SOME BOUND STATE PROBLEMS IN QUANTUM MECHANICS

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Dedicated to Barry Simon on the occasion of his 60^{th} birthday

Abstract. We give a review of semi-classical estimates for bound states and their eigenvalues for Schrödinger operators. Motivated by the classical results, we discuss their recent improvements for single particle Schrödinger operators as well as some applications of these semi-classical bounds to multi-particle systems, in particular, large atoms and the stability of matter.

In this survey, we focus on results for bound states of Schrödinger operators related to the semi-classical limit and Coulomb potentials. We will not discuss a large part of the existing literature on the general theory of bound states for Schrödinger operators. With no attempt on completeness, we would nevertheless like to mention at least some part of this literature: For one particle Schrödinger operators, see, for example, [19, 149]. Two-body cluster results are discussed in [4, 82, 140, 151, 152, 173], finiteness results of the discrete spectrum for N-particle systems can be found in [1, 40, 164], and for results on the Efimov effect see, for example, [3, 36, 123, 155, 160, 170].

1. Semi-classical bounds for single particle Schrödinger operators

The origin of semi-classical estimates can be traced back to the dawn of quantum mechanics in the beginning of the last century. Around 1912, Hermann Weyl published a series of papers [166, 167, 168], see also [169], on the frequencies of an oscillating membrane and the radiation inside a cavity, verifying a conjecture of Jeans and Lorenz on the connection between the asymptotic behavior of these frequencies and the volume of the cavity. While in itself being a classical problem, this work was the starting point

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of a substantial branch of analysis and mathematical physics, especially in quantum mechanics.

Consider a bounded domain $\Lambda \subset \mathbb{R}^d$ and the eigenvalue problem for the Dirichlet Laplacian

$$-\Delta_\Lambda^D \varphi = E\varphi,$$

that is, the partial differential equation

$$-\sum_{j=1}^{d} \frac{\partial^2}{\partial x_j^2}\varphi(x) = E\varphi(x) \text{ for } x \in \Lambda \text{ and } \varphi|_{\partial\Lambda} = 0. \tag{1}$$

Furthermore, let $E_1(\Lambda) < E_2(\Lambda) \leq E_3(\Lambda) \leq \ldots$ be an ordering of the eigenvalues of (1) and define the counting function

$$N_\Lambda^D(E) := \sum_{E_j(\Lambda)<E} 1$$

which counts the number of eigenvalues of $-\Delta_\Lambda^D$ below E. Weyl showed that

$$N^D(E) = \frac{\omega_d}{(2\pi)^d}|\Lambda|\, E^{d/2} + o(E^{d/2}) \quad \text{ as } E \to \infty. \tag{2}$$

Here $\omega_d = \frac{\pi^{d/2}}{\Gamma(1+(d/2))}$ is the volume of the unit ball in $\mathbb{R}^d$. Weyl's formula holds for all bounded domains $\Lambda \subset \mathbb{R}^d$.

The origin of Weyl's equality is easy to see: If Λ is a centered cube of side length a, then the eigenfunctions and eigenvalues of the Dirichlet Laplacian are known explicitly and given by

$$u(x) = \prod_{\nu=1}^{d} \sin(\tfrac{\pi n_\nu}{a} x_\nu), \quad n_\nu \in \mathbb{N} \text{ and}$$

$$E = \frac{\pi^2}{a^2}|n|^2 = \frac{\pi^2}{a^2}\sum_{\nu=1}^{d} n_\nu^2,$$

that is, $N_\Lambda^D(E)$ is precisely the number of points $n \in \mathbb{N}^d$ within the ball of radius $\frac{a}{\pi}E^{1/2}$, which behaves asymptotically as

$$\frac{\omega_d}{(2\pi)^d}\, a^d E^{d/2} + o(E^{d/2}) \text{ for } E \to \infty. \tag{3}$$

Similarly, the counting function $N_\Lambda^N(E)$ of the Neumann Laplacian has the same asymptotic as the Dirichlet Laplacian. They differ by a surface term which is of lower order in the high energy asymptotic, at least for domains with a nice boundary $\partial\Lambda$.

Weyl's crucial idea was to approximate a general domain $\Lambda \subset \mathbb{R}^d$ by cubes and to use (3). Using variational arguments, he showed

$$\lim_{E\to\infty} E^{-d/2} N_\Lambda^D(E) = \lim_{a\to 0} \omega_d \big(\frac{a}{2\pi}\big)^d \#\{\text{disjoint cubes of side length } a \text{ in } \Lambda\}.$$

Since $\#\{\text{disjoint cubes of side length } a \text{ in } \Lambda\} = a^{-d}(|\Lambda| + o(1))$, one obtains (2).

1.1. **Pólya's conjecture.** In 1961, Pólya [125] conjectured that the asymptotic result (2) holds as a uniform bound on $N_\Lambda^D(E)$ for all $E > 0$ with some constant $P(d)$, that is,

$$N_\Lambda^D(E) \le P(d)|\Lambda|\, E^{d/2} \text{ for all } E \ge 0, \tag{4}$$

or, equivalently[1],

$$E_n \ge (P(d)|\Lambda|)^{-2/d}\, n^{2/d} \text{ for all } n \in \mathbb{N}.$$

Pólya also conjectured that the sharp constant in (4) is given by Weyl's asymptotic result, $P(d) = \frac{\omega_d}{(2\pi)^d}$. He was able to prove this conjecture for the special class of tiling domains Λ, that is, disjoint congruents of Λ are assumed to cover $\mathbb{R}^d$. The argument is rather simple. Scaling $\Lambda_r := r\Lambda$, one gets another tiling domain with $N_\Lambda^D(E) = N_{r\Lambda}^D(r^{-2}E)$ (by scaling of the kinetic energy). So with $B =$ Ball of unit volume in $\mathbb{R}^d$, we get

$$N_{r\Lambda}^D(r^{-2}E) \le \frac{N_B^D(r^{-2}E)}{A_r}$$

where $A_r = \#\{$ disjoint congruents of $r\Lambda$ which are subsets of $B\}$. Fix $E > 0$ and let $r \to 0$. By Weyl's asymptotic we know

$$N_B^D(r^{-2}E) = r^{-d}\big(\frac{\omega_d}{(2\pi)^d} E^{d/2} + o(1)\big)$$

and, obviously, $A_r = r^{-d}\big(|\Lambda|^{-1} + o(1)\big)$ as $r \to 0$. Together these estimates give the bound

$$N_\Lambda^D(E) \le \lim_{r\to 0} \frac{N_B^D(r^{-2}E)}{A_r} = \frac{\omega_d}{(2\pi)^d}|\Lambda|\, E^{d/2}$$

for a tiling domain Λ.

Unfortunately, the sharp result is not known for general bounded domains. The best result is due to Li and Yau [91], who showed

$$N_\Lambda^D(E) \le \big(\frac{d+2}{d}\big)^{d/2} \frac{\omega_d}{(2\pi)^d}|\Lambda|\, E^{d/2}. \tag{5}$$

[1] Indeed, if $N(E) \le CE^\alpha$, then putting $E = E_n$ one sees $n = N(E_n) \le CE_n^\alpha$, that is, $E_n \ge C^{-1/\alpha} n^{1/\alpha}$. Conversely, $N(E) = \sum_{E_j<E} 1 \le \sum_{n^{1/\alpha}<C^{1/\alpha}E} 1 \le CE^\alpha$.

More precisely, they proved the sharp bound

$$\sum_{j=1}^{n} E_j \geq \frac{d}{d+2}\Big(\frac{\omega_d}{(2\pi)^d}|\Lambda|\Big)^{-2/d} n^{1+\frac{2}{d}} \text{ for all } n \in \mathbb{N}$$

and deduced (5) from this simply by observing $E_n \geq \frac{1}{n}\sum_{j=1}^{n} E_j$.

Laptev [86] gave a much simpler argument than the original one by Li and Yau in 1996. Moreover, he showed that if Pólya's conjecture holds for a domain $\Lambda_1 \subset \mathbb{R}^{d_1}$, then it holds for all domains $\Lambda = \Lambda_1 \times \Lambda_2$ for all $d_2 \in \mathbb{N}$ and domains $\Lambda_2 \subset \mathbb{R}^{d_2}$. This paper was the first instance where the idea of "stripping off" dimensions appeared, which later turned out to be the key for a refined study of semi-classical inequalities for moments of eigenvalues of Schrödinger operators, see section 1.7.

1.2. **Weyl asymptotic for Schrödinger operators.** In the early 1970's, Birman–Borzov, Martin, and Tamura, [17, 121, 159], proved semi-classical asymptotic for the number of the negative eigenvalues[2] of Schrödinger operators with a Hölder continuous and compactly supported potential V. Let $E_1 < E_2 \leq E_3 \leq \cdots \leq 0$ be a counting of the negative eigenvalues of $-\Delta+V$ on $L^2(\mathbb{R}^d)$ and set

$$N(V) := \#\{\text{negative eigenvalues of } -\Delta + V\}.$$

Assume that V is non-positive for the moment and introduce a coupling constant λ. We want to study the large λ asymptotic of $N(\lambda V)$. Assuming the Dirichlet-Neumann bracketing technique developed by Courant and Hilbert, a short argument can be given as follows; for details, see [126]. We let $\Lambda_a = \{-\frac{a}{2} < x_j < \frac{a}{2}, j = 1, \ldots, d\}$ and define $\Lambda_{a,j} = j + \Lambda_a$ for $j \in a\mathbb{Z}^d$. Assume that V is constant on the cubes $\Lambda_{a,j}$, that is, $V(x) = V_{a,j}$ for $x \in \Lambda_{a,j}$. Using Dirichlet-Neumann bracketing, one gets

$$\sum_{j\in a\mathbb{Z}^d} N^D_{\Lambda_{a,j}}(\lambda V_{a,j}) \leq N(\lambda V) \leq \sum_{j\in a\mathbb{Z}^d} N^N_{\Lambda_{a,j}}(\lambda V_{a,j}).$$

Applying Weyl's asymptotic result (2) with $E = \lambda|V_{a,j}|$,

$$N(\lambda V) = \frac{\omega_d}{(2\pi)^d}\lambda^{d/2} a^d \sum_{j\in a\mathbb{Z}^d} |V_{a,j}|^{d/2} + o(\lambda^{d/2}) \text{ as } \lambda \to \infty.$$

So if V is continuous, non-positive, and of compact support,

$$N(\lambda V) = \frac{\omega_d}{(2\pi)^d}\lambda^{d/2}\int_{\mathbb{R}^d} V(x)_-^{d/2}\,dx + o(\lambda^{d/2}). \tag{6}$$

This formula is, in fact, a semi-classical asymptotic. Let $|\xi|^2 + \lambda V(x)$ be the so-called classical symbol associated with the operator $-\Delta + \lambda V$. Using the

[2]For a probabilistic proof, see [76] or [150].

Fubini-Tonelli theorem and scaling, the volume of the negative energy region in phase space is given by

$$\iint_{|\xi|^2+\lambda V(x)<0} 1\, d\xi dx = \omega_d \lambda^{d/2} \int_{\mathbb{R}^d} V(x)_-^{d/2}\, dx.$$

Thus, formula (6) says that the number of negative eigenvalues of $-\Delta + \lambda V$ asymptotically, for large λ, behaves like the classical allowed phase-space volume divided by $(2\pi)^d$,

$$\lim_{\lambda\to\infty} \lambda^{-d/2} N(\lambda V) = \frac{1}{(2\pi)^d} \iint (|\xi|^2 + V(x))_-^0\, d\xi dx,$$

where we set $r_-^0 = 1$ for $r < 0$ and 0 for $r \geq 0$. So each eigenfunction corresponding to an negative eigenvalue occupies a volume $(2\pi)^d$ in phase-space. This is in perfect agreement with the Heisenberg uncertainty principle, according to which an electron occupies a volume of at least $(2\pi)^d$ in phase space.

One should also note that Weyl's original result fits very well into this more general framework. Indeed, and again somewhat formally, for a bounded open set Λ one can recover the Weyl asymptotic by setting $V = \infty \mathbf{1}_{\Lambda^c} - \mathbf{1}_\Lambda$ (with the convention $\infty \cdot 0 = 0$). Then (6) gives

$$\begin{aligned} N_\Lambda^D(E) &= N(EV) \\ &= \frac{1}{(2\pi)^d} \iint_{|\xi|^2+EV(x)<0} d\xi dx + o(E^{d/2}) \\ &= \frac{\omega_d}{(2\pi)^d} |\Lambda|\, E^{d/2} + o(E^{d/2}) \end{aligned}$$

which is Weyl's asymptotic.

1.3. **The Birman-Schwinger principle.** Around 1961, Birman [16] and Schwinger [137] independently found a way to reduce an estimate on the number of negative bound states to the study of a bounded integral operator. The idea of their argument is as follows: First assume that $V = -U$ is non-positive. Let φ be an eigenvector of $-\Delta - U$ for the negative energy E. That is, $(-\Delta - U)\varphi = E\varphi$, with $E < 0$. Rearranging gives $(-\Delta - E)\varphi = U\varphi$, which in turn is equivalent to $\varphi = (-\Delta - E)^{-1} U\varphi$, since for $E < 0$, $(-\Delta - E)$ is boundedly invertible. Multiplying this with $\sqrt{U}$ and setting $\psi = \sqrt{U}\varphi$ we see $-\Delta - U$ has a negative eigenvalue E if and only if the Birman-Schwinger operator

$$K_E = \sqrt{U}(-\Delta - E)^{-1}\sqrt{U} \tag{7}$$

has eigenvalue 1. Moreover, since the map $E \to n^{\text{th}}$ eigenvalue of K_E is (strictly) monotone increasing, a careful analysis shows that the corresponding eigenspaces have the same dimension. In short, denoting $\lambda_1(K_E) \geq \lambda_2(K_E) \geq \cdots \geq 0$ the eigenvalues of the Birman-Schwinger operator K_E and by $E_1 < E_2 \leq E_3 \leq \ldots \leq 0$ the negative eigenvalues of $-\Delta - U$, the Birman-Schwinger principle is the statement that

$$1 = \lambda_n(K_{E_n}) \quad \text{for all } n. \tag{8}$$

If V is not non-positive, one uses the min-max principle to see that $N_E(V) \leq N_E(-V_-)$. Here $N_E(V) = \#\{\text{eigenvalues of} - \Delta + V \leq E\}$ Thus, setting $U = -V_-$, using the Birman-Schwinger principle, and the monotonicity of $\lambda_n(K_E)$, one sees

$$N_E(V) \leq \#\{\text{eigenvalues of } K_E \geq 1\}.$$

In particular, $N_E(V) \leq \operatorname{tr}[K_E^n]$ for all $n \in \mathbb{N}$. On $\mathbb{R}^3$, K_E is a Hilbert-Schmidt operator with integral kernel

$$K_E(x,y) = \sqrt{V_-(x)}\, \frac{e^{-\sqrt{-E}|x-y|}}{4\pi|x-y|} \sqrt{V_-(y)},$$

implying the bound

$$N_E(V) \leq \operatorname{tr}[K_E^2] = \frac{1}{(4\pi)^2} \iint \frac{V_-(x)V_-(y)}{|x-y|^2}\, e^{-2\sqrt{-E}|x-y|}\, dxdy.$$

As $E \to 0$, we get the Birman-Schwinger [16, 137] bound

$$N(V) = N_0(V) \leq \frac{1}{(4\pi)^2} \iint \frac{V_-(x)V_-(y)}{|x-y|^2}\, dxdy. \tag{9}$$

Note that (the negative part of) a potential V_- is in the Rollnik class [146] if and only if the right-hand side of (9) is finite.

