Asymptotic Properties of Atomic Hamiltonians

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Outline

- Setting of Problem
- Results
  - Decay Rates
- Sketch of Proofs
  - 1D Toy Model
  - Partition of Unity
  - Energy Estimates
- Concluding Remarks

Introduction

- Existence of bound states is directly related to stability of the quantum system
- Decay rates give estimates on localization of the system
- Existence of atoms crucial for our existence
- Critical charge which holds N electrons still open
- Convexity of the ground state energy of atoms not known

N Electron Atom

- Atomic Hamiltonian using units $\frac{\hbar^2}{2m} = 1$, $\frac{e^2}{4\pi\epsilon_0} = 1$

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

  with the domain $\mathcal{H}_a^N = \wedge_{j=1}^N L^2(\mathbb{R}^3)$ or $\mathcal{H}_a^N = \wedge_{j=1}^N \left(L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 \right)$

- Ground state energy $E_{N,Z} = \inf \left\{ \langle \psi, H_{N,Z}\psi \rangle : \psi \in \mathcal{H}_a^N, \|\psi\| = 1 \right\}$
- Simple variational result:

$$E_{N,Z} \leq E_{N-1,Z} \leq E_{N-2,Z} \leq \ldots \leq E_{1,Z} < 0$$

- HVZ Theorem:

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

Known Results

Existence of Atoms

- Existence of H^-
  (Bethe 1929)
- Existence of bound states for $N - 1 < Z$
  (Zhislin 1960)
- Absence of bound states for $N > 2Z + 1$
  (Lieb 1984)
- Absence of bound states for $N > 1.22Z + 3Z^{\frac{1}{3}}$
  (Nam 2012)
- Absence of bound states for $N > 1.12Z + 4Z^{\frac{1}{3}}$
  (Hundertmark, Pattakos, Schulz 2024)

Convexity of Ground state

- open problem if ground state energy is convex in number of electrons
- counterexample for special case of multiple charges (Marino, Lewin, Nenna 2024)

Notation

- Given $N \in \mathbb{N}$: $x = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$ and $[N] = \{1, 2, \ldots, N\}$
- the distance of the outermost particle from the nucleus

$$|x|_1 = \max_{j \in [N]} |x_j|$$

- the distance of the innermost particle from the nucleus

$$|x|_N = \min_{j \in N} |x_j|$$

- the distance of the l^{th} outermost particle from the nucleus

$$|x|_l = \max_{\substack{B \subset [N] \\ |B| = \ell}} \min_{j \in B} |x_j| = \min_{\substack{A \subset [N] \\ |A| = N-\ell}} \max_{j \in A} |x_j|$$

- The total potential

$$V(x) = -\sum_{j=1}^{N} \frac{Z}{|x_j|} + \sum_{1 \leq j < k \leq N} \frac{1}{|x_j - x_k|}$$

- The potential of $N - l$ innermost electrons

$$U_{N-\ell}(x) = U_{N-\ell}(y) = -\sum_{j=N-\ell+1}^{N} \frac{Z}{|y_j|} + \sum_{N-\ell < j < k \leq N} \frac{1}{|y_j - y_k|}$$

General Case

- Let ψ be a weak eigenfunction of $H_{N,Z}$ with eigenenergy E define

$$\alpha_1 = E_{N-1,Z} - E, \alpha_2 = E_{N-1,Z} - E_{N-2,Z}, \ldots, \alpha_{N-1} = E_{2,Z} - E_{1,Z}, \alpha_N = E_{1,Z}$$

- For $\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_n)$, $0 < \beta, \gamma < 1$, and $\kappa > 0$ define

$$F^{(1)}_{\alpha,\beta;\kappa,\gamma}(x) = \sqrt{\alpha_1}\left(|x|_1 - \kappa |x|_1^{\beta}\right) + \sum_{j=2}^{N} \sqrt{\alpha_j}\Big(|x|_j - 2|x|_1^{\gamma}\Big)_+ ,$$

