Lieb's estimate on maximum ionization

A summary of the seminar talk given for the course *Advanced Mathematical Physics*

Sabiha Tokus

Consider an atom with nuclear charge Z. Neutral atoms with a number of electrons equal to Z form stable systems. An interesting question to ask is: How many electrons can a nucleus maximally bind to form a stable system? In other words, to what maximum (negative) charge number can an atom ionize by binding additional electrons and still form a stable system?

Experimental data shows that the *electron affinity* is positive for most of the elements ([5] gives data and large number of references for these). The electron affinity measures the energy difference between the initial and final state in the process of "adding" an electron to an atom to form a negatively charged ion. It thus seems that most nuclei actually can bind $Z + 1$ electrons. It might even be possible to form double negatively charged stable ions and the guess is that the maximal number of electrons a nucleus can bind N_{max} is bounded by $Z + 1$ or possibly $Z + 2$.

Though strongly believed to be true, this statement remains an unproven claim on the level of a mathematical description of quantum theory. It is sometimes referred to as the *ionization conjecture* (cf. [3]) and despite activity in this research question for some decades, there is no rigorous proof for this conjecture derived from first principles of quantum mechanics.

Yet, progress has been made in this and related questions and in the following a short and simple proof as given by Lieb in 1984 [2] and showing that $N_{max} \leq 2Z + 1$ for all $Z > 0$ is presented. For a long time this was the best known rigorous result, not using any approximation models (such as Thomas-Fermi or Hartree-Fock theory) and first in 2011 Nam improved Lieb's upper bound for $Z \geq 6$ [3] by showing that $N_{max} \leq 1.22Z + 3Z^{1/3}$.

1 The setting

We seek, at first, a more formal way for posing the question and start with a model for a classical nucleus of charge $Z > 0$ with a number N non-relativistic electrons interacting with each other and the charged nucleus via a Coulomb interaction. As a model in

quantum mechanics it is described by the Hamiltonian

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

which acts on the space of totally antisymmetric functions $\bigwedge^N (L^2(\mathbb{R}^3))$[1], that is, the space of square-integrable functions of $3N$ variables ψ for which

$$\psi(x_1, \ldots, x_N) = \operatorname{sgn}(\sigma)\psi(x_{\sigma(1)} \ldots x_{\sigma(N)}) \tag{2}$$

is true for any of permutation σ of the variables $x_1, \ldots, x_N \in \mathbb{R}^3$. It is the projection of the N-fold tensor product of one-particle spaces $L^2(\mathbb{R}^3)$ to the subspace of functions for which (2) holds, reflecting the antisymmetric nature of fermions related to the Pauli exclusion principle.

What actually is needed in the proof for maximum ionization is the symmetry of the absolute square of the wave functions, i.e.

$$|\psi(x_1, \ldots, x_N)|^2 = \left|\psi(x_{\sigma(1)} \ldots x_{\sigma(N)})\right|^2 \tag{3}$$

which also holds in the bosonic case when (2) is satisfied without taking into account the sign of the permutation. The proof thus is valid for fermions as well as bosons.

The ground state energy of the system is obtained by minimising the expectation of the Hamiltonian, i.e. by

$$E(N, Z) = \inf_{\|\psi\|=1} \langle \psi, H_{N,Z}\psi \rangle. \tag{4}$$

In fact, this is equivalent to defining the ground state energy as the infimum of the spectrum, $E_{N,Z} = \inf \sigma(H_{N,Z})$.

In general the ground state energy of a Hamiltonian neither has to be finite nor to be an eigenvalue but if so, then we call the associated eigenfunction a ground state.

In the specific case of our atomic model, $H_{N,Z}$ is indeed bounded from below. By the *Min-Max Theorem* (see e.g. Chapter 4.4 in [4]) we then already know that $E_{N,Z}$ is either an eigenvalue with finite multiplicity of $H_{N,Z}$ or it is the bottom of the essential spectrum.

We now define what we mean by a bound system:

Definition 1. *We say the atomic system of N electrons is* bound *if the* binding condition

$$E(N, Z) < E(N - 1, Z) \tag{5}$$

is satisfied.

The question we pose is: what is the maximum number N_{max} such that (5) is still satisfied?

[1]For simplicity we are neglecting the spin of the electrons here which, however, is easy to include by letting $H_{N,Z}$ act on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$.

Remark.

1. It was shown by Zhislin ([6]) that binding occurs at least if $N < Z + 1$. So asking about the maximum number is a valid question.