On the other hand, this simple bound does not have the right large coupling behavior since it only shows that $N(\lambda V) \leq (\text{const})\lambda^2$ which grows much faster than the asymptotic growth $\lambda^{3/2}$ shown by large coupling asymptotic. Nevertheless, the Birman-Schwinger principle is at the heart of all proofs of semi-classical eigenvalue bounds.

1.4. **The CLR and Lieb-Thirring bounds.** The semi-classical Weyl-type asymptotic for the number of bounds states leads naturally to the question whether there is a robust bound of the form

$$\begin{aligned} N(V) &\leq \frac{C_{0,d}}{(2\pi)^d} \iint_{|\xi|^2+V<0} 1\, d\xi dx \\ &= L_{0,d} \int_{\mathbb{R}^d} V_-(x)^{d/2}\, dx \end{aligned} \tag{10}$$

for *arbitrary* potentials V for which the right hand side is finite[3]. Here $L_{0,d} = C_{0,d}\omega_d/(2\pi)^d$, where ω_d is the volume of ball of radius one in d dimensions.

More generally, one can ask a similar question for higher moments[4] of the negative eigenvalues. That is, whether there is a semi-classical bound for

$$S^\gamma(V) = \mathrm{tr}[(-\Delta + V)_-^\gamma], \tag{11}$$

of the form

$$S^\gamma(V) \le \frac{C_{\gamma,d}}{(2\pi)^d} \iint (|\xi|^2 + V(x))_-^\gamma \, d\xi dx. \tag{12}$$

Or, equivalently, whether

$$S^\gamma(V) \le L_{\gamma,d} \int V(x)_-^{\gamma+d/2} \, dx \tag{13}$$

with $L_{\gamma,d} = C_{\gamma,d} L^{\mathrm{cl}}_{\gamma,d}$, where $L^{\mathrm{cl}}_{\gamma,d} = \frac{1}{(2\pi)^d} \int (|\xi|^2 - 1)_-^\gamma \, d\xi = \frac{\Gamma(\gamma+1)}{2^d \pi^{d/2} \Gamma(\gamma+1+d/2)}$ is the so-called classical Lieb-Thirring constant. In particular, $L^{\mathrm{cl}}_{0,d} = \omega_d/(2\pi)^d$ and $L^{\mathrm{cl}}_{1,d} = \frac{2}{d+2} \frac{\omega_d}{(2\pi)^d}$. Of course, one has to assume that the negative part of the potential $V_- \in L^{\gamma+d/2}(\mathbb{R}^d)$. One recovers $N(V)$ from $S^\gamma(V)$ by $N(V) = S^0(V) = \lim_{\gamma\to 0} S^\gamma(V)$.

Of course, the physically most interesting cases are $\gamma = 0$, the counting function for the number of bound states, and $\gamma = 1$, which gives a bound for the total energy of a system of non-interacting fermions in an external potential given by V. Also a simple approximation argument, see, for example, [147], shows that a bound of the form (10) allows to extend the semi-classical asymptotic (6) to all potentials in $L^{d/2}(\mathbb{R}^d)$.

It is easy to see that bounds of the type (12) can only hold for $\gamma > 0$ in $d \le 2$ and $\gamma \ge 0$ in $d \ge 3$. In fact, since any non-trivial attractive potential has at least one bound state [148, 81] and [85, pages 156-157], there can be no semi-classical bound of the form (13) for $\gamma = 0$ in $d = 2$, and in one dimension, this bound is even impossible[5] for $0 \le \gamma < 1/2$.

The inequalities (12) and (13) were proven by Lieb and Thirring [114, 115] in 1975-76 in the cases $\gamma > 1/2$ in $d = 1$ and $\gamma > 0$ for $d \ge 2$.

The proof of (10), the famous Cwikel-Lieb-Rozenblum bound, is considerably more complicated than the proof for $\gamma > 0$. It also has an interesting

[3]More precisely, V_+ should be locally integrable and $V_- \in L^{d/2}(\mathbb{R}^d)$.

[4]Often called Riesz' moments.

[5]Let $c > 0$, δ be the Dirac measure at 0, and note that, by a one-dimensional Sobolev embedding, the operator $-\partial^2 - c\delta$ is well-defined as a sum of quadratic forms. Take a sequence of approximate delta-functions δ_n converging weakly to δ. Then $-\partial^2 - c\delta_n$ converges to $-\partial^2 - c\delta$ in strong resolvent sense. If $\gamma < 1/2$, the right-hand side of (13) goes to zero, but the ground state of $-\partial^2 - c\delta_n$ stays bounded away from zero (it converges, in fact, to $-c^2/4 =$ single negative eigenvalue of $-\partial^2 - c\delta$).

history: Rozenblum announced his proof of (10), which is based on an extension of a machinery developed by Birman and Solomyak [18], in 1972 in [128]. This announcement went unnoticed in the west. Independently of Rozenblum, Simon established in [147] a link between the bound (10) and the then conjectured fact that the Birman-Schwinger operator K_0 given in (7) for $E = 0$ is a certain weak trace ideal[6] for $d \geq 3$. This conjecture by Simon on the asymptotic behavior of the singular values of K_0 motivated Cwikel and Lieb for their proofs of the CLR bound. In [30], Cwikel proved Simon's conjecture and Lieb, [92], used semigroup methods to bound $\mathrm{tr}[F(K_0)]$ for suitable functions F. Rozenblum's proof appeared in 1976 in [129], Lieb's was announced in [92] in 1976 and Cwikel's proof was published in 1977. Of the three methods, Lieb's gives by far the best estimates for the constants $C_{0,d}$. A very nice and readable discussion of Lieb's method can be found in Chapter 9 of [150] and Chapter 3.4 of Röpstorff's book [127]. In particular, Röpstorff discusses the fact that an extension of Lieb's method to higher moments $\gamma > 0$ gives the upper bound $C_{\gamma,d} \leq \sqrt{2\pi(\gamma + d/2)}(1+O((\gamma+d/2)^{-1}))$ as $\gamma + d/2 \to \infty$.

Later proofs of the CLR bound were given by Li and Yau [91], and Conlon, [26], see also [90, 130].

The Lieb-Thirring inequalities (12)fit beautifully into the large coupling asymptotic. At least on a formal level, it is easy to lift the asymptotic for $N(\lambda V) = S^0(\lambda V)$ to moments $\gamma > 0$ by the following observation: For any $\gamma > 0$,

$$(s_-)^\gamma = \gamma \int_0^{s_-} t^{\gamma-1}\, dt = \gamma \int_0^\infty (s+t)_-^0\, t^{\gamma-1}\, dt$$

for all real s (here $s_-^0 = 1$ if $s < 0$ and zero if $s \geq 0$). Freely interchanging integrals and traces gives

$$\begin{aligned} S^\gamma(\lambda V) = \mathrm{tr}(-\Delta + \lambda V)_-^\gamma &= \gamma \int_0^\infty \mathrm{tr}(-\Delta + \lambda V + t)_-^0\, t^{\gamma-1} dt \\ &= \gamma \int_0^\infty \Big(\frac{1}{(2\pi)^d} \iint (|\xi|^2 + \lambda V(x) + t)_-^0\, d\xi dx\, + o(\lambda^{d/2}) \Big)\, t^{\gamma-1} dt \\ &= \frac{1}{(2\pi)^d} \iint (|\xi|^2 + \lambda V(x))_-^\gamma\, d\xi dx + o(\lambda^{\gamma+d/2}). \end{aligned}$$

[6] A compact operator is in a trace ideal $\mathcal{S}^p$ if its singular values are in the space $l^p(\mathbb{N})$ and it is in the weak trace ideal $\mathcal{S}^p_w$ if its singular values are in the weak-l^p space $l^p_w(\mathbb{N})$, see, for example, [154].

Thus

$$
\begin{aligned}
\lim_{\lambda\to\infty} \lambda^{-(\gamma+d/2)} S^\gamma(\lambda V) &= \frac{1}{(2\pi)^d} \iint (|\xi|^2 + V(x))_-^\gamma \, d\xi dx \\
&= L^{\mathrm{cl}}_{\gamma,d} \int V(x)_-^{\gamma+d/2} \, dx.
\end{aligned} \tag{14}
$$

Of course, to make this sketch rigorous, one needs to handle the error terms more carefully, which we skip. This large coupling asymptotic shows that the best possible constants $L_{\gamma,d}$ in the Lieb-Thirring inequality have the natural lower bound $L_{\gamma,d} \geq L^{\mathrm{cl}}_{\gamma,d}$, or, equivalently, $C_{\gamma,d} \geq 1$.

1.5. **A Sobolev inequality for fermions.** Besides being mathematically very appealing, the $\gamma = 1$ version of the Lieb-Thirring bound gives a Sobolev inequality for fermions whose $d = 3$ version has a nice application to the Stability-of-Matter problem. For notational simplicity, we will not take the spin of the particles into account. The following gives a duality between a Lieb-Thirring type bound and a lower bound for the kinetic energy of an N-particle fermion system. It is an immediate corollary of the Lieb-Thirring bound for $\gamma = 1$.

Theorem 1. *The following two bounds are equivalent for non-negative convex functions G and $F : \mathbb{R}_+ \to \mathbb{R}_+$ which are Legendre transformation of each other. The Lieb-Thirring bound:*

$$
\sum_j |E_j| = \mathrm{tr}_{L^2(\mathbb{R}^d)}(H_0 + V)_- \leq \int G((V(x))_-) \, dx. \tag{15}
$$

(*Usually with $H_0 = -\Delta$, but this does not matter in the following.*)
The Thomas-Fermi bound:

$$
\langle \psi, \sum_{n=1}^N H_0 \psi \rangle_{\bigwedge^N L^2(\mathbb{R}^d)} \geq \int F(\rho_\psi(x)) \, dx, \tag{16}
$$

for all antisymmetric states $\psi \in \bigwedge^N L^2(\mathbb{R}^d)$ with norm one. Here

$$
\rho_\psi(x) := N \int_{R^{N-1}d} |\psi(x, x_2, \ldots, x_N)|^2 \, dx_2 \ldots dx_N
$$

is the so-called one particle density associated with the antisymmetric N-particle state ψ.

For an explicit relation between F and G see (18) and (19).

Using the traditional Lieb-Thirring bound with $\gamma = 1$, one gets the following immediate

Corollary 2. *For normalized $\psi \in \bigwedge^N L^2(\mathbb{R}^d)$,*

$$\big\langle \psi, -\sum_{j=1}^N \Delta_j \psi \big\rangle_{L^2(\mathbb{R}^{Nd})} \geq C_{1,d}^{-2/d} K_d^{\mathrm{TF}} \int_{\mathbb{R}^d} \rho_\psi(x)^{\frac{d+2}{d}}\, dx$$

with

$$K_d^{\mathrm{TF}} = \frac{d}{d+2}\big(\frac{d+2}{2} L_{1,d}^{cl}\big)^{-2/d} = \frac{d}{d+2}\frac{4\pi^2}{\omega_d^{2/d}}.$$

On should note that the right hand side of this bound is exactly the Thomas-Fermi prediction for the kinetic energy of N fermions and K_d^{TF} is the Thomas-Fermi constant, see section 2.2. In particular, if $C_{1,d}$ is one, then the Thomas-Fermi ansatz for the kinetic energy, a priori only supposed to be asymptotically correct for large N, should be a true lower bound for all N. This is a situation very much similar in spirit to Pólya's conjecture.

Remark 3. Taking the spin of electrons into account, i.e., assuming that $\psi \in \bigwedge^N (L^2(\mathbb{R}^d, \mathbb{C}^q))$ is normalized (and $q = 2$ for real electrons) one has the lower bound

$$\langle \psi, \sum_{j=1}^N -\Delta_j \psi \rangle \geq (qC_{1,d})^{-2/d} K_d^{TF} \int \rho_\psi(x)^{(d+2)/d}\, dx. \tag{17}$$

Proof of Theorem 1: This proof is certainly known to the specialist, but we include it for completeness. In fact, the reverse implication is the easy one, (15) $\Leftarrow$ (16):
Fix $N \in \mathbb{N}$ and let $E_1 < E_2 \leq \cdots \leq E_N \leq 0$ be the first N negative eigenvalues of the one-particle Schrödinger operator $H = H_0 + V$. Usually, $H_0 = -\Delta$, but this does not really matter. By the min-max principle, we can assume without loss of generality that V is non-positive, $V = -V_- = -U$. If H has only $J < N$ negative eigenvalues, then we put $E_j = 0$ for $j = J+1, \ldots, N$.

Consider $H_N = \sum_{j=1}^N (H_{0,j} - U(x_j))$ on $\bigwedge^N L^2(\mathbb{R}^d)$ be the sum of N independent copies of H (more precisely, one should write $H_N = \sum_{j=1}^N H_j$ with $H_j = \underbrace{\mathbf{1} \times \cdots \times \mathbf{1}}_{j \text{ times}} \times H \times \underbrace{\mathbf{1} \times \cdots \times \mathbf{1}}_{N-j-1 \text{ times}}$).

Let $\varphi_1, \ldots, \varphi_N$ be the normalized eigenvectors corresponding to the eigenvalues E_j (if $J < N$ pick any orthonormal functions for $j > J$) and put

$$\psi := \varphi_1 \wedge \ldots \wedge \varphi_N \in \bigwedge^N L^2(\mathbb{R}^d),$$

the normalized antisymmetric tensor product of the φ_j's. Then

$$\sum_{n=1}^{N}|E_n| = -\sum_{n=1}^{N}E_n = -\langle\psi,\sum_{n=1}^{N}H_n\psi\rangle$$
$$= -\langle\psi,\sum_{n=1}^{N}H_0\psi\rangle + \langle\psi,\sum_{n=1}^{N}U_n\psi\rangle.$$

Since $\sum_{n=1}^{N}U_n$ is a sum of one-body (multiplication) operators, we have $\langle\psi,\sum_{n=1}^{N}U_n\psi\rangle = \int U(x)\rho_\psi(x)\,dx$, by the definition of the one-particle density. Thus, taking (16) into account one gets

$$\sum_{n=1}^{N}|E_n| \le \int U(x)\rho_\psi(x)\,dx - \int F(\rho_\psi(x))\,dx$$
$$= \int (U(x)\rho_\psi(x)\,dx - F(\rho_\psi(x)))\,dx$$
$$\le \int \sup_{t\ge 0}(U(x)t - F(t))\,dx = \int G(U(x))\,dx$$

where we were forced to put

$$G(s) := \sup_{t\ge 0}(st - F(t)) \tag{18}$$

since we only know that $\rho_\psi(x) \ge 0$.

