Mathematics

An Upper Bound for the Number of Electrons in a Large Ion

Asymptotic neutrality/excess charge/quantum mechanics

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Abstract Let $E(Z,N)$ be the ground-state energy of N quantized electrons and a single nucleus of charge Z. For fixed Z, $E(Z,N)$ is independent of N for $N \geq N_{\text{critical}}(Z)$. Physically, this means that at most N_{critical} electrons can bind to the nucleus. We prove that $N_{\text{critical}} \leq Z + CZ^a$ with $a = 0.84$.

Consider the Hamiltonian for a nucleus of charge Z and N quantized electrons,

$$H_{Z,N} = \sum_{i=1}^{N} \left[(-\Delta_{x_i}) - \frac{Z}{|x_i|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} = -\Delta + V_{\text{Coulomb}}.$$

The ground state energy is then

$$E(Z) = \inf_N E(Z,N) = \inf_N \inf \left\{ \left\langle H_{Z,N}\, \psi \,,\, \psi \right\rangle \quad \Big| \quad \psi \in \wedge_{i=1}^{N} (L^2(\mathbf{R}^3) \otimes \mathbf{C}^q), \quad \|\psi\|_2 = 1 \right\}.$$

For each Z, call $N(Z)$ the smallest number for which $E(Z) = E(Z,N)$.

It is an interesting problem to obtain sharp estimates for $N(Z)$. The sharpest known result appears in (1). In particular, $N(Z)/Z \to 1$ as $Z \to \infty$, although there were no estimates for the rate of convergence. Our main result is the following:

Theorem:

$$N(Z) = Z + O(Z^{\alpha}) \qquad \text{for some } \alpha < 1$$

For the proof we will be interested only in the case $Z \leq N \leq 2Z$. Recall that $E(Z)/Z^{7/3} \to 1$ as $Z \to \infty$.

Definitions:

1. Given a ball of center 0 and radius R, call $N_R = N_R(x_1, \ldots, x_N)$ the number of x_i that belong to it.
2. We say that $\texttt{Estimate}(\bar{\epsilon}, \epsilon, R)$ holds if for a nucleus of charge Z at the origin and N quantized electrons *confined to the ball* $B(0,R)$ we have

   $$\left\langle H_{Z,N}\, \psi, \psi \right\rangle \geq E_0(Z) + \frac{\bar{\epsilon} Z}{R} \Big(N - (1+\epsilon) Z \Big)$$

   where

   $$E_0(Z) = \inf_{0 \leq N \leq (1+\epsilon_\sharp) Z} E(Z,N)$$

   for $\epsilon_\sharp$ to be picked later.

By N *quantized electrons confined to the ball* $B(0,R)$ we mean that the support of ψ is included in the set $\{\mathbf{x} | N_R(\mathbf{x}) = N\}$.

3. Fix once and for all an even approximation to the identity, ϕ, supported in $B(0, Z^{-2/3})$. Given points $x_1, \ldots, x_N$ set $\rho(x) = \sum_i \phi(x - x_i)$.
4. Take a smooth function χ_R that is equal to 1 if $|x| < R$ and 0 if $|x| > 2R$, and define $N_{\chi,R}(x) = \sum_{i=1}^{N} \phi(x - x_i) \cdot \chi_R(x)$. Obviously, $N_{R/2} \le N_{\chi,R} \le N_{2R}$.
5. If ρ_{TF} is the Thomas-Fermi density, $N_{\chi,R}^{TF} = \int_{B(0,R)} \rho_{TF}(x)\, \chi(x)\, dx$. Note that if $R = Z^{-1/3+\gamma}$, then $Z \ge N_{\chi,R}^{TF} \ge Z - cZ^{1-3\gamma}$, $\gamma > 0$.

Key Result:

$$\left\langle H_{Z,N}\, \psi, \psi \right\rangle \ge E_0(Z) + C \frac{|\langle N_\chi \psi, \psi\rangle - N_\chi^{TF}|^2}{R} - O(Z^{7/3 - b})$$

for any ψ; in particular we do not assume that there are any number of electrons confined to any ball.

Proof of Key Result:

It follows from W. Hughes (2) and H. Siedentop-R. Weikard (3) that if we set

$$K(x_1, \ldots, x_N) = \iint \frac{(\rho - \rho_{TF})(x)(\rho - \rho_{TF})(y)}{|x - y|} dx\, dy$$

then $H_{Z,N} \ge E_0(Z) + K(x_1, \ldots, x_N) - O(Z^{7/3 - b})$.