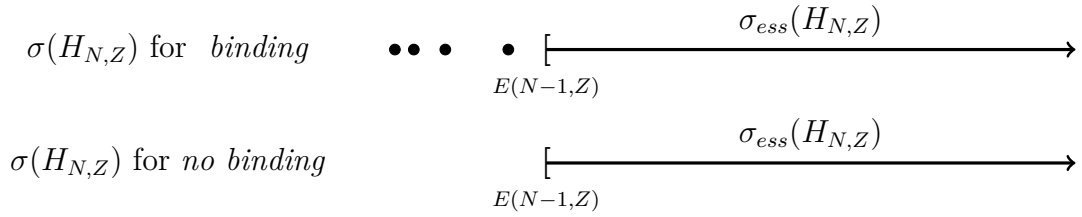
2. Heuristically we make the observation that $E(N, Z) \leq E(N-1, Z)$ is always true, simply because we can place an additional particle with arbitrarily small kinetic energy arbitrarily far away from the nucleus and other electrons. Mathematically this means we can find a Weyl sequence $\{\psi_n\}$ such that $\|(H_{N,Z} - E(N-1, Z))\psi_n\| \to 0$ as $n \to \infty$. Hence, $E(N-1, Z)$ is then in the spectrum of $H_{N,Z}$ and gives an upper bound to the ground state energy.

Indeed, the last point we could also directly conclude from the so-called HVZ theorem (e.g. Chapter 11.2 in [4]) which states that the essential spectrum is exactly given by

$$\sigma_{ess} = [E(N-1, Z), \infty). \tag{6}$$

But the theorem together with the Min-Max Theorem allows for more conclusions: namely, *if* binding occurs then the ground state energy $E(N, Z)$ is an isolated eigenvalue with finite multiplicity.

The following picture illustrates the different situtations when binding and no binding occurs, respectively. If there is binding, then there must exist eigenvalues below the essential spectrum (indicated by dots) of which the lowest one is the ground state energy. In the other case, the lowest point of the spectrum lies at $E(N-1, Z)$, the minimum of the essential spectrum:



2 Lieb's upper bound for ionization

This section presents Lieb's proof for the upper bound on the maximum number of electrons a nucleus can bind, $N_{max} < 2Z + 1$.

The proof is simple and uses the fact, that $E(N, Z)$ is an eigenvalue of $H_{N,Z}$ along with the following lemma. We state and prove it for very convenient conditions which allow to rewrite terms in a suitable way without having to dive into complicated details. The Lemma is proven in Lieb's paper ([2], in Appendix A for more general cases). Indeed, it should be possible to relax the assumptions to $f \in H^1(\mathbb{R}^3)$ (cf. [3]).

Lemma 2. *Let $f \in H^2(\mathbb{R}^3)$. Assume that g defined by $g(x) \coloneqq f(x)|x|$ is in $H^1(\mathbb{R}^3)$ and $|x|\bar{f}\Delta f$ is $L^1(\mathbb{R}^3)$.*

Then the inequality

$$\mathrm{Re}\langle |x|f, -\Delta f\rangle \geq 0 \tag{7}$$

holds.

Proof. We calculate by using partial integration

$$\begin{aligned}
&-\mathrm{Re}\int_{\mathbb{R}^3} \bar{g}(x)\Delta\left[g(x)\frac{1}{|x|}\right]\mathrm{d}x \\
=&\,\mathrm{Re}\int \nabla\bar{g}(x)\nabla(g(x)\frac{1}{|x|})\mathrm{d}x \\
=&\,\mathrm{Re}\int \nabla\bar{g}(x)\left[\frac{1}{|x|}\nabla g(x) + g(x)\nabla\frac{1}{|x|}\right]\mathrm{d}x \\
=&\int \frac{1}{|x|}\left|\nabla g\right|^2\mathrm{d}x + \frac{1}{2}\nabla\frac{1}{|x|}\left[g(x)\nabla\bar{g}(x) + \bar{g}(x)\nabla g(x)\right]\mathrm{d}x \\
=&\int \frac{1}{|x|}\left|\nabla g\right|^2\mathrm{d}x + \frac{1}{2}\int \nabla\frac{1}{|x|}\nabla\left|g(x)\right|^2\mathrm{d}x \\
=&\int \frac{1}{|x|}\left|\nabla g\right|^2\mathrm{d}x - \frac{1}{2}\int |g(x)|^2\Delta\frac{1}{|x|}\mathrm{d}x
\end{aligned} \tag{8}$$

In the last step we understand the second term in a distributional sense and use that $\Delta\frac{1}{|x|} = -C\delta$. Since $f \in L^2$ we have $g(0) = 0$ and the second term vanishes. The remaining term is > 0. □

We now state and prove the following theorem (following Lieb's [2] proof and Nam's presentation of it [3]):

Theorem 3. *Let $H_{N,Z}$ be given as above. Assume $E(N,Z)$ is an eigenvalue of $H_{N,Z}$ with corresponding normalised eigenfunction $\psi_{N,Z}$. Then $N < 2Z + 1$.*

