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21. Ionization conjecture

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Experimental observation: a neutral atom can bind at most one or two extra electrons.

Born-Oppenheimer approximation:

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

We are interested in the ground state problem:

$$E_N = \inf \sigma(H_N) = \inf_{\|\psi\|=1} \langle \psi, H_N \psi \rangle$$

We know already that E_N is bounded from below, i.e. $E_N > -CN$, but we don't know whether a minimizer exist. If a minimizer for E_N exists then it satisfies Schrödinger eq.

$$H_N \psi = E_N \psi$$

Heuristics:

- if $N < Z+1$, then the outermost electron is attracted by the rest of the system which is of effective charge $Z - (N-1) > 0$.
  Existence (of minimizers) is likely to hold in that case.

•) $N > Z+1$, then the outermost electron prefers to "escape to infinity" due to the Coulomb repulsion. The nonexistence is in favor.

The first part of this heuristics, namely the existence of positive ions and neutral atoms, was proved by Zhislin in 1960.

Thm If $N < Z+1$, then E_N has a minimizer.

On the other hand, the second part of the heuristics above, namely the nonexistence of highly negative ions, is much more difficult and is often reffered to as the "ionization conjecture".

To be precise, let us denote by $N_c = N_c(Z)$ the largest number of electrons such that E_{N_c} has a minimizer. Then we have the following:

Conjecture (ionization)

$$N_c \leq Z + 1 \quad \text{with a constant } C>0.$$

Digression: essential spectrum

$\sigma(T)$ – spectrum of operator T. Then

$$\sigma(T) =: \sigma_{disc}(T) \cup \sigma_{ess}(T)$$

discrete spectrum

$\lambda \in \sigma_{disc}(T)$ iff λ is an isolated eigenvalue of finite multiplicity.

the rest

"fails badly to be invertible"

$$\sigma_{disc}(T) := \{ \lambda \in \sigma(T) : \exists \varepsilon > 0 \ \dim 1\!\!1_{[\lambda-\varepsilon, \lambda+\varepsilon]}(T) < \infty \}$$

$$\sigma_{ess}(T) := \{ \lambda \in \sigma(T) : \forall \varepsilon > 0 \ \dim 1\!\!1_{[\lambda-\varepsilon, \lambda+\varepsilon]}(T) = \infty \}$$

One-body Schrödinger operators: $H = -\Delta + V(x)$, V - real

- if $\lim_{|x| \to \infty} V(x) = 0 \Rightarrow \sigma_{ess}(H) = [0, \infty)$
- if $\lim_{|x| \to \infty} V(x) = \infty \Rightarrow \sigma_{ess}(H) = \emptyset$

Different for many-body operators. H_N.

Thm (HVZ) (Hunziker - von Winter - Zhislin)

$$\sigma_{ess}(H_N) = [E_{N-1}, \infty)$$

As a consequence of the HVZ theorem, we

always have $E_N \leq E_{N-1}$.

Moreover, if $E_N < E_{N-1}$, then H_N has a bound state with eigenvalue E_N.

The conjecture above implies that

$$E_N = E_{N_c} \quad \forall N \geq N_c.$$

It is believed that E_N is not only strictly decreasing for $N \leq N_c$ but also convex.

<u>Conjecture</u> The function E_N is convex in N.

We are still far off the ionization conjecture. There are however non-asymptotic bounds

<u>Thm</u> (Lieb 1984)
We have $N_c(Z) < 2Z+1 \quad \forall Z > 0$.

<u>Lemma</u>

If $f \in H^2(\mathbb{R}^3)$, then $\mathrm{Re}\, \langle |x| f, -\Delta f \rangle_{L^2} \geq 0$.

Proof of lemma under stronger assumptions
$f \in H^2(\mathbb{R}^3)$, $|x| f \in H^1(\mathbb{R}^3)$.

Then by Cauchy-Schwarz $x \bar{f} \Delta f \in L^1(\mathbb{R}^3)$.

