules and solids. Adv. Math. **23**(1), 22–116 (1977)
153. Lieb, E.H., Solovej, J.P., Yngvason, J.: Asymptotics of heavy atoms in high magnetic fields I. Lowest Landau band regions. Commun. Pure Appl. Math. **47**(4), 513–591 (1994)
154. Lieb, E.H., Solovej, J.P., Yngvason, J.: Asymptotics of heavy atoms in high magnetic fields II. Semiclassical regions. Commun. Math. Phys. **161**(1), 77–124 (1994)
155. Lieb, E.H., Thirring, W.E.: Gravitational collapse in quantum mechanics with relativistic kinetic energy. Ann. Phys. **155**(2), 494–512 (1984)
156. Lieb, E.H., Yau, H.-T.: The Chandrasekhar theory of stellar collapse as the limit of quantum mechanics. Commun. Math. Phys. **112**(1), 147–174 (1987)
157. Loss, M., Yau, H.T.: Stability of Coulomb systems with magnetic fields. III. Zero energy bound states of the Pauli operator. Commun. Math. Phys. **104**, 283–290 (1986)
158. Macke, W.: Wave mechanical treatment of the Fermi gas. Phys. Rev. **100**(4), 992 (1955)
159. Macke, W.: Zur wellenmechanischen Behandlung von Vielkörperproblemen. Ann. Physik **17**(1), 1–9 (1955)
160. Mancas, P., Klaus Müller, A.M., Siedentop, H.: The optimal size of the exchange hole and reduction to one-particle Hamiltonians. Theor. Chem. Acc. Theory Comput. Model. (Theoretica Chimica Acta) **111**(1), 49–53 (2004)
161. March, N.H.: The Thomas–Fermi approximation in quantum mechanics. Adv. Phys. **6**(21), 1–101 (1957)
162. March, N.H.: A variational method for the calculation of particle densities and sums of eigenvalues in wave mechanics. Proc. Phys. Soc. Sect. A **70**(3), 169 (1957)
163. March, N.H., Young, W.H.: Variational methods based on the density matrix. Proc. Phys. Soc. **72**, 182–192 (1958)
164. Massey, H.S.W.: Negative Ions, 3rd edn. Cambridge University Press, London (1976)
165. Massey, H.S.W.: Negative ions. Adv. Atom Mol. Phys. **15**, 1–36 (1979)
166. Matte, O., Stockmeyer, E.: Spectral theory of no-pair Hamiltonians. Rev. Math. Phys. **22**(01), 1–53 (2010)
167. Mawhin, J., Ronveaux, A.: Schrödinger and Dirac equations for the hydrogen atom, and Laguerre polynomials. Arch. Hist. Exact Sci. **64**(4), 429–460 (2010)
168. Merz, K.: Über die Grundzustandsdichte relativistischer Coulomb-Systeme. PhD thesis, Ludwig-Maximilians-Universität München (2019)
169. Merz, K., Siedentop, H.: The atomic density on the Thomas–Fermi length scale for the Chandrasekhar Hamiltonian. Rep. Math. Phys. **83**(3), 387–391 (2019)
170. Merz, K., Siedentop, H.: Proof of the strong Scott conjecture for heavy atoms: the Furry picture. Annales Henri Lebesgue **5**, 611–642 (2022)
171. Mittleman, M.H.: Theory of relativistic effects on atoms: configuration-space Hamiltonian. Phys. Rev. A **24**(3), 1167–1175 (1981)
172. Morozov, S.: Multiparticle Brown–Ravenhall operators in external fields. PhD thesis, Ludwig-Maximilians-Universität München (2008)
173. Morozov, S., Müller, D.: On the minimax principle for Coulomb–Dirac operators. Math. Z. **280**(3–4), 733–747 (2015)
174. Morozov, S., Vugalter, S.: Stability of atoms in the Brown–Ravenhall model. Ann. Henri Poincaré **7**(4), 661–687 (2006)

175. Müller, A.M.K.: Explicit approximate relation between reduced two- and one-particle density matrices. Phys. Lett. A **105**(9), 446–452 (1984)
176. Müller, A.M.K.: Ausgewählte Methoden und Probleme der Mehrteilchentheorie. (unpublished), Lecture Notes by H. Siedentop (1978)
177. Müller, D.: Minimax principles, Hardy–Dirac inequalities, and operator cores for two and three dimensional Coulomb–Dirac operators. Doc. Math. **21**, 1151–1169 (2016)