Proof. We start with the Schrödinger equation

$$(H_{N,Z} - E(N,Z))\psi_{N,Z} = 0, \tag{9}$$

which we multiply by $|x_N|\psi_{N,Z}$ to obtain

$$0 = \langle |x_N|\psi_{N,Z}, (H_{N,Z} - E(N,Z))\psi_{N,Z}\rangle. \tag{10}$$

We can split the Hamiltonian into a system with $N-1$ electrons and contributions from the Nth electron:

$$H_{N,Z} = \underbrace{\sum_{i=1}^{n-1}\left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|}\right) + \sum_{1\leq i<j\leq N-1}\frac{1}{|x_i - x_j|}}_{H_{N-1,Z}} + \left(-\frac{1}{2}\Delta_N - \frac{Z}{|x_N|}\right) + \sum_{j=1}^{N-1}\frac{1}{|x_j - x_N|}. \tag{11}$$

Hence we have three terms that sum up to zero:

$$\begin{aligned}
&\langle |x_N|\psi_{N,Z}, (H_{N-1,Z} - E(N,Z))\psi_{N,Z}\rangle \\
&+ \frac{1}{2}\langle |x_N|\psi_{N,Z}, -\Delta_N \psi_{N,Z}\rangle \\
&+ \left\langle \psi_{N,Z}, \left[-Z + \sum_{j=1}^{N-1} \frac{|x_N|}{|x_j - x_N|}\right]\psi_{N,Z}\right\rangle \\
&= 0.
\end{aligned} \tag{12}$$

Using the fact that $H_{N,Z}$ does not act on the variable x_N we estimate for the first term:

$$\begin{aligned}
&\langle |x_N|\psi_{N,Z}, (H_{N-1,Z} - E(N,Z))\psi_{N,Z}\rangle \\
=&\int_{\mathbb{R}^3} |x_N| \int_{\mathbb{R}^{3(N-1)}} \bar{\psi}_{N,Z}(x_1,\dots,x_N)(H_{N-1,Z} - E(N,Z))\psi_{N,Z}(x_1,\dots,x_N)\mathrm{d}x_1\dots\mathrm{d}x_{N-1}\mathrm{d}x_N \\
=&\int_{\mathbb{R}^3} |x_N| \langle \psi_{N,Z}(\cdot,x_N), (H_{N,Z} - E(N,Z))\psi_{N,Z}(\cdot,x_N)\rangle_{L^2(\mathbb{R}^{3(N-1)})} \\
\geq&\int_{\mathbb{R}^3} |x_N| (E(N-1,Z) - E(N,Z))\|\psi_{N,Z}\|^2_{L^2(\mathbb{R}^{3(N-1)})}\mathrm{d}x_N.
\end{aligned} \tag{13}$$

But since $E(N-1,Z) \geq E(N,Z)$ this is obviously non-negative.

For the second term of (12), noting tht $\psi_{N,Z}$ is an eigenfunction, we can use Lemma 1 to conclude that also this term is ≥ 0.

Hence, the last term in (12) must be non-positive. By the symmetry (3) of $|\psi_{N,Z}|^2$, we have an invariance under exchanging x_N with any other variable x_j, $j \neq i$ and we can rewrite the sum in this expression by

$$\left\langle \sum_{j=1}^{N-1} \frac{|x_N|}{|x_j - x_N|}\right\rangle = \left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i} \frac{|x_i|}{|x_j - x_i|}\right\rangle, \tag{14}$$

where the brackets indicate an evaluation within the scalar product between $\psi_{N,Z}$ as in (12). This can be further rewritten as

$$\left\langle \frac{1}{N}\sum_{i=1}^{N}\left(\sum_{j>i}\frac{|x_i|}{|x_j - x_i|} + \sum_{j<i}\frac{|x_i|}{|x_j - x_i|}\right)\right\rangle = \left\langle \frac{1}{N}\sum_{i=1}^{N-1}\left(\sum_{j>i}\frac{|x_i|}{|x_j - x_i|} + \sum_{j>i}\frac{|x_j|}{|x_i - x_j|}\right)\right\rangle, \tag{15}$$

and the condition for the third term to be non-negative now reads:

$$\left\langle \psi_{N,Z}, \left[-Z + \frac{1}{N}\sum_{1\leq i<j\leq N}\frac{|x_i| + |x_j|}{|x_i - x_j|}\right]\psi_{N,Z}\right\rangle \leq 0 \tag{16}$$

Then from $|x_i| + |x_j| \geq |x_i - x_j|$ it follows:

$$\frac{1}{N} \sum_{1 \leq i < j \leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|} \geq \frac{1}{N} \sum_{1 \leq i < j \leq N} 1 = \frac{N-1}{2}. \tag{17}$$

Since equality for the triangle inequality only holds on a set of measure zero in $\mathbb{R}^{3N}$ the inequality in (17) holds strictly almost everywhere. Hence,

$$Z > \frac{N-1}{2} \tag{18}$$

and thus

$$N < 2Z + 1. \tag{19}$$

□

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