Since

$$K = \int_{\mathbf{R}^3} |\xi|^{-2} |\hat{\rho}(\xi) - \hat{\rho}_{TF}(\xi)|^2 d\xi$$

and

$$N_\chi - N_\chi^{TF} = \int (\rho - \rho_{TF}) \chi\, dx = \int (\hat{\rho} - \hat{\rho}_{TF}) \hat{\chi}\, d\xi$$

Cauchy-Schwarz yields

$$|N_\chi - N_\chi^{TF}|^2 \le \int |\chi(\xi)|^2 \cdot |\xi|^2\, d\xi \int |(\hat{\rho} - \hat{\rho}_{TF})|^2 \cdot |\xi|^{-2}\, d\xi \le CR \cdot K$$

And Cauchy-Schwarz again gives the result.

Corollary 1: For any β_1, β_2, satisfying

$$2\beta_1 + \beta_2 < b \tag{ineq 1}$$

for some c depending on $b - 2\beta_1 - \beta_2$ and sufficiently large Z, $\texttt{Estimate}(\bar{\epsilon}_0, \epsilon_0, R_0)$ holds for $\epsilon_0 \geq Z^{-\beta_1}$, $\bar{\epsilon}_0 \leq cZ^{-\beta_1}$ and $R_0 \leq \frac{1}{2} Z^{\beta_2 - \frac{1}{3}}$.

Proof: Use the key result for $R = 2R_0$. Note that $N_{R/2} = N$. If $N \geq Z + Z^{1-\beta_1}$, since $N_\chi^{TF} \leq Z$, we have

$$C\frac{|N-Z|^2}{R} - O(Z^{7/3 - b}) \geq C' \frac{|N-Z|^2}{R}$$

and therefore

$$\langle H_{Z,N}\psi, \psi\rangle ; \geq E_0(Z) + C'\frac{|N-Z|^2}{R} \geq E_0(Z) + \frac{cZ^{1-\beta_1}}{R}(N - Z - Z^{1-\beta_1})$$

Corollary 2: If $R = Z^{-1/3 + \gamma_2}$ and $\left\langle N_{2R}\psi, \psi \right\rangle < Z - cZ^{1-\gamma_1}$, and

$$3\gamma_2 > \gamma_1 \qquad 7\gamma_2 < b \tag{ineq 2}.$$

Then

$$\langle H_{Z,N}\psi, \psi\rangle ; \geq E_0(Z) + cZ^{7/3 - 7\gamma_2}$$

c becomes 0 as $3\gamma_2 - \gamma_1$ and $7\gamma_2 - b$ go to 0.

Proof: Since $N_{\chi,R}^{TF} \geq Z - cZ^{1-3\gamma_2}$

$$\frac{|N_R - N_{\chi,R}^{TF}|^2}{R} \geq cZ^{7/3 - 7\gamma_2}.$$

Now, we study a system of N quantized electrons in $B(0,R)$, and N' quantized electrons in $B(0,2R) - B(0,R/2)$, for $R > 2Z^{-1/3+\gamma}$, with

$$\gamma > \gamma_2 \qquad \gamma > \beta_2 \tag{ineq 3}$$

Let's rewrite the Hamiltonian $H_{Z,N+N'}$ as

$$H_{Z,N+N'} = -\Delta_{x_i \ldots x_N} + V - \Delta_{\text{extra}} + V_{\text{extra}}$$

with

$$\begin{aligned}
\Delta_{\text{extra}} &= \Delta_{x'_1,\ldots,x'_{N'}} \\
V &= -\sum_{i=1,\ldots,N} \frac{Z}{|x_i|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|x_i - x_j|} \\
V_{\text{extra}} &= -\sum_{i=1,\ldots,N'} \frac{Z}{|x'_i|} + \sum_{\substack{i=1,\ldots,N' \\ j=1,\ldots,N}} \frac{1}{|x'_i - x_j|} + \frac{1}{2}\sum_{\substack{i=1,\ldots,N' \\ j=1,\ldots,N' \\ i\neq j}} \frac{1}{|x'_i - x'_j|}
\end{aligned}$$