178. Nam, P.T.: New bounds on the maximum ionization of atoms. Commun. Math. Phys. **312**(2), 427–445 (2012)
179. Nam, P.T.: The ionization problem. Eur. Math. Soc. Newsl. **118**, 22–27 (2020)
180. Nam, P.T.H.: The ionization problem in quantum mechanics. In: The Physics and Mathematics of Elliott Lieb. The 90th Anniversary, vol. II, pp. 93–120. European Mathematical Society (EMS), Berlin (2022)
181. Nenciu, G.: Self-adjointness and invariance of the essential spectrum for Dirac operators defined as quadratic forms. Commun. Math. Phys. **48**(3), 235–247 (1976)
182. Oelker, M.: On domain, self-adjointness, and spectrum of Dirac operators for two interacting particles. PhD thesis, Ludwig-Maximilians-Universität München (2019)
183. Onsager, L.: Electrostatic interaction of molecules. J. Phys. Chem. **43**(2), 189–196 (1939)
184. Østergaard, T.S.: The large-Z behavior of pseudorelativistic atoms. J. Math. Phys. **46**(5), 052307 (2005)
185. Pidduck, F.B.: Laguerre's polynomials in quantum mechanics. J. Lond. Math. Soc. **4**(3), 163–166 (1929)
186. Pilkuhn, H.: Relativistic Quantum Mechanics. Texts and Monographs in Physics, Springer, Berlin (2005)
187. Rakowsky, N.: Über eine asymptotisch genaue obere Schranke der Elektronendichte am Kern für Ionen im Grundzustand. Master's thesis, Universität Münster, Mathematisches Institut (1995)
188. Rakowsky, N., Siedentop, H.: An upper bound on the ionic ground state density at the nucleus. Rep. Math. Phys. **36**(1), 91–98 (1995)
189. Raynal, J.C., Roy, S.M., Singh, V., Martin, A., Stubbe, J.: The Herbst Hamiltonian and the mass of boson stars. Phys. Lett. B **320**(1–2), 105–109 (1994)
190. Reed, M., Simon, B.: Methods of Modern Mathematical Physics. II. Fourier Analysis, Self-Adjointness. Academic Press, New York (1975)
191. Reed, M., Simon, B.: Methods of Modern Mathematical Physics. Analysis of Operators, vol. 4, 1st edn. Academic Press, New York (1978)
192. Reiher, M., Wolf, A.: Relativistic Quantum Chemistry: The Fundamental Theory of Molecular Science. Wiley-VCH, Weinheim (2009)
193. Richard, S., de Aldecoa, R.T.: On the spectrum of magnetic Dirac operators with Coulomb-type perturbations. J. Funct. Anal. **250**(2), 625–641 (2007)
194. Sapirstein, J.: Theoretical methods for the relativistic atomic many-body problem. Rev. Mod. Phys. **70**(1), 55 (1998)
195. Saue, T.: Relativistic Hamiltonians for chemistry: a primer. ChemPhysChem **12**(17), 3077–3094 (2011)
196. Schimmer, L., Solovej, J.P., Tokus, S.: Friedrichs extension and min-max principle for operators with a gap. Ann. Henri Poincaré **21**(2), 327–357 (2020)
197. Schmincke, U.-W.: Distinguished selfadjoint extensions of Dirac operators. Math. Z. **129**, 335–349 (1972)
198. Schwinger, J.: Thomas-Fermi model: the leading correction. Phys. Rev. A **22**(5), 1827–1832 (1980)
199. Schwinger, J.: Thomas–Fermi model: the second correction. Phys. Rev. A **24**(5), 2353–2361 (1981)
200. Scott, J.M.C.: The binding energy of the Thomas–Fermi atom. Philos. Mag. **43**, 859–867 (1952)
201. Sharma, S., Dewhurst, J.K., Lathiotakis, N.N., Gross, E.K.U.: Reduced density matrix functional for many-electron systems. Phys. Rev. B (Condensed Matter and Materials Physics) **78**(20), 201103 (2008)
202. Siedentop, H.: An upper bound for the atomic ground state density at the nucleus. Lett. Math. Phys. **32**(3), 221–229 (1994)
203. Siedentop, H.: Das asymptotische Verhalten der Grundzustandsenergie des Müllerfunktionals für schwere Atome. J. Phys. A **42**(8), 08520,19, (2009)