Exponential decay in the subcritical case; General Case

Let ψ be a weak eigenfunction of $H_{N,Z}$ with energy $E < E_{N-1,Z}$ and let α be ionization energies with at least $\alpha_1 > 0$. For any $\kappa > 0$ and $0 < \beta, \gamma < 1$ such that

$$1 - \gamma^{N-1} < \beta < 1 ,$$

we have the L^2 exponential upper bound

$$\| e^{F^{(1)}_{\alpha,\beta;\kappa,\gamma}} \psi \|_{L^2(\mathbb{R}^{3N})} < \infty$$

Remarks

- $0 < \beta < 1$ can be in principle arbitrary but γ needs to be close to 1 for large N
- For $\kappa > 0$ and $1 - \frac{1}{N} < \beta < 1$ there exists C s.t.

$$|\psi(x)| \leq C \exp\left(-\sum_{j=1}^{N} \sqrt{\alpha_j}|x|_j + \kappa|x|_1^{\beta}\right)$$

  holds for a.e. $x \in \mathbb{R}^{3N}$.
- Leading order in $\sqrt{\alpha_j}|x|_j$ is sharp

Positive Ionization Energies

- Let ψ be a weak eigenfunction of $H_{N,Z}$ with eigenenergy E define

$$\alpha_1 = E_{N-1,Z} - E, \alpha_2 = E_{N-1,Z} - E_{N-2,Z}, \ldots, \alpha_{N-1} = E_{2,Z} - E_{1,Z}, \alpha_N = E_{1,Z}$$

- For $\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_n)$, $\alpha_j > 0$, $0 < \beta, \gamma < 1$, and $\kappa > 0$ define

$$F^{(2)}_{\alpha,\beta;\kappa,\gamma}(x) = \sqrt{\alpha_1}\big(|x|_1 - \kappa |x|_1^{\beta}\big) + \sum_{j=2}^{N} \sqrt{\alpha_j}\Big(|x|_j - \frac{Z}{2\alpha_j}\ln(1+|x|_j) - 2|x|_1^{\gamma}\Big)_+ .$$

Exponential decay in the subcritical case; All $\alpha_j > 0$

Let ψ be a weak eigenfunction of $H_{N,Z}$ with energy $E < E_{N-1,Z}$ and let α be ionization energies with all $\alpha_j > 0$. For any $\kappa > 0$ and $0 < \beta, \gamma < 1$ such that

$$1 - 2\gamma^{N-1} < \beta < 1,$$

we have the L^2 exponential upper bound

$$\big\| e^{F^{(2)}_{\alpha,\beta;\kappa,\gamma}} \psi \big\|_{L^2(\mathbb{R}^{3N})} < \infty$$

Road map

- Modified Agmon method
- Partition of unity
- Energy estimates

1D Toy Model

- Consider the Hamiltonian

$$H = -\Delta - \frac{1}{|x|}$$

- ground state ψ with energy $E = -\frac{1}{4}$

1st step (Projecting onto the region of interest)

- Define smooth function $\chi_R(x) = \begin{cases} 0 & |x| < R \\ 1 & |x| > 2R \end{cases}$
- As a decay rate function we use $F = \frac{1}{2}|x| - \kappa|x|^\beta$ with $\kappa > 0$, $0 < \beta < 1$
- Also set $F_\epsilon = \frac{F}{\epsilon|x|+1}$
- Evaluate eigenequation $H\psi = E\psi$ by functional $\left\langle \chi_R^2 e^{F_\epsilon}\psi \right|$

$$\mathrm{Re}\left(\left\langle \chi_R^2 e^{F_\epsilon}\psi, H\psi\right\rangle\right) = E\left\langle \chi_R^2 e^{F_\epsilon}\psi, \psi\right\rangle$$

1D Toy Model

2nd step (Identifying the good and the bad part)