(15) $\Rightarrow$ (16): This is certainly standard, the argument in the original case goes through nearly without change. By min-max and the Lieb-Thirring inequality (15), we know that for any non-negative function U and any normalized antisymmetric N-particle ψ,

$$\langle\psi,\sum_{n=1}^{N}(H_0 - U)\psi\rangle \ge -\operatorname{tr}(H_0 - U)_- \ge -\int G(U(x))\,dx.$$

Thus

$$\langle\psi,\sum_{n=1}^{N}H_0\psi\rangle \ge \langle\psi\sum_{n=1}^{N}U_n\psi\rangle - \int G(U(x))\,dx$$
$$= \int U(x)\rho_\psi(x)\,dx - \int G(U(x))\,dx$$
$$= \int \big[U(x)\rho_\psi(x) - G(U(x))\big]\,dx$$

again by the definition of the one-particle density. Hence

$$\begin{aligned}\langle\psi, \sum_{n=1}^{N} H_0\psi\rangle &\geq \sup_{U\geq 0}\int \big[U(x)\rho_\psi(x) - G(U(x))\big]\,dx\\ &= \int \sup_{U(x)\geq 0}\big[U(x)\rho_\psi(x) - G(U(x))\big]\,dx\\ &= \int \sup_{s\geq 0}\big[s\rho_\psi(x) - G(s)\big]\,dx = \int F(\rho_\psi(x))\,dx,\end{aligned}$$

where, of course, we put

$$F(t) := \sup_{s\geq 0}(st - G(s)). \tag{19}$$

□

Remark 4. Since F and G are Legendre transforms of each other and since the double Legendre transform of a convex function reproduces the function (under suitable semi-continuity and convexity assumptions), we see that the Lieb-Thirring type inequality (15) and the Thomas-Fermi type kinetic energy bound (16) are dual to each other. In particular, one implies the other with the corresponding optimal constants. This could be interesting in the hunt for sharp constants, since Eden and Foias gave in [35] a direct and rather simple proof of the kinetic energy lower bound in one dimension.

Following Lieb and Thirring, the bound in Theorem 1 has a beautiful application to the Stability-of-Matter problem which we will discuss a little bit in section 2.3.

The Lieb-Thirring inequalities also found other applications, especially in the theory of non-linear evolution equations, as a tool to bound the dimension of attractors [28, 53, 57, 98, 131, 162].

1.6. **Classical results for the Lieb-Thirring constants.** The moment inequalities due to Lieb and Thirring are an important tool in the theory of Schrödinger operators since they connect a purely quantum mechanical quantity with its classical counterpart. Moreover, as we saw already, a dual version of it, the Sobolev inequality for fermions, is related to the theory of bulk matter. So a good understanding of the Lieb-Thirring coefficients is of some importance for our understanding of quantum mechanics.

In general dimensions $d \in \mathbb{N}$ one now knows the following properties of $C_{\gamma,d}$:

- $C_{\gamma,d} \geq 1$, which follows from the Weyl-asymptotic.
- Monotonicity in γ: $C_{\gamma,d} \leq C_{\gamma_0,d}$ for all $\gamma \geq \gamma_0$ (Aizenman and Lieb [2]).

- $C_{\gamma,d} > 1$ as soon as $\gamma < 1$ (Helffer and Robert [62][7]).
- The best bounds on $C_{\gamma,d}$ are due to Lieb [98], but they are explicitly dimension dependent and grow like $C_{\gamma,d} = \sqrt{2\pi a}$ as $a = \gamma + d/2 \to \infty$, see [127, Chapter 3.4].
- Some special bounds in small dimensions: The bounds

$$C_{1,1} \leq 2\pi$$
$$C_{1,2} \leq 6.03388$$
$$C_{1,3} \leq 5.96677$$

are due to Lieb [98] and, after 12 years of additional work, were slightly improved by Blanchard and Stubbe [20] in 1996

$$C_{1,1} \leq 5.81029$$
$$C_{1,2} \leq 5.17690$$
$$C_{1,3} \leq 5.21809.$$

- There is a natural lower bound on $C_{0,d}$ using the fact that the CLR bound implies a Sobolev inequality[8] [56], [115, eq. (4.24)], see also the discussion in [150, page 96–97], In three dimensions it gives

$$4.6189 \leq C_{0,3} \leq 6.869$$

where the upper bound is from Lieb [92]. In particular, this shows that in dimension 3, Lieb's result is at most 49% off the best possible. In fact, the above lower bound is conjectured to be the correct value [56, 115, 150].

The monotonicity in γ is probably easiest to understand in the phase space picture (12) of the Lieb-Thirring bounds: Let $s_- = (s)_- = \frac{1}{2}(|s| - s)$ be the negative part of s. For any $0 \leq \gamma_0 < \gamma$ there exists a positive (!) measure μ on $\mathbb{R}_+$ such that[9]

$$(s)_-^\gamma = \int_0^\infty (s+t)_-^{\gamma_0} \, \mu(dt).$$

[7]In particular, this disproved part of a conjecture of Lieb and Thirring made in [115].

[8]More surprisingly, the Sobolev inequality together with the fact that $-\Delta$ generates a Markov semigroup implies the CLR bound, see [90].

[9]In fact, $\mu(dt) = ct^{\gamma-\gamma_0-1}\, dt$ for an explicit constant c; just do the integral on the right hand side by scaling.

With this we have

$$\begin{aligned}\operatorname{tr}(-\Delta+V)_-^{\gamma} &= \int_0^\infty (\operatorname{tr}(-\Delta+V+t)_-^{\gamma_0}\,\mu(dt)\\ &\le \frac{C_{\gamma_0,d}}{(2\pi)^d}\int_0^\infty \iint_{\mathbb{R}^{2d}} (|\xi|^2+V(x)+t)_-^{\gamma_0}\,d\xi dx\,\mu(dt)\\ &= \frac{C_{\gamma_0,d}}{(2\pi)^d}\iint_{\mathbb{R}^{2d}}\int_0^\infty (|\xi|^2+V(x)+t)_-^{\gamma_0}\,\mu(dt)\,d\xi dx\\ &= \frac{C_{\gamma_0,d}}{(2\pi)^d}\iint_{\mathbb{R}^{2d}} (|\xi|^2+V(x))_-^{\gamma}\,d\xi dx,\end{aligned}$$

by freely interchanging the integrations (and the trace). In particular, this shows

$$C_{\gamma,d} \le C_{\gamma_0,d}.$$

Thus monotonicity in γ is just a simple consequence of the Fubini-Tonelli theorem and scaling.

In one dimension much more is known:

- $C_{3/2,1} = 1$ (Gardener, Greene, Kruskal, and Miura 1974 [55]; Lieb and Thirring 1976 [115]). By monotonicity, this implies, $C_{\gamma,1} = 1$ for $\gamma \ge \frac{3}{2}$.
- For $\frac{1}{2} \le \gamma \le \frac{3}{2}$, an explicit solution[10] of the variational problem $\sup_{V\neq 0} \frac{|E_1(V)|}{\int V^{\gamma+1/2}}$ leads to

$$C_{\gamma,1} \ge 2\left(\frac{\gamma-1/2}{\gamma+1/2}\right)^{\gamma-1/2}.$$

  (Keller 1961 [77], later rediscovered by Lieb and Thirring 1976 [115]). In particular, $C_{\gamma,d} > 1$ for $\gamma < \frac{3}{2}$.
- $C_{1/2,1} < \infty$ (Timo Weidl 1996 [165]).

The sharp result $C_{3/2,1} = 1$ follows from the lower bound $C_{\gamma,d} \ge 1$ and a sum rule for one dimensional Schrödinger operators from the theory of the KdV equation. It reads

$$\frac{3}{16}\int_{-\infty}^\infty V(x)^2\,dx = \sum_j |E_j|^{3/2} + \text{“scattering data”}.$$

As noted on page 115 of [55], the contribution from the scattering data is non-negative, so one can drop it to get an inequality for the $\frac{3}{2}$ moment of the negative eigenvalues[11]. It remains to note that $L^{\mathrm{cl}}_{3/2,1} = \frac{3}{16}$.

---

[10]See also the very nice discussion in [15].

[11]It might be amusing to note that dropping the contribution of the eigenvalues gives an upper bound for the contribution of the scattering data which was the key to proof of a

Lieb and Thirring [115] did not settle the critical case $\gamma = 1/2$ in one dimension. The question whether $C_{1/2,1}$ is finite or not was open for twenty years until Weidl [165] showed that $C_{1/2,1} < 4.02$. But, despite some considerable interest, and in contrast to other results on sharp inequalities (see, e.g., on [23, 24, 97] on Sobolev inequalities) the only sharp bound for the Lieb-Thirring inequalities for more than twenty years was the original result by Lieb and Thirring.

This was especially tantalizing since, depending on the dimension, there are obvious conjectures for the sharp Lieb-Thirring constants,

Conjecture 5. *In dimension $d \geq 3$: $C_{1,d} = 1$. In particular, the Thomas-Fermi type bound for the kinetic energy of N fermions should hold with the Thomas-Fermi constant.*
In one dimension:

$$C_{\gamma,1} = 2\left(\frac{\gamma - 1/2}{\gamma + 1/2}\right)^{\gamma-1/2} \qquad \text{for } 1/2 < \gamma \leq \tfrac{3}{2}$$

(*with* $C_{1/2,1} = \lim_{\gamma\to 1/2} C_{\gamma,1} = 2$) *and the extremizers in the one-bound-state variational problem studied by Keller* [77] *and by Lieb and Thirring in* [115] *should also be extremizers in the Lieb-Thirring inequality. That is, up to scaling and translations the extremizing potentials V in* (13) *for $d = 1$ and $1/2 \leq \gamma < \frac{3}{2}$ are of the form*

$$V(x) = -\frac{1}{\gamma^2 - 1/4}\left(\cosh\left(\frac{x}{\gamma^2 - 1/4}\right)\right)^{-2}.$$

In particular, for $\gamma = \frac{1}{2}$, $C_{1/2,1} = 2$ and the extremizing potential should be a multiple and translate of a delta function. For the first moment one should have $C_{1,1} = 2/\sqrt{3} < 1.155$.

Shortly after Weidl's result, Hundertmark, Lieb, and Thomas proved the $\gamma = \frac{1}{2}$ part of the one-dimensional Lieb-Thirring conjecture in [68].

Theorem 6 (Hundertmark-Lieb-Thomas, 1998)**.** *Suppose ν is a non-negative measure with $\nu(\mathbb{R}) < \infty$ and let $E_1 < E_2 \leq E_3 \leq \ldots \leq 0$ be the negative eigenvalues counting multiplicity of the Schrödinger operator $-\partial_x^2 - \nu$ (if any) given by the corresponding quadratic form. Then*

$$\sum_{i=1}^{\infty} \sqrt{|E_i|} \leq \frac{1}{2}\,\nu(\mathbb{R})$$

with equality if and only if the measure ν is a single Dirac measure.

---

conjecture of Kiselev–Last–Simon, [80] on the ac spectrum of one dimensional Schrödinger operators with L^2 potentials by Deift and Killip [32]. Sum rules have also turned out to be instrumental in the study of other related spectral problems, [78, 79, 83, 122, 134, 135]

Since $L^{\mathrm{cl}}_{1/2,1} = 1/4$, this shows $C_{1/2,1} = 2$, confirming the left endpoint of the one-dimensional Lieb-Thirring Conjecture 5. It might be interesting to note that Schmincke, [136], proved a corresponding sharp *lower* bound for one-dimensional Schrödinger operators with a potential. That is, for $-\partial_x^2 + V$, he showed

$$-\frac{1}{4}\int_{\mathbb{R}} V(x)\,dx \le \sum_{i=1}^{\infty} \sqrt{|E_i|}.$$

Schmincke's proof uses Schrödinger's factorization method, see also [29, 31], and has been extended in [124] to some higher moments.

1.7. **The Laptev–Weidl extension of the Lieb-Thirring bounds.** The last few years saw a dramatic increase in our understanding of the Lieb-Thirring inequalities:

- $C_{\gamma,d} = 1$ for $\gamma \ge \frac{3}{2}$ all d (Laptev and Weidl 2000 [88]).
- $C_{1,d} \le 2$ for all d (Hundertmark, Laptev, and Weidl 2000 [67]). Hence also $C_{\gamma,d} \le 2$ for $1 \le \gamma < \frac{3}{2}$, by monotonicity in γ.
- $C_{0,d} \le 81$ all $d \ge 3$ (Hundertmark 2002 [66]).

The key observation of Laptev and Weidl [88], which was already noted in Laptev [86], was to do something seemingly crazy: Extend the Lieb-Thirring inequalities from scalar to *operator-valued* potentials. They considered Schrödinger operators of the form $-\Delta \otimes \mathbf{1}_{\mathcal{G}} + V$ on the Hilbert space $L^2(\mathbb{R}^d, \mathcal{G})$, where V now is an operator-valued potential with values $V(x)$ in the bounded self-adjoint operators on the auxiliary Hilbert space $\mathcal{G}$, and asked whether a bound of the form

$$\operatorname{tr}_{L^2(\mathbb{R}^d,\mathcal{G})}(-\Delta \otimes \mathbf{1}_{\mathcal{G}} + V)_-^{\gamma} \le \frac{C^{\mathrm{op}}_{\gamma,d}}{(2\pi)^d} \iint\limits_{\mathbb{R}^d\mathbb{R}^d} d\xi dx\ \operatorname{tr}_{\mathcal{G}}(|\xi|^2 + V(x))_-^{\gamma} \tag{20}$$

holds. Or, again doing the ξ integral explicitly with the help of the spectral theorem and scaling,

$$\operatorname{tr}_{L^2(\mathbb{R}^d,\mathcal{G})}(-\Delta \otimes \mathbf{1}_{\mathcal{G}} + V)_-^{\gamma} \le L^{\mathrm{op}}_{\gamma,d} \int_{\mathbb{R}^d} dx\ \operatorname{tr}_{\mathcal{G}}(V(x)_-^{\gamma+d/2}). \tag{21}$$

This seemingly purely technical extension of the Lieb-Thirring inequality turned out to be the key in proving at least a part of the Lieb-Thirring conjecture. In fact, using this type of inequality Laptev and Weidl noticed the following[12] monotonicity properties of the operator-valued Lieb-Thirring constants $C^{\rm op}_{\gamma,d}$ in the dimension:

$$
\begin{aligned}
&1 \le C^{\rm op}_{\gamma,d} \le C^{\rm op}_{\gamma,1} C^{\rm op}_{\gamma,d-1} \quad \text{and} \\
&1 \le C^{\rm op}_{\gamma,d} \le C^{\rm op}_{\gamma,1} C^{\rm op}_{\gamma+\frac{1}{2},d-1}
\end{aligned} \tag{22}
$$

Assume that one knows $C^{\rm op}_{3/2,1} = 1$. Then using the first part of (22) repeatedly, we get

$$1 \le C^{\rm op}_{3/2,2} \le C^{\rm op}_{3/2,1} C^{\rm op}_{3/2,1} = 1 \cdot 1 = 1,$$

that is, $C^{\rm op}_{3/2,2} = 1$ and hence

$$1 \le C^{\rm op}_{3/2,3} \le C^{\rm op}_{3/2,1} C^{\rm op}_{3/2,2} = 1$$

also. Thus an obvious induction in d shows

$$1 \le C^{\rm op}_{3/2,d} \le C^{\rm op}_{3/2,1} C^{\rm op}_{3/2,d-1} = 1$$

and with the monotonicity in γ one concludes

$$C^{\rm op}_{\gamma,d} = 1 \text{ for } \gamma \ge 3/2 \text{ and all } d \in \mathbb{N}.$$

The beauty (and simplicity!) of this observation is that $C_{3/2,1} = 1$ is well-known (already in [115]) and Laptev and Weidl were able to prove that $C^{\rm op}_{3/2,1} = 1$ by extending the Buslaev-Faddeev-Zakharov sum rules for the KdV equation,[22, 171], to matrix-valued potentials.