204. Siedentop, H.: The quantum energy agrees with the Müller energy up to third order. In: Many-Electron Approaches in Physics, Chemistry and Mathematics, pp. 207–217. Springer (2014)

205. Siedentop, H.: A statistical theory of heavy atoms: asymptotic behavior of the energy and stability of matter. In: Partial Differential Equations, Spectral Theory, and Mathematical Physics—The Ari Laptev Anniversary Volume, EMS Ser. Congr. Rep., pp. 389–403. EMS Press, Berlin (2021)
206. Siedentop, H.: Mathematical elements of density functional theory. In: B.-G. Englert, H. Siedentop, and M.-I. Trappe (eds): Density Functionals for Many-Particle Systems: Mathematical Theory and Physical Applications. Lecture Notes Series, Institute of Mathematical Sciences, National University of Singapore, vol. 41, pp. 1–55, World Scientific, Singapore (2023)
207. Siedentop, H., Weikard, R.: On some basic properties of density functionals for angular momentum channels. Rep. Math. Phys. **28**, 193–218 (1986)
208. Siedentop, H., Weikard, R.: On the leading energy correction for the statistical model of the atom: interacting case. Commun. Math. Phys. **112**, 471–490 (1987)
209. Siedentop, H., Weikard, R.: On the leading correction of the Thomas–Fermi model: lower bound—with an appendix by A. M. K. Müller. Invent. Math. **97**, 159–193 (1989)
210. Siedentop, H., Weikard, R.: A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators. Annales Scientifiques de l'École Normale Supérieure **24**(2), 215–225 (1991)
211. Siedentop, H., Weikard, R.: Asymptotically correct lower bound for the sum of negative eigenvalues of Schrödinger operators through a decomposition of unity given by Macke. Asympt. Anal. **8**, 65–72 (1994)
212. Siedentop, H.K.H.: On the relation between the Hellmann energy functional and the ground state energy of an N-Fermion system. Z. Phys. A **302**, 213–218 (1981)
213. Siedentop, H.K.H., Weikard, R.: On the leading energy correction for the statistical model of the atom: non-interacting case. Abh. Braunschweig. Wiss. Ges. **38**, 145–158 (1986)
214. Simon, B.: Fifteen Problems in Mathematical Physics. In: Perspectives in Mathematics. Birkhäuser (1984)
215. Simon, B.: On the infinitude or finiteness of the number of bound states of an N-body quantum system. I. Helv. Phys. Acta **43**(6–7), 607–630 (1970)
216. Simon, B.: Functional Integration and Quantum Physics. Academic Press Inc., New York (1979)
217. Simon, B.: Convexity: An Analytic Viewpoint. Cambridge Tracts in Mathematics, vol. 187. Cambridge University Press, Cambridge (2011)
218. Slater, J.C.: A note on Hartree's method. Phys. Rev. **35**, 210–211 (1930)
219. Sobolev, A.V.: Discrete spectrum asymptotics for the Schrödinger operator with a singular potential and a magnetic field. Rev. Math. Phys. **8**(6), 861–903 (1996)
220. Sobolev, A.V.: Eigenvalue asymptotics for the one-particle density matrix. Duke Math. J. **171**(17), 3481–3513 (2022)
221. Sobolev, A.V.: Eigenvalue asymptotics for the one-particle kinetic energy density operator. J. Funct. Anal. **283**(8), 109604,35, (2022)
222. Solovej, J.P.: Universality in the Thomas–Fermi–von Weizsäcker model of atoms and molecules. Commun. Math. Phys. **129**, 561–598 (1990)
223. Jan Philip Solovej: The ionization conjecture in Hartree–Fock theory. Ann. Math. **158**(2), 509–576 (2003)
224. Solovej, J.P., Sørensen, T.Ø., Spitzer, W.L.: The relativistic Scott correction for atoms and molecules. Commun. Pure Appl. Math. **63**, 39–118 (2010)