- Applying a variant of IMS formula we obtain

$$\langle \chi_R e^{F_\epsilon}\psi, H\chi_R e^{F_\epsilon}\psi\rangle - \langle \psi, |\nabla e^{F_\epsilon}\chi_R|^2\psi\rangle = E\|e^{F_\epsilon}\chi_R\psi\|^2$$

- IMS error is

$$\left|\nabla\left(\chi_R e^{F_\epsilon}\right)\right|^2 = |\nabla\chi_R + \chi_R\nabla\left(F_\epsilon\right)|^2 e^{2F_\epsilon}$$

- Terms containing $\nabla\chi_R$ are good terms because they are compactly supported

1D Toy Model

3rd step (Estimating and rearranging)

- Estimating G and rearranging the remaining terms gives

$$\left\langle \chi_R e^{F_\epsilon}\psi, (H-E-B)\,\chi_R e^{F_\epsilon}\psi \right\rangle \leq \|G\psi\|^2 \leq K\,.$$

- Good part

$$G = \left(|\nabla \chi_R|^2 + 2\chi_R \nabla \chi_R \cdot \nabla F_\epsilon \right) e^{2F_\epsilon}$$

- Bad part

$$B = \chi_R^2\, |\nabla F_\epsilon|^2\, e^{2F_\epsilon} \leq \chi_R^2 \left(\frac{1}{4} - C|x|^{\beta-1} \right) e^{2F_\epsilon}$$

1D Toy Model

Final step (The magic happens // Showing positivity)

- Show that $H - E - B$ is positive operator
- We have the estimate

$$G \geq \left\langle \chi_R e^{F_\epsilon} \psi, (H - E - B) \chi_R e^{F_\epsilon} \psi \right\rangle$$
$$\geq \left\langle \chi_R e^{F_\epsilon} \psi, \frac{1}{|x|} \left(C|x|^\beta - 1 \right) \chi_R e^{F_\epsilon} \psi \right\rangle$$

- Implying $e^{F_\epsilon} \psi$ has bounded norm independent on ϵ
- We have $\left\| \frac{e^{\frac{1}{2}|x| - \kappa |x|^\beta}}{|x|+1} \psi \right\| < \infty$

Partition of Unity - 4 Particle Example

- Split space according to electrons relatively close to nucleus and far from it
- Localization to paraboloidal regions
- Parameters $R \gg 1, 0 < \gamma < 1$
- the largest distance od electron $|x|_1 = \max_{j\in[N]} |x_j|$, the second largest $|x|_2$ etc.

Region	Conditions	Loc. function
Compact part	$|x|_1 < 2R$	χ_0
A_1	$|x|_1 > R, |x|_2 < 2|x|_1^\gamma$	χ_1
A_2	$|x|_1 > R, |x|_2 > |x|_1^\gamma, \ |x|_3 < 2|x|_2^\gamma$	χ_2
A_3	$|x|_1 > R, |x|_2 > |x|_1^\gamma, |x|_3 > |x|_2^\gamma, |x|_4 < 2|x|_3^\gamma$	χ_3
A_4	$|x|_1 > R, |x|_2 > |x|_1^\gamma, |x|_3 > |x|_2^\gamma, |x|_4 > |x|_3^\gamma$	χ_4

Partition of Unity

Partition

For a given $0 < \gamma < 1$ we define

$$B_1 := \mathbb{R}^{3N}$$
$$B_\ell := \bigcap_{m=2}^{\ell} \{|x|_m > |x|_{m-1}^\gamma\} \text{ for } \ell = 2, \dots, N$$
$$A_\ell := B_\ell \cap \{|x|_{\ell+1} < 2|x|_\ell^\gamma\} \text{ for } \ell = 1, \dots, N-1$$
$$A_N := B_N \,.$$

Moreover, for $R > 0$ we set $B_{j,R} := B_j \cap \{|x|_1 > R\}$ and $A_{j,R} := A_j \cap \{|x|_1 > R\}$.