Theorem 7 (Laptev and Weidl, 2000 [88])**.** *One has*

$$C^{\rm op}_{3/2,1} = 1.$$

For a nice alternative proof, which avoids the use of sum rules see [14].

However, as beautiful as this result is, it sheds no light on the physically most important constants $C_{1,d}$. Recently, Benguria and Loss [15] developed a new viewpoint on the Lieb-Thirring conjecture in one dimension. They connected a simplified "2 bound state version" with an isoperimetric problem for ovals in the plane. However, no progress has been made so far using this viewpoint.

The second submultiplicativity property of $C^{\rm op}_{\gamma,d}$, together with the sharp bound due to Laptev and Weidl, shows that $C^{\rm op}_{1,2} \le C^{\rm op}_{1,1} C^{\rm op}_{3/2,1} = C^{\rm op}_{1,1}$. Again by induction this implies

$$C^{\rm op}_{1,d} \le C^{\rm op}_{1,1} \quad \text{for all } d \in \mathbb{N}.$$

[12] In fact, they observed that $L^{\rm cl}_{\gamma,d} = L^{\rm cl}_{\gamma,1} L^{\rm cl}_{\gamma+\frac{1}{2},d-1}$ by explicitly multiplying Γ-functions. So if (21) holds with the classical constant for some γ, then using monotonicity in γ one can start an induction in the dimension argument. We prefer to avoid multiplying Γ-functions and to think of this in terms of the $C^{\rm op}_{\gamma,d}$'s, using a Fubini type argument on the operator side instead.

In particular, if the one dimensional version of the Lieb-Thirring conjecture, see Conjecture 5, were true for operator-valued potentials, the uniform bound $C^{\mathrm{op}}_{1,d} < 1.16$ would follow.

Using ideas from [68], Hundertmark, Laptev, and Weidl extended the sharp bound in the critical case in one dimension to operator-valued potentials [67]. Together with the Aizenman-Lieb monotonicity in γ, this gives the uniform bound $C^{\mathrm{op}}_{\gamma,d} \leq C^{\mathrm{op}}_{\frac{1}{2},1} = 2$, for $1 \leq \gamma < \frac{3}{2}$. Together with the sharp result from Laptev and Weidl, this gives

Theorem 8 (Hundertmark-Laptev-Weidl, 2000). *The bounds*

$$C_{\gamma,d} \leq 2 \quad \textit{for } 1 \leq \gamma \textit{ and all } d \geq 1,$$
$$C_{\gamma,d} \leq 4 \quad \textit{for } 1/2 \leq \gamma < 1 \textit{ and all } d \geq 2$$

on the Lieb-Thirring constants hold.

Moreover, the *same* estimates for the Lieb-Thirring constants for magnetic Schrödinger operators hold. This follows from the proof of this estimates. One strips off one dimension, but in one dimension there are no magnetic fields, since any "vector" potential in one dimension is gauge equivalent to the zero potential. Thus, by induction in the dimension, the magnetic vector potential simply drops out, see [67] for details.

It soon became obvious, that one is not restricted to stripping off only one dimension at a time. More precisely, one has the following two general submultiplicativity properties of $C^{\mathrm{op}}_{\gamma,d}$,

Theorem 9 (Hundertmark, 2002 [66]). *For* $1 \leq n \leq d$*:*

$$1 \leq C^{\mathrm{op}}_{\gamma,d} \leq C^{\mathrm{op}}_{\gamma,n} C^{\mathrm{op}}_{\gamma,d-n} \qquad \textit{and}$$
$$1 \leq C^{\mathrm{op}}_{\gamma,d} \leq C^{\mathrm{op}}_{\gamma,n} C^{\mathrm{op}}_{\gamma+n/2,d-n}.$$

In particular, stripping off $n = 3$ dimensions, and using that $C^{\mathrm{op}}_{\gamma+3/2,d-3} = 1$ for $d \geq 3$ by the Laptev-Weidl result, one immediately sees that

$$C^{\mathrm{op}}_{\gamma,d} \leq C^{\mathrm{op}}_{\gamma,3} \quad \text{for all } \gamma \geq 0 \text{ and } d \geq 3. \tag{23}$$

Ari Laptev asked the question [87], see also [89], whether, in particular, the Cwikel-Lieb-Rozenblum estimate holds for Schrödinger operators with operator-valued potentials. The proof of this fact was also given in [66]

Theorem 10 (Hundertmark, 2002). *Let* $\mathcal{G}$ *be some auxiliary Hilbert space and* V *a potential in* $L^{d/2}(\mathbb{R}^d, \mathcal{S}^{d/2}(\mathcal{G}))$ *with* $\mathcal{S}^{d/2}$ *the von Neumann-Schatten operator ideal on* $\mathcal{G}$*. Then the operator* $-\Delta \otimes \mathbf{1}_{\mathcal{G}} + V$ *has a finite number* N *of negative eigenvalues. Furthermore, one has the bound*

$$N \leq L_{0,d} \int_{\mathbb{R}^d} \mathrm{tr}_{\mathcal{G}}(V(x)_-^{d/2})\, dx$$

with

$$L_{0,d} \le (2\pi\, K_d)^d L^{\mathrm{cl}}_{0,d},$$

where the constant K_q *is given by*

$$K_q = (2\pi)^{-d/q} \frac{q}{2} \left(\frac{8}{q-2}\right)^{1-2/q} \left(1 + \frac{2}{q-2}\right)^{1/q}.$$

This shows $C_{0,d} \le (2\pi\, K_d)^d$. The constant K_d is exactly the one given by Cwikel [30]. The proof of the above theorem is by extending Cwikel's method to an operator-valued setting. Thereby one recovers Cwikel's bound $C^{\mathrm{op}}_{0,3} \le 81$, which is 17 times larger than Lieb's estimate (however, for the scalar case). Nevertheless, using the submultiplicativity, it gives the uniform bound $C^{\mathrm{op}}_{0,d} \le C^{\mathrm{op}}_{0,3} \le 81$ which, by monotonicity in γ, also extends to moments $0 < \gamma < 1/2$.

We will not discuss the by now rather big literature on Lieb-Thirring inequalities for the Pauli operator, see, for example, the review article by Lászlo Erdős, [39], nor the quite extensive literature on quantum graphs, see [84], or the results on quantum wave guides, see, for example, [38, 41, 42], but we would like to mention one more recent and, at least for us, rather surprising result on Lieb-Thirring inequalities.

1.8. **The Ekholm-Frank result.** It is well known that an attractive potential does not necessarily produce a bound state in three and more dimensions. This follows, for example, from Hardy's inequality, which says that in dimension three and more the sharp operator inequality

$$\frac{(d-2)^2}{4|x|^2} \le -\Delta \tag{24}$$

holds. Using this, one can refine the usual Lieb-Thirring inequalities in the following way: Using Hardy's inequality, for any $\varepsilon \in (0,1)$ one has

$$-\Delta + V \ge -\varepsilon\Delta + (1-\varepsilon)\frac{(d-2)^2}{4|x|^2} + V.$$

Thus with the known Lieb-Tirring inequality, one gets

(25)

$$\begin{aligned}\operatorname{tr}(-\Delta + V)^\gamma_- &\le \frac{C_{\gamma,d}}{(2\pi)^d \varepsilon^{d/2}} \iint_{\mathbb{R}^d\times\mathbb{R}^d} \Big(|\xi|^2 + (1-\varepsilon)\frac{(d-2)^2}{4|x|^2} + V(x)\Big)^\gamma_- \, d\xi dx \\ &= L_{\gamma,d}\varepsilon^{-d/2} \int_{\mathbb{R}^d} \Big((1-\varepsilon)\frac{(d-2)^2}{4|x|^2} + V(x)\Big)^{\gamma+d/2}_- \, dx.\end{aligned}$$

Of course, as $\varepsilon \to 0$, the constant in front of the integral diverges. Very recently, Ekholm and Frank established that one can nevertheless take the limit $\varepsilon \to 0$. They proved the rather surprising result

Theorem 11 (Ekholm and Frank 2006, [37]). *For moments $\gamma > 0$ the inequality*

$$\operatorname{tr}(-\Delta + V)_-^\gamma \le \frac{C^{EF}_{\gamma,d}}{(2\pi^2)} \iint_{\mathbb{R}^d\times\mathbb{R}^d} \big(|\xi|^2 + \frac{(d-2)^2}{4|x|^2} + V(x)\big)_-^\gamma \, d\xi dx$$
$$= L^{EF}_{\gamma,d} \int_{\mathbb{R}^d} \big(\frac{(d-2)^2}{4|x|^2} + V(x)\big)_-^{\gamma+d/2} \, dx$$

holds in dimension three and more.

Thus, as far as moments are concerned, only the part of the potential *below* the critical Hardy potential is responsible for bound states. This amounts to an infinite phase-space renormalization on the level of the Lieb-Thirring inequality. Note that the Ekholm Frank bound *cannot* hold for $\gamma = 0$. Also, effective bounds on $C^{EF}_{\gamma,d}$, resp. $L^{EF}_{\gamma,d}$, are not known.

2. Multi-particle Coulomb Schrödinger operators

2.1. **The Coulomb Hamiltonian.** The Hamiltonian for N electrons in the field of M nuclei is given by

$$H = H_{N,Z,R} = T + V_c = T + V_c \tag{26}$$

where $T = \sum_{j=1}^N -\Delta_j$ is the kinetic energy of N electrons and

$$V_c = V_{en} + V_{ee} \tag{27}$$

with

$$V_{en} = -\sum_{j=1}^N \sum_{\alpha=1}^M \frac{Z_\alpha}{|x_j - R_\alpha|},$$

the electron-nucleus interaction,

$$V_{ee} = \sum_{i<j} \frac{1}{|x_i - x_j|},$$

the electron-electron repulsion. Sometimes, one also considers

$$V_{nn} = \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|},$$

the repulsion of the M nuclei at positions $R = (R_1, \dots, R_M) \in \mathbb{R}^{3M}$. We keep the position of the nuclei fixed, for simplicity. The electrons have spin q. In real life $q = 2$. Thus the N-electron operator $H_{N,Z,R}$ is defined on $\bigwedge^N(L^2(\mathbb{R}^2), \mathcal{C}^q)$, the antisymmetric subspace of $L^2(\mathbb{R}^{3N}, \mathcal{C}^{qN})$, since electrons are fermions. Note that in the unit we use, the ground state energy of Hydrogen is 1/4.

Zhislin's theorem [172], see also [145] for a simple proof, guarantees the existence of a ground state if $N < \sum_\alpha Z_\alpha + 1$. One of the problems is to compute the ground state and the ground state energy, that is,

$$E^Q(N,Z,R) = \inf\big(\langle\psi, H_{N,Z,R}\psi\rangle | \psi \in \bigwedge^N (L^2(\mathbb{R}^3,\mathbb{C}^q)),\ \|\psi\| = 1\big) \tag{28}$$

and the minimizing groundstate wavefunction. The catch is that, although the Schrödinger equation is a linear equation, even the problem of two electrons in the field of one nucleus is not exactly solvable. Moreover, due to the exponential scaling of the degrees of freedom, there are no efficient methods to solve the Schrödinger equation approximately, even for moderate numbers of electrons.

Nevertheless, one can give a rather complete answer in the limit of large atoms or molecules. As shown by Lieb and Simon, Thomas-Fermi theory becomes exact in this case.

2.2. **Thomas-Fermi theory.** Thomas-Fermi theory is a simplification of the usual Schrödinger equation. For an excellent review and proofs of results see [95]. A fundamental object in this theory (or approximation) is not the wave function any more, but the so-called single-particle density. Given a normalized wave function $\psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathcal{C}^q)$, recall that its single particle density is given by

$$\rho_\psi(x) = N \sum_{\sigma_j = 1,\dots,q} \int |\psi(x,\sigma_1,x_2,\sigma_2,\dots,x_N,\sigma_N)|^2\, dx_2 \dots dx_N. \tag{29}$$

The electron nucleus interaction is easily expressed in terms of the density,

$$\langle\psi, V_{en}\psi\rangle = -\sum_{j=1}^M \int_{\mathbb{R}^3} \frac{Z_j}{|x-R_j|}\rho_\psi(x)\, dx. \tag{30}$$

The kinetic energy $T = \langle\psi, H_0\psi\rangle$ cannot be expressed by density ρ, but it can be approximately expressed by the density. For a free electron gas in a container of sidelength L in d dimensions, with periodic boundary conditions, say, the ground state energy is given by

$$T = \sum_{\substack{(n,\sigma)\in\mathbb{Z}^d\times\{1,\dots,q\} \\ |n|\le n_0}} \left(\frac{2\pi}{L}\right)^2 |n|^2.$$

In the limit $N \to \infty$ one has

$$N = \sum_{\substack{(n,\sigma)\in\mathbb{Z}^d\times\{1,\dots,q\} \\ |n|\le n_0}} 1 \longrightarrow q\int_{|n|\le n_0} dn = q\omega_d n_0^d.$$

with ω_d the volume of the sphere of radius one. Also, again in the limit $N \to \infty$,

$$T = q\big(\frac{2\pi}{L}\big)^2 \int_{|n|\le n_0} n^2\, dn = \frac{d}{d+2}\omega_d\Big(\frac{2\pi}{L}\Big)^2 n_0^{d+2}$$
$$= \frac{d}{d+2}\frac{(2\pi)^2}{(q\omega_d)^{2/d}}\frac{N^{(d+2)/d}}{L^2}.$$

Thus the kinetic energy density should be given by

$$\frac{T}{L^d} = \frac{d}{d+2}\frac{(2\pi)^2}{(q\omega_d)^{2/d}}\Big(\frac{N}{L^d}\Big)^{(d+2)/d} = q^{-2/d}K_d^{TF}\rho^{(d+2)/d}$$

with the density $\rho = N/L^d$ and the Thomas-Fermi constant $K_d^{TF} = \frac{d}{d+2}\frac{(2\pi)^2}{\omega_d^{2/d}}$.

For slowly varying densities, the above suggest that the kinetic energy of N electrons (in the large N limit) is well-approximated by

$$T = q^{-2/d}K^{TF}\int_{\mathbb{R}^d}\rho(x)^{(d+2)/d}\, dx \qquad \text{with } K_d^{TF} = \frac{d}{d+2}\frac{4\pi^2}{\omega_d^{2/d}}. \tag{31}$$

In fact, the duality of the Lieb-Thirring bound and the kinetic energy bound for Fermions shows that as an inequality, this holds with the Thomas-Fermi constant, if the Lieb-Thirring inequality is true with the classical constant, that is if $C_{1,d} = 1$.