Let $g(x) = |x| f(x)$. We compute:

$$\mathrm{Re} \langle |x| f(x), -\Delta f \rangle_2 = -\mathrm{Re} \int_{\mathbb{R}^3} \overline{g(x)}\, \Delta \frac{g(x)}{|x|}\, dx =$$

$$= \mathrm{Re} \int_{\mathbb{R}^3} \overline{\nabla g(x)} \left(g(x) \nabla \frac{1}{|x|} + \frac{1}{|x|} \nabla g(x) \right) dx = \int_{\mathbb{R}^3} \frac{|\nabla g|^2}{|x|} dx +$$

$$+ \frac{1}{2} \int_{\mathbb{R}^3} \left(g(x) \overline{\nabla g(x)} + \overline{g}(x) \nabla g(x) \right) \nabla \frac{1}{|x|} dx$$

$$= \int_{\mathbb{R}^3} \frac{|\nabla g(x)|^2}{|x|} + \frac{1}{2} \int_{\mathbb{R}^3} (\nabla |g|^2)(x) \nabla \frac{1}{|x|} dx =$$

$$= \int_{\mathbb{R}^3} \frac{|\nabla g(x)|^2}{|x|} - \frac{1}{2} \int |g(x)|^2 \underbrace{\Delta \frac{1}{|x|}}_{-4\pi\delta} dx \geq 0$$

__Proof of thm:__

Assume

$H_N \varphi = E_N \varphi$ has a solution.

Multiplying the equation with $|x_N|$ we have

$$0 = \langle |x_N| \varphi, (H_N - E_N) \varphi \rangle = \langle |x_N| \varphi, (H_{N-1} - E_N) \varphi \rangle$$

$$+ \underbrace{\langle |x_N| \varphi, -\Delta_{x_N} \varphi \rangle_2}_{\geq 0 \text{ by lemma}} + \langle \varphi, (-Z + \sum_{1 \leq i \leq N-1} \frac{|x_N|}{|x_i - x_N|}) \varphi \rangle_2 .$$

The operator H_{N-1} does not depend on x_N thus the first term is also non-negative. Indeed:

$$\langle |x_N| \varphi, (H_{N-1} - E_N) \varphi \rangle_2 = \int_{\mathbb{R}^3} |x_N| \int_{\mathbb{R}^{3(N-1)}} \overline{\varphi(x_1, \dots, x_N)} (H_{N-1} - E_N) \varphi(x_1, \dots, x_N)$$

$$\geq \int |x_N| \int (E_{N-1} - E_N) |\varphi|^2 \geq 0$$

Thus the third term has to be non-positive.

$$0 \geq \langle \varphi, (-2 + \sum_{1 \leq i \leq N-1} \frac{|x_N|}{|x_i - x_N|}) \varphi \rangle =$$

$$= \langle \varphi, (-2 + \frac{1}{N} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \frac{|x_j|}{|x_i - x_j|}) \varphi \rangle$$

$$= \langle \varphi, (-2 + \frac{1}{N} \sum_{i<j} \frac{|x_i| + |x_j|}{|x_i - x_j|}) \varphi \rangle$$

Using the triangle inequality $|x_i| + |x_j| \geq |x_i - x_j|$ and the fact that there are $\frac{N(N-1)}{2}$ terms in the sum, we get

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

This inequality is strict almost everywhere

$$\Rightarrow \quad 0 > -2 + \frac{N-1}{2}.$$

$\blacksquare$

Remark

The inequality from the lemma can be stated as

$$(-\Delta)|x| + |x|(-\Delta) \geq 0 \quad \text{on } L^2(\mathbb{R}^3)$$

Interesting generalization:

$$|\nabla_x|^a |x|^b + |x|^b |\nabla_x|^a \geq 0 \quad \text{on } L^2(\mathbb{R}^d)$$

for $[a, b] \in [0, 2]$ and $a + b \leq d$.

The method of "multiplying the equation by $|x|$" is called the Benguria–Lieb argument. It is nowadays a standard technique in the analysis of Coulomb systems.

Below we present two results based on this method.

Thm (Nam 2012)

We have $N_c(Z) < 1{,}22\, Z + 3 Z^{1/3}$. ⊠

The proof is based on a multiplication of the equation by $|x_N|^2$.

In 2013, Lenzmann and Lewin proved a stronger version of the nonexistence, where the absence of not only the ground state but also all eigenfunctions is concerned.

Thm If $N \geq 4Z+1$, then H_N has no eigenvalue. ⊠

Idea of proof: $0 = \langle \varphi, i[H_N, A_{x_N}]\varphi\rangle$

for an operator $A = i[\Delta, f(x)]$, $f(x) = |x|^3$.

This is related to time-dependent methods as $\frac{d}{dt}\langle \varphi_t, A_{x_N}\varphi_t\rangle$ for $\varphi_t = e^{-itH_N}\varphi$. The thm above motivates a stronger conjecture

Conj $\exists\, C>0$ st for $N > Z+C$ H_N has no eigenvalues.