225. Solovej, J.P., Spitzer, W.L.: A new coherent states approach to semiclassics which gives Scott's correction. Commun. Math. Phys. **241**(2–3), 383–420 (2003)
226. Sommerfeld, A.: Zur Quantentheorie der Spektrallinien. Annalen der Physik **356**(17), 1–94 (1916)
227. Sommerfeld, A.: Asymptotische Integration der Differentialgleichung des Thomas-Fermischen Atoms. Z. Phys. A **78**, 283–308 (1932)
228. Stell, G.: Fluids with long-range forces: toward a simple analytic theory. In: Berne, B.J. (ed.) Statistical Mechanics. Modern Theoretical Chemistry, vol. 5, pp. 47–84. Springer, New York (1977)
229. Sucher, J.: Foundations of the relativistic theory of many-electron atoms. Phys. Rev. A **22**(2), 348–362 (1980)
230. Sucher, J.: Relativistic many-electron Hamiltonians. Phys. Scripta **36**, 271–281 (1987)
231. Talman, J.D.: Minimax principle for the Dirac equation. Phys. Rev. Lett. **57**(9), 1091–1094 (1986)
232. Thaller, B.: The Dirac Equation. Texts and Monographs in Physics, 1st edn. Springer, Berlin (1992)
233. Thaller, B.: Advanced Visual Quantum Mechanics. With 1 CD-ROM (Windows and Macintosh). Springer, New York (2005)

234. Thirring, W.: A lower bound with the best possible constant for Coulomb Hamiltonians. Commun. Math. Phys. **79**, 1–7 (1981)
235. Thomas, L.H.: The calculation of atomic fields. Proc. Camb. Philos. Soc. **23**, 542–548 (1927)
236. Tix, C.: Lower bound for the ground state energy of the no-pair Hamiltonian. Phys. Lett. B **405**(3–4), 293–296 (1997)
237. Tix, C.: Strict positivity of a relativistic Hamiltonian due to Brown and Ravenhall. Bull. Lond. Math. Soc. **30**(3), 283–290 (1998)
238. Tomishima, Y.: A relativistic Thomas–Fermi theory. Prog. Theor. Phys. **42**(3), 437–447 (1969)
239. Unsöld, A.: Beiträge zur Quantenmechanik der Atome. Annalen der Physik **387**(3), 355–393 (1927)
240. von Weizsäcker, C.F.: Zur Theorie der Kernmassen. Z. Phys. **96**, 431–458 (1935)
241. Vallarta, M.S., Rosen, N.: The relativistic Thomas–Fermi atom. Phys. Rev. **41**(6), 708 (1932)
242. Vogelsang, V.: Absolutely continuous spectrum of Dirac operators for long-range potentials. J. Funct. Anal. **76**(1), 67–86 (1988)
243. Warmt, C.: Semiklassische Asymptotik der Resolvente eines Diracoperators. PhD thesis, Ludwig-Maximilians-Universität, Fakultät für Mathematik, Informatik und Statistik (2011)
244. Weder, R.A.: Spectral properties of one-body relativistic spin-zero Hamiltonians. Ann. Inst. H. Poincaré Sect. A (N.S.) **20**, 211–220 (1974)
245. Weidmann, J.: Oszillationsmethoden für Systeme gewöhnlicher Differentialgleichungen. Math. Z. **119**, 349–373 (1971)
246. White, H.E.: Pictorial representations of the Dirac electron cloud for hydrogen-like atoms. Phys. Rev. **38**, 513–520 (1931)
247. Whittaker, E.T., Watson, G.N.: A Course of Modern Analysis; An Introduction to the General Theory of Infinite Processes and of Analytic Functions, with an Account of the Principal Transcendental Functions, 4th edn. Cambridge University Press, Cambridge (1927)
248. Wüst, R.: Distinguished self-adjoint extensions of Dirac operators constructed by means of cut-off potentials. Math. Z. **141**, 93–98 (1975)
249. Yafaev, D.: Sharp constants in the Hardy–Rellich inequalities. J. Funct. Anal. **168**(1), 144–212 (1999)
250. Yonei, K., Tomishima, Y.: On the Weizsäcker correction to the Thomas–Fermi theory of the atom. J. Phys. Soc. Japan **20**(6), 1051–1057 (1965)
251. Zislin, G.M.: A study of the spectrum of the Schrödinger operator for a system of several particles. Trudy Moskov. Mat. Obsc. **9**, 81–120 (1960)