Now let's concentrate on the physical relevant case of three space dimensions. Similarly as for the kinetic energy, the Coulomb repulsion of the electrons cannot be expressed by the density alone, but, keeping fingers crossed, it should be well-approximated by the Coulomb integral. In fact, up to a small error, the Coulomb integral is a lower bound, see Lieb and Oxford [111], Lieb [94]:

(32)
$$\langle\psi, \sum_{i<j}\frac{1}{|x_j - x_j|}\psi\rangle \ge \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|}\, dxdy - c^{\text{LO}}\int_{\mathbb{R}^d}\rho_\psi(x)^{4/3}\, dx$$

where $1.234 < c^{\text{LO}} \le 1.68$. For an alternative derivation, with a slight loss in the constants, see, for example, [119].

Ignoring the error terms and putting the above together, one is lead to the Thomas-Fermi energy functional

$$\begin{aligned}\mathcal{E}(\rho) = \mathcal{E}(\rho, Z, R) &= q^{-2/3}K_3^{TF}\int_{\mathbb{R}^3}\rho(x)^{5/3}\, dx - \int_{\mathbb{R}^3}V(x)\rho(x)\, dx \\ &+ \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|}\, dxdy\end{aligned} \tag{33}$$

with $V(x) = \sum_{n=1}^{M} \frac{Z_n}{|x-R_n|}$ for Coulomb matter. $N(\rho) = \int_{\mathbb{R}^3} \rho(x)\,dx = N$ is the number of electrons (although in this formulation it does not have to be an integer). The functional is well-defined on the spaces $S = \{\rho | \rho \geq 0, \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)\}$, $S_\lambda = \{\rho \in S | \int \rho(x)\,dx \leq \lambda\}$, and $S_{\partial\lambda} = \{\rho \in S | \int \rho(x)\,dx = \lambda\}$.

The Thomas-Fermi energy is given by

$$E^{TF}(N, Z, R) = \inf_{\rho} \{\mathcal{E}(\rho, Z, R) | \rho \in S_{\partial N}\}. \tag{34}$$

The catch with this definition is that $S_{\partial\lambda}$ is not a convex set. But for $N \leq \sum Z_n$, it is shown in [112], that the minimum over the convex set S_N exists and gives the same energy as $E^{TF}(N, R, Z)$. This follows from the strict convexity of the Thomas-Fermi functional.

One can show, see [112, 95] that for Coulomb matter the function $\lambda \to E^{TF}(\lambda, Z, R)$ is strictly convex on $[0, \sum Z_n]$ and constant if λ is bigger than the total charge of the nuclei. Moreover, for λ less or equal to the total charge, the minimizing density of the TF functional exists and is unique and is a solution of the so-called Thomas-Fermi equations.

The Thomas-Fermi energy functional and the Thomas-Fermi energy have a natural scaling. For any $\delta > 0$, let $\rho_\delta(x) = \delta^2 \rho(\delta^{1/3} x)$. Then

$$\mathcal{E}(\rho_\delta, \delta Z, \delta^{-1/3} R) = \delta^{7/3} \mathcal{E}(\rho, Z, R). \tag{35}$$

So for a Coulomb system with nuclear charges $Z = (Z_1, \ldots, Z_M)$ at positions $R = (R_1, \ldots, R_M)$, this implies the scaling law

$$E^{TF}(\delta N, \delta Z, \delta^{-1/3} R) = \delta^{7/3} E^{TF}(N, Z, R). \tag{36}$$

The main quantum mechanical limit theorem, proved by Lieb and Simon in [112] is that asymptotically, the Thomas-Fermi energy gives the correct answer for the ground state energy of atoms or molecules with a large nuclear charge.

Theorem 12 (Lieb and Simon 1977)**.**

$$\lim_{\delta\to\infty} \frac{E^Q_{\delta\lambda}(\delta Z, \delta^{-1/3} R)}{\delta^{7/3}} = E^{TF}(\lambda, Z, R).$$

Moreover, the quantum m-point densities, suitably rescaled, converge to a product $\rho(x_1)\ldots\rho(x_m)$ of Thomas Fermi densities. Originally, the above result was proved using a decomposition of the space into boxes together with Dirichlet Neumann decoupling techniques. Motivated by a result of Thirring, [163], Lieb used in [95] coherent states techniques.

In addition, much more is known by now about lower order terms in the asymptotic for large atoms and in part for molecules. The energy has the asymptotic

$$E^Q(Z,R) = -\alpha^{TF}\sum_n Z_n^{7/3} + \frac{1}{2}\sum_n Z_N^2 + c_1 Z^{5/3} + O(Z^{5/3-\varepsilon})$$

here α^{TF} is the Thomas-Fermi prediction. The second term in this asymptotic is the Scott correction, see [138], for molecules it was formulated in [95]. The second term asymptotic was established in a series of papers for atoms by Hughes [65] and Siedentop and Weikard [142, 143, 144]. For molecules it was established by Ivrii and Sigal [75], see also [158]. There are also some results on the convergence of suitably scaled ground-states, the so-called strong Scott conjecture, see [71, 72, 73]. The next higher correction due to Dirac and Schwinger was established for atoms in a monumental series of papers by Fefferman and Seco [52]. The Fefferman-Seco proof is a 2 step proof. First one reduces the problem, with an error less than $O(Z^{5/3-\varepsilon})$, to the study of an effective one-particle Hamiltonian which is given by the mean-field approximation. The second step then consists of a very detailed analysis of the bound states of this mean-field Hamiltonian. Based on his work on error bounds for the Hartree-Fock approximation in [5], Bach gave in [6] a much simpler proof of the first step, the reduction to the mean-field Hamiltonian. For a variation on Bach's proof, see [58]. Bach's proof also works for molecules and not only atoms, but the spectral properties of the mean-field Hamiltonian have been established to the needed accuracy only for atoms. In this case, the mean-field Hamiltonian is rotationally symmetric and the study of its bounds states, within accuracy of $O(Z^{5/3-\varepsilon})$, can be done by a quite delicate WKB analysis.

The above mentioned landmark paper of Simon and Lieb established many more interesting results for the Thomas Fermi theory of matter, for example, a rigorous treatment of the Thomas Fermi theory of solids. Also Teller's no-binding result for Thomas Fermi theory. It says that, taking the nucleus-nucleus repulsion into account, the Thomas-Fermi energy of a molecule is always bigger than the sum of the energies of the individual atoms. Thus binding, which is due to the outermost electrons in atoms, is not correctly described by TF theory.

For any nuclear charge vector $Z = (Z_1, \dots, Z_M)$ and positions of nuclei $R = (R_1, \dots, R_M)$ define

$$e^{TF}(\lambda, Z, R) = E^{TF}(\lambda, Z, R) + \sum_{n<m} \frac{Z_n Z_m}{|R_n - R_m|}$$

the energy with nucleus-nucleus repulsion. Then

Theorem 13 (Teller's no-binding theorem)**.** *For any strictly positive* $Z = (Z_1, \ldots, Z_M)$*, that is,* $Z_j >$ *for all* j*, and* R *and* $\lambda > 0$*, one has*

$$e^{TF}(\lambda, Z, R) > \min_{0 \le \lambda' \le \lambda} \left[e^{TF}(\lambda', Z_A, R_A) + e^{TF}(\lambda - \lambda', Z_B, R_B) \right]$$

for any decomposition $Z_A = (Z_1, \ldots, Z_k)$*,* $Z_B = (Z_{k+1}, \ldots, Z_M)$ *and similarly for* R_A *and* R_B*.*

This theorem is at the heart of the proof of stability of matter by Lieb and Thirring.

The no-binding lower bound and the behavior of the Thomas-Fermi energy in terms of λ together with scaling implies, in particular, that

$$e^{TF}(\lambda, Z, R) \ge \sum_{n=1}^{K} E^{TF}(Z_n, Z_n) = E^{TF}(1,1) \sum_{n=1}^{K} Z_n^{7/3}. \tag{37}$$

By scaling, one has

$$E^{TF}(1,1) = -\frac{\epsilon^{TF}}{K}.$$

with $K = q^{-2/3} K_3^{TF}$. Numerically, it is known that $\epsilon^{TF} = 2.21$. So with the classical value of K^{TF} and $q = 2$ for real electrons, one has $E^{TF}(1,1) \ge -0.385$.

On the other hand, it is known by now that molecules do bind in modifications of the Thomas-Fermi model, for example, the Thomas-Fermi-von Weizsäcker model, as was established by Catto and Lions [25].

2.3. **Stability of matter.** Following Lieb and Thirring, Teller's no-binding theorem for Thomas Fermi theory and the kinetic energy lower bound in Theorem 1 has a beautiful application to the Stability-of-Matter problem. A basic fact of astrophysics claims that bulk matter undergoes gravitational collapse in the absence of nuclear forces. Onsager asked in the 1930's why bulk matter does not undergo an electrostatic collapse, too. This is due to the Pauli principle. The first proof of this fact is due to Dyson and Lennard in the 1960's [33, 34]. However their proof was rather complicated.

On the other hand, this defect of Thomas-Fermi theory is in turn a chance to give a physically motivated and very appealing proof of stability of quantum mechanical matter, as soon as one can give a lower bound of the quantum mechanical energy of an antisymmetric N-fermion wave function ψ in terms of the Thomas Fermi energy of its one-particle density ρ_ψ. The lower bound provided in Theorem 1 was the main tool of Lieb and Thirring [114], leading to a much simpler proof of stability of matter than the original one by Dyson and Lennard. At the same time, by relating the stability of matter question to the Thomas-Fermi model, it provided considerable new physical insight in the mechanism which prevents this collapse. (See [93, 100, 101] for a nice presentation of the physical and mathematical aspects of this problem.) Also, it turned out that not only the existence of these bounds, but good estimates on the constants in these inequalities are of considerable importance for a rigorous understanding of the properties of matter [27, 44, 45, 61]

We will only sketch this application here. Note that the kinetic energy lower bound and the Lieb-Oxford bound give the following lower bound for the quantum mechanical energy

$$\langle\psi, (H_C + V_{nn})\psi\rangle \geq \mathcal{E}^{TF}_K(\rho_\psi) - c^{\mathrm{LO}} \int \rho_\psi(x)^{4/3}\, dx.$$

Here $\mathcal{E}^{TF}_K$ is the Thomas-Fermi functional with K^{TF} in the kinetic energy term replaced by $(qC_{1,d})^{-2/3}K^{TF}$. Recall that $q = 2$ for electrons, $c^{\mathrm{LO}} \leq 1.68$, and that the equality $C_{1,d} = 1$ is a longstanding open conjecture. The best known bounds so far say that $C_{1,d} \leq 2$.

Using Hölder's inequality, one has

$$\int \rho_\psi(x)^{4/3}\, dx \leq \Big(\int \rho_\psi(x)\, dx\Big)^{1/2}\Big(\int \rho_\psi(x)^{5/3}\, dx\Big)^{1/2} \leq \frac{\tilde\gamma}{4}N + \frac{1}{\tilde\gamma}\int \rho_\psi(x)^{5/3}\, dx$$

for any $\tilde\gamma > 0$. Thus, with $\tilde\gamma = c^{\mathrm{LO}}\gamma$,

$$\begin{aligned}\langle\psi, (H_C + V_{nn})\psi\rangle &\geq \mathcal{E}^{TF}_K(\rho_\psi) - \frac{(c^{\mathrm{LO}})^2}{4}\gamma N - \frac{1}{\gamma}\int \rho_\psi(x)^{5/3}\, dx \\ &= \mathcal{E}^{TF}_{K-1/\gamma}(\rho_\psi) - \frac{(c^{\mathrm{LO}})^2}{4}\gamma N.\end{aligned}$$

Taking the no-binding result of Thomas-Fermi theory into account the right hand side is bound below by

$$-\frac{\epsilon^{TF}}{K-1/\gamma}\sum_n Z_n^{7/3} - \frac{(c^{\mathrm{LO}})^2}{4}\gamma N = -\epsilon^{TF} N\Big(\frac{1}{K-1/\gamma}\frac{\sum_n Z_n^{7/3}}{N} - c\gamma\Big)$$

with $c = (c^{\mathrm{LO}})^2/(4\epsilon^{TF}) < 0.3193$. Maximizing w.r.t. γ leads to the bound

$$\langle\psi, (H_C + V_{nn})\psi\rangle \geq -(qC_{1,3})^{2/3}\frac{\epsilon^{TF}}{K^{TF}} N\Big(\sqrt{c} + \sqrt{\sum_n Z_n^{7/3}/N}\Big)^2$$

Using this, together with the easy bound $2ab \leq a^2 + b^2$ one gets

$$\langle\psi, (H_C + V_{nn})\psi\rangle \geq -(qC_{1,3})^{2/3}\frac{\epsilon^{TF}}{K^{TF}}\big(1+c\big)\big(N + \sum_n Z_n^{7/3}\big)$$

which, in the case of real fermions with $q = 2$, the estimates $C_{1,3} \leq 2$, and $c \leq 0.3193$ gives

$$\langle \psi, (H_C + V_{nn})\psi\rangle \geq -0.804\big(N + \sum_n Z_n^{7/3}\big). \tag{38}$$

As shown by Thirring, [163], it is also known that, asymptotically, Thomas-Fermi theory is, indeed, the correct lower bound for the stability of matter result,

$$\langle \psi, (H_C + V_{nn})\psi\rangle \geq -0.385 \sum_{n=1}^{K} Z_n^{7/3}(1 + O(Z_n^{-2/33}),$$

where the constants in the error term $O(Z_n^{-2/33})$ depend on the number of electrons. Somewhat better error estimates were established in [120]. In particular, the robust estimate in (38) is not far from the truth. Note also that, following the route leading to (38), the best possible lower estimate for the Coulomb energy is $-0.5078(N + \sum_n Z_n^{7/3})$ (using the conjectured value $C_{1,3} = 1$ and $q = 2$).

Remark 14. On can also use Thomas-Fermi theory to get a lower bound for the electron-electron repulsion: Reshuffling the terms in the stability result for Thomas-Fermi theory[13],

$$\frac{1}{\gamma}\int \rho^{5/3}\,dx - \sum_{j=1}^{N}\int \frac{1}{|x_j - y|}\rho(y)\,dy + D(\rho,\rho) + \sum_{1<i<j<N} \frac{1}{|x_j - x_i|} \geq -\epsilon^{TF}\gamma N,$$

gives

$$\sum_{1<i<j<N} \frac{1}{|x_j - x_i|} \geq \sum_{j=1}^{N}\int \frac{1}{|x_j - y|}\rho(y)\,dy - D(\rho,\rho) - \epsilon^{TF}\gamma N - \frac{1}{\gamma}\int \rho^{5/3}\,dx.$$

Noting $\langle \psi, \sum_{j=1}^{N}\int \frac{1}{|x_j-y|}\rho(y)\,dy\psi\rangle = 2D(\rho_\psi,\rho)$ and choosing $\rho = \rho_\psi$ one sees

$$\langle \psi, \sum_{i<j} \frac{1}{|x_i - x_j|}\psi\rangle \geq D(\rho_\psi,\rho_\psi) - \epsilon^{TF}\gamma N - \frac{1}{\gamma}\int \rho_\psi^{5/3}\,dx.$$

This way one get's the lower bound

$$\langle \psi, (H_C + V_{nn})\psi\rangle \geq -\frac{\epsilon^{TF}}{K} N\big(1 + \sqrt{\sum_n Z_n^{7/3}/N}\big)^2$$

Again, using Cauchy-Schwartz, a similar lower bound as before follows from this, with the factor $1 + c$ replaced by 2. The "best possible" lower bound

[13]This was the route originally taken by Lieb and Thirring in [114]

for the energy of real matter this way is

$$\langle \psi, (H_C + V_{nn})\psi\rangle \geq -0.77(N + \sum_n Z_n^{7/3}),$$

see, for example [20, 121], which should be compared with (38). Of course, this is not best possible, since, as demonstrated above, using the Lieb-Oxford bound improves the estimate quite a bit.