Corollary 2 now implies that

$$\langle V_{\text{extra}}\psi, \psi\rangle\, ; \geq \frac{c\epsilon Z}{R} N' \tag{A}$$

or else

$$\left\langle H_{Z,N+N'}\, \psi,\, \psi\right\rangle \geq E_0(Z) + cZ^{7/3 - 7\gamma_2}$$

since the fact that $\left\langle N_{R/Z^{\gamma-\gamma_2}}\psi, \psi\right\rangle$ is at least $Z - Z^{1-\gamma_1}$ makes the interaction of the nucleus and of the electrons in $B(0, R/Z^{\gamma-\gamma_2})$ with a fixed electron x'_j in $B(0,2R) - B(0,R/2)$ contribute approximately with $(-Z + N_{R/Z^{\gamma-\gamma_2}})/|x'_j| \geq -Z^{1-\gamma_1}/|x'_j|$ to the potential energy. We omit the details and we simply point out that you need enough electrons to almost cancel the effect of the nucleus. Precisely,

$$Z^{-\gamma_2} > \epsilon \tag{ineq 4}$$

We now use this estimate to go from $\texttt{Estimate}(\bar{\epsilon}, \epsilon, R)$ to $\texttt{Estimate}(\bar{\epsilon}, \epsilon', 2R)$. To see this, simply take a wave function ψ living in $B(0,2R)$ and a partition of unity θ_0, θ_1, adapted to $B(0,R)$ and $B(0,2R) - B(0,R/2)$, and set

$$\psi_{i_1,\ldots,i_N}(x_1,\ldots,x_N) = \theta_{i_1}(x_1)\cdots\theta_{i_N}(x_N)\cdot\psi(x_1,\ldots,x_N)$$

For each $\psi_{i_1,\ldots,i_N}$ we have N_1 electrons living in $B(0,R)$ and N_2 electrons living in $B(0,2R) - B(0,R/2)$, with $N_1 + N_2 = N$; now, assume $\texttt{Estimate}(\bar{\epsilon},\epsilon,R)$ holds, apply Corollary 1 and 2 and estimate (A), and sum over all possible choices of $i_1,\ldots,i_N$ to obtain

$$\begin{aligned}\Big\langle H_{Z,N}\psi,\psi\Big\rangle &\geq E_0(Z) + \frac{\bar{\epsilon}Z}{R}\Big(N_1 - (1+\epsilon)Z\Big) + \langle V_{\text{extra}}\psi,\psi\rangle\,; - \frac{CN}{R^2}\\ &\geq E_0(Z) + \frac{\bar{\epsilon}Z}{R}\Big(N_1 + N_2 - (1+\epsilon)Z\Big) - \frac{CN}{R^2}\\ &= E_0(Z) + \frac{\bar{\epsilon}Z}{R}\Big(N - (1+\epsilon)Z\Big) - \frac{CN}{R^2} \qquad (\bar{\epsilon} \leq c\epsilon)\end{aligned}$$

The terms CN/R^2 come from the Laplacian hitting θ_0 and θ_1. Again we omit the details. Now observe that

$$\max\left(0, \frac{\bar{\epsilon}Z}{R}\big(N - (1+\epsilon)Z\big) - \frac{CN}{R^2}\right) \geq \frac{\bar{\epsilon}Z}{2R}\big(N - (1+\epsilon')Z\big)$$

for $\epsilon' - \epsilon = \frac{4C}{\bar{\epsilon}RZ}$; we also need that $R \geq \frac{2C}{\bar{\epsilon}Z}$, which certainly holds in this case. This proves that $\texttt{Estimate}(\bar{\epsilon},\epsilon',2R)$ holds.

If

$$\beta_2 > \gamma_2 \qquad \text{(ineq 5)}$$

we can use corollary 1 and conclude that $\texttt{Estimate}(\bar{\epsilon}_0,\epsilon_n,2^nR_0)$ holds for

$$\epsilon_{n+1} = \epsilon_n + \frac{4C}{2^n\bar{\epsilon}_0R_0Z}.$$

Note that $\epsilon_n \leq C\epsilon_0 = \epsilon_\sharp$, for C independent of n. Therefore, $\texttt{Estimate}(\bar{\epsilon}_0,C\epsilon_0,R)$ holds for all $R \geq R_0$ and so

$$N(Z) - Z \leq C\epsilon_0 \leq CZ^{1-\beta_1}$$

The value for $\alpha = 1 - \beta_1$ depends on b and on the parameters β_1, β_2, γ_1 and γ_2 subject to the constraints (ineq1)—(ineq5). For each b, the optimum value in the closure of this set of parameters is attained for $\beta_1 = {}^{3b}\!/_7$. The value for α is then $1 - {}^{3b}\!/_7$. From Hughes and Siedentop-Weikard it follows that we can take $b = {}^{21}\!/_{56}$. This allows us to take any $\alpha > {}^{47}\!/_{56} \approx 0.84$. Further improvement of b will lead to a better estimate for α. What Hughes and Siedentop-Weikard did is something in fact much harder that just estimate K, and it is clear that better estimates can be obtained; maybe we can take b to be ${}^{2}\!/_{3}$; this would give the result for any $\alpha > {}^{5}\!/_{7}$.

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