- From the definition one immediately sees that

$$B_\ell = B_{\ell-1} \cap \{|x|_\ell > |x|_{\ell-1}^\gamma\}$$
$$A_\ell \cap B_{\ell+1} = B_\ell \cap \{|x|_\ell^\gamma < |x|_{\ell+1} < 2|x|_\ell^\gamma\}$$
$$A_\ell \cup B_{\ell+1} = B_\ell$$

and the same for $A_{\ell,R}$ and $B_{\ell,R}$.

Partition of Unity

- Let $u, v \in C^\infty$
- $0 \leq u, v \leq 1$, $u = 1$ and $v = 0$ on $[0, 1]$, $u = 0$ and $v = 1$ on $[2, \infty)$
- $u^2 + v^2 = 1$

Quadratic partition of unity adapted to paraboloidal sets

For $0 < \gamma < 1$ we set

$$\chi_0(x) = \chi_{0,R}(x) = u\big(|x|_1/R\big) \text{ and } \rho_1(x) = \rho_{1,R}(x) = v\big(|x|_1/R\big)\,.$$

Moreover, for $j = 2, \dots, N$ let

$$u_j(x) = u\big(|x|_j/|x|_{j-1}^\gamma\big)\,, v_j(x) = v\big(|x|_j/|x|_{j-1}^\gamma\big) \text{ and}$$

$$\rho_j = \rho_{j,R} \coloneqq \rho_{j-1,R}\, v_j = \rho_{1,R} \prod_{m=2}^{j} v_m\,.$$

For $j = 1, \dots, N-1$ we let

$$\chi_j = \chi_{j,R} \coloneqq \rho_{j,R} u_{j+1}\,.$$

Lastly, we set $\chi_N = \chi_{N,R} \coloneqq \rho_{N,R}\,.$

Energy Estimates

Energy bounds

For all ψ from N–particles Hilbert space with q spin degrees of freedom, we have

$$\langle \psi, H_{N,Z}\psi \rangle \geq \sum_{\ell=0}^{N} \langle \chi_{\ell,R}\psi, (E_{N-\ell,Z} - \sum_{j=1}^{\ell} \frac{Z}{|x|_j} - L_R)\chi_{\ell,R}\psi \rangle$$

where $E_{k,Z}$ is the ground state energy of an atom with k particles with the same symmetry and nuclear charge Z.

- $\sum_{j=0}^{N} \chi_{j,R}^2 = 1$ corresponds to partition of unity
- $\mathrm{supp}(\chi_{\ell,R}) \subset A_{\ell,R}$
- localization error is $L_R := \sum_{j=0}^{N} |\nabla \chi_{j,R}|^2$
- estimate for localization error

$$L_R(x) \leq C\left(R^{-2}\mathbb{1}_{\{R\leq |x|_1 \leq 2R\}} + \sum_{j=1}^{N-1} \rho_{j,R}^2 \left(|x|_j^{-2} + 4\gamma^2 |x|_j^{-2\gamma} \right) \right)$$

$$\leq C\left(R^{-2}\mathbb{1}_{\{R\leq |x|_1 \leq 2R\}} + \sum_{j=1}^{N-1} \left(|x|_1^{-2\gamma^{j-1}} + 4\gamma^2 |x|_1^{-2\gamma^j} \right) \mathbb{1}_{\{|x|_1 \geq R\}} \right)$$

Summary

Decay rate for N electron atom with charge Z

- $\frac{N-1}{N} < \beta < 1$

$$|\psi(x)| \lesssim \exp\Big(- \sum_{j=1}^{N} \sqrt{\alpha_j} |x|_j + \kappa |x|_1^{\beta} \Big)$$

- $\alpha_j > 0$, $\frac{N-1}{1+(N-1)2^{1/(N-1)}} < \beta < 1$

$$|\psi(x)| \lesssim \exp\left(-\sqrt{\alpha_1} \big(|x|_1 - \kappa |x|_1^{\beta} \big) - \sum_{j=2}^{N} \sqrt{\alpha_j} \Big(|x|_j - \frac{Z}{2\alpha_j} \ln(1 + |x|_j) \Big) \right)$$

Thank you for your attention