We will not discuss other approaches to this circle of problems, [59, 60, 43], nor the extension of the stability results to other models of real matter, for example, the Pauli operator, [54, 104, 107, 46, 47], or relativistic models, [50, 117, 118, 108, 109, 110], and, more recently, matter interacting with quantized electromagnetic fields, [48, 49, 105, 106], but point the interested reader to the excellent reviews by Lieb [102, 103]. There is also a growing literature on stability/instability of the relativistic electron–positron field in Hartree-Fock approximation, see, for example, [7, 8, 9, 21, 63, 64, 69].

3. More on bound states for atoms

It is known that an N-electron Coulomb system has a bound state as long as the number of electrons is lower than the total charge of the nuclei (plus one). This is known as Zhislin's theorem [172]. In nature, one can observe once negatively charged free atoms, but not twice or more negatively charged atoms. Formulated conservatively, one expects the maximal negative ionization to be independent of the nucleus charge Z. This is known as the ionization conjecture, see, e.g., the review article by Simon [153]. For a more precise form of this conjecture, let

$$H_{N,Z} = \sum_{j=1}^{N} \big(-\Delta_j - \frac{Z}{|x_j|}\big) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} \tag{39}$$

be the Hamiltonian for N electrons in the field of an atom of charge Z. For fermions, the Hilbert space $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$.

Define

$$E(N,Z) = \inf \sigma(H_{N,Z}) \tag{40}$$

and the ionization energy

$$I = I(N,Z) = \inf \sigma_{\mathrm{ess}}(H_{N,Z}) - \inf \sigma(H_{N,Z}). \tag{41}$$

By the HVZ theorem, $\sigma_{\mathrm{ess}}(H_N, Z) = [E(N-1,Z), \infty)$, so

$$I(N,Z) = E(N-1,Z) - E(N,Z).$$

Note that $H_{N,Z}$ has a bound state, a discrete eigenvalue below its essential spectrum, if and only if $I(N,Z) > 0$.

Due to electrostatic reasons, one expects that there should be an $N_{\text{cr}}(Z)$ such that

$$E(N,Z) = E(N-1,Z) \quad \text{for all } N \geq N_{\text{cr}}(Z).$$

that is, the atom can bind only a finite number of electrons. The picture is not that simple, however. Heuristically, ignoring all many-body effects, the potential felt by the N^{th} electron is given by the effective potential

$$U_{\text{eff}}(x) = -\frac{Z}{|x|} + \int \frac{1}{|x-y|}\rho_\psi(y)\,dy \tag{42}$$

where ρ_ψ is the single-particle density of the other $N-1$ electrons. The physics of the system should be somehow described by the effective Hamiltonian

$$H_{\text{eff}} = -\Delta + U_{\text{eff}}. \tag{43}$$

When N increases, ρ_ψ increases and hence U_{eff} should increase at least in some average sense. Moreover, when $N > Z$, Newton's theorem implies $U_{\text{eff}}(x) > 0$ for large x. But for x near zero, U_{eff} is very negative since due to the uncertainty principle, the electrons cannot concentrate too much close to zero. Hence the attraction of the nucleus is never fully screened. Nevertheless, eventually, U_{eff} will cease to have a bound state.

Note that there is a big difference between fermions and bosons from this viewpoint: Whereas in order to bind N bosonic "electrons" the effective one-particle Hamiltonian should have at least one bound state, for fermionic systems, due to the Pauli principle, if one wants to bind N electrons the effective one particle Hamiltonian needs to have at least N bound states. For real atoms, this N^{th} bound state seems to disappear precisely when $N \sim Z+1$. Bosons, however, should be much more easily bound to an atom than fermions.

Thus, one expects the atomic Hamiltonian (39) not to have a bound state if $N > N_{\text{cr}} = Z + Q$, where Z is the total charge of the nucleus and $Q > 0$ some fixed positive number, hopefully of the order of one.

This innocent looking conjecture, known as the ionization conjecture, see, e.g., the review article by Simon [153], has withstood all attempts to prove it, even for very large but fixed excess charge Q. Only partial results are known.

3.1. **Ruskai-Sigal type results.** We are far from understanding the ionization conjecture rigorously, at least for fermions. One of the first results in this direction is the result by Ruskai [132, 133] and Sigal [140, 141].

Theorem 15 (Ruskai, Sigal)**.** *For any Z there exist $N_{cr}(Z)$ such that*

$$I(N,Z) = E(N-1,Z) - E(N,Z) = 0$$

for all $N \geq N_{cr}(Z)$. In addition, for fermions, one has the bound

$$\limsup_{Z\to\infty} \frac{N_{cr}(Z)}{Z} \leq 2.$$

This theorem was proven independently by Ruskai [132, 133] and Sigal [140, 141]. A huge improvement of this theorem is due to Lieb. He showed

Theorem 16 (Lieb, 1984 [99]). *Independently of the statistics of the particles,*

$$N_{cr}(Z) < 2Z + 1$$

In fact, Lieb also treats molecules and other refinements like magnetic fields and relativistic kinetic energies, see also Ichinose [74].

Another improvement of the Ruskai-Sigal bound is given by Lieb, Sigal, Simon and Thirring, [116]. They showed that large atoms are asymptotically neutral,

$$\lim_{Z\to\infty} \frac{N_{\mathrm{cr}}(Z)}{Z} = 1. \tag{44}$$

Unfortunately, their proof used a compactness argument in the construction of suitable localizing functions and did not give any quantitative information or error estimates for finite nuclear charges Z. The first quantitative result seems to have been given by Fefferman and Seco in 1990. They proved

Theorem 17 (Fefferman and Seco 1990, [51]).

$$N_{cr}(Z) \leq Z + O(Z^\alpha) \quad \text{with } \alpha = \frac{47}{56}.$$

Shortly afterwards, this approach was simplified by Sigal, Seco, and Solovej [139] who gave the estimate

Theorem 18. *One has the bound*

$$I(N, Z) \leq C_1 Z^{4\alpha/3} - C_2(N - Z)Z^{\alpha/3}$$

for the ionization energy and as a consequence also

$$N_{cr}(Z) \leq Z + CZ^\alpha.$$

Here $\alpha = 47/56$ as in the Fefferman-Seco theorem.

Nevertheless, these bounds are still far from the (expected) truth, since $N_{\mathrm{cr}}(Z) - Z$ and $I(Z, Z)$ should be bounded in Z.

3.2. **Existence of highly negative ions for bosonic atoms.** As discussed above, for an atom to bind N electrons, the effective one particle Hamiltonian $H_{\rm eff}$ should have at least N bound states. For bosons, however, it is enough that it has at least *one* bound state. Thus a "bosonic" atom should be able to bind many more particles than one might naively expect from purely electrostatic reasons. This is indeed the case,

Theorem 19 (Benguria and Lieb, [12])**.** *For bosonic atoms*

$$\liminf_{Z\to\infty} \frac{N_{cr}(Z)}{Z} \geq 1+\gamma$$

Here $0<\gamma<1$ is defined via the ground state of the Hartree functional: Let ψ be the unique positive solution of the non-linear Hartree equation

$$-\Delta\psi - \Big(\frac{Z}{|x|} - |\psi|^2 * \Big)\psi = 0.$$

Then

$$(1+\gamma)Z = \int_{\mathbb{R}^3} |\psi(x)|^2\, dx.$$

Benguria, see [95] for a reference, showed that $0<\gamma<1$. Moreover, numerically it is known that $\gamma = 0.21$, see [11].

Later, Solovej proved a corresponding upper bound using similar ideas as in [139],

Theorem 20 (Solovej 1990,[156])**.** *For bosonic atoms*

$$N_{cr}(Z) \leq (1+\gamma)Z + CZ^{7/9}.$$

In particular,

$$\lim_{Z\to\infty} \frac{N_{cr}(Z)}{Z} = 1+\gamma.$$

3.3. **Solution of the ionization conjecture in Hartree-Fock theory.** In Hartree-Fock theory (or better in the Hartree-Fock approximation) one does not consider the full N-body Hilbert space $\bigwedge^N L^2(\mathbb{R}^3,\mathbb{C}^2)$, but restricts the attention to pure Slater determinants

$$\psi = v_1\wedge \ldots \wedge v_N \tag{45}$$

where the single particle orbitals $v_j \in L^2(\mathbb{R}^3, C^2)$. In other words, the *density matrix*

(46)

$$\gamma_\psi(x,\alpha,y,\beta) = \sum_\sigma \int\cdots\int \overline{\psi(x,\alpha,x_2,\sigma_2,\ldots,x_N,\sigma_N)}\psi(y,\beta,x_2,\sigma_2,\ldots,x_n,\sigma_N)\, dx_2\ldots dx_N$$

is assumed to be a projection operator. Note that in general, for arbitrary $\psi \in \bigwedge L^2(\mathbb{R}^3, \mathbb{C}^2)$, is a bounded operator with $0 \le \gamma_\psi \le \mathbf{1}$ on $L^2(\mathbb{R}^3, \mathbb{C}^2)$.

The Hartree-Fock energy of an atom of charge Z with N electrons is then defined to be

$$E^{\mathrm{HF}} = E^{\mathrm{HF}}(N, Z) = \inf_{\substack{\gamma_\psi^2 = \gamma_\psi \\ \langle \psi, \psi \rangle = 1}} \langle \psi, H_{N,Z} \psi \rangle. \tag{47}$$

A little bit of calculation shows that for Slater determinants ψ

$$\langle \psi, H_{N,Z} \psi \rangle = \mathcal{E}^{\mathrm{HF}}(\gamma_\psi)$$

with

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \mathrm{tr}_{L^2(\mathbb{R}^3, \mathbb{C}^2)} \big(-\Delta - \frac{Z}{|x|} \big) + D(\gamma) - Ex(\gamma) \tag{48}$$

where

$$D(\gamma) = \frac{1}{2} \iint \frac{\mathrm{tr}_{\mathbb{C}^2}(\gamma(x,x)\gamma(y,y))}{|x-y|} \, dxdy$$

is the direct part of the Coulomb energy and

$$Ex(\gamma) = \frac{1}{2} \iint \frac{\mathrm{tr}_{\mathbb{C}^2} |\gamma(x,y)|^2}{|x-y|} \, dxdy$$

the exchange term. In particular,

$$E^{\mathrm{HF}}(\gamma) = \inf \big\{ \mathcal{E}^{\mathrm{HF}}(\gamma) | \, \gamma^* \gamma = \gamma, \mathrm{tr}\, \gamma = N \big\}.$$

The existence of a minimizing projection operator γ for $N < Z+1$ was proven by Lieb and Simon, [113]. Moreover, given the Hartree-Fock functional, one can relax the assumption that γ is a projection operator, as was shown by Lieb, [96]

$$E^{\mathrm{HF}}(N, Z) = \inf \big\{ \mathcal{E}^{\mathrm{HF}}(\gamma) | 0 \le \gamma \le \mathbf{1}, \mathrm{tr}(\gamma) = N \big\}.$$

For a simple proof of this see [5].

For the Hartree-Fock approximation, Solovej gave a proof showing the ionization energy and maximum surcharge an atom can bind to be bounded uniformly in Z.

Theorem 21 (Solovej 2003, [157])**.** *For a neutral atom, the ionization energy in Hartree-Fock approximation is bounded, that is,*

$$I^{HF}(Z, Z) = E^{HF}(Z-1, Z) - E^{HF}(Z, Z) = O(1) \quad \text{as } Z \to \infty.$$

Moreover, there exists a finite $Q > 0$ such that for all $N \ge Z + Q$ there are no minimizers for the Hartree-Fock functional among N-dimensional projections.

A related result for the Thomas-Fermi-von Weizsäcker model was shown in [13]. Unfortunately, all results of this precise form are so far for models which shed no light on the Schrödinger case.

References

[1] F. Ahia: *Finiteness of the discrete spectrum of ($N \geq 3$) N-body Schrödinger operators, which have some determinate subsystems that are virtual at the bottom of the continuum.* J. Math. Phys. **33** (1992), no. 1, 189–202.

[2] M. Aizenmann and E. H. Lieb: *On semi-classical bounds for eigenvalues of Schrödinger operators.* Phys. Lett. **66A** (1978), 427–429.

[3] S. Albeverio,R. Høegh-Krohn, and T. S. Wu: *A class of exactly solvable three-body quantum mechanical problems and the universal low energy behavior.* Phys. Lett. A **83** (1981), no. 3, 105–109.

[4] M. A. Antonec, G.M. Žhislin, and I. A. Šereševskiĭ: *Discrete spectrum of the Hamiltonian of a quantum N-particle system.* (Russian. English summary) Teoret. Mat. Fiz. **16** (1973), no. 2, 235–246. {English translation: Theoret. and Math. Phys. **16** (1973), no. 2, 800–809 (1974).}

[5] V. Bach: *Error bound for the Hartree-Fock energy of atoms and molecules.* Comm. Math. Phys. **147** (1992), no. 3, 527–548.

[6] V. Bach: *Accuracy of mean field approximations for atoms and molecules.* Comm. Math. Phys. **155** (1993), no. 3, 295–310.

[7] V. Bach, J.-M. Barbaroux, B. Helffer, and H. Siedentop: *Stability of matter for the Hartree-Fock functional of the relativistic electron-positron field.* Doc. Math. **3** (1998), 353–364 (electronic).

[8] V. Bach, J.-M. Barbaroux, B. Helffer, and H. Siedentop: *On the stability of the relativistic electron-positron field.* Comm. Math. Phys. **201** (1999), no. 2, 445–460.

[9] J.-M. Barbaroux, W. Farkas, B. Helffer, and H. Siedentop: *On the Hartree-Fock equations of the electron–positron field.* Comm. Math. Phys. **255** (2005), no. 1, 131–159.

[10] B. Baumgärtner: *The Thomas-Fermi-theory as result of a strong-coupling-limit.* Comm. Math. Phys. *47* (1976), no. 3, 215–219.

[11] B. Baumgärtner: *On Thomas-Fermi-von Weizsäcker and Hartree energies as functions of the degree of ionisation.* J. Phys. A **17** (1984), no. 8, 1593–1601.

[12] R. Benguria and E. H. Lieb: *Proof of the Stability of Highly Negative Ions in the Absence of the Pauli Principle.* Phys. Rev. Lett. **50** (1983), 1771–1774.

[13] R. Benguria and E. H. Lieb: *The most negative ion in the Thomas-Fermi-von Weizsäcker theory of atoms and molecules.* J. Phys. B **18** (1985), no. 6, 1045–1059.

[14] R. Benguria and M. Loss: *A simple proof of a theorem of Laptev and Weidl.* Math. Res. Lett. **7** (2000), no. 2-3, 195–203.

[15] R. Benguria and M. Loss: *Connection between the Lieb-Thirring conjecture for Schrödinger operators and an isoperimetric problem for ovals on the plane.* In Partial differential equations and inverse problems, 53–61, Contemp. Math., **362**, Amer. Math. Soc., Providence, RI, 2004.

[16] M. S. Birman: *The spectrum of singular boundary problems.* Mat. Sb. **55** (1961), no. 2 , 125–174, translated in Amer. Math. Soc. Trans. (2) **53** (1966), 23–80.

[17] M. S. Birman and V. V. Borzov: *The asymptotic behavior of the discrete spectrum of certain singular differential operators.* (Russian) Problems of mathematical physics,

No. 5: spectral theory (Russian), pp. 24–38. Izdat. Leningrad. Univ., Leningrad, 1971.

[18] M. Sh. Birman and M. Z. Solomyak: *Piecewise polynomial approximations of functions of classes* ${W_p}^\alpha$. (Russian) Mat. Sb. (N.S.) **73 (115)** (1967), 331–355.

[19] M. Sh. Birman and M. Z. Solomyak: *Schrödinger operator. Estimates for number of bound states as function-theoretical problem.* Spectral theory of operators (Novgorod, 1989), 1–54. Amer. Math. Soc. Transl. Ser. 2, **150**, Amer. Math. Soc., Providence, RI, 1992.

[20] Ph. Blanchard and J. Stubbe: *Bound states for Schrödinger Hamiltonians: phase space methods and applications.* Rev. Math. Phys. **8** (1996), no. 4, 503–547.

[21] R. Brummelhuis, N. Röhrl, and H. Siedentop: *Stability of the relativistic electron–positron field of atoms in Hartree-Fock approximation: heavy elements.* Doc. Math. **6** (2001), 1–9 (electronic).

[22] V. S. Buslaev and L. D. Faddeev: *Formulas for traces for a singular Sturm-Liouville differential operator.* (Russian) Dokl. Akad. Nauk SSSR 132 13–16 (Russian); translated in Soviet Math. Dokl. **1** (1960), 451–454.

[23] E. A. Carlen and M. Loss: *Extremals of functionals with competing symmetries.* J. Funct. Anal. **88** (1990), no. 2, 437–456.

[24] E. A. Carlen and M. Loss: *Competing symmetries of some functionals arising in mathematical physics.* Stochastic processes, physics and geometry (Ascona and Locarno, 1988), 277–288, World Sci. Publishing, Teaneck, NJ, 1990.

[25] I. Catto and P.-L. Lions: *Binding of atoms and stability of molecules in Hartree and Thomas-Fermi type theories.*
Part 1: *A necessary and sufficient condition for the stability of general molecular systems*, C.P.D.E., **17** (1992), no. 7/8, 1051–1110.
Part 2: *Stability is equivalent to the binding of neutral subsystems,* C.P.D.E., **18** (1993), no. 1/2, 305–354.
Part 3: *Binding of neutral subsystems,* C.P.D.E., **18** (1993), no. 3/4, 381–429.
Part 4: *Binding of neutral systems for the Hartree model*, C.P.D.E. **18** (1993), no. 7/8, 1149–1159.

[26] J. G. Conlon: *A new proof of the Cwikel-Lieb-Rosenbljum bound.* Rocky Mountain J. Math. **15** (1985), no. 1, 117–122.

[27] J. G. Conlon, E. H. Lieb, and H.-T. Yau: *The Coulomb gas at low temperature and low density.* Comm. Math. Phys. **125** (1989), no. 1, 153–180.

[28] P. Constantin and C. Foias: *Navier-Stokes Equations.* Chicago Lectures in Mathematics. University of Chicago Press, Chicago 1988.

[29] M. M. Crum: *Associated Sturm-Liouville systems.* Quart. J. Math. Oxford Ser. (2) **6** (1955), 121–127.

[30] M. Cwikel: *Weak type estimates for singular values and the number of bound states of Schrödinger operators.* Ann. Math. **106** (1977), no. 1, 93–100.

[31] P. Deift: *Applications of a commutation formula.* Duke Math. J. **45** (1978), no. 2, 267–310.

[32] P. Deift and R. Killip: *On the absolutely continuous spectrum of one-dimensional Schrödinger operators with square summable potentials.* Comm. Math. Phys. **203** (1999), no. 2, 341–347.

[33] F. Dyson and A. Lennard: *Stability of matter I.* J. Math. Phys. **8** (1967), 423–434.

[34] F. Dyson and A. Lennard: *Stability of matter II.* J. Math. Phys. **9** (1967), 698–711.

[35] A. Eden and C. Foias: *A simple proof of the generalized Lieb-Thirring inequalities in one-space dimension.* J. Math. Anal. Appl. **162** (1991), no. 1, 250–254.

[36] V. Efimov: *Energy levels arising from resonant two-body forces in a three-body system.* Phys. Lett. B **33** (1970), 563–564.

[37] T. Ekholm and R. Frank: *On Lieb-Thirring inequalities for operators with virtual level.* To appear in Commun. Math. Phys.

[38] T. Ekholm and H. Kovarik: *Stability of the magnetic Schrödinger operator in a waveguide.* Commun. Partial Differential Equations **30** (2005), no. 4, 539–565.

[39] Ł. Erdős: *Recent developments in quantum mechanics with magentic fields.* Preprint 2006.

[40] Evans, W. D.(4-WALC); Lewis, Roger T.(1-AL2) *N-body Schrödinger operators with finitely many bound states.* Trans. Amer. Math. Soc. **322** (1990), no. 2, 593–626.

[41] P. Exner, H. Linde, and T. Weidl: *Lieb-Thirring inequalities for geometrically induced bound states.* Lett. Math. Phys. **70** (2004), no. 1, 83–95.

[42] P. Exner and T. Weidl: *Lieb–Thirring inequalities on trapped modes in quantum wires.* In: Proc. XIII Internat. Congr. Math. Phys. (London 2000), International Press, Boston, 2001, 437–443.

[43] P. Federbush: *A new approach to the stability of matter problem. I, II.* J. Mathematical Phys. **16** (1975), 347–351; ibid. **16** (1975), 706–709.

[44] C. Fefferman: *The N-body problem in quantum mechanics.* Frontiers of the mathematical sciences: 1985 (New York, 1985). Comm. Pure Appl. Math. **39** (1986), no. S, suppl., S67–S109.

[45] C. Fefferman: *The atomic and molecular nature of matter.* Rev. Mat. Iberoamericana **1** (1985), no. 1, 1–44.

[46] C. Fefferman: *Stability of Coulomb systems in a magnetic field.* Proc. Nat. Acad. Sci. U.S.A. **92** (1995), no. 11, 5006–5007.

[47] C. Fefferman: *On electrons and nuclei in a magnetic field.* Adv. Math. **124** (1996), no. 1, 100–153.

[48] C. Fefferman, J. Fröhlich, and G. M. Graf: *Stability of nonrelativistic quantum mechanical matter coupled to the (ultraviolet cutoff) radiation field.* Proc. Nat. Acad. Sci. U.S.A. **93** (1996), no. 26, 15009–15011 (electronic).

[49] C. Fefferman, J. Fröhlich, and G. M. Graf: *Stability of ultraviolet-cutoff quantum electrodynamics with non-relativistic matter.* Comm. Math. Phys. **190** (1997), no. 2, 309–330.

[50] C. Fefferman and R. de la Llave: *Relativistic stability of matter. I.* Rev. Mat. Iberoamericana **2** (1986), no. 1-2, 119–213.

[51] C. Fefferman and L. A. Seco: *Asymptotic neutrality of large ions.* Comm. Math. Phys. **128** (1990), no. 1, 109–130.

[52] C. Fefferman and L. A. Seco: *On the energy of a large atom.* Bull. Amer. Math. Soc. (N.S.) **23** (1990), no. 2, 525–530.
Aperiodicity of the Hamiltonian flow in the Thomas-Fermi potential. Rev. Mat. Iberoamericana **9** (1993), no. 3, 409–551.
On the Dirac and Schwinger corrections to the ground-state energy of an atom. Adv. Math. **107** (1994), no. 1, 1–185.
The density in a one-dimensional potential. Adv. Math. **107** (1994), no. 2, 187–364.
The eigenvalue sum for a one-dimensional potential. Adv. Math. **108** (1994), no. 2, 263–335.
The density in a three-dimensional radial potential. Adv. Math. **111** (1995), no. 1,

88–161. *Weyl sums and atomic energy oscillations.* Rev. Mat. Iberoamericana **11** (1995), no. 1, 165–226.
The eigenvalue sum for a three-dimensional radial potential. Adv. Math. **119** (1996), no. 1, 26–116.

[53] C. Foias, O. Manley, and R. Temam: *Attractors for the Bnard problem: existence and physical bounds on their fractal dimension.* Nonlinear Anal. **11** (1987), no. 8, 939–967.

[54] J. Fröhlich, E. H. Lieb, and M. Loss: *Stability of Coulomb systems with magnetic fields. I. The one-electron atom.* Comm. Math. Phys. **104** (1986), no. 2, 251–270.

[55] C. S. Gardner, J. M. Greene, M. D. Kruskal, and R. M. Miura: *Korteweg-deVries equation and generalization. VI. Methods for exact solution.* Comm. Pure Appl. Math. **27** (1974), 97–133.

[56] V. Glaser, H. Grosse, A. Martin, and W. Thirring: *A family of optimal conditions for the absence of bound states in a potential.* Studies in Math. Phys., Essays in Honor of Valentine Bargmann, Princeton University Press, New Jersey (1976).

[57] J.-M. Ghidaglia, M. Marion, and R. Temam: *Generalization of the Sobolev-Lieb-Thirring inequalities and applications to the dimension of attractors.* Differential Integral Equations **1** (1988), no. 1, 1–21.

[58] G. M. Graf and J.-Ph. Solovej: *A correlation estimate with applications to quantum systems with Coulomb interactions.* Rev. Math. Phys. **6**, no. 5A, 977-997.

[59] G. M. Graf: *Stability of matter through an electrostatic inequality.* Papers honouring the 60th birthday of Klaus Hepp and of Walter Hunziker, Part II (Zü"rich, 1995). Helv. Phys. Acta **70** (1997), no. 1-2, 72–79.

[60] G. M. Graf: *Stability of matter in classical and quantized fields.* Proceedings of the International Congress of Mathematicians, Vol. III (Berlin, 1998). Doc. Math. 1998, Extra Vol. III, 153–162 (electronic).

[61] G. M. Graf and D. Schenker: *On the molecular limit of Coulomb gases.* Comm. Math. Phys. **174** (1995), no. 1, 215–227.

[62] B. Helffer and D. Robert: *Riesz means of bound states and semi-classical limit connected with a Lieb-Thirring conjecture. I, II.* Asymptotic Anal. **3** (1990), no. 2, 91–103. Ann. Inst. H. Poincaré Phys. Théor. **53** no. 2 (1990), 139–147.

[63] C. Hainzl, M. Lewin, and E. Séré: *Existence of a stable polarized vacuum in the Bogoliubov-Dirac-Fock approximation.* Comm. Math. Phys. **257** (2005), no. 3, 515–562.

[64] C. Hainzl, M. Lewin, and J. Ph. Solovej: *Mean-field approximation in Quantum Electrodynamics. The no-photon case.* Preprint 2005.

[65] W. Hughes: *An atomic energy lower bound that agrees with Scott's corrections.* Adv. Math. **79** (1990), no. 2, 213–270.

[66] D. Hundertmark: *On the number of bound states for Schrödinger operators with operator-valued potentials.* Arkiv för matematik **40** (2002), 73-87.

[67] D. Hundertmark, A. Laptev, and T. Weidl: *New bounds on the Lieb-Thirring constant.* Invent. Math. **140** no. 3 (2000), 693–704.

[68] D. Hundertmark, E. H. Lieb, and L. E. Thomas: *A sharp bound for an eigenvalue moment of the one-dimensional Schrödinger operator.* Adv. Theor. Math. Phys. **2**, no. 4 (1998), 719–731.

[69] D. Hundertmark, N. Röhrl, and H. Siedentop: *The sharp bound on the stability of the relativistic electron–positron field in Hartree-Fock approximation.* Comm. Math. Phys. **211** (2000), no. 3, 629–642.

[70] D. Hundertmark and B. Simon: *Lieb-Thirring inequalities for Jacobi matrices.* J. Approx. Theory **118**, no. 1, 106–130.

[71] A. Iantchenko, *The electron density in intermediate scales.* Comm. Math. Phys. **184** (1997), no. 2, 367–385.

[72] A. Iantchenko, E. H. Lieb, and H. Siedentop: *Proof of a conjecture about atomic and molecular cores related to Scott's correction.* J. Reine Angew. Math. **472** (1996), 177–195.

[73] A. Iantchenko and H. Siedentop: *Asymptotic behavior of the one-particle density matrix of atoms at distances Z^{-1} from the nucleus.* Math. Z. **236** (2001), no. 4, 787–796.

[74] T. Ichinose: *Note on the kinetic energy inequality leading to Lieb's negative ionization upper bound.* Lett. Math. Phys. **28** (1993), no. 3, 219–230.

[75] V. Ja. Ivrii and I. M. Sigal: *Asymptotics of the ground state energies of large Coulomb systems.* Ann. of Math. (2) **138** (1993), no. 2, 243–335.

[76] M. Kac: *On the asymptotic number of bound states for certain attractive potentials.* Pages 159–167, in Topics in Functional Analysis, I. Gohberg and M. Kac, eds., Academic Press, New York,1978.

[77] J. Keller: *Lower bounds and isoperimetric inequalities for eigenvalues of the Schrödinger equation.* J. Math. Phys. **2** (1961), 262–266.

[78] R. Killip and B. Simon: *Sum rules for Jacobi matrices and their applications to spectral theory.* Annals of Math. **158** (2003), 253–321.

[79] R. Killip and B. Simon: *Sum rules and spectral measures of Schrödinger operators with L^2 potentials.* Preprint 2006.

[80] A. Kiselev, Y. Last, and B. Simon: *Modified Prüfer and EFGP transforms and the spectral analysis of one-dimensional Schrödinger operators.* Commun. Math. Phys. **194** (1998), 1–45.

[81] M. Klaus: *On the bound state of Schrödinger operators in one dimension.* Ann. Physics **108** (1977), no. 2, 288–300.

[82] M. Klaus and B. Simon: *Coupling constant thresholds in nonrelativistic quantum mechanics. II. Two-cluster thresholds in N-body systems.* Comm. Math. Phys. **78** (1980/81), no. 2, 153–168.

[83] S. Kupin: *Spectral properties of Jacobi matrices and sum rules of special form.* J. Funct. Anal. **227** (2005), no. 1, 1–29.

[84] P. Kuchment: *Quantum graphs: I. Some basic structures.* Waves Random Media **14** (2004), S107–S128.

[85] L. D. Landau and E. M. Lifshitz: *Quantum Mechanics. Non-relativistic theory.* Volume **3** of Course of Theoretical Physics, Pergamon Press 1958.

[86] A. Laptev: *Dirichlet and Neumann eigenvalue problems on domains in Euclidian spaces.* J. Funct. Anal. **151** (1997), 531–545.

[87] A. Laptev: Private communication.

[88] A. Laptev and T. Weidl: *Sharp Lieb-Thirring inequalities in high dimensions.* Acta Math. **184** (2000), no. 1, 87–111.

[89] A. Laptev and T. Weidl: *Recent results on Lieb-Thirring inequalities.* Journées "Équation aux dérivées partielles" (La Chapelle sur Erdre, 2000), Exp. No. **10**, 14 pp., Univ. Nantes, Nantes, 2000.

[90] D. Levin and M. Z. Solomyak: *The Rozenblum-Lieb-Cwikel inequality for Markov generators.* J. Anal. Math. **71** (1997), 173–193.

[91] P. Li and S.-T. Yau: *On the Schrödinger equation and the eigenvalue problem.* Comm. Math. Phys., **88** (1983), 309-318.

[92] E. H. Lieb: *Bounds on the eigenvalues of the Laplace and Schrödinger operators.* Bull. Amer. Math. Soc., **82** (1976), 751–753. See also *The number of bound states of one-body Schrödinger operators and the Weyl problem.* Geometry of the Laplace operator (Univ. Hawaii, Honolulu, Hawaii, 1979), pp. 241–252, Proc. Sympos. Pure Math., **36**, Amer. Math. Soc., Providence, R.I., 1980.

[93] E. H. Lieb: *The stability of matter.* Rev. Modern Phys. **48** (1976), no. 4, 553–569.

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

[95] E. H. Lieb: *Thomas-Fermi and related theories of atoms and molecules.* Rev. Modern Phys. **53** (1981), no. 4, 603–641.
Erratum: "Thomas-Fermi and related theories of atoms and molecules". Rev. Modern Phys. **54** (1982), no. 1, 311.

[96] E. H. Lieb: *Variational principle for many-fermion systems.* Phys. Rev. Lett. *46* (1981), no. 7, 457–459.

[97] E. H. Lieb: *Sharp constants in the Hardy-Littlewood-Sobolev and related inequalities.* Ann. of Math. (2) **118** (1983), no. 2, 349–374.

[98] E. H. Lieb: *On characteristic exponents in turbulence.* Comm. Math. Phys. **92**, no. 4 (1984), 473–480.

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

[100] E. H. Lieb: *Kinetic energy bounds and their application to the stability of matter.* Schrödinger operators (Sønderborg, 1988), 371–382, Lecture Notes in Phys., **345**, Springer, Berlin, 1989.

[101] E. H. Lieb: *The stability of matter: from atoms to stars.* Bull. Amer. Math. Soc. (N.S.) **22** (1990), no. 1, 1–49.

[102] E. H. Lieb: *The stability of matter and quantum electrodynamics.* Milan J. Math. **71** (2003), 199–217.

[103] E. H. Lieb: *Quantum mechanics, the stability of matter and quantum electrodynamics.* Jahresber. Deutsch. Math.-Verein. **106** (2004), no. 3, 93–110.

[104] E. H. Lieb and M. Loss: *Stability of Coulomb systems with magnetic fields. II. The many-electron atom and the one-electron molecule.* Comm. Math. Phys. **104** (1986), no. 2, 271–282.

[105] E. H. Lieb and M. Loss: *Stability of a model of relativistic quantum electrodynamics.* Comm. Math. Phys. **228** (2002), no. 3, 561–588.

[106] E. H. Lieb and M. Loss: *The thermodynamic limit for matter interacting with Coulomb forces and with the quantized electromagnetic field: I. The lower bound.* Commun. Math. Phys. **258** (2005), no. 3, 675–695.

[107] E. H. Lieb, M. Loss, and J. Ph. Solovej: *Stability of matter in magnetic fields.* Phys. Rev. Lett. **75** (1995), no. 6, 985–989.

[108] E. H. Lieb, M. Loss, and H. Siedentop: *Stability of relativistic matter via Thomas-Fermi theory.* Papers honouring the 60th birthday of Klaus Hepp and of Walter Hunziker, Part I (Zürich, 1995). Helv. Phys. Acta **69** (1996), no. 5-6, 974–984.

[109] E. H. Lieb, H. Siedentop, and J. Ph. Solovej: *Stability of relativistic matter with magnetic fields.* Phys. Rev. Lett. **79** (1997), no. 10, 1785–1788.

[110] E. H. Lieb, H. Siedentop, and J. Ph. Solovej: *Stability and instability of relativistic electrons in classical electromagnetic fields.* Dedicated to Bernard Jancovici. J. Statist. Phys. **89** (1997), no. 1-2, 37–59.

[111] E. H. Lieb and S. Oxford: *Improved Lower Bound on the Indirect Coulomb energy.* In. J. Quant. Chem. texbf19 (1981), 427–439.

[112] E. H. Lieb and B. Simon: *The Thomas-Fermi theory of atoms, molecules and solids.* Advances in Math. **23** (1977), no. 1, 22–116.

[113] E. H. Lieb and B. Simon: *The Hartree-Fock theory for Coulomb systems.* Comm. Math. Phys. **53** (1977), no. 3, 185–194.

[114] E. H. Lieb and W. Thirring: *Bound for the kinetic energy of fermions which proves the stability of matter.* Phys. Rev. Lett., **35** (1975), 687-689. Errata **35** (1975), 1116.

[115] E. H. Lieb and W. Thirring: *Inequalities for the moments of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities.* Studies in Math. Phys., Essays in Honor of Valentine Bargmann, Princeton (1976).

[116] E. H. Lieb, I. M. Sigal, B. Simon, and W. Thirring: *Approximate neutrality of large-Z ions.* Comm. Math. Phys. **116** (1988), no. 4, 635–644.

[117] E. H. Lieb and H.-T. Yau: *Many-body stability implies a bound on the fine-structure constant.* Phys. Rev. Lett. **61** (1988), no. 15, 1695–1697.

[118] E. H. Lieb and H.-T. Yau: *The stability and instability of relativistic matter.* Comm. Math. Phys. **118** (1988), no. 2, 177–213.

[119] P. Mancas, A. M. K. Müller, and H. Siedentop: *The Optimal Size of the Exchange Hole and Reduction to One-Particle Hamiltonians.* Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta) **111** (2004), no. 1, 49–53.

[120] P. B. Matesanz and J. Ph. Solovej: *On the asymptotic exactness of Thomas-Fermi theory in the thermodynamic limit.* Ann. Henri Poincaré **1** (2000), no. 2, 281–306.

[121] A. Martin: *Bound states in the strong coupling limit.* Helv. Phys. Acta **45** (1772), 140–148.

[122] S. Molchanov, M. Novitskii, and B. Vainberg: *First KdV integrals and absolutely continuous spectrum for 1-D Schrödinger operator.* Comm. Math. Phys. **216** (2001), no. 1, 195–213.

[123] Yu. N. Ovchinnikov and I. M. Sigal: *Number of bound states of three-body systems and Efimov's effect.* Ann. Physics **123** (1979), no. 2, 274–295.

[124] N. Pavlović: *Bounds for sums of powers of eigenvalues of Schrödinger operators via the commutation method.* In Advances in differential equations and mathematical physics (Birmingham, AL, 2002), 271–281, Contemp. Math., **327**, Amer. Math. Soc., Providence, RI, 2003.

[125] G. Pólya: *Onthe eigenvalues of a vibrating membrane.* Proc. London Math. Soc. **11**, 419–433.

[126] M. Reed and B. Simon: *Methods of Modern Mathematical Physics IV: Analysis of Operators.* Academic Press, New York (1978).

[127] G. Roepstorff: *Path Integral Approach to Quantum Physics.* Springer Berlin 1994.

[128] G.V. Rozenblum: *Distribution of the discrete spectrum of singular differential operators.* Dokl. AN SSSR **202** (1972), 1012–1015; translated in Soviet Math. Dokl. **13** (1972), 245–249.

[129] G.V. Rozenblum: *Distribution of the discrete spectrum of singular differential operators.* (Russian) Izv. VUZov Matematika **1** (1976), 75–86; translated in English translation: Soviet Math. (Iz. VUZ) **20** (1976), no. 1, 63–71.

[130] G. V. Rozenblum and M. Z. Solomyak: *The Cwikel-Lieb-Rozenblyum estimator for generators of positive semigroups and semigroups dominated by positive semigroups.*

(Russian) Algebra i Analiz **9** (1997), no. 6, 214–236; translation in St. Petersburg Math. J. **9** (1998), no. 6, 1195–1211

[131] D. Ruelle: *Large volume limit of the distribution of characteristic exponents in turbulence.* Comm. Math. Phys. **87** (1982), 287–302.

[132] M. B. Ruskai: *Absence of discrete spectrum in highly negative ions.* Comm. Math. Phys. **82** (1981/82), no. 4, 457–469.

[133] M. B. Ruskai: *Absence of discrete spectrum in highly negative ions. II. Extension to fermions.* Comm. Math. Phys. **85** (1982), no. 2, 325–327.

[134] A. Rybkin: *On the absolutely continuous and negative discrete spectra of Schrödinger operators on the line with locally integrable globally square summable potentials.* J. Math. Phys. **45** (2004), no. 4, 1418–1425.

[135] A. Rybkin: *On the spectral* $L^2 2$ *conjecture,* $3/2$*-Lieb-Thirring inequality and distributional potentials.* J. Math. Phys. **46** (2005), no. 12, 123505, 8 pp.

[136] U.-W. Schmincke: *On Schrödinger's factorization method for Sturm-Liouville operator.* Proc. Roy. Soc. Edinburgh Sect. A **80** (1978), 67–84.

[137] J. Schwinger: *On the bound states of a given potential.* Proc. Nat. Acad. Sci. U.S.A. **47** (1961), 122–129.

[138] J. M. C. Scott: *The binding energy of the Thomas-Fermi atom.* Phys. Rev. **43** (1952), 859–867.

[139] L. A. Seco, I. M. Sigal, and J. Ph. Solovej: *Bound on the ionization energy of large atoms.* Comm. Math. Phys. **131** (1990), no. 2, 307–315.

[140] I. M. Sigal: *Geometric methods in the quantum many-body problem. Nonexistence of very negative ions.* Comm. Math. Phys. **85** (1982), no. 2, 309–324.

[141] I. M. Sigal: *How many electrons can a nucleus bind?* Ann. Physics**157** (1984), no. 2, 307320;

[142] H. Siedentop and R. Weikard: *Upper bound on the ground state energy of atoms that proves Scott's conjecture.* Phys. Lett. A **120** (1987), no. 7, 341–342.

[143] H. Siedentop and R. Weikard: *On the leading energy correction for the statistical model of the atom: interacting case.* Comm. Math. Phys. **112** (1987), no. 3, 471–490.

[144] H. Siedentop and R. Weikard: *On the leading correction of the Thomas-Fermi model: lower bound. With an appendix by A. M. Klaus Müller.* Invent. Math. **97** (1989), no. 1, 159–193.

[145] B. Simon: *On the infinitude or finiteness of the number of bound states of an N-body quantum system, I.* Helv. Phys. Acta **43** (1970), 607-630.

[146] B. Simon: *Quantum Mechanics for Hamiltonians Defined as Quadratic Forms.* Princeton Series in Physics, Princeton University press, New Jersey (1971).

[147] B. Simon: *Analysis with weak trace ideals and the number of bound states of Schrödinger operators.* Trans. Amer. Math. Soc. **224** (1976), 367-380

[148] B. Simon: *The bound state of weakly coupled Schrödinger operators in one and two dimensions.* Ann. Physics **97** (1976), no. 2, 279–288.

[149] B. Simon: . In Studies in Mathematical Physics, Essays in Honor of Valentine Bargmann, Princeton University Press, 1976

[150] B. Simon: *Functional Integration and Quantum Physics.* Volume 86 of *Pure and Applied Mathematics.* Academic Press, New York, (1977).

[151] Simon, Barry *Geometric methods in multiparticle quantum systems.* Comm. Math. Phys. **55** (1977), no. 3, 259–274.

[152] Simon, Barry *N body scattering in the two-cluster region.* Comm. Math. Phys. **58** (1978), no. 2, 205–210.

[153] B. Simon: *Schrödinger operators in the twenty-first century.* Mathematical physics 2000, 283–288, Imp. Coll. Press, London, 2000.

[154] B. Simon: *Trace Ideals and Their Applications: Second Edition* Mathematical Surveys and Monographs, AMS, Rhode Island, 2005;

[155] V. A. Sobolev: *The Efimov effect. Discrete spectrum asymptotics.* Comm. Math. Phys. **156** (1993), no. 1, 101–126.

[156] J. Ph. Solovej: *Asymptotics for bosonic atoms.* Lett. Math. Phys. **20** (1990), no. 2, 165–172.

[157] J. Ph. Solovej: *The ionization conjecture in Hartree-Fock theory.* Ann. of Math. (2) **158** (2003), no. 2, 509–576.

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

[159] H. Tamura: *The asymptotic eigenvalue distribution for non-smooth elliptic operators.* Proc. Japan Acad. **50** (1974), 19–22.

[160] H. Tamura: *The Efimov effect of three-body Schrödinger operators: asymptotics for the number of negative eigenvalues.* Nagoya Math. J. **130** (1993), 55–83.

[161] E. Teller: *On the stability of molecules in the Thomas-Fermi theory.* Rev. Mod. Physics **34** (1962), 627–631.

[162] R. Temam: *Infinite-Dimensional dynamical systems in Mechanics and Physics.* Second edition, Springer Berlin (1997).

[163] W. Thirring: *A lower bound with the best possible constant for Coulomb Hamiltonians.* Comm. Math. Phys. **79** (1981), no. 1, 1–7.

[164] S. A. Vugal′ter, G. M. Zhislin: *The spectrum of the Schrödinger operators of multiparticle systems with short-range potentials.* (Russian) Trudy Moskov. Mat. Obshch. **49** (1986), 95–112, 239.

[165] T. Weidl: *On the Lieb-Thirring constants $L_{\gamma,1}$ for $\gamma \geq 1/2$.* Comm. Math. Phys. **178** no. 1 (1996), 135–146.

[166] H. Weyl: *Über die Abhängigkeit der Eigenschwingungen einer Membrane von deren Begrenzung.* J. Reine Angew. Math. **141** (1912), 1–11.

[167] H. Weyl: *Das asymptotische Verteilungsgesetz der Eigenwerte linearer partieller Differentialgleichungen.* Math. Ann. **71** (1912), 441–479.

[168] H. Weyl: *Über das Spektrum der Hohlraumstrahlung.* J. Reine Angew. Math. **141** (1912), 163–181.

[169] H. Weyl: *Ramifications, old and new, of the eigenvalue problem.* Bull. Amer. Math. Soc. **56**, (1950). 115–139.

[170] D. R. Yafaev: *On the theory of the discrete spectrum of the three-particle Schrödinger operator.* (Russian) Mat. Sb. (N.S.) **94**(136) (1974), 567–593, 655–656.

[171] V. E. Zakharov and L. D. Faddeev: *The Korteweg-de Vries equation is a fully integrable Hamiltonian system.* (Russian) Funkcional. Anal. i Priložen. **5** (1971), no. 4, 18–27; English translation in Functional Anal. Appl. **5** (1971), 280–287.

[172] G.-M. Zhislin: *Discussion of spectrum of Schrödinger operators for systems of many particles.* (Russian) Trudy Moskovskogo matematiceskogo obscestva **9** (1960), 81–120.

[173] G.-M. Zhislin: *Finiteness of the discrete spectrum in the quantum problem of n particles.* (Russian. English summary) Teoret. Mat. Fiz. **21** (1974), 60–73. {English translation: Theoret. and Math. Phys. **21** (1974), no. 1, 971–980 (1975).}

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